

## Polymer Processing

### 1.1 Introduction

Polymers form a very important class of materials: the total volume produced exceeds that of metals. Used for structural applications, household goods, packaging, fibres .....

Most engineering polymers (>90% of market) are *thermoplastics* (i.e. can be melted and resolidify without damage, do not contain permanent cross-links between chains)

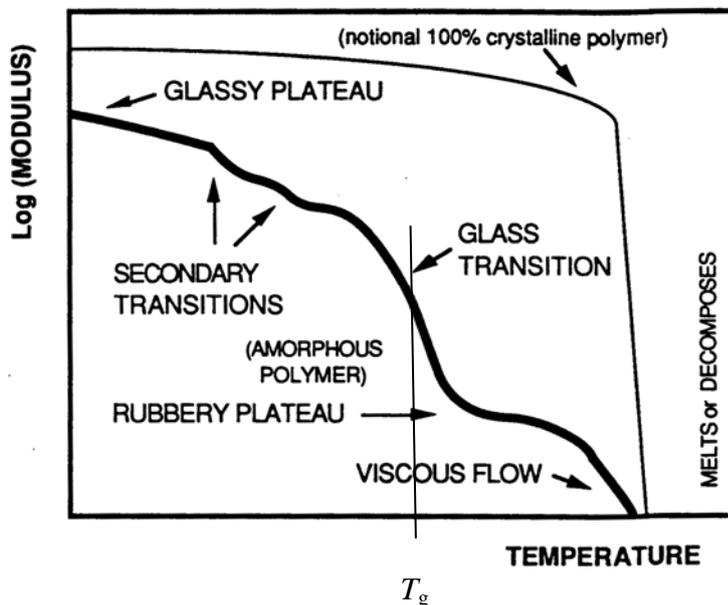
Thermoplastics have:

- long-chain molecules – typically of  $10^3 - 10^5$  monomer (repeat) units
- strongly bonded (covalent) backbones
- weak inter-chain bonds (van der Waals or hydrogen bonds)

They may be *amorphous* (= *glassy* i.e. with randomly oriented chains) or *semi-crystalline* (with some amorphous component).



Amorphous polymers have a *glass transition temperature*  $T_g$  above which the chains can rotate; their behaviour above  $T_g$  is rubbery but below  $T_g$  they are glasses. Elastic modulus falls by a factor of about 100 above  $T_g$ . Crystalline regions have a sharp melting point  $T_m$  at which the chains become fully mobile (i.e. liquid).  $T_g$  is often approximately  $2/3 T_m$  (in K).



The most important thermoplastics (in terms of Western European consumption) are:

- semi-crystalline:
  - PE polyethylene 30% (LDPE 11%; HDPE 19%)
  - PP polypropylene 16%
  - PET polyethylene terephthalate 6%
- amorphous
  - PVC poly(vinyl chloride) 16%
  - PS polystyrene 6%
- The other 27% includes mixed plastics and *thermosets*.

(Source: WRAP Market Situation Report Autumn 2007 [www.wrap.org.uk](http://www.wrap.org.uk))

Semicrystalline polymers contain crystalline regions (analogous to grains in a metal) and amorphous regions. A polymer molecule is usually very stiff when it is strained parallel to the molecular backbone – but if the molecules are randomly oriented as in an isotropic amorphous polymer, the behaviour is dominated by the weak inter-chain bonds.

By *aligning* the molecules parallel to the applied stress, we can achieve much greater stiffness. The degree of molecular alignment and the degree of crystallinity are both important in controlling the properties of a polymer product.

Optically transparent polymers are usually amorphous, because crystallites scatter light giving a milky/opaque appearance.

## 1.2. Additives and polymer alloys

Most polymers have small amounts of other materials blended with them to change their properties in some way. Note the problem which additives pose when trying to recycle polymers: they effectively become impurities.

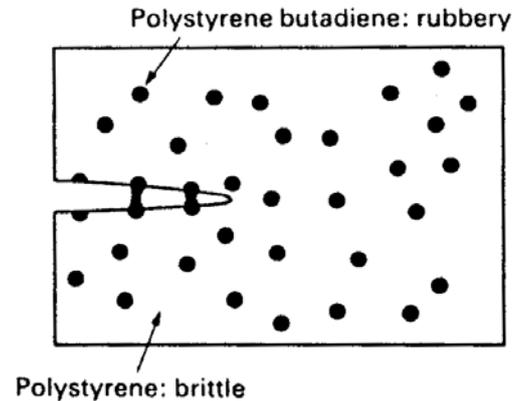
Main classification	Subdivision
<b>1. Processing additives</b>	Stabilisers (to prevent degradation at high T) Lubricants Viscosity depressants
<b>2. Flexibilisers</b>	Plasticisers (e.g. PVC plasticized by small molecules such as tricresyl phosphate TCP)
<b>3. Anti-ageing additives</b>	Antioxidants Ultraviolet stabilisers (e.g. carbon in rubber)
<b>4. Surface property modifiers</b>	Antistatic agents
<b>5. Coatings</b>	Metallising; Ceramic surface (powder bonded onto polymer); barrier layers (e.g. gas-impermeable film on some packaging films and bottles)
<b>6. Optical property modifiers</b>	Pigments and dyes
<b>7. Fire retardants</b>	Ignition inhibitors Self-extinguishing additives Smoke suppressants
<b>8. Foaming agents</b>	Blowing agents. For making polymer foams (closed cell or open cell)
<b>9. Fillers</b>	Increase rigidity (elastic modulus) Increase creep resistance (e.g. glass fiber in PTFE) 'Bulk out' expensive polymer with cheap inert substance

Alloys can be produced by blending two or more polymers, for example:

**Vinyl chloride + vinyl acetate** co-polymerised produce a polymer which is less brittle than PVC (chain irregularities lead to less dense packing; extra free volume allows more chain mobility).

**Styrene-acrylonitrile** co-polymer reinforced with **polystyrene-butadiene** co-polymer, to make **ABS**.

**Styrene + butadiene** to make **High Impact Polystyrene (HIPS)**: polystyrene is brittle, polystyrene-butadiene 'precipitates' are rubbery giving higher toughness.



