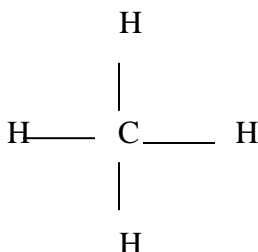


CHAPTER 8

POLYMERS

8.1 Polymer building blocks: The polymer materials are all built from carbon atoms in association with other elements such as oxygen, hydrogen, nitrogen, chlorine and fluorine. Carbon atoms have four chemical bonds or as chemists would say a valency of four. Hydrogen atoms have a valency of one. So if hydrogen and carbon are combined in the simplest way to give a molecule of methane (natural gas), the molecule would appear as:



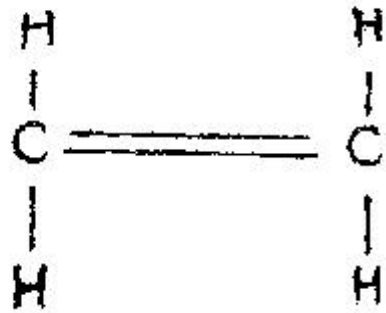
Thus four hydrogen atoms combine with one carbon atom to make one molecule of methane gas. This molecule is given the chemical formula CH_4 and because it consists solely of hydrogen and carbon it is referred to as a 'hydrocarbon'. The hydrocarbons are found in crude oil, coal and natural gas.

8.2 Paraffins: These are the simplest of the four groups of hydrocarbons. They have a general formula of $\text{C}_n\text{H}_{2n+2}$. For example, in the methane molecule just considered, there is only one carbon atom, so $n=1$ and the number of hydrogen atoms is $2(1)+2=4$. This agrees with the formula already stated as CH_4 . One way of recognizing paraffin is the fact that their names always end in -ane (as in methane, propane, octane etc.). This is because the paraffins are saturated hydrocarbons or alkanes, that is, they contain the maximum number of hydrogen atoms in each case as shown in Fig 8.2.1 and this makes them rather inactive chemically. The paraffins are the most common group of hydrocarbons appearing in crude oil.

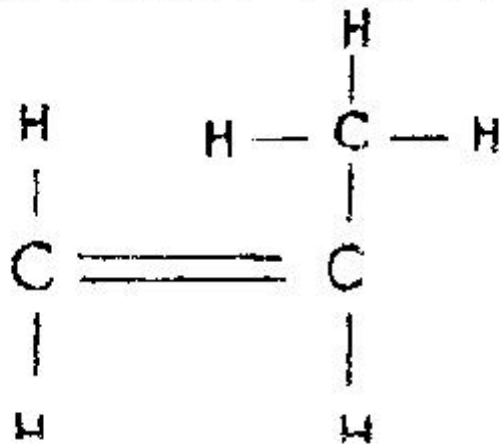
FORMULA	NAME	USE
$ \begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array} $	CH ₄ Methane	Natural gas
$ \begin{array}{c} \text{H} \qquad \text{H} \\ \qquad \\ \text{H}-\text{C} - \text{C}-\text{H} \\ \qquad \\ \text{H} \qquad \text{H} \end{array} $	C ₂ H ₆ Ethane	Converted into Plastic
$ \begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{C} - \text{C} - \text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array} $	C ₃ H ₈ Propane	Heating fuel
$ \begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ \text{H}-\text{C} - \text{C} - \text{C} - \text{C}-\text{H} \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array} $	C ₄ H ₁₀ Butane	1. Heating fuel 2. Converted to synthetic rubbers.
This series continues to C ₁₀₀ to become the asphalts and tars used for roads and roofing.		

Fig 8.2.1 Common paraffins

8.3 Olefins: These are unsaturated hydrocarbons or alkanes, that is , additional hydrogen atoms have to be added to olefins in order to saturate them. This unsaturated condition makes them chemically reactive and olefins form the basis of many thermoplastic and elastomer materials. When their general formula is C_nH_{2n} they are called mono-olefins and are given names ending in -ylene (as in ethylene, propylene etc.). They are used as a feed stock for the polymer industry where they are known as chemical intermediates. Two typical examples are shown in Fig 8.3



ETHYLENE (derived from ethane)



Propylene (derived from propane)

H=Hydrogen C=Carbon

Fig 8.3 Common olefins

8.4 Napthenes and aromatics: These both have ring shaped molecules as shown in Fig 8.4. Materials made from a ring shaped molecule have improved mechanical properties, for example the high tensile strength of nylon.

