Mustansiriyah University
Materials Engineering Department

POLYMER PROCESSING

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POLYMER PROCESSING

At the end of this lecture, you should be able to:

- Explain what is meant by polymer processing
- Understand Plastic Processing Techniques
- Understand Fibre Processing Techniques
- Understand Elastomer Processing Techniques
- List polymer additives
- Select the appropriate processing methods

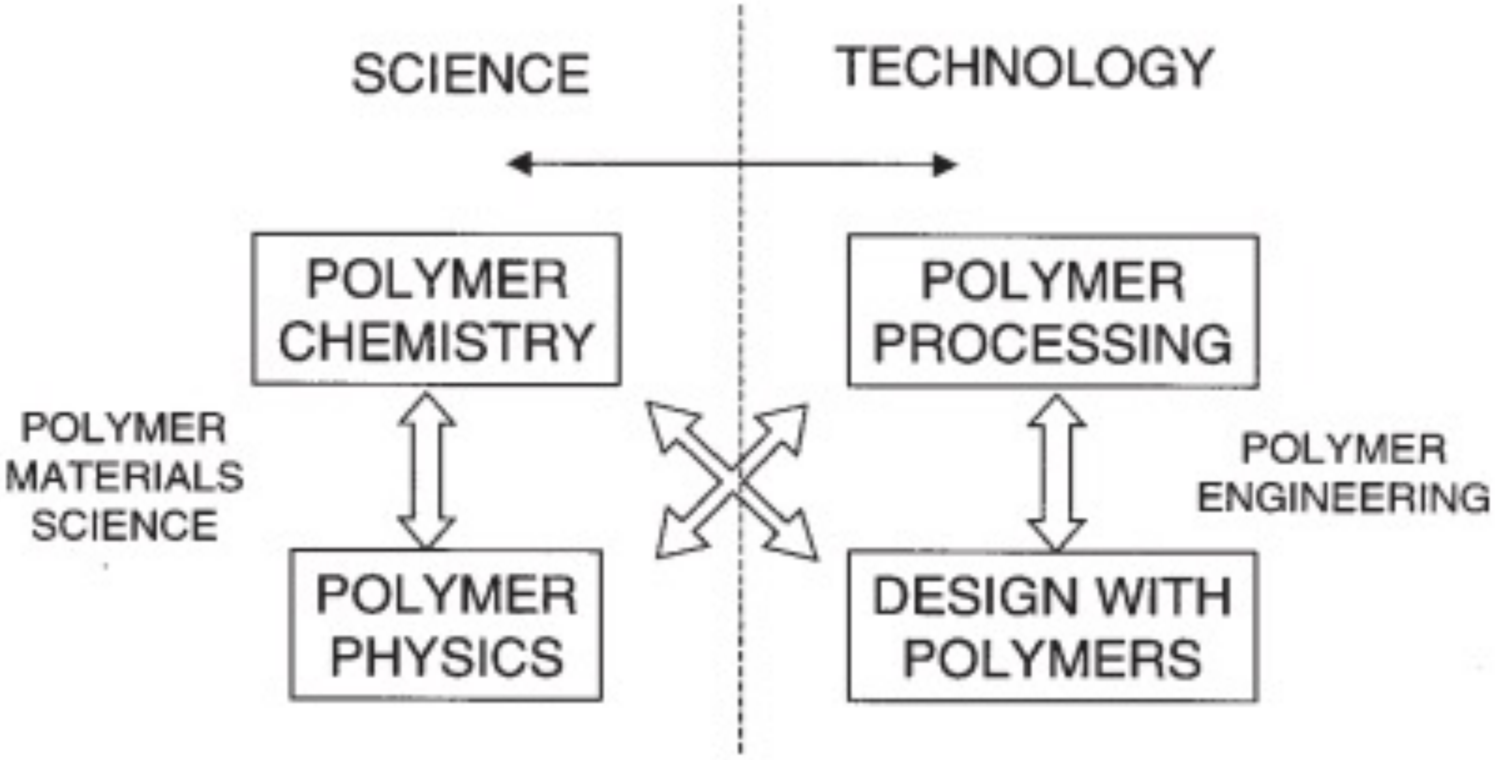


Fig. 1. Areas of interest in Polymer Science and Technology.

- **Polymer processing:** it is an operation in which solid or liquid polymers are converted to finished products.

- **Polymer processing consists of several steps:**

1) **Pre-shaping operations involve all or some of the following individual operations:**
    - Handling of particulate solids (particle packing, agglomeration, gravitational flow, compaction, and others);
    - Melting or heat softening;
    - Pressurization and pumping of the polymer melt;
    - Mixing for melt homogenization or dispersion of additives;
    - Devolatilization and stripping of residual monomers, solvents, contaminants, and moisture

The common goal of the above operations is to deliver thermoplastics or crosslinkable thermosets in a deformable fluid state that will allow them to be shaped by a die or mold; thereafter, they can be solidified by cooling below Tg or Tm (thermoplastics) or by a chemical reaction (thermosets).

2**) Shaping operations** during which structuring occurs (morphology development and molecular orientation that modify and improve physical and mechanical properties). Principal shaping methods include **die forming**, **molding**, **casting**, **calendaring**, and **coating**.

3) **Post-shaping operations**, such as decorating, bonding, sealing, welding, dyeing, printing, and metallizing.

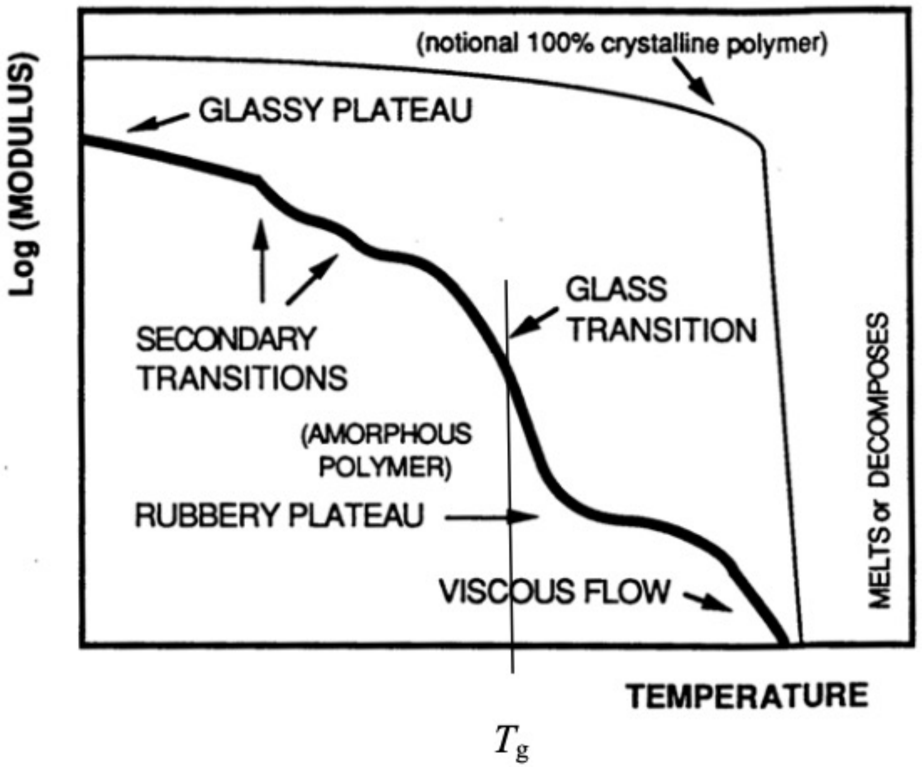
Most engineering polymers (>90% of market) are thermoplastics (i.e. can be melted and resolidify without damage, do not contain permanent cross-links between chains)
Thermoplastics have:

- long-chain molecules – typically of 103 – 105 monomer (repeat) units
- strongly bonded (covalent) backbones
- weak inter-chain bonds (van der Waals or hydrogen bonds)

For **thermoplastics, extrusion** is the most popular with approximately 50% of all the commodity thermoplastics being used in extrusion process equipment to produce profiles, pipe and tubing, films, sheets, wires, and cables.

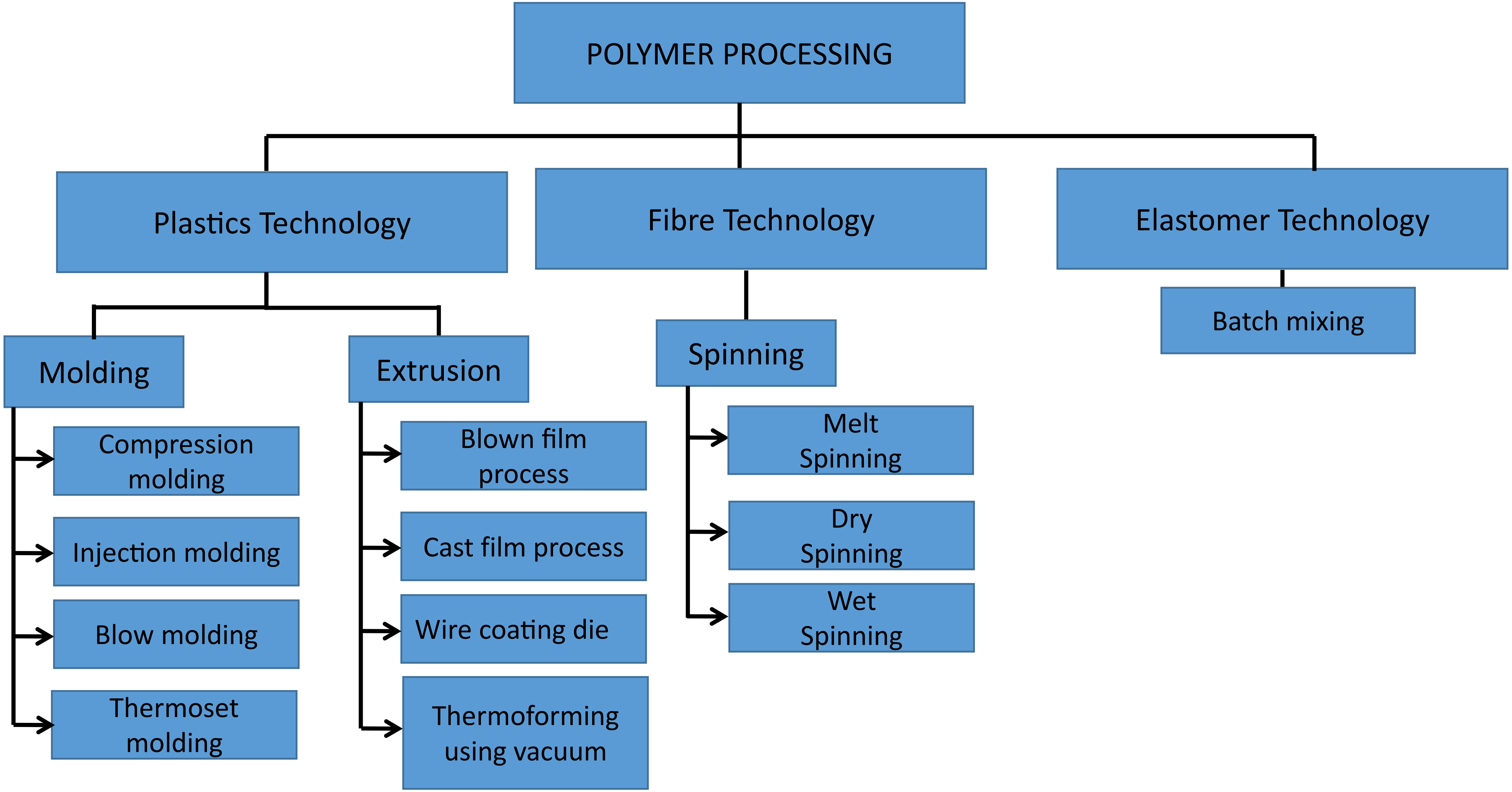
Injection molding follows as the next most popular processing method, accounting for about 15% of all the commodity thermoplastics processed. Other common methods include blow molding, Compression molding, thermoforming, and calendaring.

