

Chapter 4

Polymerization Techniques and Processing

4.1 Polymerization Techniques

On the basis of factors such as nature of the monomer, the type of polymerisation mechanism chosen, the required physical form of the polymer and the viability of the process for industrial production, there can be different polymerisation techniques. They are:

4.1.1 Bulk Polymerisation

Bulk polymerisation is widely used to prepare condensation polymers. In this only monomer and initiators are taken for the process. The monomer is taken in the liquid state and the initiator is dissolved in the monomer. The chain transfer agent whenever used to control the molecular weight is also dissolved in the monomer itself. The whole system is, therefore, in a homogeneous phase. The reaction mass is heated or exposed to a radiation source for initiating the polymerisation and is kept under agitation for proper mass and heat transfers. When the viscosity is high, the termination becomes difficult; and we get an unusable mass. It is known as auto acceleration or transdorf effect(Gel Effect). For dissipation of heat liberated with progress of polymerisation continuous stirring of the reaction system is essential. But the stirring process and heat dissipation , becomes progressively difficult due to rapid increase of viscosity of the reaction system.

Disadvantages

1. As the polymerisation proceeds, the viscosity of the medium increases and mixing becomes progressively difficult, leading to products with very broad molecular weight distribution.
2. Bulk polymerisation is that the medium get viscous, diffusibility of the growing polymer chains becomes restricted, the probability of chain collision becomes less, termination becomes difficult, active radical sites accumulate and the rate of polymerisation increases enormously, leading to an explosion.

Advantages

1. Bulk polymerisation, however, is quite simple and the product obtained as a high purity, since except the initiator and the chain transfer agent, no other additive that could contaminate the product is used.
2. The polymer obtained can also be used as such since no isolation from other components is involved.

Application

The bulk polymerisation technique is used in the free radical polymerisation of methyl methacrylate or styrene to get transparent moulding powders and caste sheetings and also of vinyl chloride to get PVC resin.

4.1.2 Solution Polymerisation

In solution polymerisation the monomer is dissolved in a suitable inert solvent along with the chain transfer agent, whenever used. The free radical initiator is also dissolved in the solvent medium, while the ionic and coordination catalysts, can either be dissolved or suspended. The presence of inert solvent medium helps to control the viscosity increase and promote a proper heat transfer.

Disadvantages

1. The major disadvantage of solution polymerisation technique is that however inert the selected solvent may be chain transfer to the solvent cannot be completely ruled out and hence it is difficult to get very high molecular weight products.
2. The polymer formed will also have to be isolated from the solution either by evaporation of the solvent or by precipitation of a non solvent, and
3. Removal of their final traces is always extremely difficult.

Advantages

1. Solution polymerisation techniques is advantageous in the sense that where the polymer is used in the solution form as in the case of certain adhesives and coating compositions.
2. In systems, where the polymer formed is insoluble in its monomer or solvent and precipitates out as a slurry and is amenable for easy isolation.

Applications

- It is applied in the industrial production of poly acrylonitrile by free radical polymerisation and that of polyisobutylene by cationic polymerisation use the solution technique.
- Block co polymers are made exclusively by this technique.

4.1.3 Suspension Polymerisation

Only water insoluble monomers can be polymerised by this technique. The monomer is suspended in water, in the form of fine droplets, which are stabilised and prevented from coalescing using suitable water soluble protective colloids, surface active agents [carboxy methyl cellulose (CMC), methyl cellulose, polyvinyl alcohol, gelatin] and by stirring. Sometimes water insoluble inorganic compounds like bentonite, kaolin, Magnesium silicate, aluminium hydroxide etc. in finely divided state are used to prevent the agglomeration of the monomer droplets. The size of the monomer droplets formed depends on the monomer-to-water ratio, the type and concentration of the stabilising agents and also on the type and speed of agitation employed.

The initiators are monomer soluble, Since each monomer droplet is isolated and independent of the other droplets, it can be visualised to act as an independent bulk polymerisation nucleus, The continuous aqueous phase separating the monomer droplets acts as an efficient heat transfer medium and hence the exothermicity is well controlled. Since water is used as the heat transfer medium, the process also economical as compared to solution polymerisation

As the entire bulk of the monomer is divided into innumerable tiny droplets, control on the initial chain length of the polymer formed is also quite good, resulting in a fairly narrow molecular weight distribution of the product. Polymerisation proceeds to 100% conversion and the product is obtained as spherical beads or pearls. For these reason this technique is also known as 'bead pearl' polymerisation. Isolation of the product becomes easy as this involves only filtration of the beads and removal of the surface active agents and protective colloids by water washing. The water washed and dried product can be used as such for moulding purposes or can be dissolved in a suitable medium for use as adhesives and coatings.