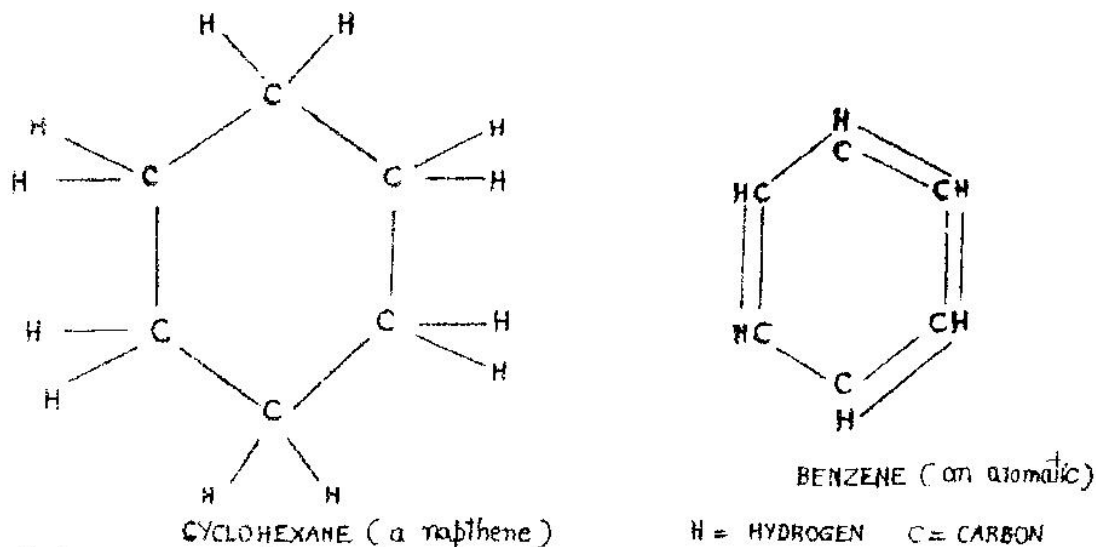


Fig 8.4 Common naphthenes and aromatics

Naphthenes have saturated molecules and names beginning with 'cyclo' (as in cyclohexane) Aromatics, on the other hand, are unsaturated and are chemically highly reactive, being used in solvents and explosives. Aromatics are rare in crude oils but occur in coal. They form the styrene group of plastics.

8.5 Polymers: Consider the manufacture of simple polymeric material such as polyethylene. The paraffin ethane is first converted into its corresponding olefin. (Hence the term 'chemical intermediate'). A single molecule of the olefin ethylene is referred to as a monomer and the next stage of process is to combine several monomers together to form a much larger molecule called a 'polymer' (poly means many). In this example, it is polyethylene. In the form of a polymer, the olefin takes the characteristics of a plastic material. Two examples are shown in Fig 8.5.

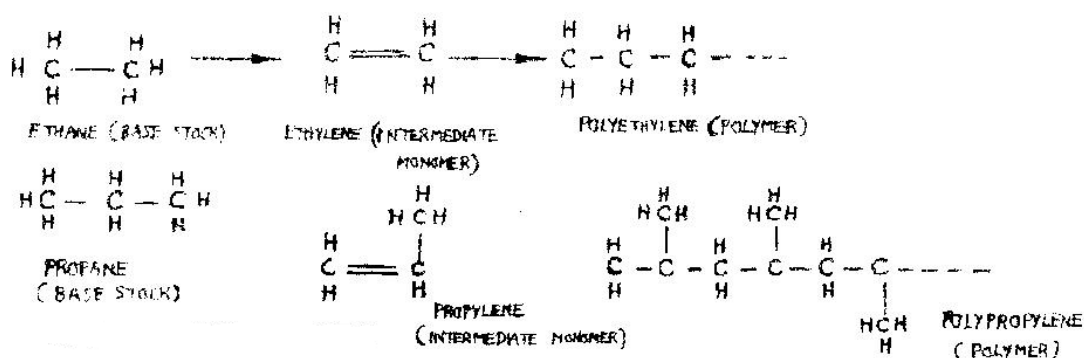


Fig 8.5 Simple polymers

There are simple basic rules which govern the number of monomers which can be brought together to form a polymer. For example, at room temperature ethylene which is made up of single molecule is a gas. A polymer of six monomers of ethylene is a liquid; a polymer of 36 monomers is grease; a polymer of 140 monomers is a wax and a polymer of 500 or more monomers is a solid plastic material. The upper limit is about 2000 monomers. At this point, there is little further increase in strength, but a considerable increase in hardness and brittleness. This rule applies to most plastic materials.

All polymeric materials have two things in common:

1. They are all made up of long chains of individual unit molecules. These individual unit molecules are called monomers; and when large numbers of these monomers are repeated over and over again to form a long chain molecule they are referred to as polymers. Hence such materials are known as polymeric materials. This is a much more accurate description of these materials than the popular word 'plastic'.
2. They are all based on a chain of monomers which builds up a giant molecule. It is the shape of this chain as well as its composition which determines the properties of polymeric materials.

8.6 Thermoplastics & thermosets: Fig 8.6 shows some of the shapes which the molecular chain of a polymeric material may take. The linear chain shown in Fig 8.6 (a) and the linear chain with side branches shown in Fig 8.6 (b) are typical of thermoplastic materials. The simple linear chains with no side branches can easily move past each other. This results in non-rigid thermoplastic materials which can be flexed and stretched. Such materials melt at low temperatures and easily return to their original state when they

cool down. Polyethylene is an example of such a material.