### 1.3 End uses of polymer products (British Plastics Federation 2009)

- 38%: Packaging e.g. film, bottles, pots
- 22%: Construction e.g. building components, plumbing, gutters
- 6%: Cable/electrical insulation
- 7%: Transport e.g. automotive parts
- 7%: Furniture/homewares
- 7%: Agriculture e.g. containers, crop protection
- 2%: Medical e.g. disposables, containers, implants
- 11%: Other

### 1.4 Costs

Polymer costs depend on specification, grade and quantity. Very roughly, most high-volume virgin polymers currently (2012) cost £1300-£1800 / tonne – and fluctuate with the oil price. (The current steel price is about £220 per tonne).

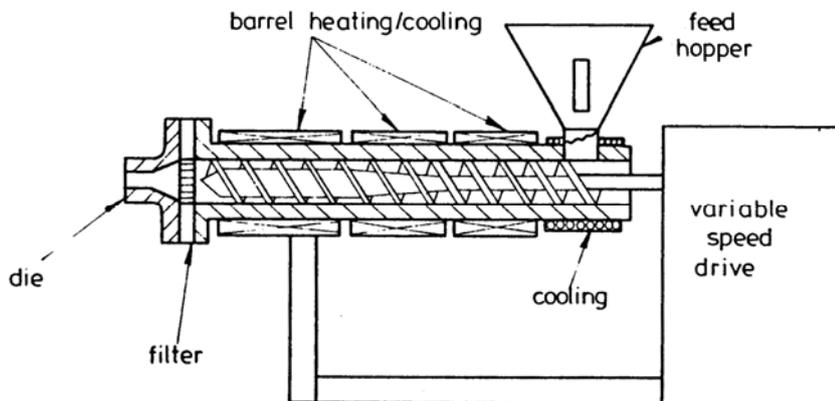
## 2 Polymer processing methods

### 2.1. Processing - the main categories

Polymer process	Characteristics	Analogous metal forming process
<b>Extrusion</b>	Continuous process. Very common. Polymer melted and compressed by the screw in a barrel screw extruder, and forced out of dies in wide range of shapes, geometries and sizes.	Extrusion (with hydraulic ram)
<b>Injection moulding</b>	Discontinuous process. Molten polymer forced into metal mould (die).	Pressure die casting
<b>Thermoforming</b>	Thermoplastic sheet heated to plasticise; then formed to shape by pressure	Creep forming
<b>Rotational moulding</b>	Rotate heated mould containing polymer granules to form thin shell.	Centrifugal casting (limited to pipes)

## 2.2. Extrusion and related processes.

### The screw extruder



Extrusion is the most important processing method for thermoplastics. Granules of polymer are fed into the hopper. The screw turns and drags the polymer along the extruder. Heat from friction with barrel walls, and also external heat source. The polymer granules are melted and compacted, and the screw movement also mixes and homogenises the melt. The molten polymer leaves the extruder through a shaped die

which defines the geometry of the product (e.g. sheet, film, pipe, rod, or more complex sections such as channels for constructing windows/doors).

**Pressures:** High (typically 100 MPa). **Temperature:** Above  $T_m$  for a crystalline polymer

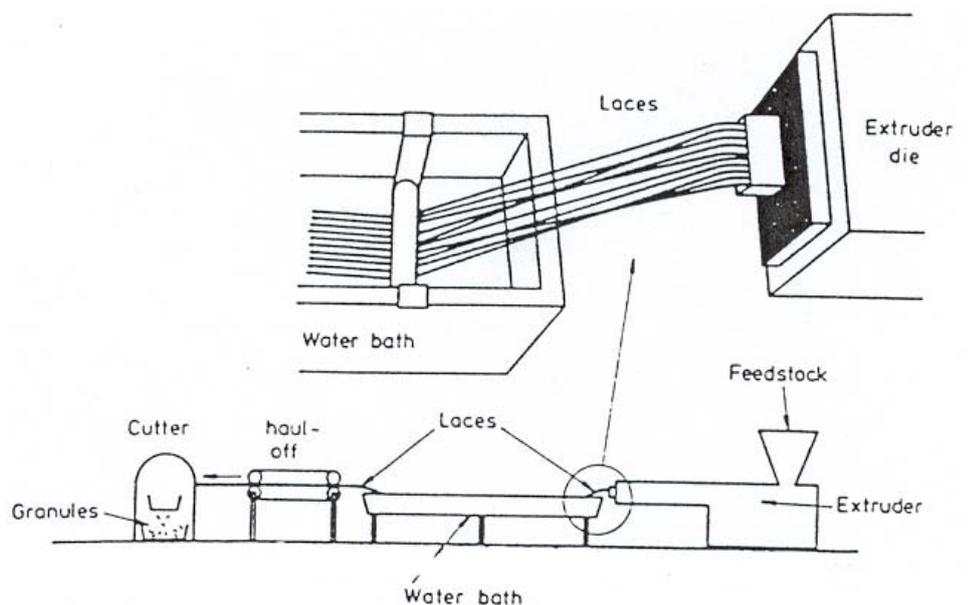
Two or more polymers can be extruded together (co-extrusion), so that the product has a multi-layer structure.

### Extrusion-based processes.

The following variants of the basic process give some idea of the range of possible product shapes.

#### a. Granules.

After the polymer is synthesised (usually from oil), it is passed on to processors in the form of granules. The polymer is extruded through multi-hole dies to form laces 3-6mm in diameter. The laces are cooled and chopped into regular granules.

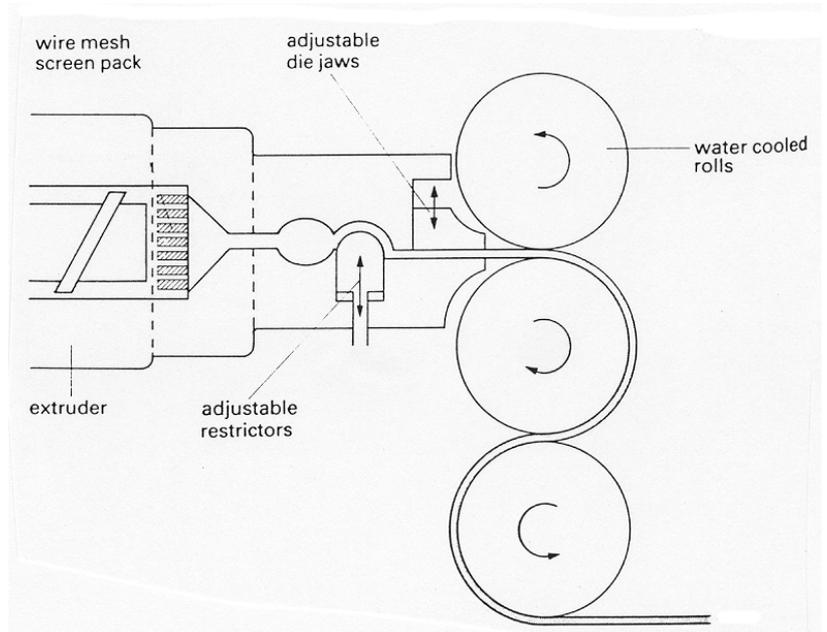


**b. Thick Film / Sheet.**

Several related processes for making the thicker grades of film, sheet (which may be corrugated) or multilayer films. Multilayer films are common for packaging, as the different properties of polymers can be combined.