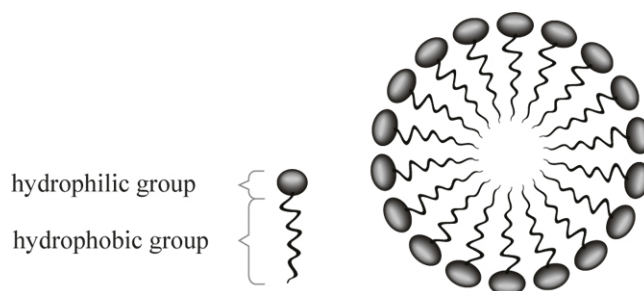
Applications

- Expandable polystyrene beads(for making polystyrene foams).
- Styrene-divinyl benzene co-polymer beads(for the preparation of ion exchange resins) and
- Polyvinyl acetate beads(further conversion to polyvinyl alcohol) are produced by the suspension technique using free radical initiators.

4.1.4 Emulsion Polymerisation

Just like solution polymerisation, in emulsion polymerisation, the monomer is dispersed in the aqueous phase not as discrete droplets, but as a uniform emulsion. The emulsion is stabilised by surface active agents(surfactants), protective colloids and also by certain buffers. The surfactants can be anionic (alkali salts of fatty acids and of aryl and alkyl sulfonic acids), cationic(alkyl amine hydrochloride and alkyl ammonium halides) or non-ionic (alkyl glycosides and saccharose esters of fatty acids). Surfactants get fully dissolved or molecularly dispersed only at low concentrations. Beyond a particular concentration, the excess quantity do not get molecularly dispersed, but forms molecular aggregates known as ‘micelles’, and an equilibrium is set up between the dissociated surfactant molecules on the aggregated ones, The highest concentration, wherein all the molecules are in a dispersed state, or the concentration beyond which only micelles formation is possible, is known as the ‘critical micelles concentration’(CMC).

The emulsifier molecules are made of two parts, a long non-polar hydrocarbon chain to which is attached a polar group such as $-\text{COONa}$, $-\text{SO}_3\text{Na}$, $-\text{NH}_2\text{Cl}$, or $-\text{NBr}$. In micelle formation the emulsifier molecules aggregate in such a way that the polar end of the molecules align themselves outward and the hydrocarbon ends come close to each other at the interior.



Due to the close proximity of the hydrocarbon ends of the all emulsifier molecules, the interior of the micelle acts as a hydrocarbon phase where the monomer can be solubilised. When the monomer is added and agitated emulsification takes place. The resultant emulsion is a complex system; a molecular solution of the emulsifier in water is the continuous phase wherein the monomer droplets and micelles are uniformly dispersed. If the monomer slightly soluble in water, then the aqueous emulsifier solution phase will also contain a part of the monomer dissolved in it. The difference between the suspension system and emulsion system is that, while both have monomer droplets, in the case of emulsion polymerisation, in addition to monomer droplet formation, there is the formation of micelles in which the monomer is solubilised. If the quantity of emulsifier added is less than CMC, the system becomes solution polymerisation and if there is enough emulsifier concentration, it forms emulsion polymerisation system.

Emulsion system generally utilise water soluble initiators such as persulfates or hydrogen peroxide, redox initiators are also widely used. When the initiator is water soluble, and the monomer is insoluble there is hardly any initiator in the monomer droplet and hence no appreciable polymerisation occurs inside the monomer droplet. At the micelle we have a favourable condition for the polymerisation to occur.