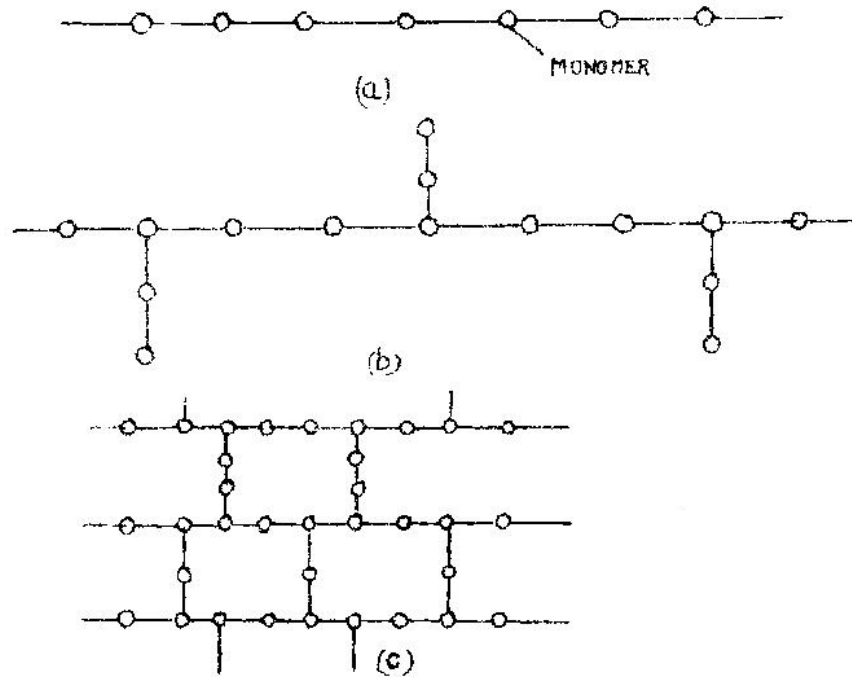


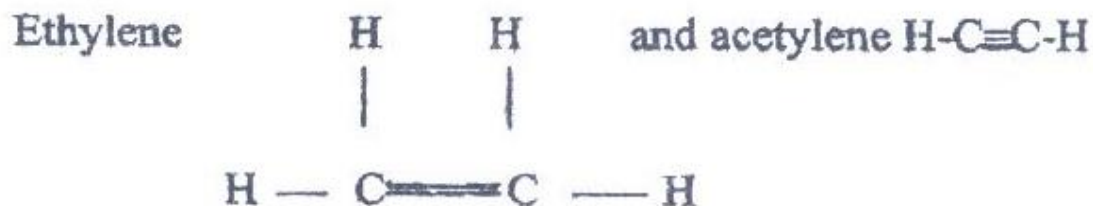
Fig 8.2 TYPICAL POLYMER CHAINS (a) Linear polymer chain (b) Branched polymer chain (c) Cross linked polymer chain

Since it is more difficult for branched linear chains to move past each other, materials with monomers in this configuration are more rigid, harder and stronger. Also they are less dense since the side branches prevent the chains being packed so closely together. Heat energy is required to break down the side branches and this rises the melting temperature above that for materials with a simple linear chain. An example of a thermoplastic material with a branched linear chain is 'polypropylene'. The cross-linked molecular chain shown in Fig 8.2 (c) is typical of the thermosetting plastics. These are rigid and tend to be brittle once the links have been formed by curing the material during the molding process. Once curing has occurred the material can not be softened by reheating as the process is not reversible. If heated sufficiently they char or burn and are destroyed.

Thermosetting plastics differ from thermoplastic materials in the way in which polymerization (curing takes place). In thermoplastics, polymerization occurs through the addition of monomers at the time of manufacture and no further curing occurs during the molding process. In thermo-setting plastics polymerization usually occurs through condensation.

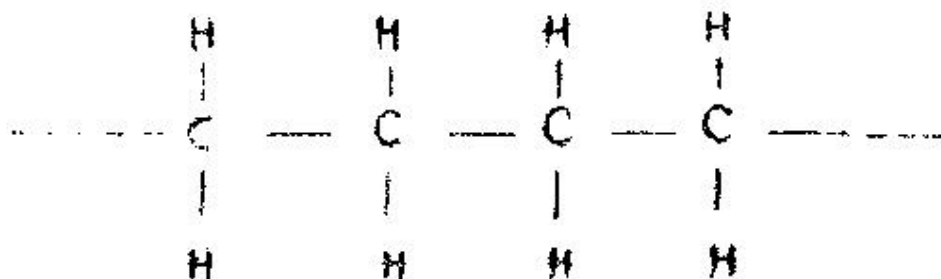
8.7 Polymerization: Ethylene and acetylene are the corresponding unsaturated compounds. Some of the valence bonds of the carbon atoms are not satisfied and these are indicated by double or triple lines.

If ethylene is subjected to the influence of suitable pressures, temperatures and catalyst



catalysts the saturated bonds permit joining of a number of ethylene molecules to form a long chain:

This



formation of larger molecules from small ones is known as polymerization. Polymerisation is accompanied by increase in the boiling points of liquid compounds and increase in the melting points of solid compounds. Polymerization of ethylene, when the process has progressed sufficiently, results in converting an ordinary gaseous substance to a solid. As the size of the polymer molecule grows, a liquid forms whose viscosity then increases until solidification occurs. Polymerization of ethylene involves the least complicated type of reaction known as a linear addition. As the name linear addition implies, a number of molecules add to one another to form long chain type molecules. Another type of chain molecule is formed by linear condensation reactions such as shown in Fig 8.3.1. The nylon forms from adipic acid and hexamethylene diamine.

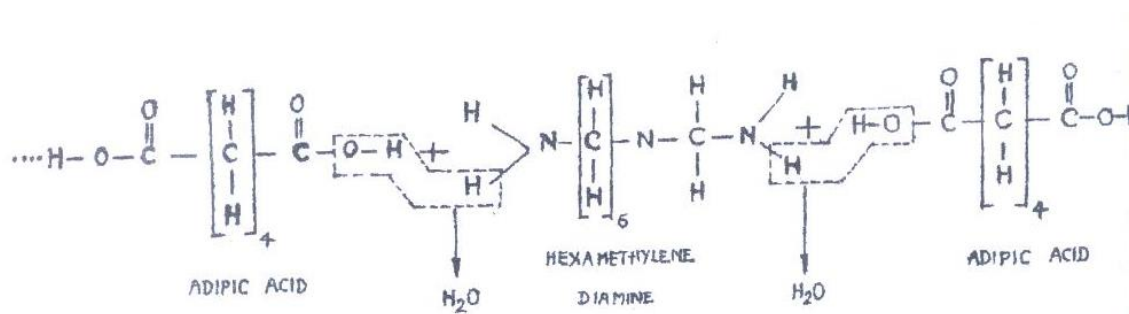


Fig 8.3.1 LINEAR CONDENSATION REACTION

In the above reaction, a molecule of water is split off (condensed) for each bond formed between an adipic acid molecule and hexamethylene diamine molecule.

In some type of plastics, polymerization produces cross-linking between the long chain molecules. An example of this is the condensation reaction which occurs between phenol and formaldehyde to form the plastic commonly known as bakelite.