Extrusion of one or more polymers through a long slit can be followed by quenching:

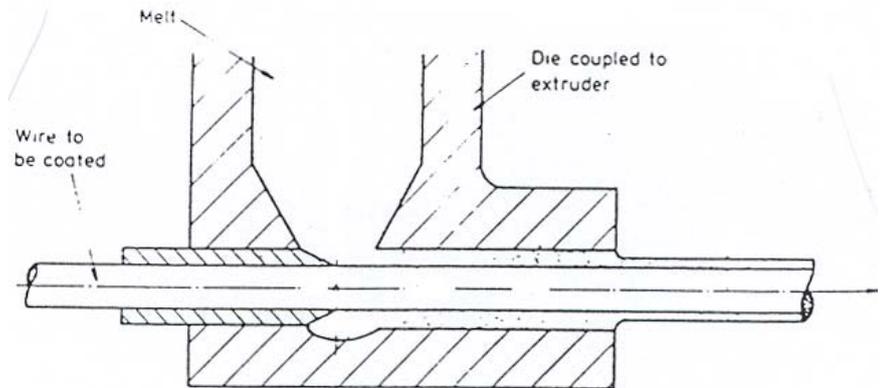
- With air jets or
- On to cooled metal rolls and the product may then be stacked (panels) or rolled (sheet). As air-cooled surfaces are rough, the polymer must be cooled in contact with a metal surface if the surface roughness is important. (Even so, smooth surfaces are not guaranteed, as the slower cooling rate of the interior results in compressive stresses in the surface layer which can give a wrinkled surface)



**c. Coating**

Fabric or paper can be coated with polymer (often LDPE).

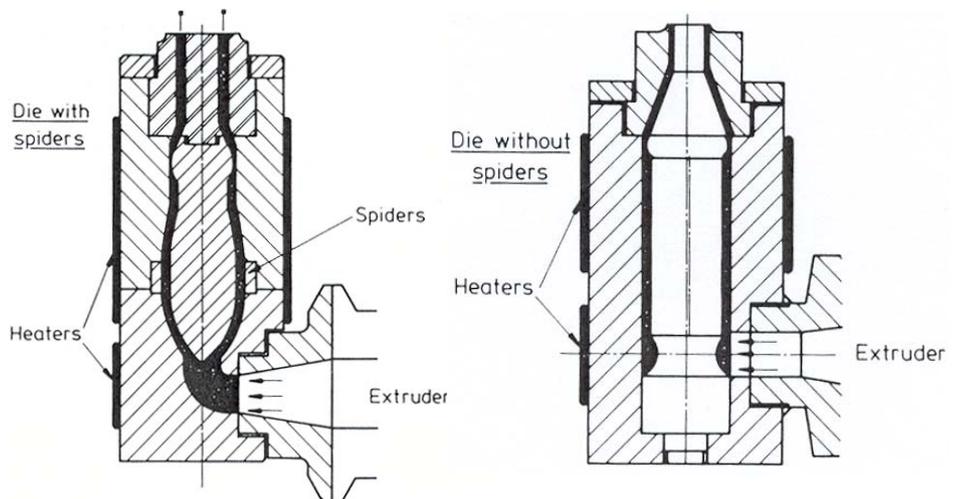
A high-volume use is wire or cable insulation (e.g. with PVC or nylon for electrical purposes).



**d. Pipes and hollow sections**

The melt flow is divided. The most common way is by a floating mandrel, held in place by a 'spider' of fine wires. The melt welds up after passing the wires, so there should be no damage line in the final article.

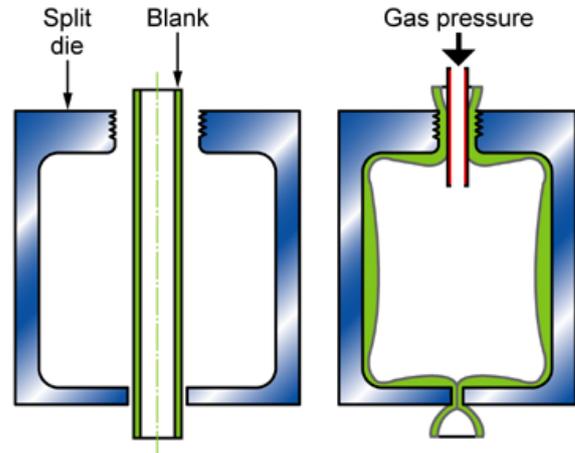
For simple sections, the die may be made with a solid central part, and the melt flows around it.



**e. Extrusion blow moulding**

Bottles can be made directly from the extruded polymer in a continuous process. Fast (cycle time ~10 s) and automated, avoids need for reheating (cf. stretch blow moulding).