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



The methods of polymer processing can be classified according polymer end-use as:

- Plastics technology
- Fibre technology
- Elastomer technology



- POLYMER PROCESSING
  - Plastics Technology
    - Molding
      - Compression molding
      - Injection molding
      - Blow molding
      - Thermoset molding
    - Extrusion
      - Blown film process
      - Cast film process
      - Wire coating die
      - Thermoforming using vacuum
  - Fibre Technology
    - Spinning
      - Melt Spinning
      - Dry Spinning
      - Wet Spinning
  - Elastomer Technology
    - Batch mixing

Plastics Technology

The most important polymer processing are **molding and extrusion processes** which involve the following sequence of steps:

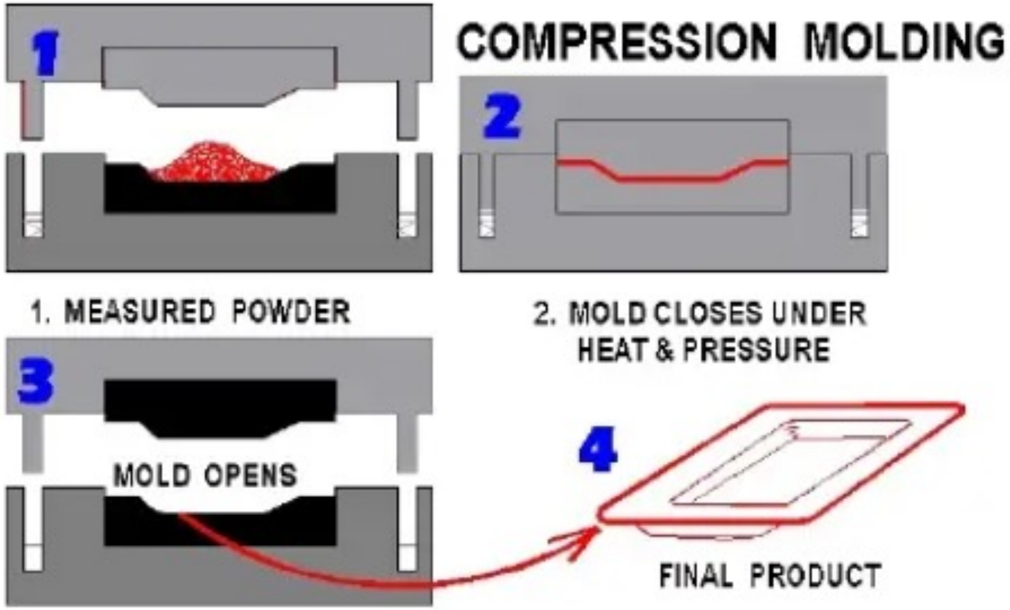
- Heating and melting the polymer
- Pumping the polymer to the shaping unit
- Forming the melt into the required shape and dimensions
- Cooling and solidification

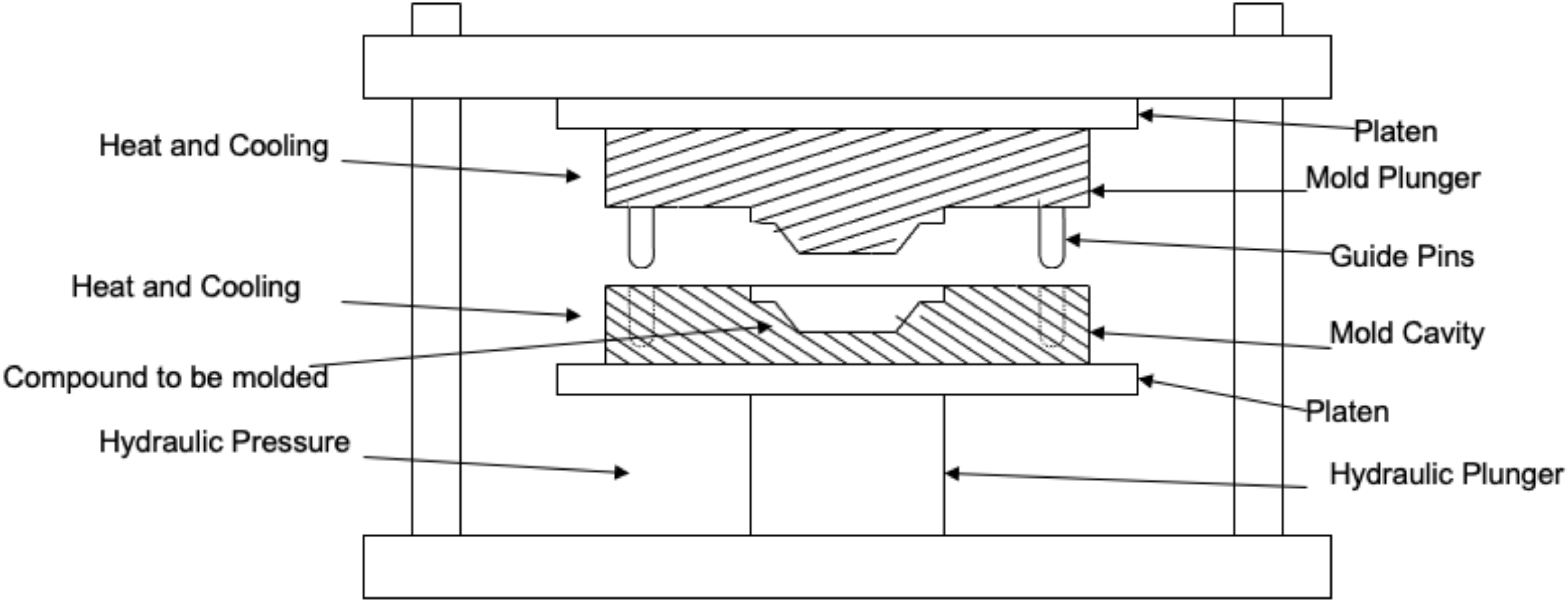
Molding

- The molding process starts by the forcing of divided plastic by the application of heat and pressure to flow, fill, and conform to the shape of a cavity (mold).
- Thermoplastic materials have to be cooled below T_m or T_g before being removed from the mold.
- Thermoset materials and rubbers have to be heated long enough for some chemical reaction to occur that brings about a stable, network structure.
- Although some thermosets are cooled before ejection from the mold, most can be ejected hot.

Compression Molding

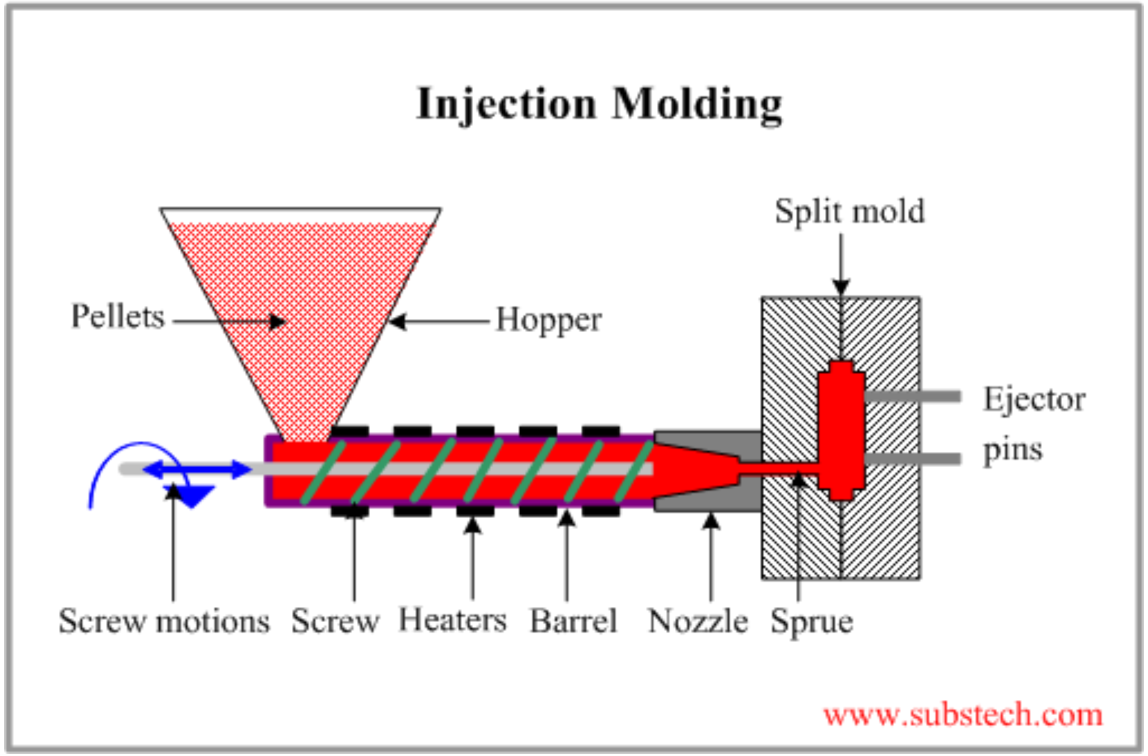
- In compression molding, the preform (pre-weighed) amount of polymer is put between stationary (heated mold cavity) and movable members of mold and closing the mold.
- Heat and pressure cause the material to liquefy and flow into the voids in the mold where it chemically reacts and hardens into the final shape.
- For a typical compression molding, the temperature are near 150℃ and pressure of 1000-3000 psi.
- The material is then allowed to cure and ejected from the mold.
- Parts made in this way would have sprues and runners which must be trimmed.