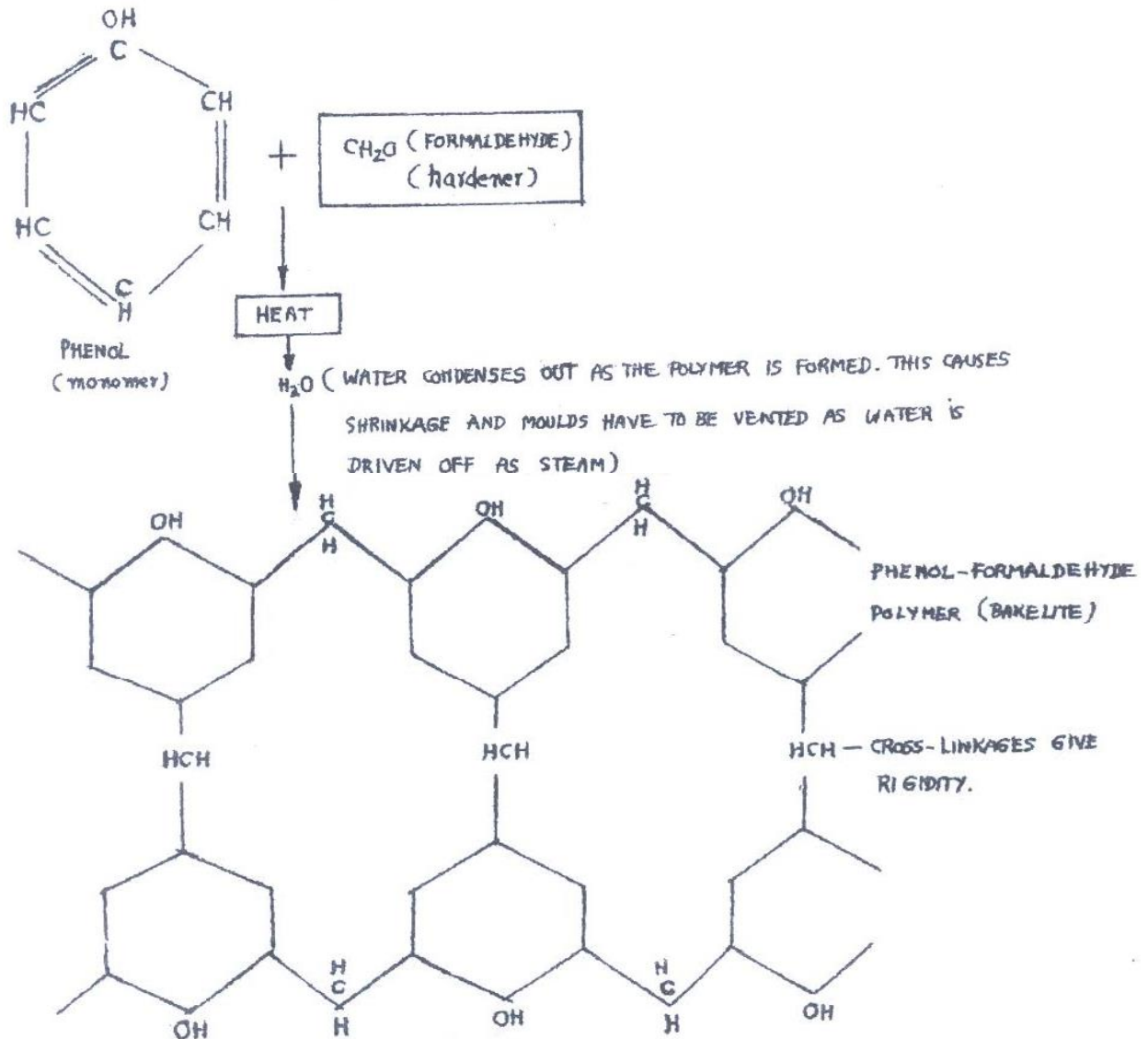


Fig 8.3.2 Polymerization of thermoplastics

8.4 Properties: The properties of polymeric materials can vary widely, but they all have the following properties in common.

8.4.1 Electrical insulation: All polymeric materials exhibit good electrical insulation properties. However their usefulness in this field is limited by their low heat resistance and their softness. Thus they are useless as formers on which to wind electric radiator

elements and as insulators for use out of doors where their relatively soft surface would soon be roughened by the weather. Dirt collecting on this roughened surface would then provide conductive path causing a short circuit.

8.4.2 Strength/weight ratio: Polymeric materials vary in strength considerably. Some of the stronger, such as nylon compare favorably with the weaker metals. All polymeric materials are much lighter than any of the metals used for engineering purpose. Therefore, properly chosen and proportioned, their strength/weight ratio compares favorably with many light alloys and they are steadily taking over engineering duties which, until recently, were considered the prerogative of metal.

8.4.3 Corrosion resistance: All polymeric materials are inert to most inorganic chemicals and can be used in environments which are hostile even to the most common resistant metals. The synthetic rubbers which are a product of polymer chemist are superior to natural rubber (polyisoprene) since they are not attacked by oils and grease.

8.4.4 Chemical properties: From the chemical standpoint, the plastics are generally more resistant to environments which attack common engineering materials such as steel, wood and rubber. Most plastics are rather inert to the atmosphere and to salt, fresh or soil water. Fairly good resistance is usually offered by plastics to attack by inorganic acids, bases and salts. The thermosetting plastics have good resistance to organic chemicals. On the other hand, thermoplastics are more generally attacked or dissolved by common organic solvents. The polyamides (nylon) are important thermoplastics which resist organic solvents. Tetrafluoroethylene (Teflon) is outstanding because of excellent resistance to almost all chemicals, both organic and inorganic, in dilute or concentrated solutions. With the exception of cellulose nitrate (celluloid and gunpowder) which is very flammable, the plastics in many cases are non-inflammable, self-extinguishing or burn very slowly.