The surface layer of the micelle formed by the polar ends of the emulsifier molecules is highly hydrophilic and, hence, an appreciable concentration of the initiator is found at this place. At the same time the interior of the micelle is filled with the solubilised monomer, Polymerisation

therefore, starts at the surface layer of the micelle and proceeds inwards. As and when the monomer inside the micelle is consumed, more monomer diffuses into the micelle from the monomer droplets present in the aqueous phase. The chain growth continues till another radical species enters and arrests the chain growth. With more and more polymer formation, the polymer chains agglomerate into fine particles and get surrounded and then stabilised by the emulsifier layer of the micelle. As the polymer particle concentration increases, it absorbs the monomer and swells in size, which in turn enlarges the size of the micelle. At a particular stage, however, the micelle bursts and loses its identity; all the emulsifier molecules originally forming the micelle now form an absorption layer around the polymer particles. Further supply of the monomer to the growing chain inside the swollen polymer particle comes again, from the monomer droplets. Monomer droplets in this emulsion system, therefore, act only as a reservoir where from the monomer diffuses into micelles or polymer particles, as the case may be.

At the end of polymerisation, we have fine particles of polymer, stabilised by the emulsifier layer and dispersed uniformly in the aqueous phase. This milky white dispersion is often called latex. The latex can be used either be used as such for making adhesives, water soluble emulsion paints etc., or the polymer can be isolated from the latex by destabilising the emulsion (using some electrolytes) by spray drying or freezing. Depending upon the whether monomer is slightly soluble or completely insoluble in water, whether the initiator is soluble in water or monomer or in both, and the monomer/water and emulsifier/water ratios, the polymerisation can occur at one or more spots.

- a. At the dissolved phase of the monomer in water.
- b. At the interface between the monomer droplet and water.
- c. Inside the monomer droplet.
- d. At the surface layer of the micelle.
- e. At the hydrocarbon phase of the micelle.
- f. At the surface of the polymer particle.
- g. At the interior of the swollen mass.

The ultimate result is the same in that the monomer droplets as well as the micelles lose their identity and the polymer is formed as fine particles and is then stabilised into an emulsion.

Advantages

1. Since the polymerisation proceeds at the micelles, where the surface/volume ratio is very high, the rate of polymerisation is quite high.
2. Also, since the number of radicals in a micelle is very much limited and since there is a continuous supply of monomer to the growing chain, a very high molecular weight product is achieved by this technique.

Applications

1. Emulsion polymerisation is the most widely used industrial technique and monomers such as vinyl chloride, butadiene, chloroprene, vinyl acetate, acrylates and methacrylates are polymerise by this technique.
2. Heat transfer is very efficient and the viscosity build-up of the polymerisation mass is quite low as compared to that in the bulk and solution techniques.

Comparison Between Solution and Emulsion Polymerisation

Suspension Polymerisation	Emulsion Polymerisation
In suspension system, there is the formation of monomer droplets	Here also monomer droplets, in addition micelles in which the monomer is solubilised
The quantity of the emulsifier added is less than CMC, the system becomes solution polymerisation	If there is enough emulsifier to form the micelles, it forms the emulsion polymerisation system

4.1.5 Melt Condensation

This technique is used for the polymerisation of monomers which have at least one solid component and do not decompose around their melting points. The temperatures involved in melt polycondensation are rather high and hence, the reaction has to be carried out in an inert atmosphere of N_2 , CO_2 , to avoid such side reactions as can lead to oxidation, decarboxylation, degradation etc. In some cases the reaction is carried out under reduced pressure to facilitate removal of the by product, which becomes essential if a high molecular weight product is aimed at.

Disadvantages

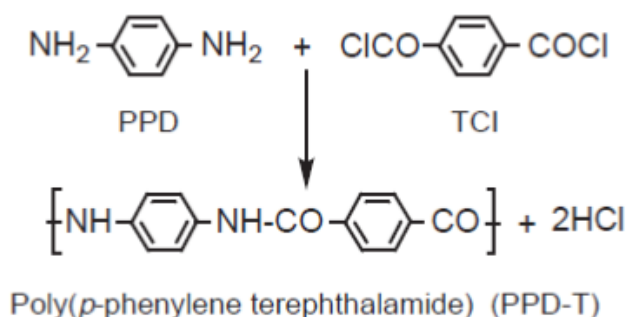
1. Removal of the by product becomes extremely difficult at later stages of the reaction as there is considerable increase in the viscosity of the medium, like in bulk polymerisation.
2. The polymer formed in the molten state at the reaction temperature and is discharged from the reactor while hot as otherwise, it will solidify inside the reactor and removal will become extremely difficult.
3. In most of the cases, the hot melt from the reactor is passed on directly to the processing equipments for extrusion, casting or spinning.