Heat and Cooling
Heat and Cooling
Compound to be molded
Hydraulic Pressure
Platen
Mold Plunger
Guide Pins
Mold Cavity
Platen
Hydraulic Plunger

Thermoplastic Injection Molding

In *injection molding*, polymer granules are compressed by a ram or screw, heated until molten and squirted into a cold, split mold under pressure. The molded polymer is cooled below T_G, the mold opens and the product is ejected. Excess polymer is injected to compensate for contraction in the mold. The molecules are oriented parallel to the flow direction during injection, giving useful strengthening, but properties that are ***anisotropic***.



The process gives high-precision moldings, because the polymer cools with the pressure still on but **is slow (the cycle time is between 1 and 5 min)**, and **the molds are expensive**. Typically, molding temperatures for thermoplastics are between **150 and 350 °C** (1.3 and 1.6 T_G) and **the pressures needed to give good detail are high—typically 30–120 MN m^{-2}**.

Design Considerations

- Design for gating and feed system for the die is crucial to ensure complete die fill. It is important to design the molding so that solidification does not prevent complete mold filling. The design and location of the gates for entry of polymer is a crucial design details. For large part more than one gate may be required for proper flow of material.

- Mold must be designed in such a way that the solid part can be ejected without distortion. By considering proper orientation at the beginning, in may be possible to avoid expensive mold cost. If possible, design the part so that it can be ejected in the direction of mold closure.

- To minimize the shrinkage, fillers like glass fiber, wood flour, are added during molding. With some part geometries, post mold shrinkage can lead to generation of high residual stress.

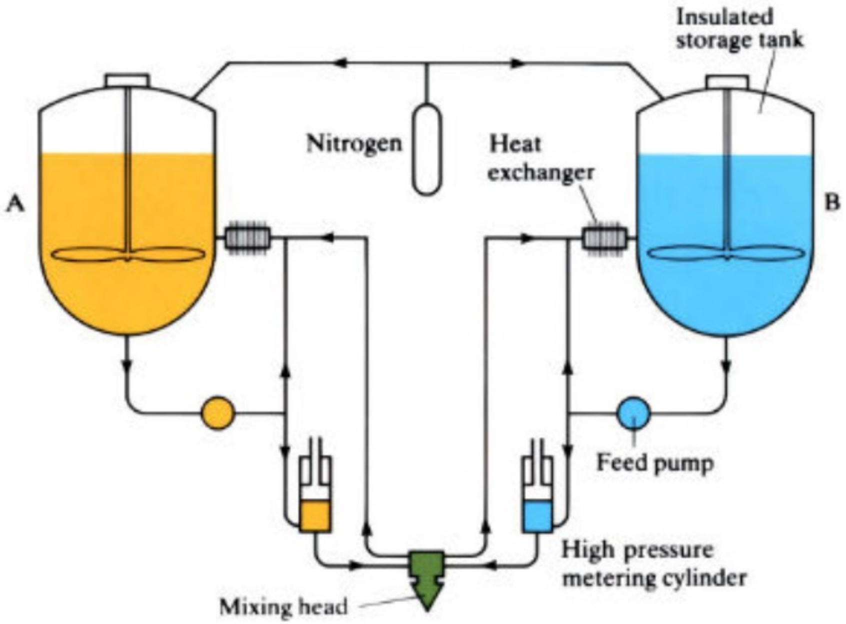
Thermoset Injection Molding

Most the forementioned engineering processes are for thermoplastics. For thermoset polymer, the modeling process can be achieved as follows:

- The polymer are heated just enough to make them fluid but not to initiate cure.
- Molds are usually heated, and this plus the heating generated as the resin is injected into the mold raise its temperature enough to initiate cure.
- The part may be removed from the mold when it is form stable but before the cure is completed.
- Stored heat in the part allows the cure to be completed in a minute, before the part can cool.

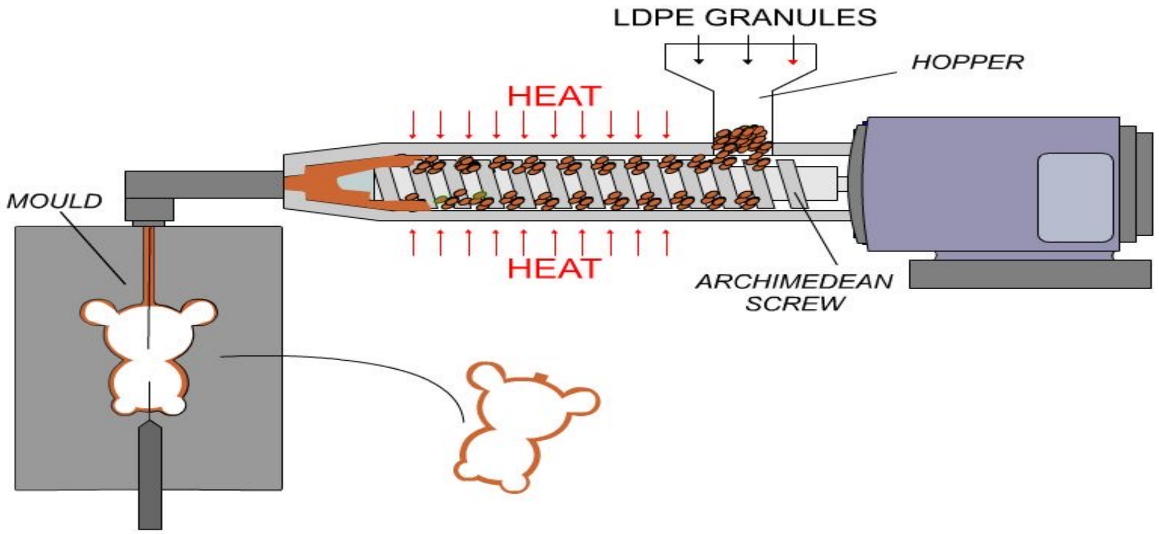
Reaction Injection Molding (RIM) for Thermoset Polymers

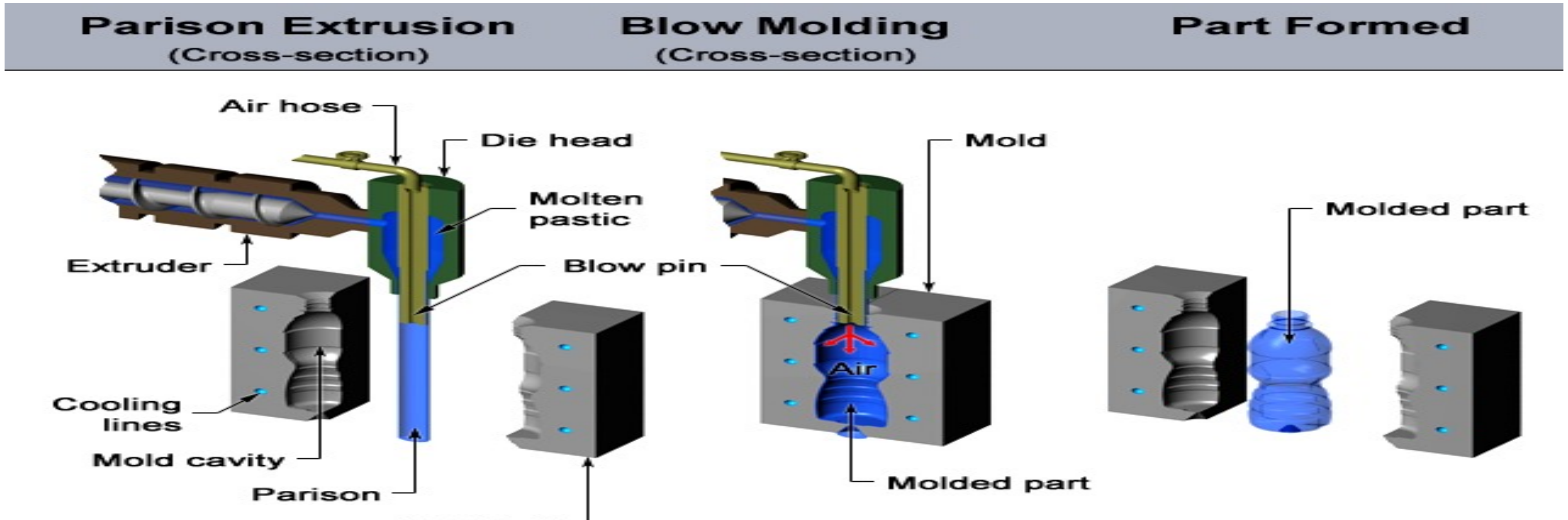
In reaction injection molding, two types of monomers are mixed together before being injected into a mold, where they polymerise to form the plastic component. This method is usually used to form polyurethane parts.



Blow Molding

- Using this manufacturing process **hollow parts** are made like **bottle or sphere** etc.
- **Air is blown** (20 – 40 Mpa) into a thin walled plastic cylinder called the **parison**. The parison is formed by melted plastic material being pushed through an extruder.
- When the parison reaches **a certain length**, the two halves of the mould close around the **parison sealing** it at the bottom.
- Compressed air is then used to inflate the parison to form the **shape of the cavity** inside the mould.





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Extrusion

Extrusion is one of the few continuous plastic processes . Extrusion is similar to injection molding can be defined as the act of shaping a material by forcing it through a die. It is a Polymer conversion operation.

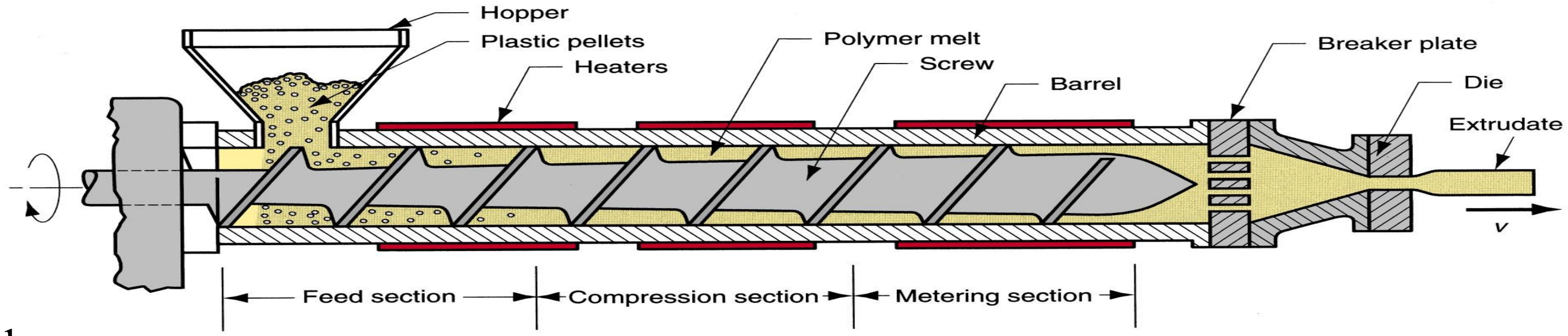
Principle:

- It comprises of forcing of a plastic material through an die by means of pressure.
- The chief concern with extrusion of polymers is the die swell and the orientation.
- In die swell, the extrudate swells to a size greater than the die from which it just exited. Thus the design must compensate for the swell.
- Polymer molecules become highly oriented in one or two directions as a result of the strongly oriented flow inherent in the extrusion process.
- Control of orientation can improve the property of the material.