8.4.5 Physical properties: The range of specific gravities is between approximately 1 and 2. The plastics are good thermal and electric insulators, all having high dielectric strengths. The plastics are transparent, translucent or opaque. The transparent plastics can be produced in any color. Although plastics are chemically inert with respect to water, all except tetrafluoroethylene (Teflon) tend to absorb or lose moisture with changes in humidity.

8.4.6 Mechanical properties: As compares to metals, the tensile and compressive strengths of plastics fall below the values for magnesium. The strength/weight ratio improves the relative standing of plastics considerably. The modulus of elasticity of non-flexible plastics are about of the same order of magnitude as for concrete. Impact strengths as measured by notched Izod specimen are rather low. In general, the thermosetting plastics are essentially void of ductility and thermoplastic resins range from moderately to very ductile. The ductility of the thermoplastics is affected by the compounding of the resin. Ductile plastics are in some respects similar to metals in their response to service conditions. Higher rates of tensile loading result in raising the elastic limit. Raising the temperature tends to lower the elastic limit and modulus of elasticity.

The crystallinity of a polymeric material has profound influence on the ultimate tensile strength and percentage elongation. (Refer Fig 8.4.6.1)

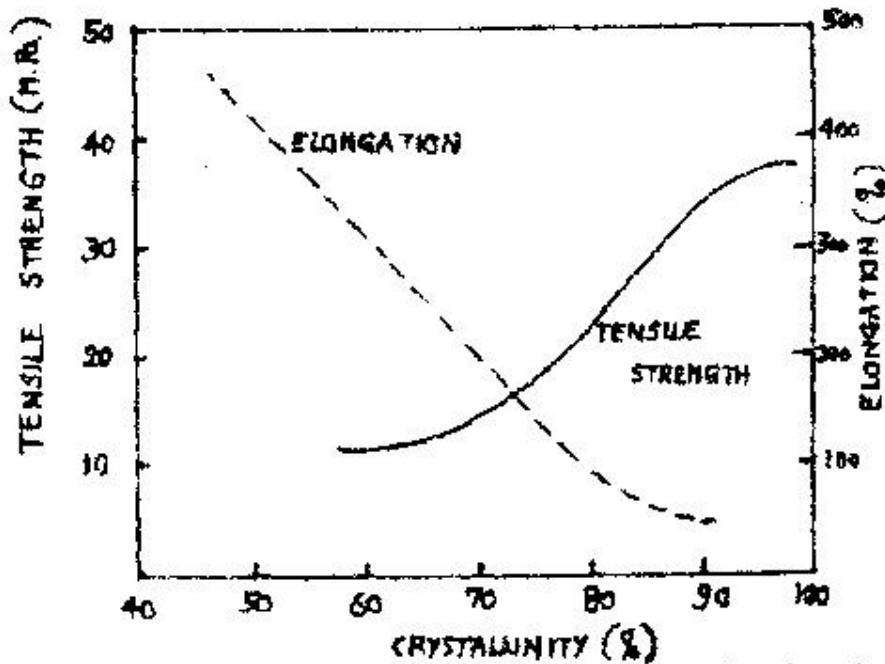


Fig 8.4.6.1 Effect of crystallinity on the properties of polyethylene

Increasing the crystallinity of a material increases its melting point, increases the resistance of the material to the absorption of water and to solvent attack, prevents the penetration of plasticizers reducing the ultimate elongation of the material and makes the material more impervious to gases.

Amorphous solids do not show clearly defined melting point when heated but merely becomes less rigid progressively until they eventually become liquid. Amorphous thermoplastic materials behave in this way. Other thermoplastic materials show some crystallinity and for these it is possible to determine a melting temperature (T_m). The melting temperature is determined by plotting the specific volume of the material against temperature rise as shown in Fig 8.4.6.2

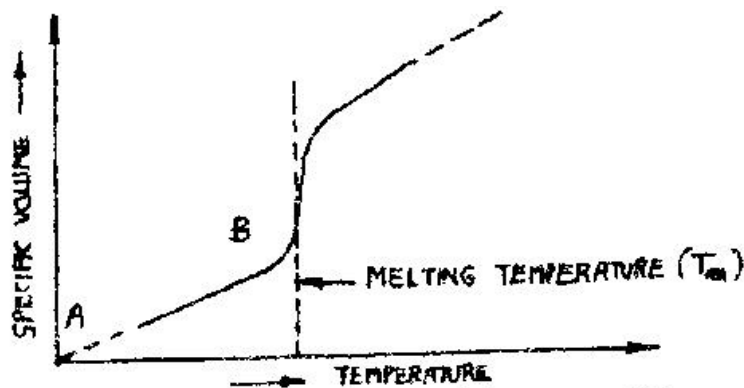


Fig 8.4.6. 2 Melting temperature (T_m) of a partially crystalline polymer

Initially the smaller, less perfect crystallites become amorphous and this is indicated by the portion of the curve marked AB. At the point (B), a rapid increase in specific volume with temperature occurs. This point is regarded as the melting temperature (T_m) and is defined as the point where the material loses its crystallinity completely and becomes amorphous. The greater the crystallinity of any thermoplastic material, the higher will be its melting temperature. Table 8.4.6 lists the melting points for some typical crystalline polymers.

Material	T_m °C
Polyethylene (low density)	120
Polyethylene (high density)	135
Polypropylene	180
Polyvinyl chloride	212
Poly tetra Fluoroethylene (PTFE)	327
Natural Rubber	30

Table 8.4.6 Melting temperatures T_m for some partially crystalline polymers

8.5 Testing of plastics: Some of the tests used for metals are modified and used for testing of plastics. In addition, there are other special tests applicable only to plastics.