Applications

- Production of polyethylene terephthalate from dimethyl terephthalate and ethylene glycol is carried out by the melt condensation technique.
- Preparation of Nylon 6.6 is another example, illustrative of the melt condensation technique.

4.1.6 Interfacial Poly condensation

In this technique, polymerisation is allowed to proceed at the interface between an aqueous and an organic medium. Reactants having highly reactive functional groups, which can readily react at ambient temperatures to form condensation products, are suited to this technique. Preparation of fully aromatic poly amides from terephthaloyl chloride and paraphenylene diamine is a typical example:



The diamine is dissolved in water and the acid chloride in chloroform or carbon tetrachloride. When the two solutions are brought in contact with each other, at the interface, the diamine molecules diffuse into the organic phase and react with the acid chloride resulting in the formation

of a polymer which precipitates out aqueous phase and gets dissolved, The precipitate is formed at the interface in the form of a thin film and, when removed from the system exposes a fresh surface of the acid chloride to the organic phase, resulting in the formation of the fresh quantity of the polymer.

Advantages

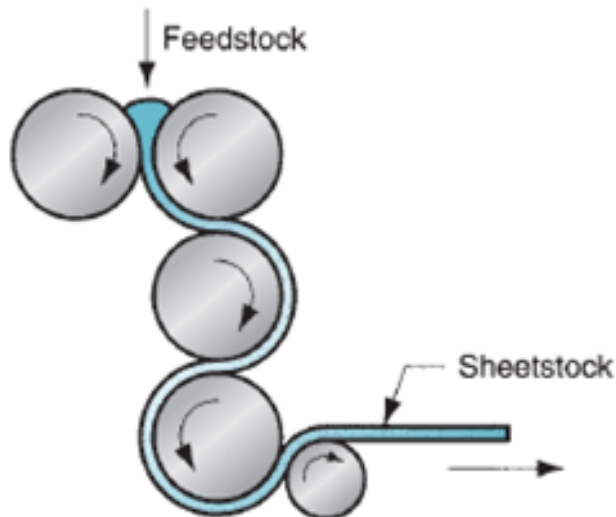
1. Since the polymer formation at the interface is a diffusion controlled process, very high molecular weight products can be achieved by this technique.
2. In actual production, the two solutions are very thoroughly agitated so as to form an emulsion wherein the interface/volume ratio is increased tremendously and hence both the rate and degree of polymerisation become very high.
3. As the polymer is formed, it precipitates out and, under the influence of high-speed agitation, forms a slurry. The polymer is isolated from the slurry and washed free of adherent reactants.

4.2 Calendering

The calendering process is employed to produce continuous films and sheets.

The main part of a calendering machine is a set of highly polished metal rollers rotating in opposite directions with provision for precise adjustment of the gap between them. The gap between the rollers determines the thickness of the sheet calendered out.

Compounded polymeric material is fed between the rollers which are maintained at an elevated temperature and the sheet emerging from the rollers is cooled by passing through cold rollers. The sheets are finally wound up in rolls.



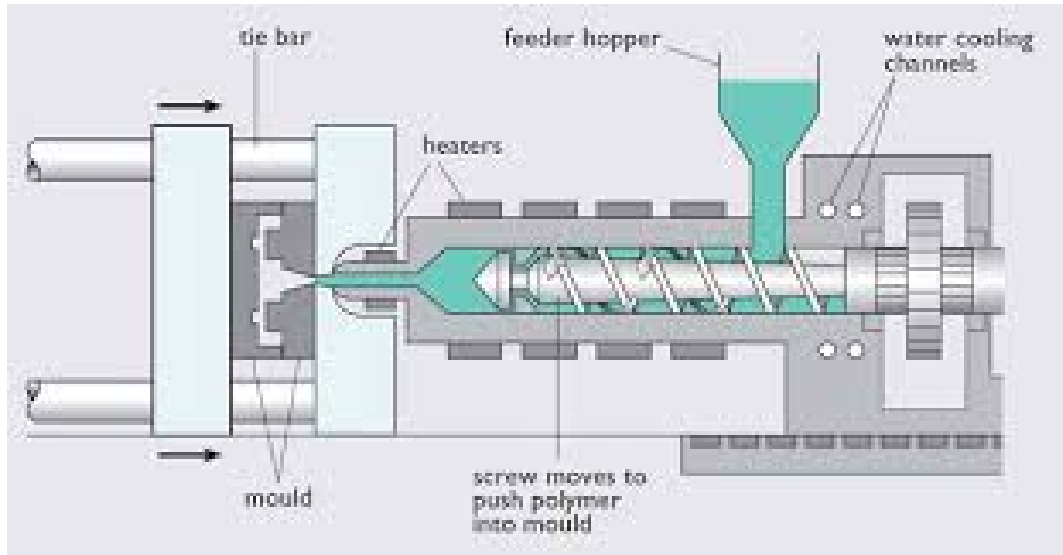
If thin films are required instead of sheets, a series of rollers with a successive diminishing gap between them is employed.