Applications

- For compounding plastics
- Production of tubes ,pipes ,sheets ,film , wire coating and other continuous profiles.
- It is generally used in case of thermoplastic polymers and some thermosets too.
- Commonly used polymers are PE, PP, PS, PVC, polyamide, polyester.

Extrusion is divided into several sections:



Feed Scetion

In this 1st zone, the polymer pellets are conveyed to the subsequent zone.

Main function is to preheat the polymer.

Here the screw depth is constant.

Compression Section

Here the screw depth increases.

It repels the air gap between the granules.

Heat transfer from the barrel wall is improved.

Density change is accommodated.

Metering Section

Here screw depth is constant.

It homogenizes the melt and supply it to the die.

Die zone

The final zone to shape the polymer melt.

It usually comprises of the perforated steel plate called ***breaker plate and a sieve pack.***

It sieves out the extraneous materials(foreign particles).

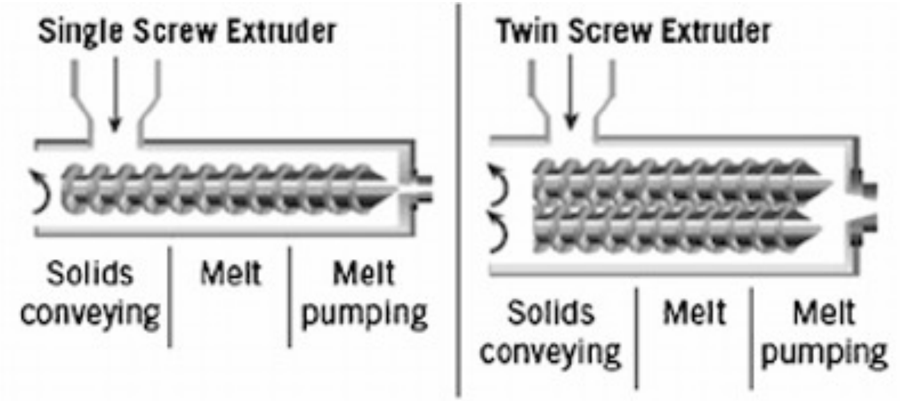
It removes the turning memory from the polymer melt.

It allows head pressure to develop by providing a resistance for pumping action of metering zone.

Extruders are basically helical screw pumps that convert solid polymer material into melt , which is then delivered to the die.

TYPES:

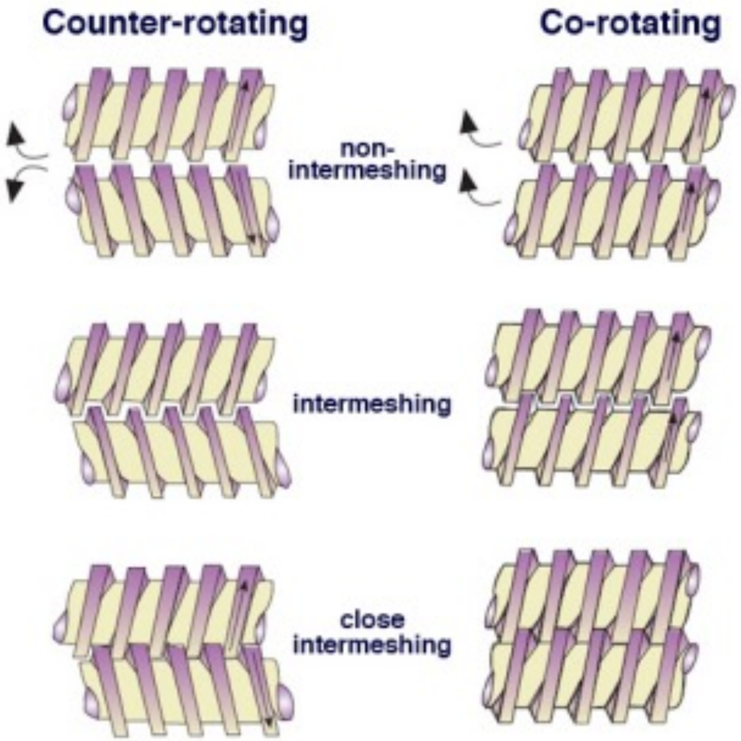
- Single screw extruder
- Twin screw extruder



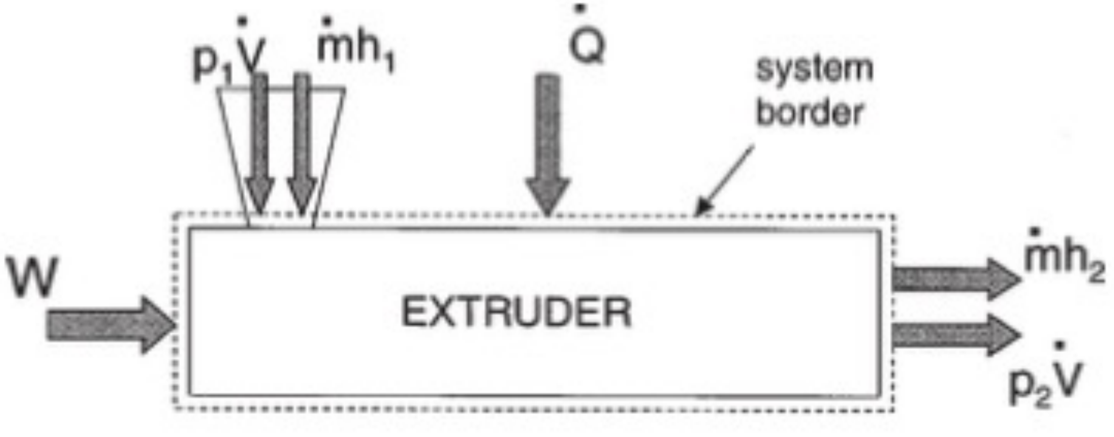
What happens inside a Single screw extruder ?

- Raw materials in the form of thermoplastic pellets, granules, or powder, placed into a hopper and fed into extruder barrel.
- The barrel is equipped with a screw that blends the pellets and conveys them down the barrel
- Heaters around the extruder's barrels heats the pellets and liquefies them

Types of Twin screw extruder



ENERGY ANALYSIS IN THE EXTRUSION OF PLASTICS

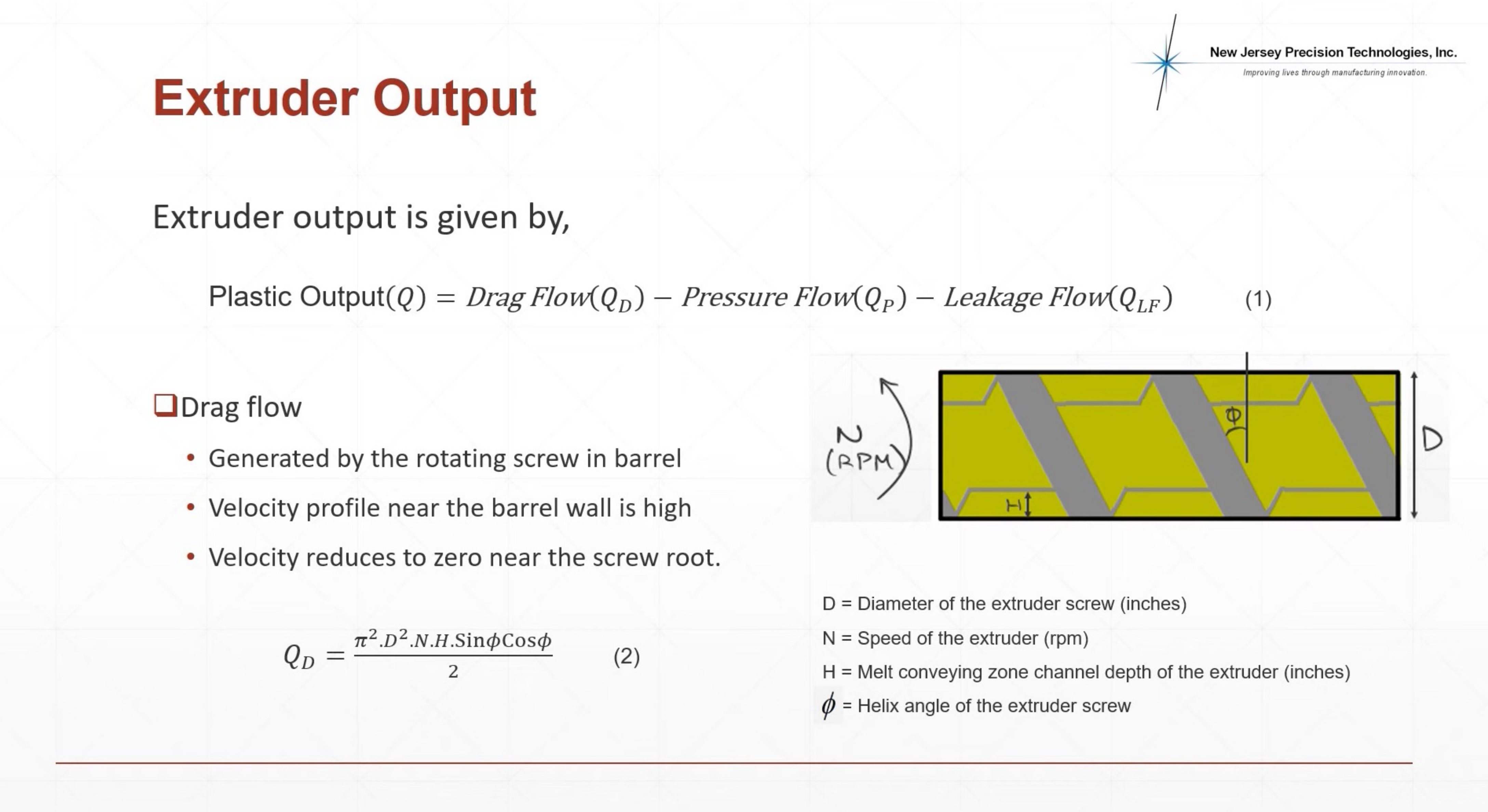


W : average technical power
$\dot{Q}$: net heat flow
$\dot{m}$: mass flow rate

$\dot{V}$: volume flow rate
h : enthalpy
p : pressure
V **: velocity**

$$\frac{dE_{CV}}{dt} = \dot{Q} - \dot{W}_{CV} + \dot{m}_1\left(h_1 + \frac{V_1^{\,2}}{2} + gz_1\right) - \dot{m}_2\left(h_2 + \frac{V_2^{\,2}}{2} + gz_2\right)$$

FLOW ANALYSIS IN THE EXTRUDER



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Extruder Output

Extruder output is given by,

$$\text{Plastic Output}(Q) = \textit{Drag Flow}(Q_D) - \textit{Pressure Flow}(Q_P) - \textit{Leakage Flow}(Q_{LF}) \qquad (1)$$

- Drag flow
  - Generated by the rotating screw in barrel
  - Velocity profile near the barrel wall is high
  - Velocity reduces to zero near the screw root.

$$Q_D = \frac{\pi^2 . D^2 . N . H . \mathrm{Sin}\phi \mathrm{Cos}\phi}{2} \qquad (2)$$

D = Diameter of the extruder screw (inches)
N = Speed of the extruder (rpm)
H = Melt conveying zone channel depth of the extruder (inches)
ϕ = Helix angle of the extruder screw

Extruder Output

❑Pressure flow

- Due to the pressure that exists before the die packing.