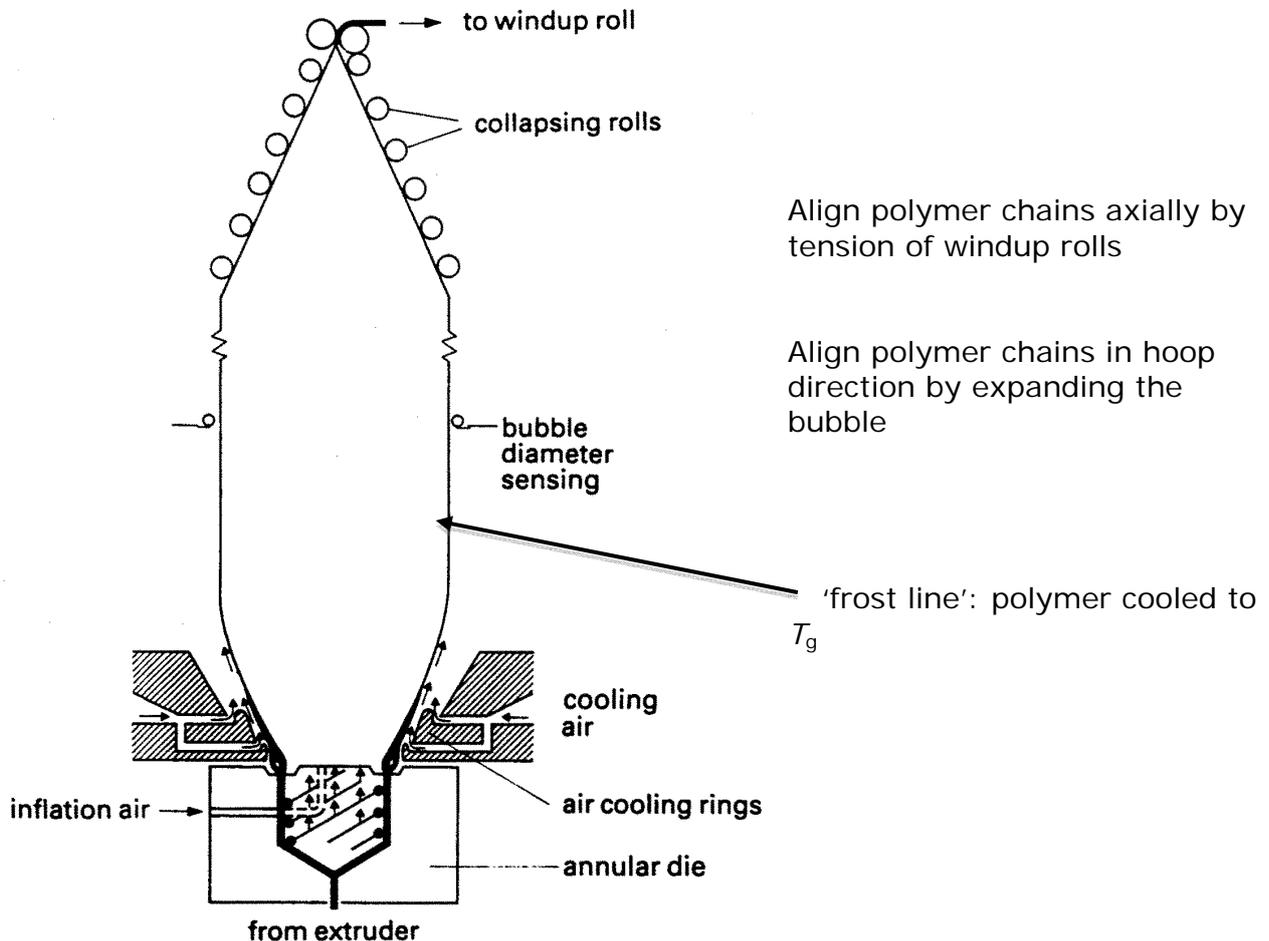
A tube of polymer is extruded vertically from an annular die. A mould is clamped around the tube while it is still hot, and the tube is inflated with compressed air until it fills the mould. After cooling it is removed from the mould and cut from the remaining tube. Widely used for containers.



**f. Film blowing.**

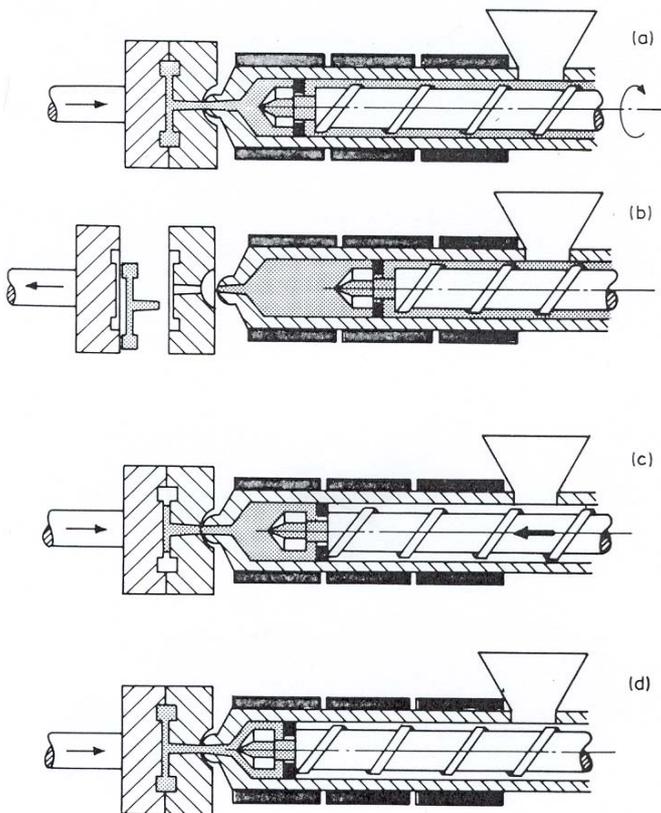
Most polymer film is made by blowing, which allows *biaxial alignment* of the polymer molecules in the film. Molten polymer is extruded through an annular die and inflated, providing circumferential hoop stresses and resulting in molecular alignment in this direction. Tensile stress is provided by pulling rolls, resulting in molecular alignment in this direction as well. The alignment increases the film strength, so it can be made thinner. Typically, a polymer film 1 mm thick extruded from the die is reduced to 0.1 - 0.2 mm, using a blow-up ratio (final bubble diameter/die diameter) of 3-5. The film is cooled by external air jets. Co-extrusion allows multilayer films to be produced (e.g. for food packaging).

The bubble is usually split and flattened onto a coiling drum, and the film is used for plastic bags or sheeting.



## 2.3. Injection moulding and related processes

### Injection moulding.



Very versatile process (can also incorporate inserts of metal, other polymers – ‘over-moulding’). Molten polymer is forced into a shaped metal mould at high speed and pressure. It cools and solidifies rapidly, and the mould is then opened to release the article. Very short cycle times can be achieved (~seconds – but determined by the cooling time).

The moulded items have some waste polymer in the form of *sprues* attached to them (remnants from the feeding system to get the polymer into the mould). These are often cut off immediately after the item is removed from the mould.

The operation generally uses a screw extruder to mix and melt the polymer, but the process differs from the continuous processes discussed above in a critical respect. The molten polymer accumulates in a chamber in front of the screw, and only once the chamber is full is the whole charge ejected into the mould cavity. This is achieved by the whole screw moving forwards, acting as a hydraulic ram. Once the polymer in the mould is solid, the screw can be drawn back so that the molten polymer can be collected again.

A variant use a separate ram to inject the polymer.