Polyvinyl chloride, polyethylene, acrylonitrile-butadiene-styrene copolymer and rubbers are among the main polymers which are usually calendered into sheets.

By incorporating a suitably engraved embossing roller in the calendering machine, embossed sheets of suitable design could be produced. and also special decorative effects could be achieved.

4.3 Injection Moulding

Injection moulding is almost similar to Extrusion



It is the most widely used cyclic process for product manufacture. This technique is widely used with thermoplastics. The process involves forcing or injecting the polymer into a closed mould where it takes the shape of the cavity.

4.3.1 Working

The screw injection moulding machine consists of a reciprocating screw enclosed with a barrel. The screw and the barrel can be heated electrically. It has three sections, feed zone, compression zone, and metering zone. The polymer in the form of pellets and powder is introduced through the hopper into the barrel. As the screw rotates the polymer is plasticized, melted, mixed thoroughly and pushed forward to accumulate at the tip of the screw where the nozzle is placed. The melt is then injected through the nozzle into the mould cavity.

The mould is made of two or more pieces depending on the structure of the product. It includes a stationary part and a non stationary part. When properly closed the mould enclose a the shape of the product, which is known as the mould cavity. When more than one product is made in the same mould it is called a multi cavity mould. The mould has the provisions for cooling and the ejection of the product.

The first step is closing the mould to get the mould cavity. Immediately the screw rotates to melt and collect molten resin which is the conveyed to the space at the end of the screw where it accumulates as a pool. Then the entire screw moves forward and injects the exact amount of melt in to the mould cavity. During injection the melt flows through the sprue, runner, and gate before entering the mould cavity.

4.3.2 Process

The gate is the end of runner and entry path to the mould. The runner is used to carry the melt uniformly to the mould cavity . The Screw is driven using hydraulic pressure. As the melt touches the cold walls of the mould, it start solidification. Once the solidification is complete, the mould plates open and the product is ejected. This makes one cycle. The cycle is continued to produce many product units. Depending upon the size and shape of the product cycle time varies..

Advantages

1. Screw injection moulding offer uniform melting. mixing and dispersion of additives.
2. High production rate resulting in less manufacturing cost.
3. Multi cavity moulds are used to increase number of articles per cycle.

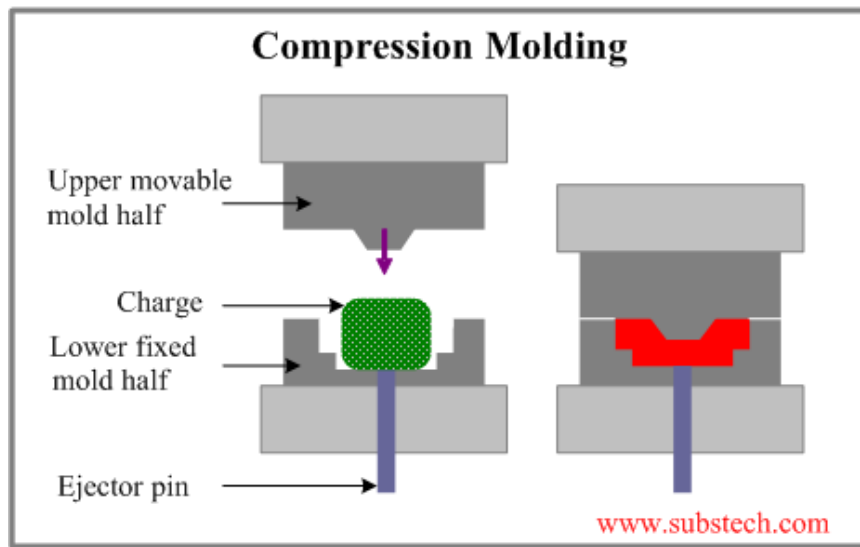
Applications

Injection moulding is used to produce the following items.