Velocity flow profile of pressure flow

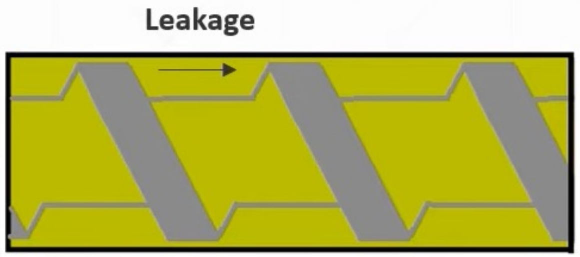
$$Q_P = \frac{\pi.D.H^3.\text{Sin}^2\phi.dP}{12.\eta.dL} \qquad (3)$$

P = Back pressure inside the extruder (Pa)

η = Viscosity of the polymer (Pa s)

❑Leakage flow

- Flow of polymer over the screw flight.
- Occurs when the clearance between the screw flight and barrel is high.
- Generally happens when the screw is worn out and thus leads to leakage.
- Negligible in most cases.



Leakage flow due to clearance

Extruder Output

Extruder output can be derived as, (substituting eqn. 2 and 3 into 1)

$$\text{Plastic Output}(Q) = \mathit{Drag\ Flow}(Q_D) - \mathit{Pressure\ Flow}(Q_P) - \mathit{Leakage\ Flow}(Q_{LF})$$

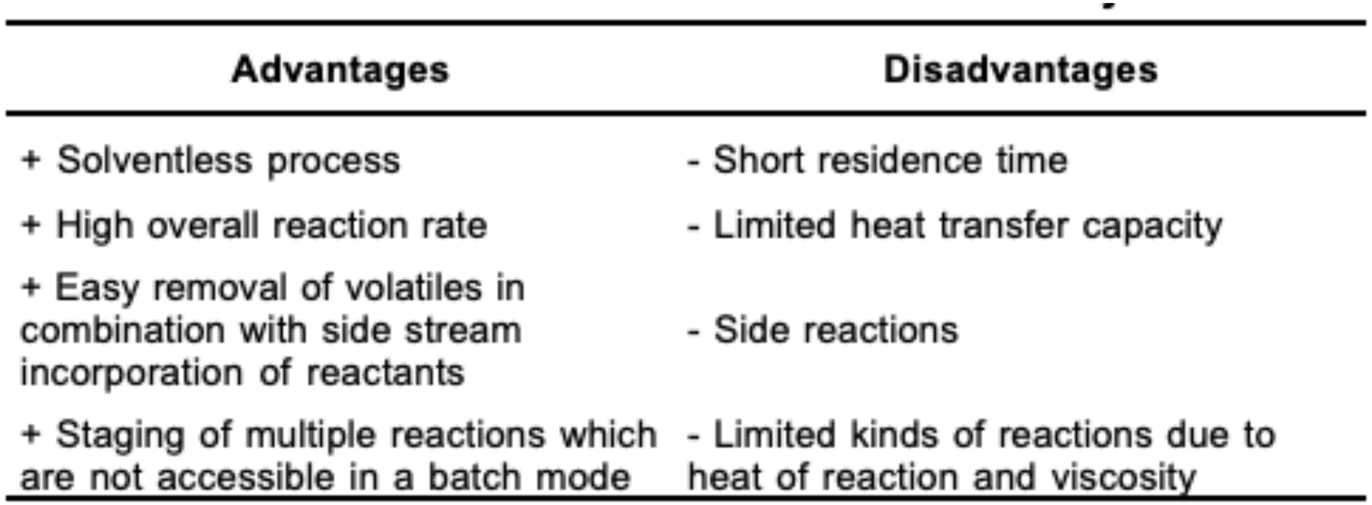
$$Q = \frac{\pi^2.D^2.N.H.\mathrm{Sin}\phi\mathrm{Cos}\phi}{2} - \frac{\pi.D.H^3.\mathrm{Sin}^2\phi.P}{12.\eta.L} - 0 \qquad (4)$$

- Leakage flow is assumed to be neglected as sufficient accuracy is already achieved.
- This flow rate is the throughput through the extruder.
- Can be derived into two cases,
  - ❖ In case there is no back pressure which means P = 0, $Q_{\max} = \frac{\pi^2.D^2.N.H.\mathrm{Sin}\phi\mathrm{Cos}\phi}{2}$ (5)
  - ❖ The maximum pressure at the extruder end which means Q = 0, $P_{\max} = \frac{6.\pi.D.N.L.\eta}{H^2.\tan\phi}$ (6)

Reactive Extrusion for Thermoset Polymers

Lately solventless processes have gained significant interest due to environmental and economical concerns. Therefore the use of extruders as chemical reactors and reactive blenders or compounders, commonly called reactive extrusion (REX), has proven to be an important technology in the polymer industry. So REX combines the classical extrusion process with the use of the extruder as chemical reactor. Basically the REX is used for two major processes: i) For the polymerization of monomers and the chemical modification of existing polymers, and ii) for the use as blender to reactively blend existing polymers sometimes in the presence of fillers and other additives.

Table 1: Pro and Cons of a reactive extrusion system



Advantages	Disadvantages
+ Solventless process	- Short residence time
+ High overall reaction rate	- Limited heat transfer capacity
+ Easy removal of volatiles in combination with side stream incorporation of reactants	- Side reactions
+ Staging of multiple reactions which are not accessible in a batch mode	- Limited kinds of reactions due to heat of reaction and viscosity

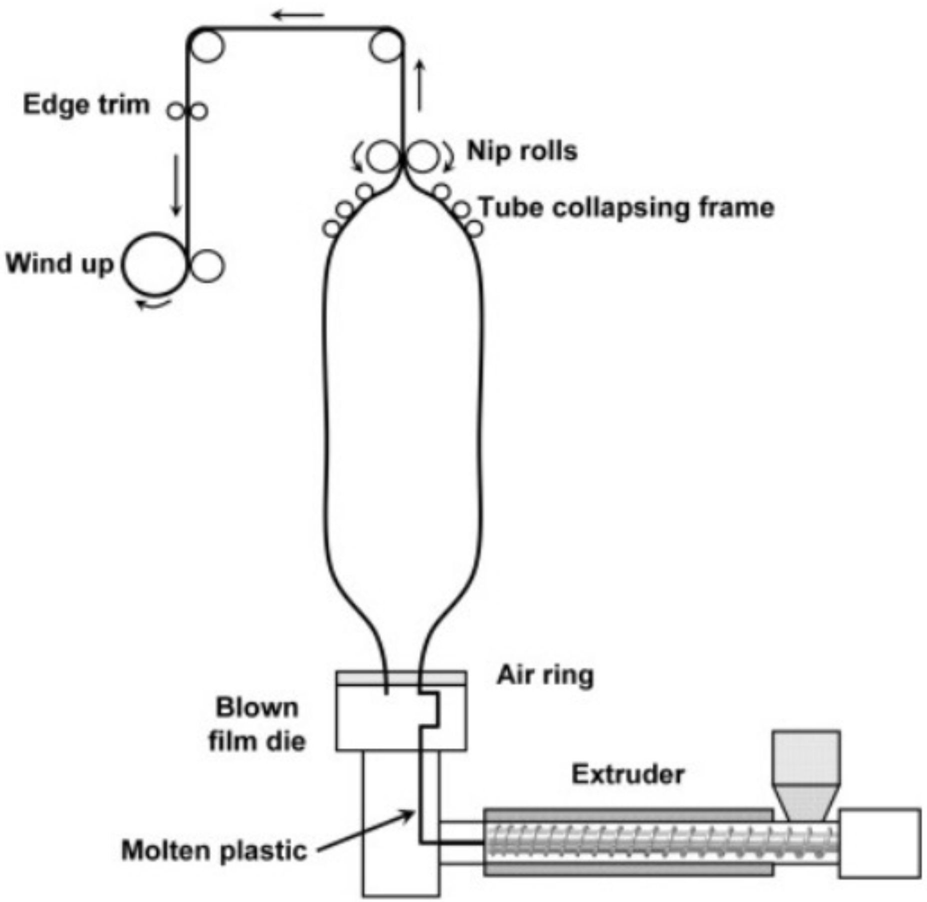
http://www.chemie.unibayreuth.de/mci/en/lehre/html/32556/P104_Extrusion_final_11_.pdf

Extrusion Process Types

- Blown film process (Film extrusion)
- Cast film Process
- Wire coating die
- Thermoforming by application of vacuum

Blow film process (Film extrusion)

- Blown film extrusion is the most important process for the production of thin plastic films . The Film is generally defined as a product thinner than 0.1 mm, while sheet is thicker than this.
- The molten polymer is extruded through an annular die. In most cases the blown film bubble is formed vertically upwards. The maximum bubble diameter is usually 1.2 – 4 times larger than the die diameter.
- The solidified film passes through a frame which pinches the top of the bubble and is taken up by rollers. Coextruded films with 3 – 8 layers (sometimes up to 11) are also produced by this process.