The process needs to be well-controlled to deliver high quality products.

#### Injection pressure:

The polymer shrinks as it cools and crystallizes. High pressures allow some compensation.

#### Component thickness:

Increased thickness reduces cooling rates, so increases shrinkage especially in semicrystalline polymers, as there is then more crystalline material which has a higher density.

#### Hold-on times:

Time that the die is under pressure. Longer time counterbalances shrinkage (as long as the polymer is still molten at gate).

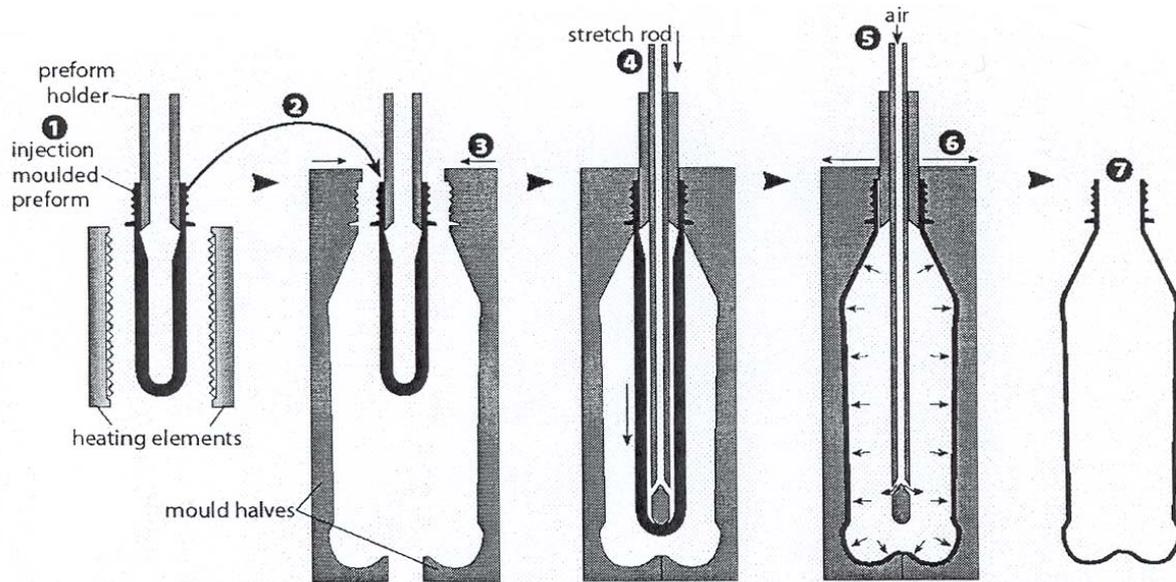
#### Mould temperature:

Increasing mould temperature reduces cooling rate, increases crystallisation. Implications for shrinkage.

### Stretch blow moulding

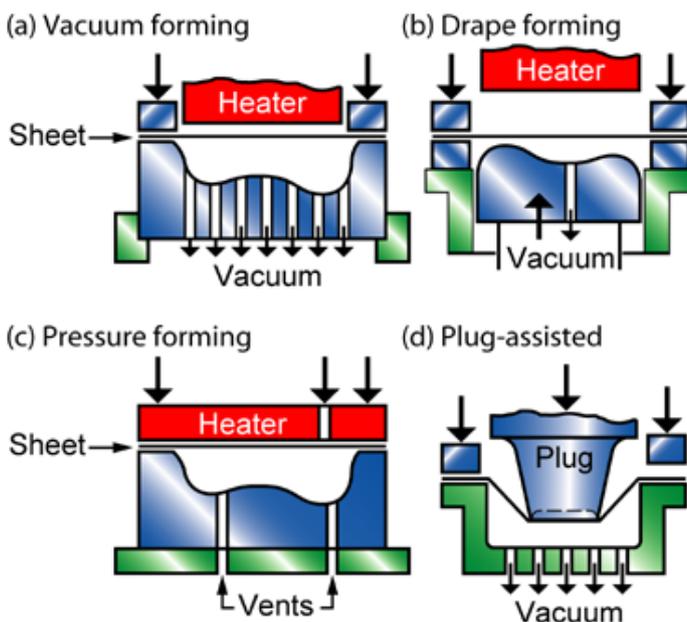
Used for containers – differs from extrusion blow moulding as the polymer is biaxially oriented and walls can be made thinner. An injection-moulded **pre-form** is heated and stretched longitudinally before also being inflated. Polymer chains are aligned in both the hoop and axial directions (ie in the plane of the wall) giving higher strength and stiffness in this plane. Process control is critical to optimize the properties.

**Example:** PET bottles for fizzy drinks: low permeability to carbon dioxide.



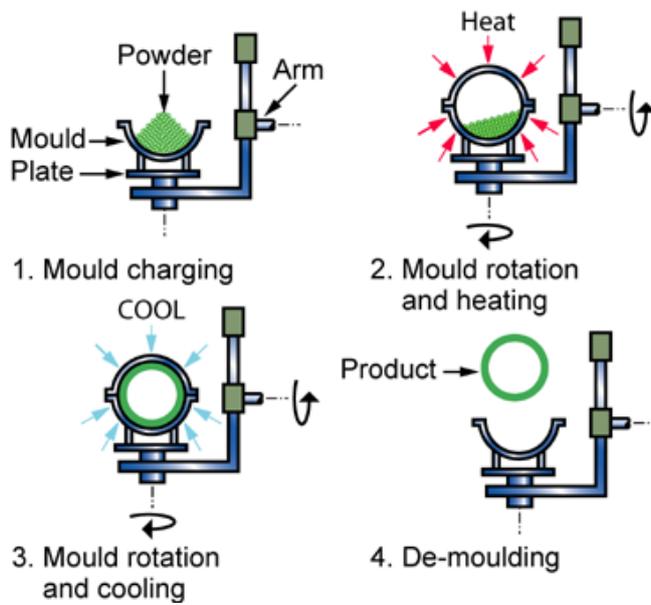
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| <p>1 An injection moulded preform is attached to a pin and softened by heating. The preform may be moulded at another site.</p> <p>2 The warm, soft preform is transferred to a mould, made from aluminium alloy.</p> | <p>3 The mould halves close around the preform.</p> <p>4 The preform is stretched downwards by a stretch rod.</p> <p>5 Air is then blown into the preform, pushing it firmly against the walls of the mould.</p> | <p>6 When cooled, the mould halves open.</p> <p>7 The moulded bottle is ejected. The cycle continues.</p> |
|---|--|---|

### 2.4. Thermoforming.



Used for large thermoplastic parts in simple shapes: heated sheet deforms onto a mould. Various methods can be used to achieve this (vacuum, air pressure, moving die)

## 2.5. Rotational Moulding



Hollow mould is charged with thermoplastic granules, then heated and rotated. The granules adhere together to form the component (but do not fully melt).