1. Buckets, mugs, tumblers
2. shopping bags, decorative items, ice buckets, radio cabinets.
3. furniture, automotive parts

4.4 Compression moulding

Compression moulding is a very widely used techniques used to produce articles from thermosetting materials. The mould is made of two halves- the upper and lower halves or male and the female. the lower half usually contains a cavity and the upper half has a projection which fits into the cavity when the mould is closed. The gap between the projected upper half and the cavity in the lower one gives the shape of the moulded article.

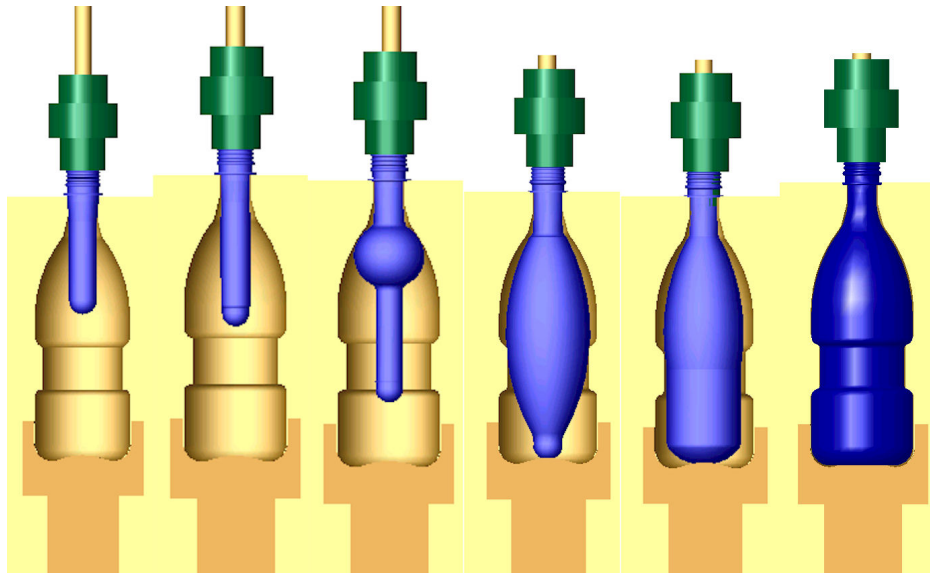
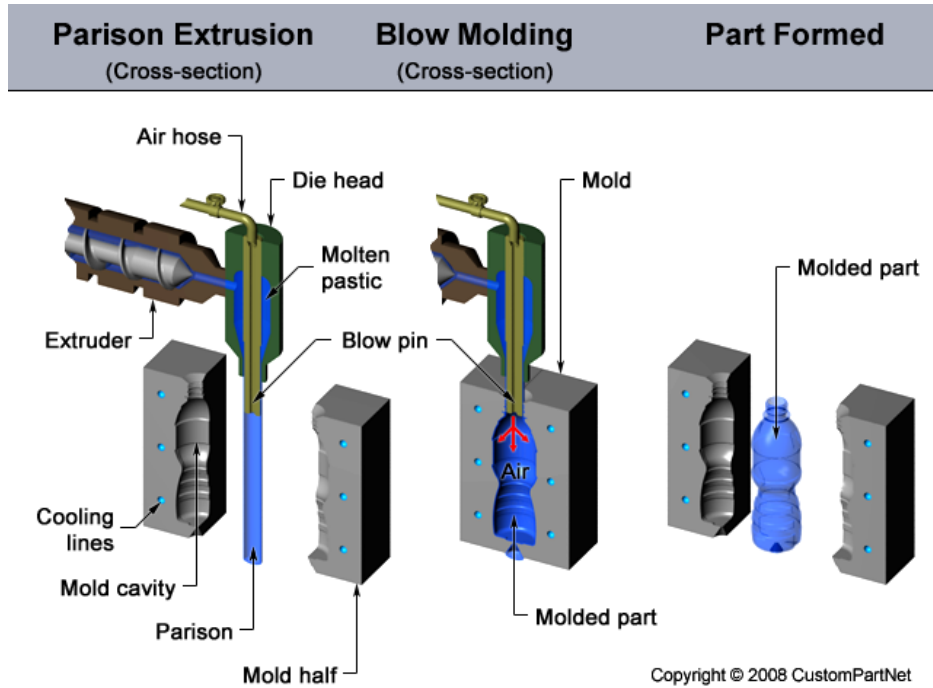