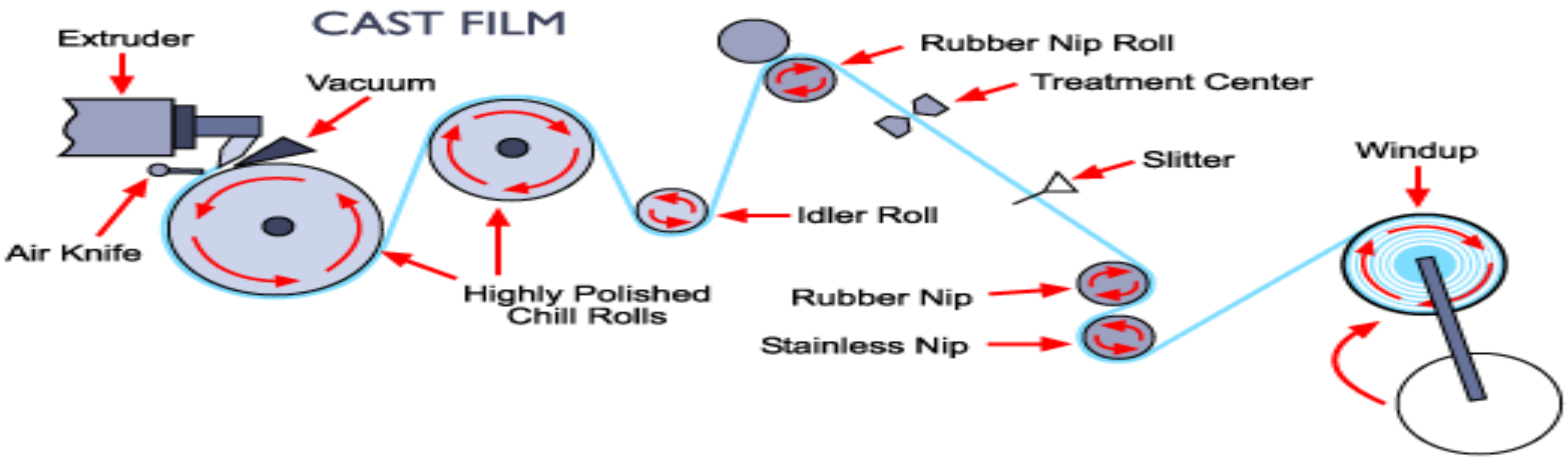


Cast film Process

Cast film and sheet extrusion involves extruding a polymer through a flat die with a wide opening (up to 10 m), onto a chilled steel roller or rollers which quench and solidify the molten material.

The cast film process is used for very tight tolerances of thin film, or for low viscosity resins. Most dies are of T slot design, which contain a manifold to spread the flowing polymer across the width of the die, followed downstream by alternating narrow and open slits to create the desired flow distribution and pressure drop.

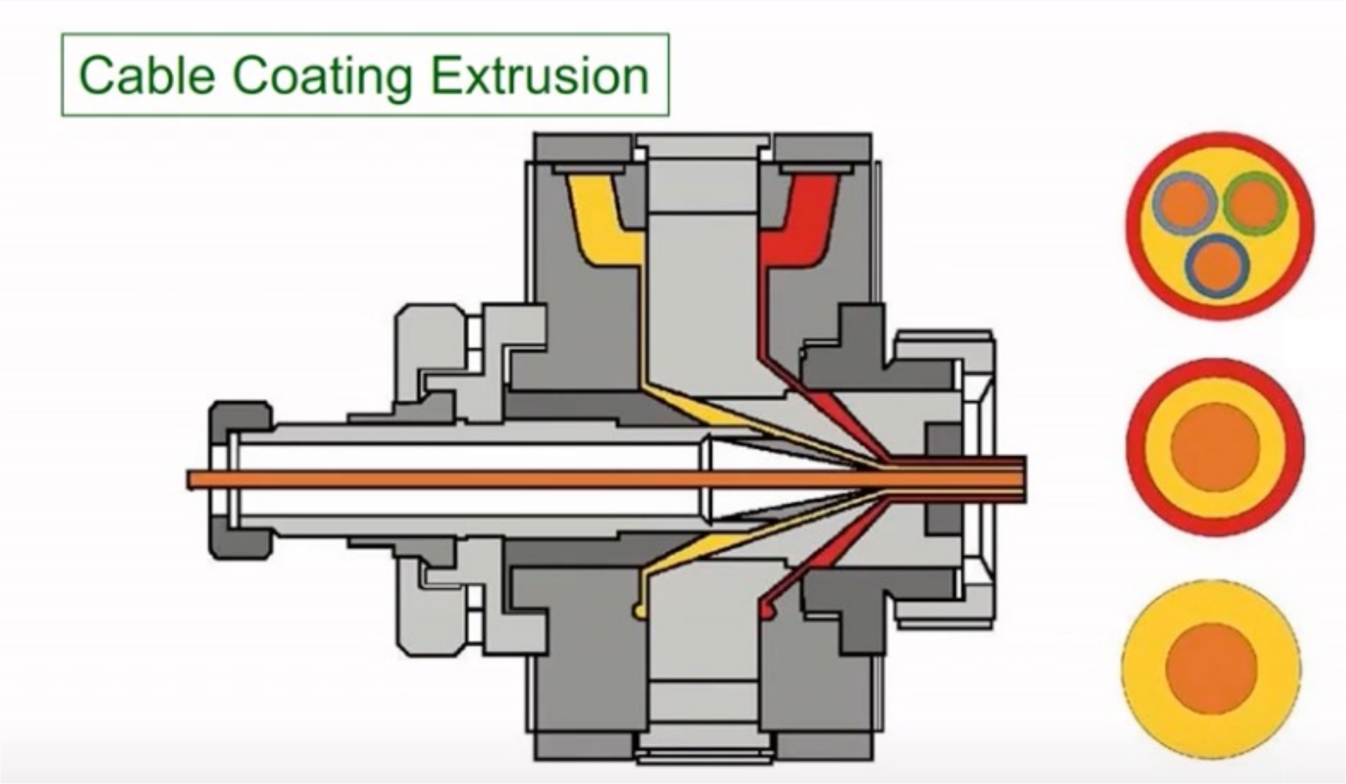
Most cast film lines manufactured today are coextrusion lines, combining layers from as many as seven extruders into the product through multi-manifold dies, or single manifold dies with the aid of feed blocks.



Wire Coating Die

In wire and cable coating processes, individual wires or wire assemblies are pulled at very high speed through a crosshead die, at right angles to the extruder axis.

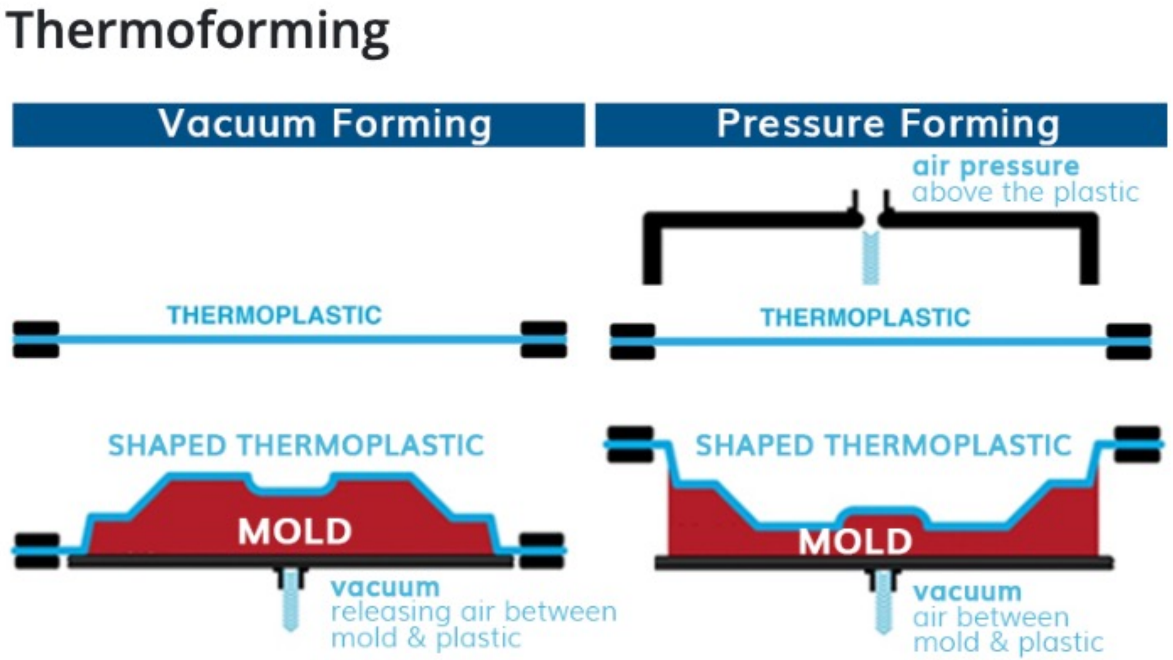
In high pressure extrusion, the polymer melt meets the wire or cable **before the die exit**, for example insulating of individual wires. In low pressure extrusion, the melt meets the cable **after the die exit**, for example jacketing of assemblies of insulated cables.



Thermoforming

Thermoforming refers to heating a sheet of plastic material until it becomes soft and flexible and then forming it either by vacuum, by air pressure or between matching mold halves. Following are the typical sequences used in thermoforming of polymers.

- A sheet of thermoplastic material is placed over a die and heated until it becomes soft.
- A vacuum is then created inside the die cavity which draws down the heated plastic sheet into the shape of the die.
- The material is then cooled, the vacuum is released and the final product is taken out



The main advantages of this process are the relatively low cost of thermoforming machines and the very low cost of the molds, and the ease of forming large area, thin section parts.

Disadvantages are the limited product shapes possible, difficulties in obtaining the required thickness distribution, difficulties in controlling molecular orientation and limitations in service temperature which may induce strain recovery or shrinkage.

Fibre Technology

Spinning

Spinning is the process in which a polymer melt is forced through a small orifice called spinner jet which shapes it into a fiber form.

Spinning types:

a) Melt spinning
b) Dry spinning
c) Wet spinning

NOTES:

- All three types involve the formation of continuous filament strands by forcing a viscous fluid or solution of the polymer through the small orifices of a spinneret plate and immediately solidifying or precipitating the resulting filaments.

- In dry and wet spinning, the solvent is removed to form the solid filament. In dry spinning the solvent evaporates into a gas and in wet spinning the solvent is leached into a liquid path.