8.5.1 Tensile tests: The tensile test for plastics provides information on mechanical properties similar to that obtained by tensile testing of metals. However, since the properties of plastics are more sensitive to changes in moisture content, temperature and rate of cooling, these variables must be closely controlled.

Flat, tubular or rod specimens are used for tensile testing. The rod specimen, longer and of different shape than the specimen used for metals, is shown in Fig 8.5.1. Specimens to be tested are carefully finished with abrasive paper (No.00 or finer) and subjected to controlled temperatures and relative humidity prior to and during testing. Five specimens are tested for isotropic materials and ten specimens are used for anisotropic plastics (five normal and five parallel to the principal axes of anisotropy). The speed of testing specifies a cross-head speed of 0.20 – 25 inch per minute.

Tensile strength, percentage elongation and modulus of elasticity are calculated in the usual way. Tensile tests (and compressive tests) are also run at elevated or reduced

temperatures

if

required.

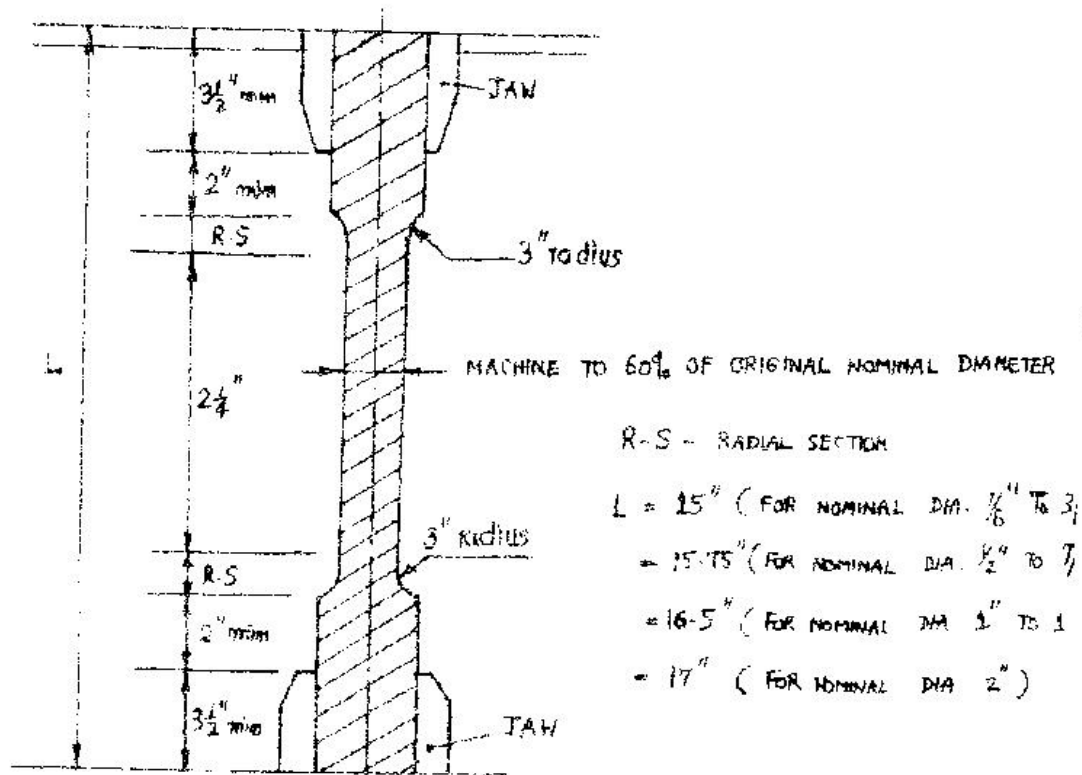


Fig 8.5.1 End tension specimen for plastics. Dimensions of plastic rod tension specimen and diagram showing location of specimen in testing machine

8.5.2 Hardness tests: These are carried out on plastics with a Rockwell hardness tester using the M or R scales. The M-scale employs a 1/4 inch ball penetrator with a 10 kg minor load and 100 kg major load. The R-scale uses a 1/2 inch ball penetrator with minor and major loads of 10 kg and 60 kg respectively. As in tensile testing, the conditioning procedure aims at controlling variables such as temperature and moisture content which properties of plastic are sensitive.

8.5.3 Impact tests: Both Charpy and Izod types are carried out at normal, elevated or subnormal temperatures. A cantilever beam (Izod) specimen is shown in Fig 8.5.3. Charpy specimens are similar to this except that they are 5 inches rather than 2.5 inches long. The values of impact strength are expressed in foot pounds of energy absorbed per inch of notch. These values are determined by dividing the energy absorbed by the length of the notch. Careful conditioning of specimens prior to testing is necessary

for the greatest precision.

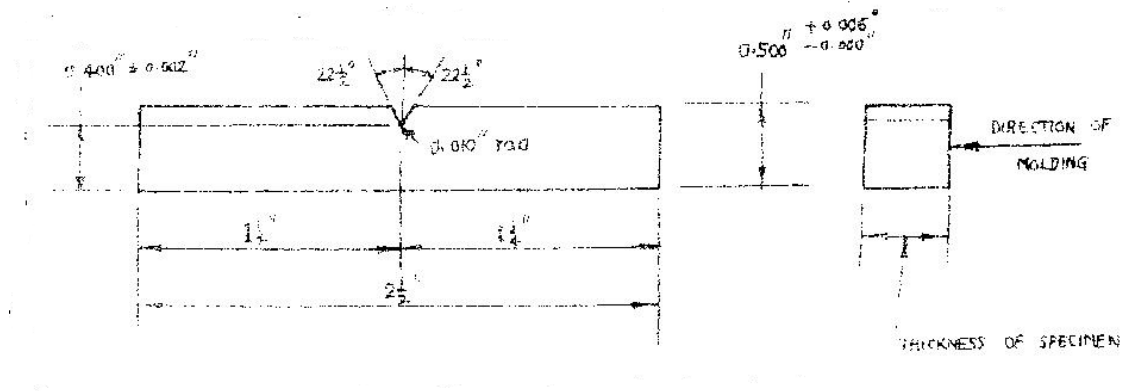


Fig 8.5.3 Izod (cantilever beam) impact specimen for sheet plastic material

The thickness of the specimen is the thickness of the sheet unless the sheet is more than $\frac{1}{2}$ inch thick. if the sheet is more than $\frac{1}{2}$ inch thick, it shall be machined sown to this thickness.