In compression moulding, the thermosetting material is subjected to heat and pressure in a single stroke. This is accomplished by using a hydraulic press with heated plattens. Moulding temperature and pressure can be high as 200°C and $70 \text{ kg}\cdot\text{cm}^{-2}$, respectively. The actual temperature and pressure depends on the rheological, thermal and other properties of the plastic material to be moulded. The compounded material is places in the cavity of the mould so as to fully fill the cavity. As the mould closes down under pressure, the material is squeezed or compressed between the two halves and compacted to shape inside the cavity. The excess material flows out of the mould as a thin film. This film, expelled out of the mould is known as 'flash'. Under the influence of heat the compacted mass gets cured and hardened to shape. Th mould can be opened while it is still hot to release the moulded product.

4.5 Blow moulding

Blow moulding in fact, basically belongs to the glass industry. A hot softened thermoplastic tube, usually called 'parison' is properly placed inside a two piece hollow mould. When the two halves of the mould are closed, it pinches and closes one end of the parison and encloses a blowing pin at the other end, The parison is now blown by pressurising from within by blowing compressed air through the blowing pin.

The hot parison is inflated like a balloon and goes on expanding until it comes in intimate contact with the relatively cold interior surface of the hollow mould. Under pressure, the parison ultimately assumes the shape of the hollow cavity of the mould. The mould is allowed to cool and the right thermoplastic article formed is removed by opening the mould.



4.5.1 Types of blow moulding

Based on the techniques used for the preparation of parison, blow moulding is categorized into different types.

1. Extrusion blow moulding.
2. Injection blow moulding.
3. Stretch blow moulding.

4.5.2 Extrusion blow moulding

Extrusion blow moulding uses an extruder die to prepare the parison. The parison thus formed is transferred into a blowing mould where it is blown to get the shape.

This method is more popular and extensively used for small and medium sized products.

4.5.3 Injection Blow Moulding

In injection moulding parison is formed by injecting a definite mass of the melt into a closed mould. Then it is transferred to the blowing mould.

4.5.4 Stretch Blow Moulding

In stretch blow moulding the plastics given a biaxial stretching which introduces a high amount of molecular orientation as a result the product gets higher strength and physical properties.

The stretching process also offers considerable cost saving and improvement in mechanical and optical properties.

This method is largely used for the manufacture of transparent bottles. PET bottles for carbonated drinks are manufactured by this method.

Applications of Blow Moulding

- Most of the hollow plastic articles are produced by this technique.
- Containers, soft drink bottles and numerous other hollow articles are produced by this process.
- Thermoplastic materials such as polyethylene, polycarbonate, PVC, polystyrene, nylon, polypropylene, acrylates, acrylo nitrile and ABS polymer can be blow moulded.
- High density polyethylene tops list in terms of annual consumption.