Melt spinning

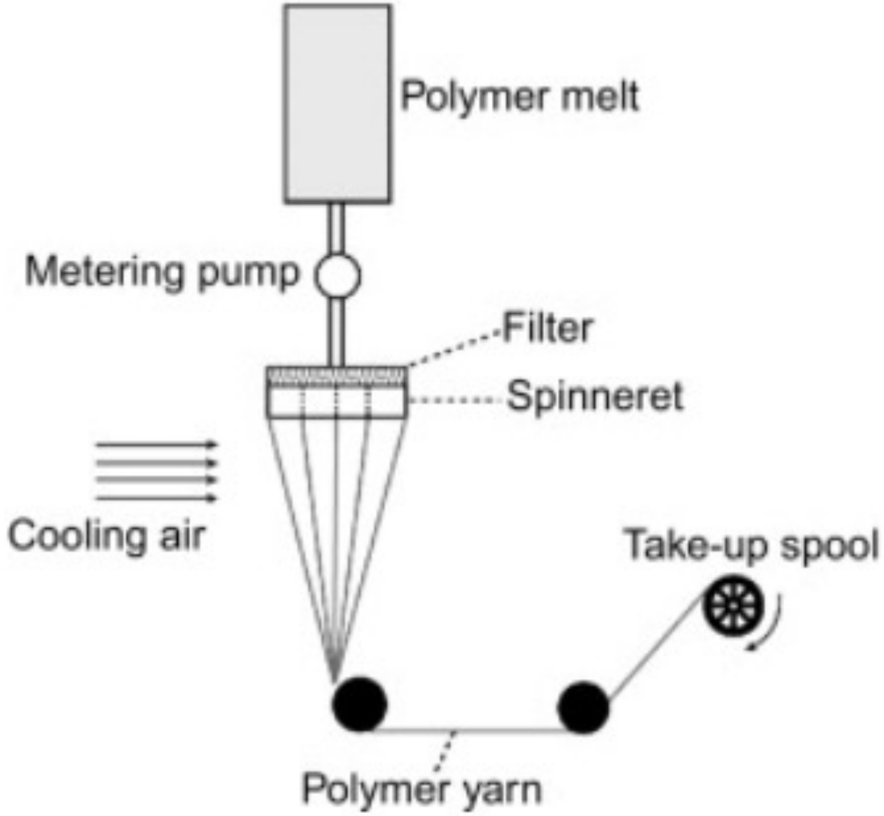
- Melt spinning uses heat to melt the polymer to a viscosity suitable for extrusion. This type of spinning is used for polymers that are not decomposed or degraded by the temperatures necessary for extrusion.

- Melt spinning process use heat to melt the fiber to a viscosity suitable for extrusion through a spinneret (die) with numerous holes (one to thousands)

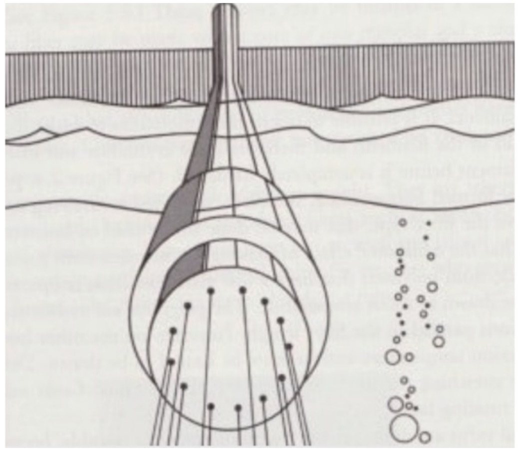
- The molten polymer is extruded at high pressure and constant rate through a spinneret into a relatively cooler air stream that solidifies the filaments. Lubricants and finishing oils are applied to the fibers in the spin cell. Lubricants are used to reduce fibers friction against themselves and against elements of the processing machinery.

- Once formed, the filament yarn either is immediately wound onto bobbins or is further treated for certain desired characteristics or end use.

- Polymers such as poly(ethylene terephthalate) and nylon 6,6 are melt spin in high volumes



Spinneret



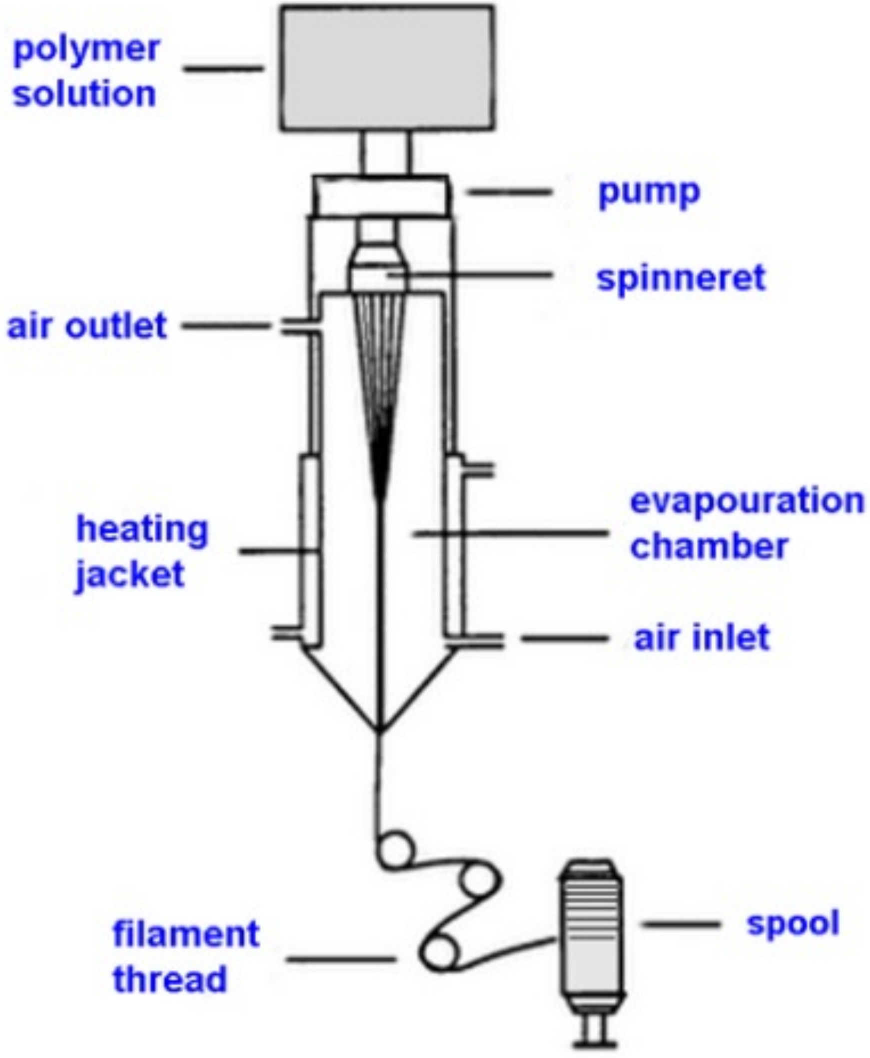
Dry spinning

- The dry spinning process begins by dissolving the polymer in an organic solvent. This solution is blended with additives and is filtered to produce a viscous polymer solution, referred to as "dope", for spinning.

- The polymer solution is then extruded through a spinneret as filaments into a zone of heated gas or vapor. The solvent evaporates into the gas stream and leaves solidified filaments, which are further treated using one or more methods.

- This type of spinning is used for easily dissolved polymers such as cellulose acetate, acrylics, and modacrylics. Dry spinning is the fiber formation process potentially emitting the largest amounts of volatile organic compounds.

- Air pollutant emissions include volatilized residual monomer, organic solvents, additives, and other organic compounds used in fiber processing. The largest amounts of un-recovered solvent are emitted from the fiber spinning step and drying the fiber.



Dry spinning process

Wet spinning

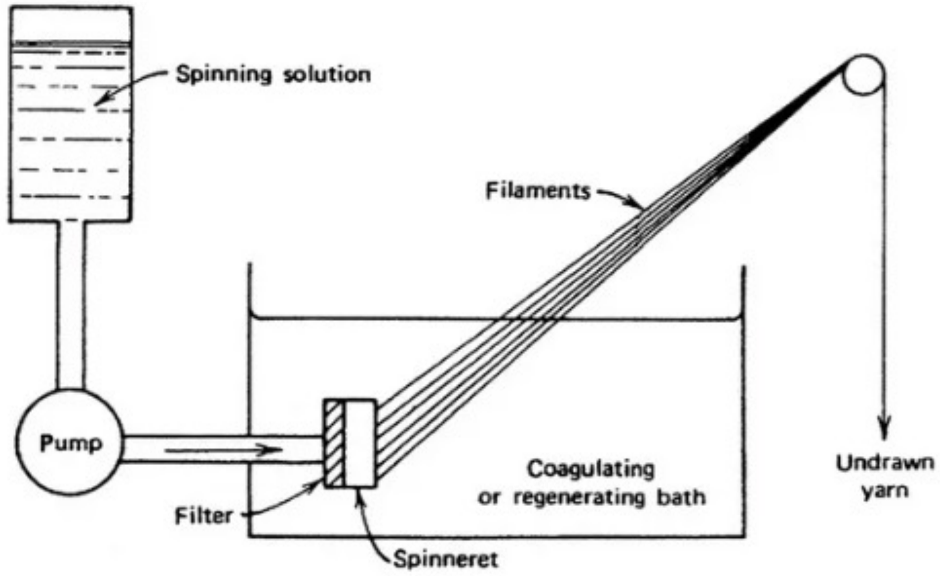
- Wet spinning is required when polymer’s solvents are not sufficiently volatile to permit rapid evaporation. Wet spinning also uses solvent to dissolve the polymer to prepare the spinning dope.

- The process begins by dissolving polymer chips in a suitable organic solvent, such as dimethyl formamide (DMF), or acetone. The spinning solution is extruded through spinnerets into a precipitation bath that contains a coagulant (or precipitant) such as aqueous dimethyl acetamide (DMAc) or water.

- The polymer is not soluble in coagulant but the coagulant is miscible with spinning dope solvent.

- The essential feature in wet spinning is the transfer of the mass of the solvent from the polymer to the coagulating bath. When the solvent is solubilized out, the polymer structure precipitates into solid form.

- Air pollution emissions in the wet spinning organic solvent are similar to those of dry spinning. Emissions occur as solvent evaporates from the spinning bath and from the fiber in post-spinning operations.



Elastomer technology

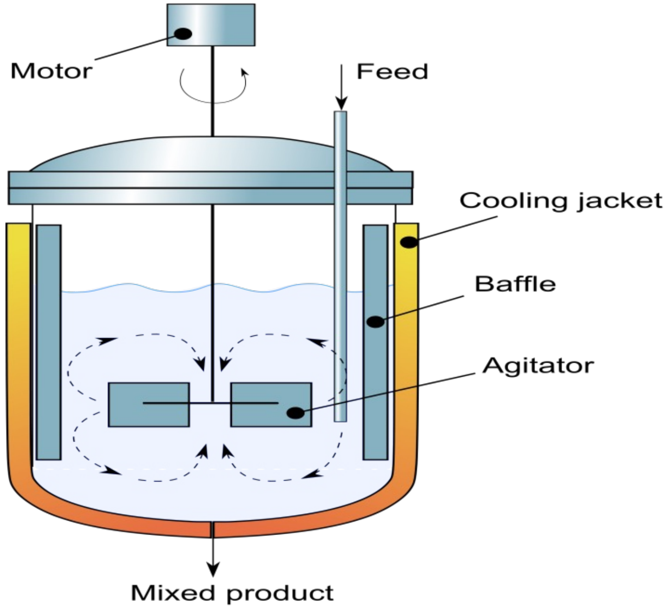
Batch Mixing

- Batch mixing is generally carried out using two specially designed blades inside temperature controlled chamber.