8.5.4 Heat distortion temperature tests: For plastics these are indicative of the temperatures at which softening of the resin commences. To determine the distortion temperature, a beam specimen 5 inches long and 0.5 inch wide having a thickness between 0.125 inch and 0.5 inch is used. The beam is supported on round supports 4 inches apart in a temperature bath at $25 \pm 1^\circ \text{C}$ as shown in Fig 8.5.4

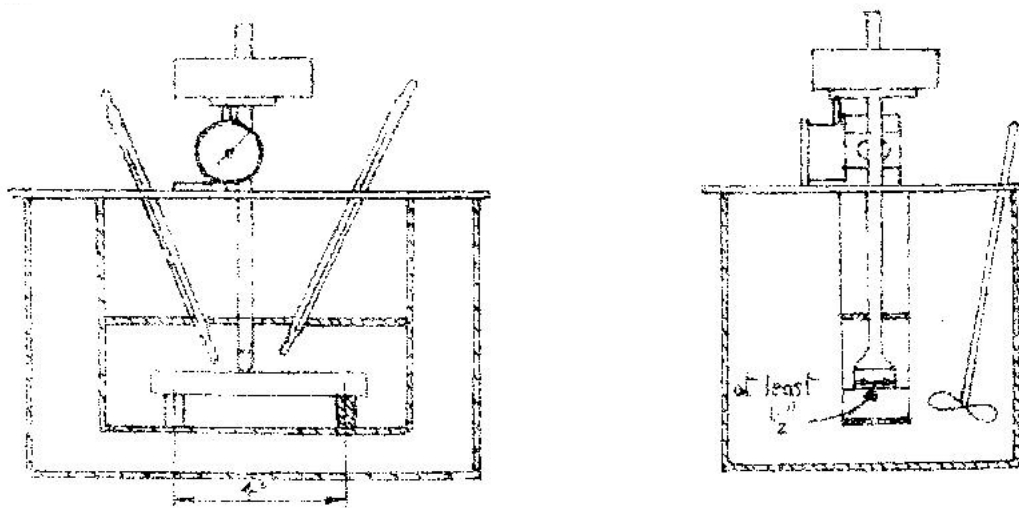


Fig 8.5.4 Apparatus for heat distortion test

Weights applied at the centre of the beam will produce one of two arbitrarily selected maximum fiber stresses in the beam. The larger maximum fiber stress is 264 psi and the

smaller maximum fiber stress is 66 psi. The proper weight is applied for five minutes and the dial gauge is zeroed. Heating at a rate of $2+0.2^{\circ}\text{C}$ per minute is then commenced. The temperature, at which a 0.010 inch deflection is reached, is reported as the heat distortion temperature for the particular stress. Tabulated data present a single figure for heat distortion temperature, specifying the corresponding stress or two figures, a higher one corresponding to 66 psi and a lower one corresponding to 264 psi. The results of this test can rarely, if ever, be used directly in design work. They are however, a useful general indication of relative resistance to softening at elevated temperatures.

8.5.4 Embrittling temperature: Measurements are made by striking a small specimen (1.5 inch X 0.25 inch X 0.075 inch) at an arbitrary velocity (6.5 feet per second). Specimens held in a constant temperature bath are struck at various temperatures. A specimen is said to fail when it is fractured completely into at least two pieces.

8.5.5 Flammability tests: These are of several kinds. The simplest test consists of heating one end of a horizontally supported specimen for 30 seconds with a small (one – half inch) Bunsen flame. If after two attempts, five inches of the specimen has not burned away, the plastic is said to be self extinguishing. If the combustion is supported, the rate of burning in inches per minute is determined by means of a stop watch. The specimens are strips of 6 inches long, 0.5 inch wide and of thickness as supplied.

Other tests are also carried out such as water absorption, accelerated weathering (alternate exposure to fog and ultraviolet light) mar resistance (impairment of surface glass by No. 80 carborundum and moldability and flow resistance).

8.6 Fabrication of plastic objects: A variety of interesting and ingenious methods have been devised for the fabrication of plastic objects. The method used depends largely upon the properties of the resin (i.e thermoplastic or thermosetting) and the geometry of the finished object. It is interesting to note the many similarities between plastic and metal fabrication processes.