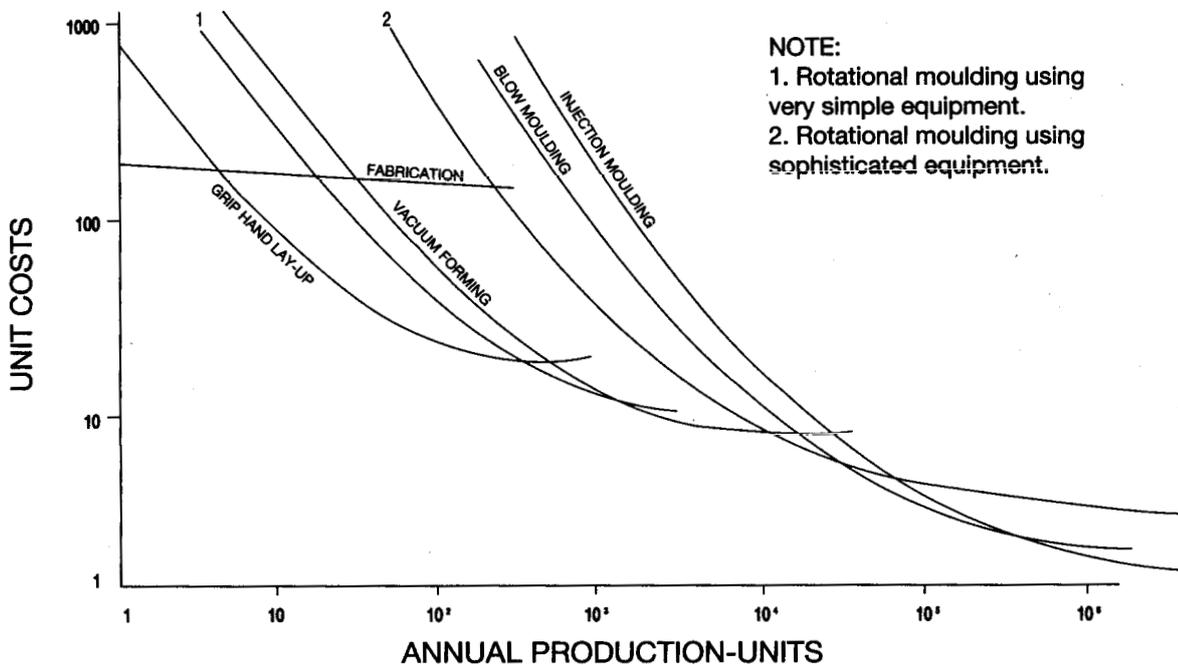
Typically used for PE or PP parts. Cheap: does not need expensive equipment; moulds made from aluminium sheet so easily made and customised; can be large. External heat provided by hot gas.

There is no molecular alignment. Product hollow, but with poor control of wall thickness.

Typical products: Traffic cones, tanks, canoes, pallets, toys.

## 2.6. Process selection

COMPARATIVE PRODUCTION COSTS FOR A 200g COMPONENT



### 3.1. Influence of polymer architecture on properties

<b>Molecular chain length</b>		
Average chain length; distribution range of length	Determined by how the polymer was made (e.g. what catalysts, temperature and pressure).	Longer chains give higher strength, higher softening temperatures, often higher crystallinity
<b>Molecular shape</b>		
Linear or branched chains?	Determined by how the polymer was made.	Linear chains show less entanglement and are more likely to crystallize
<b>Side groups on chain backbone</b>		
Nature and distribution of side groups attached to chain backbone	Nature determined by chemical formula. Distribution determined by how polymer was made.	Influences how easily chains are able to move past each other under stress. Large side groups inhibit crystallization giving an amorphous polymer
<b>Nature of bonds between polymer chains</b>		
Van der Waals bonds	Weak 'proximity bonds' which break and re-form easily around $T_G$ . Intrinsic to the polymer.	Number and nature determine glass transition temperature $T_G$ . Provide polymer rigidity below $T_G$
Entanglements	Friction between polymer chains.	Important for strength above $T_G$
Secondary bonds	Strong chemical bonds between chains, similar to those within the chains. Determined by nature of polymer and processing conditions.	Thermosets have many secondary bonds and therefore cannot melt, retaining stiffness when heated  Elastomers and rubbers have a few.  Thermoplastics have none (and thus melt when heated)

Because of variation in molecular weight, branching etc. the 'same polymer' from different manufacturers may well have different properties. Any particular polymer may have a range of physical properties ( $T_g$ , elastic modulus, strength, failure strain, toughness, transparency) which will also depend on processing history.

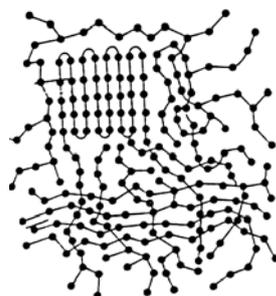
### 3.2. Effects of processing on properties

The two major ways in which processing affects the properties of thermoplastics are through *crystallinity* and *molecular alignment*.

**(a) Crystallinity** (Note that some polymers cannot crystallise and remain amorphous ) Crystalline regions have denser chain packing than amorphous material, with higher elastic modulus and tensile strength. Density can be used to indicate degree of crystallinity. Because of the geometry of chain folding (which normally requires amorphous regions between crystalline regions), the maximum amount of crystallinity does not normally exceed about 80%.

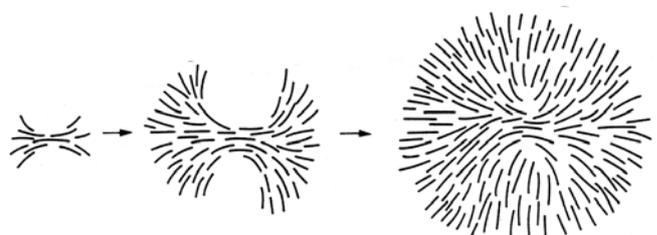
Crystals may be dispersed through the material, or may form regions with spherical symmetry (spherulites).