- It is most commonly used for compounding and mixing of rubber formulations.

- Its most important commercial use in the incorporation of carbon black and other additives into rubber for the manufacture of automobile tires.

- Laboratory size batch intensive mixers are extensively used for characterization of materials and processes.



Vulcanization

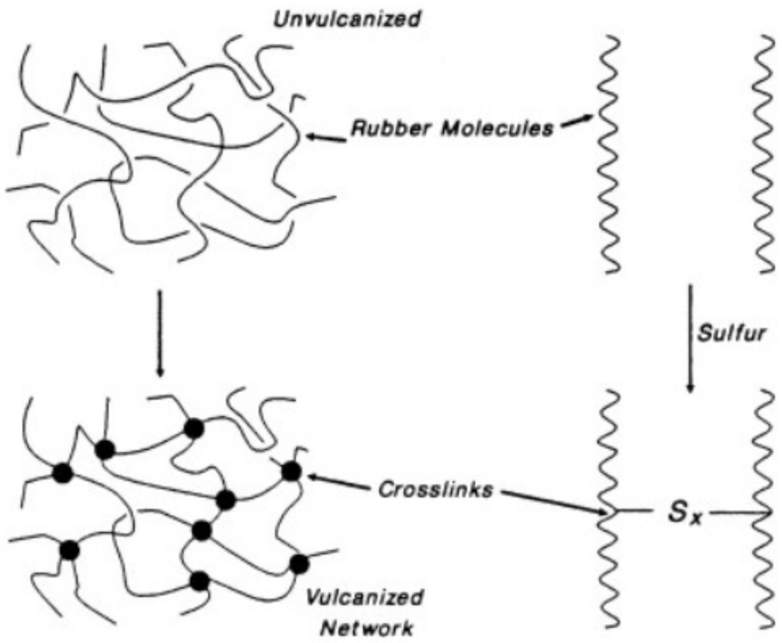
- It is the process by which a network of crosslinks is introduced into an elastomer. Vulcanization effects are: It transforms an elastomer from a weak thermoplastic mass without useful mechanical properties into a strong elastic, tough rubber.

- Vulcanization takes place by heat in the presence of sulfur alone and this process is relatively low. It can be speeded by the addition of small amounts of organic or inorganic compounds known as accelerators.

- Vulcanization with sulfur takes place when 0.5-5 parts (by weight) of sulfur is combined with 100 parts of rubber. Sulfur chloride can vulcanize rubber without heat.

- Non sulfur compounds that can vulcanize rubber fall into three groups:

  1. Oxidizing agents such as organic peroxide and nitro compounds
  2. Generators of free radicals such as organic peroxides and azo compounds.
  3. Phenolic resins .



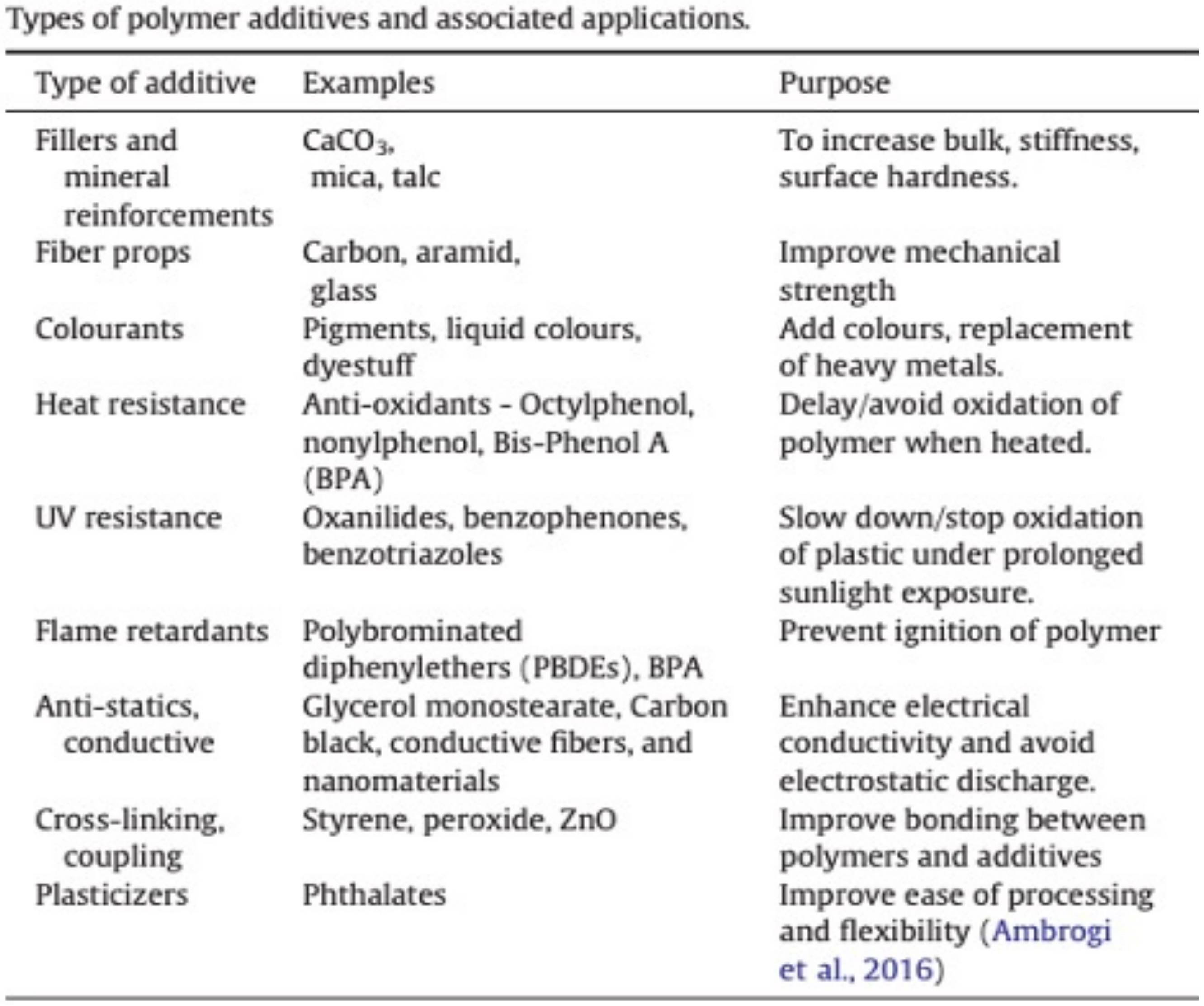
Polymer Additives

Usually, additives are added to polymeric materials to:

- improving and controlling the processing characteristics

- Enhancing properties, opening up the possibility for more applications.

- Reducing the overall cost.



Types of polymer additives and associated applications.

Type of additive	Examples	Purpose
Fillers and mineral reinforcements	$CaCO_3$, mica, talc	To increase bulk, stiffness, surface hardness.
Fiber props	Carbon, aramid, glass	Improve mechanical strength
Colourants	Pigments, liquid colours, dyestuff	Add colours, replacement of heavy metals.
Heat resistance	Anti-oxidants - Octylphenol, nonylphenol, Bis-Phenol A (BPA)	Delay/avoid oxidation of polymer when heated.
UV resistance	Oxanilides, benzophenones, benzotriazoles	Slow down/stop oxidation of plastic under prolonged sunlight exposure.
Flame retardants	Polybrominated diphenylethers (PBDEs), BPA	Prevent ignition of polymer
Anti-statics, conductive	Glycerol monostearate, Carbon black, conductive fibers, and nanomaterials	Enhance electrical conductivity and avoid electrostatic discharge.
Cross-linking, coupling	Styrene, peroxide, ZnO	Improve bonding between polymers and additives
Plasticizers	Phthalates	Improve ease of processing and flexibility (Ambrogi et al., 2016)

Fred-Ahmadu, O.H., Bhagwat, G., Oluyoye, I., Benson, N.U., Ayejuyo, O.O. and Palanisami, T., 2020. Interaction of chemical contaminants with microplastics: principles and perspectives. *Science of the Total Environment*, *706*, p.135978.

Plastics =
Polymer + Additives

Heat Stability

Light Stability

Processing Stability

Antistaticity

Fungicide

Flame Retardants

Biocide

Recycling

Scratch Resistance

Copper Contact

A diagram showing the most common polymer additives

https://gulfstrategy.net/polymer-additives/

Process Selection Criteria

The following parameters play a key role in selecting the best suited process to produce a specific product for a specific application.

1. Material Processibility Limitations
2. Volume of production
3. Size & shape of the product (configuration)
4. Cost to performance balance
5. Quality

MATERIAL PROCESSIBILITY LIMITATIONS

If a specific material is suitable for a particular application, then material processibility will decide the specific method of Processing / Production.

Case :1

Product : PET bottle

Process : Blow Moulding

Specific process : Injection stretch Blow moulding

Not possible by : Extrusion Blow moulding or Extrusion Stretch blow moulding

Reason:

PET material used today does not have the required hot melt strength to hold/self support a parison.

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CASE :2

Product : PTFE sheets

Process : Compression molding following by sintering process.-The sintered sheets are subsequently machined to the required dimension.

Other Conventional Process:

Extrusion - Not possible.

Reason:

PTFE exhibits - very high melt viscosity above its melting temperature. Hence only best suited process is compression molding followed by sintering.

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CONFIGURATION OF PRODUCT

- Size & shape governs the process selection.

Case 1:

Narrow neck containers like Shampoo bottles, Pharmaceutical containers, soft drink bottles will have to be produced by Blow moulding only.

Case 2:

Hollow containers such as Tanks (20,000ltrs) will have to be produced by Roto moulding inspite of higher initial cost on plant & machinery.

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COST / PERFORMANCE BALANCE

If more than one process is suitable for producing a product based on performance, then cost plays a crucial role in process selection.

Case:

Product : 200 litres chemical container

Material : HDPE

Process : 1. Blow Moulding 2. Roto Moulding

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Sl. No.	Parameter	Blow Moulding	Roto Moulding
1.	Specific Process	Accumulator Blow Moulding	Three arm rotomoulding
2.	Volume of Production	High	Low
3.	Initial investment on plant & machine	High	Moderate
4.	Performance	Good	Good
5.	Cost/performance	Best	good

Hence accumulator type blow molding process can be selected.

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THANK YOU
FOR YOUR ATTENTION