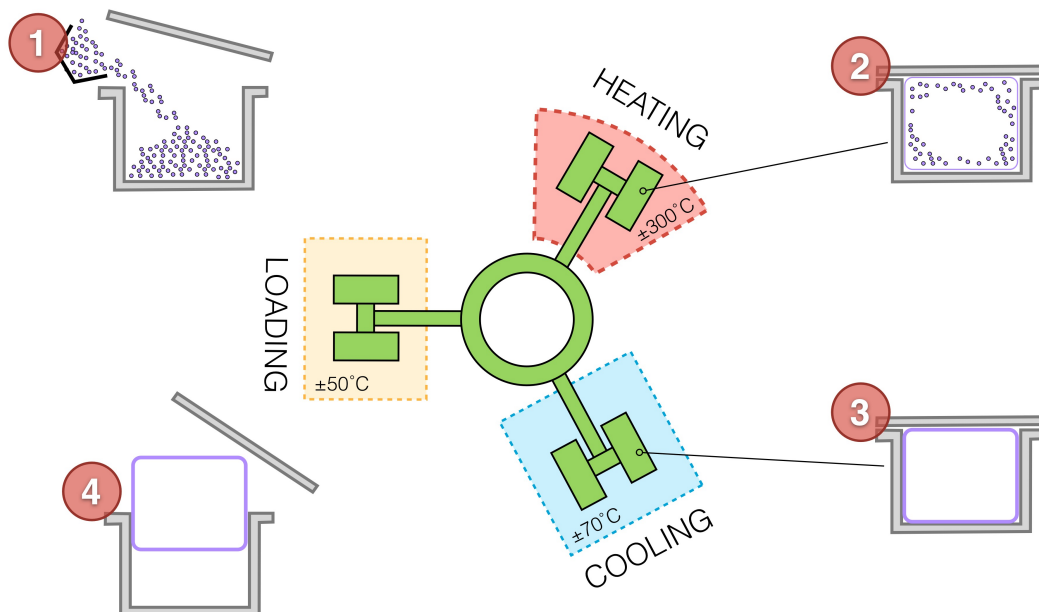
4.6 Rotational moulding

Rotational moulding is used for the production of hollow configurations especially large products by blow moulding. It is mainly used with thermoplastics.

The moulding machine consists of a frame with three arms that can be rotated in two planes at right angles to each other. On the frame one or more moulds can be mounted. Major steps are involved in the rotational moulding are

1. Loading.
2. Heating.
3. Cooling and unloading.

4.6.1 Working



Loading

This involves the loading of correct amount of polymer into the cold mould. This is done in the loading compartment.

Heating

This mould is then moved into an oven where it is heated so that fusion of the polymer takes place. At the same time it is rotates biaxially so that a uniform layer of plastic is deposited on the inner surface of the mould. Heating period is the longest part in the mould cycle.

Cooling and Unloading

When the fusion becomes complete the mould is transferred into a cooling station. The rotation is continued until cooling sets the shape of the product. Cooling is done using cold air or by spraying cold water. After cooling the mould moves into the unloading compartment to take out the product.

4.6.2 Advantages and Applications

Advantages:-

1. Lower cost of equipment and mould.
2. The process requires no pressure.

Disadvantage

The main disadvantage is that it has large cycle time.

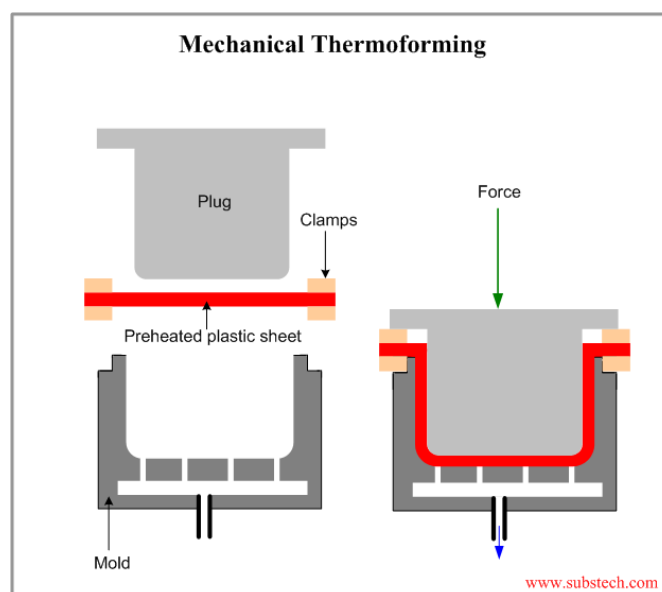
Applications

Rotational moulding is used to make large water storage tanks, drums, floats, containers, furnitures, and sandwiched structures.

4.7 Thermoforming

Thermoforming is a highly useful process for fabricating three dimensional articles from plastic sheets. Even some large products, such as submarine hulls are made of ABS sheets by thermoforming techniques.

The technique was can be out lined as follows. The thermoplastic sheet is heated to its softening temperature. The warm flexible sheet is then pressed into the female half of a matched metal die duly assisted by male half. Now the sheet assumes the required shape of the mould. On cooling, the shaped article becomes rigid and can be removed from the mould.



In a modified method, the hot plastic sheet is sucked into the cavity of the female mould under the influence of vacuum to give the desired shape. This method is called vacuum forming