Lamellar crystals



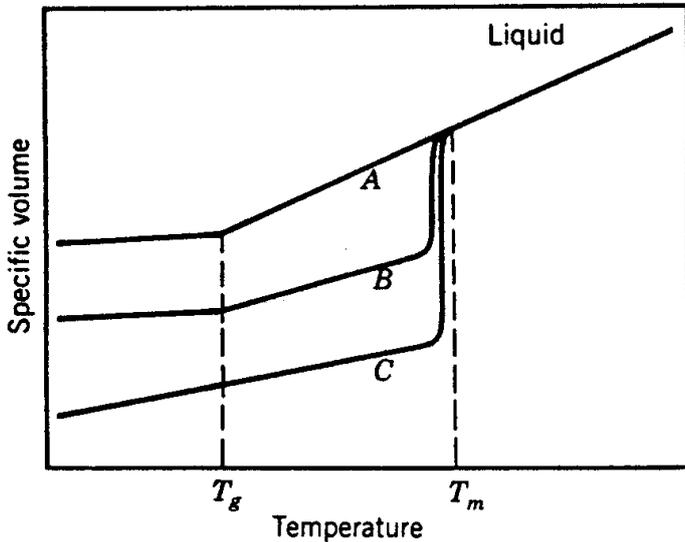
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Spherulites: crystalline regions growing from a central nucleation point



Crystallization causes significant volume reduction during solidification. Crystallization in polymers follows C-curves for extent of transformation in a similar way to phase changes in metals and other materials.

Volume / density curves for the same polymer with different cooling rates



A: Fast cooling: Fully amorphous (no crystallization)  
 B: Intermediate cooling rate: Partially crystalline  
 C: Slow cooling: "Fully" crystalline (as much crystallinity as possible in the system)

$T_m$  is the melting point of the crystalline phase

Glass transition temperature is  $T_g$ . Below this the polymer chains are essentially immobile

During processing of thermoplastics, thick sections will generally cool more slowly than thin sections, and may therefore have a higher proportion of crystallinity. This leads to differential contraction within the component, and can cause shape distortion.

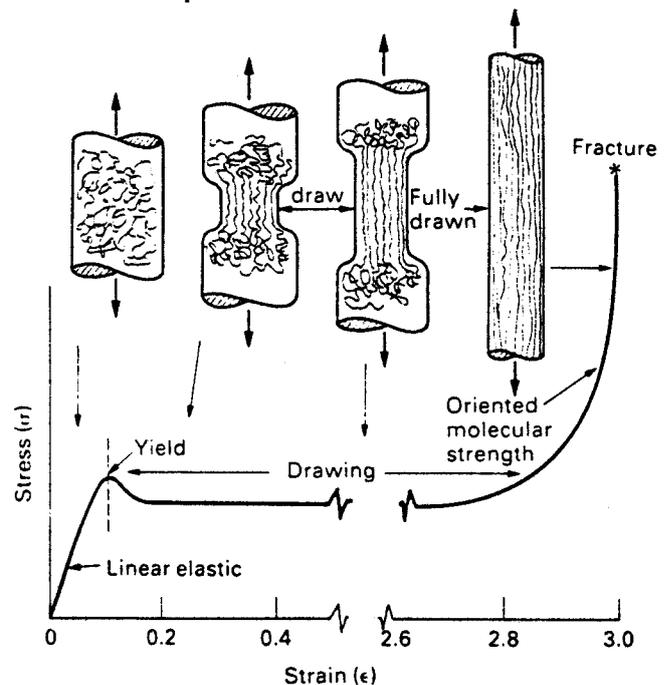
**(b) Chain alignment: by cold drawing of fibres or tapes**

Strength and elastic modulus increase enormously in the direction of chain alignment, but there is an equivalent deterioration in properties normal to this direction.

Chain alignment allows very strong fine threads of polymers to be created: the effect of **draw-strengthening**.

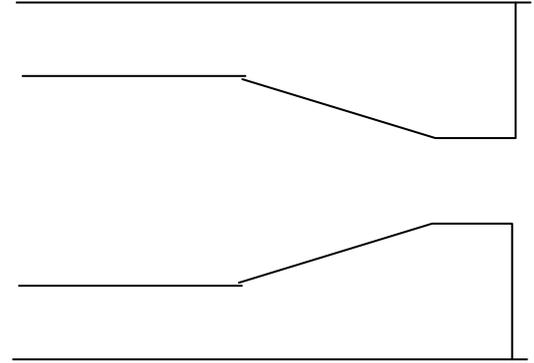
**Example:**

Nylon fibres can be made by melt spinning: the molten polymer is extruded through a fine nozzle and then pulled (with a draw ratio of about 4), and quenched to freeze the orientation of the molecules. The molecules are now reasonably well aligned along the fibre axis. The strength and modulus of this nylon fibre are about 10 times higher than for the bulk polymer.



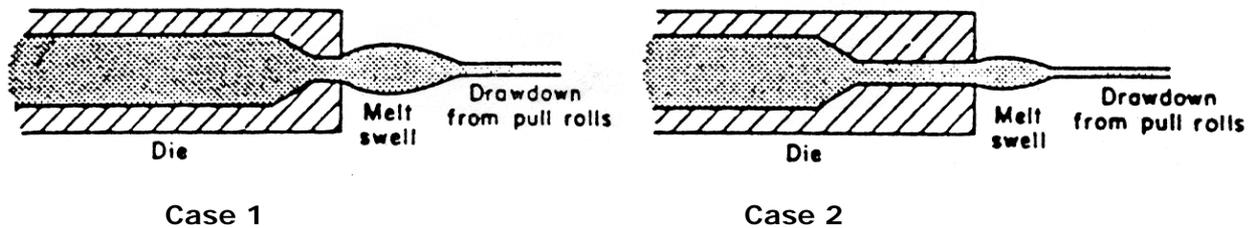
**(c) Chain alignment: during extrusion and injection moulding**

*Extensional flow* leading to *chain alignment* occurs when the polymer is subjected to drag from the walls. This typically occurs close to the walls in channel flow, and is also associated with extrusion of the polymer through a die. Polymer molecules become aligned parallel to the flow direction:



Molecules are naturally randomly coiled (highest entropy state). Due to friction on the wall of the die they become aligned parallel to the flow direction.

This can lead to change in shape as the extruded product emerges from the die: melt swell or post-extrusion swelling.



**Case 1:** Polymer expands as it leaves the die because of an elastic response as the compressive stresses encountered in the die are released. This causes some adiabatic heating, and the viscosity drops.

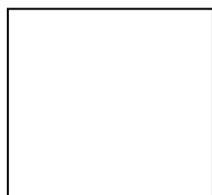
The polymer chains then coil up, giving expansion normal to the extrusion direction. This is melt swell. The product can be tensioned whilst still hot: using *draw down* to reduce melt swell.

**Case 2:** The die has a long 'land', and this reduces melt swell. The polymer molecules which became aligned as they entered the die now have time to coil up again (creep) as the polymer passes through the long die 'land'. Some elastic expansion still occurs as the polymer leaves the die, but melt swell is much reduced.

**Other remedies for melt swell are:**

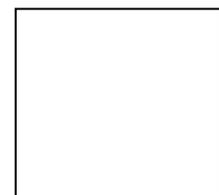
Rapidly cool the product : generate a 'frost line' (used for pipes)

Modify die shape to give required product shape:



Die shape

product shape



Die shape

product shape

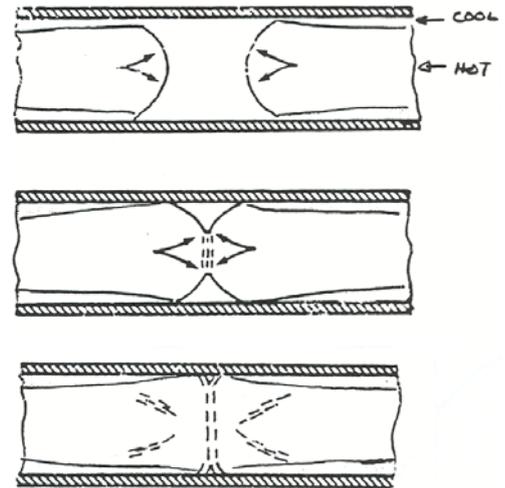
Not all polymer processing leads to chain alignment. *Shear flow* dominates in injection moulding; this does not lead to significant molecular alignment, and what there is becomes randomised rapidly as the chains coil up again.



### 3.3 Some processing defects

#### Weld lines

When two polymer streams meet (e.g. in injection moulding), lines of weakness can form. These are the result not only from incomplete fusion (as in metals – ‘cold shuts’) but also from molecular alignment variations. Weld lines have low local density, strength and stiffness, and are susceptible to solvent-induced cracking.

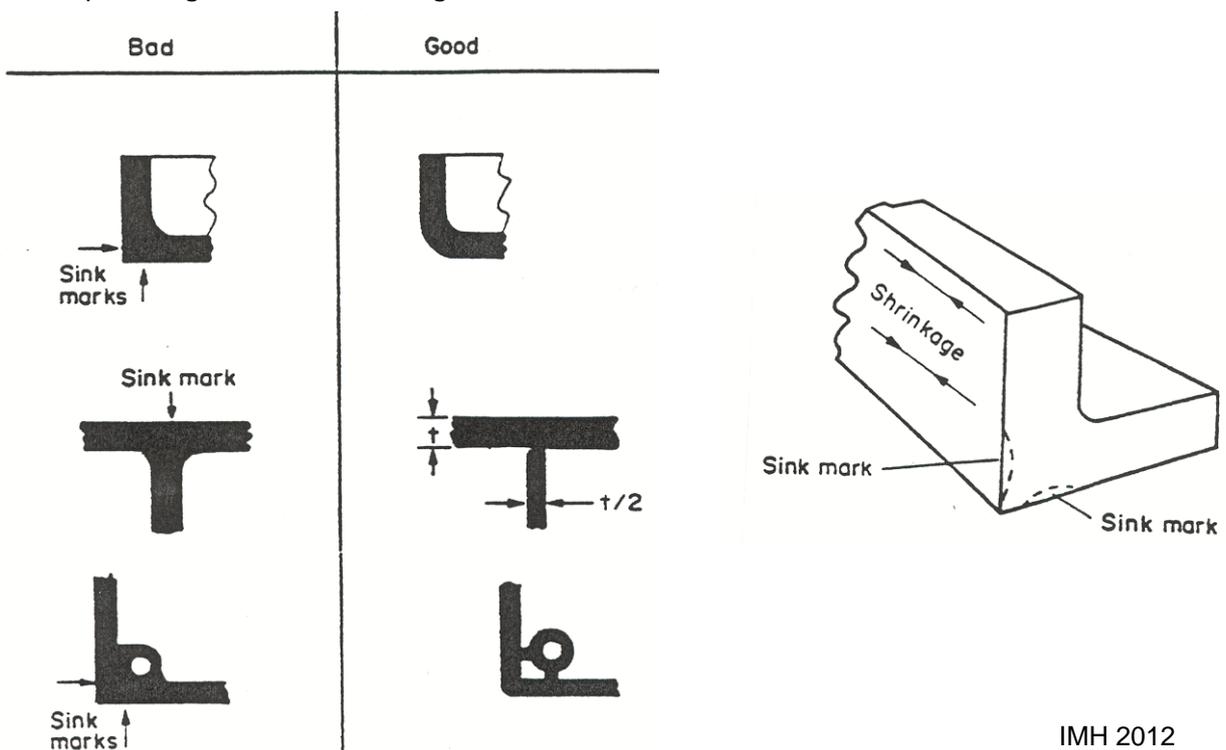


#### Sink marks at section variations

Injection mouldings often suffer from **sink marks** at section changes, or where ribs meet a structural member, caused by slower cooling at this point.

To avoid, keep ribs small and slender; avoid abrupt section changes and consider local cooling rates in design of parts and moulds.

Examples of good and bad design:



## Further information and sources

### Books:

**Ashby MF, Jones DRH.** *Engineering Materials 2*. Pergamon.

Excellent general introduction to polymers and polymer processing: chapters 21-24

**A. Brent Strong.** *Plastics - Materials and Processing*.

**Brydson JA.** *Plastics Materials*. Butterworth Heinemann.

Details of properties of individual polymers.

**Callister WD.** *Materials Science and Engineering*. John Wiley.

More detailed 'materials science' view of polymers.

**Crawford RJ.** *Plastics Engineering*. Detailed information on processes.

**Edwards L, Endean M.** *Manufacturing with Materials*. Open University/Butterworth-Heinemann Ltd. Lots of information about materials processing.

### Software and web:

#### CES (Process Universe)

[www.bpf.co.uk](http://www.bpf.co.uk) Polymer properties and uses; helpful animations of processes

[www.matweb.com](http://www.matweb.com) Very useful for all materials. Useful links to other specialist sites