8.6.1 Compression molding: It is analogous to hot pressing of powdered metals. A definite amount of thermosetting resin, filler and other ingredients are placed in a mold cavity having the desired shape, as shown in Fig 8.6.1

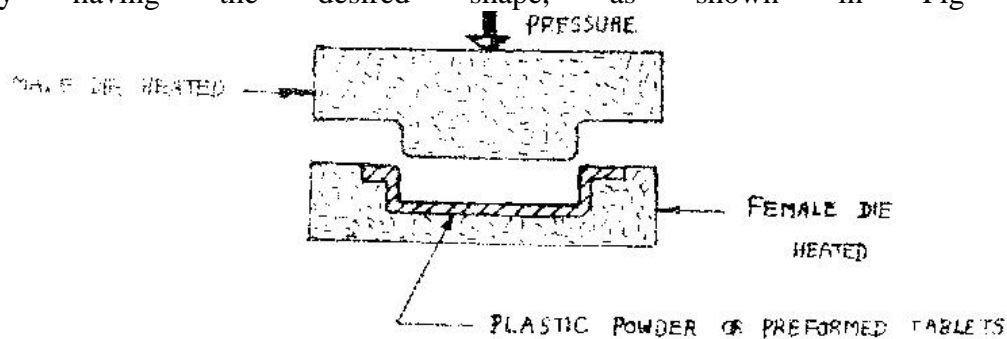


Fig 8.6.1 Diagram of compression molding

The quantity of plastic must be carefully predetermined so that the volume of the compacted plastic is slightly greater than the volume of the mould carefully. In this way complete filling of the cavity is ensured. The amounts of plastic are controlled by hand or automatic weighing or by cold pressing a correctly sized tablet or perform. Both male and

female portions of the die are heated, usually by steam. If performs are used, they are frequently preheated by high frequency dielectric heating or infrared heating lamps. Preheating shortens the time cycle during molding, increases die life, reduces pressure requirements and results in a more uniform product less likely to contain trapped gases, molding temperatures range between 130°C and 180°C, with pressures varying from 1500 to 8000 psi. Pressure and temperature requirements are determined by the kind of resin and the kind filler being used, the size and shape of the object and whether or not preheating is used. The time required for molding varies from portions of a minute to several minutes, depending upon much the same factors as determine the temperature and pressure requirements. Thermoplastics can not be economically shaped by compression molding because of time consuming and expensive alternate heating and cooling cycles

8.6.2 Cold molding: It corresponds to cold pressing powder metallurgy techniques. It involves cold pressing of thermosetting plastic powders, followed by a curing treatment. Cold molding is not widely used and produces articles of inferior surface finish, strength and density.

8.6.3 Injection molding: It is analogous to die casting of metals. Thermoplastic molding compound is loaded into a hopper from which it is fed into an upper cylinder of the molding machine. One stroke of a piston meters the proper amount of compound from the upper to a lower cylinder as shown in Fig 8.6.3. A ram in the lower cylinder forces the charge forward into a heating chamber. Here the granular powder becomes plastic and is forced into a viscous liquid through a nozzle into the mold cavity. The mould is water-cooled which keep it below the melting range of the compound. Pressure is maintained on the plastic until it has cooled sufficiently to solidify. The mold is then opened and object is removed. This process is used principally for thermoplastic resins, though modification, known as jet molding, has been developed for thermosetting materials.

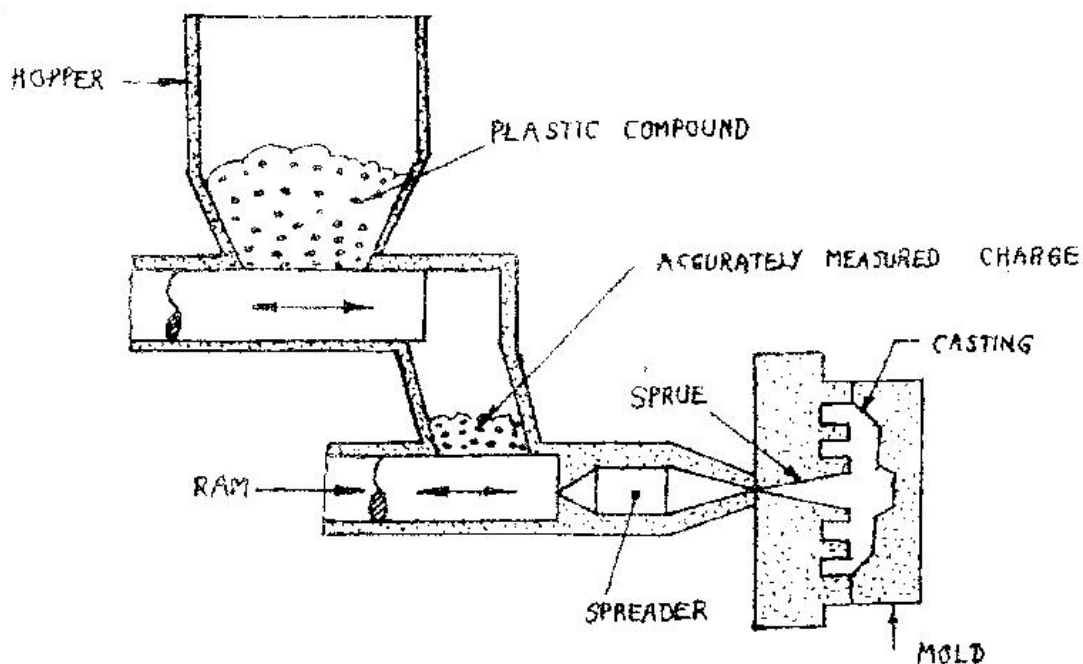


Fig 8.6.3 Diagram of injection molding

8.6.4 Jet molding: It differs from injection molding in that the mold cavity must be heated to cure the plastic and force it into mold cavity. The hot nozzle by which the plastic is initially softened before being forced into the mold is hot only shortly before and during the time the mould is being filled. It is quickly cooled after this portion of the cycle to prevent curing of the plastic remaining in it. As in injection molding, pressure is maintained until the plastic in the mold hardens. Jet molding finds only limited application. Compression molding allows part design of greater complexity than either jet or injection methods and also permits greater flexibility with respect to fillers and inserts.

8.6.5 Transfer molding: It is a modification of compression molding, illustrated in Fig 8.6.5. It is used for making parts of thermosetting resins in which the design involves delicate or complex shapes or critically positioned inserts. If such objects were made by compression molding, application of pressure to the solid powder in the mold cavity might result in breakage or distortion of delicate mould sections or misalignment of inserts.

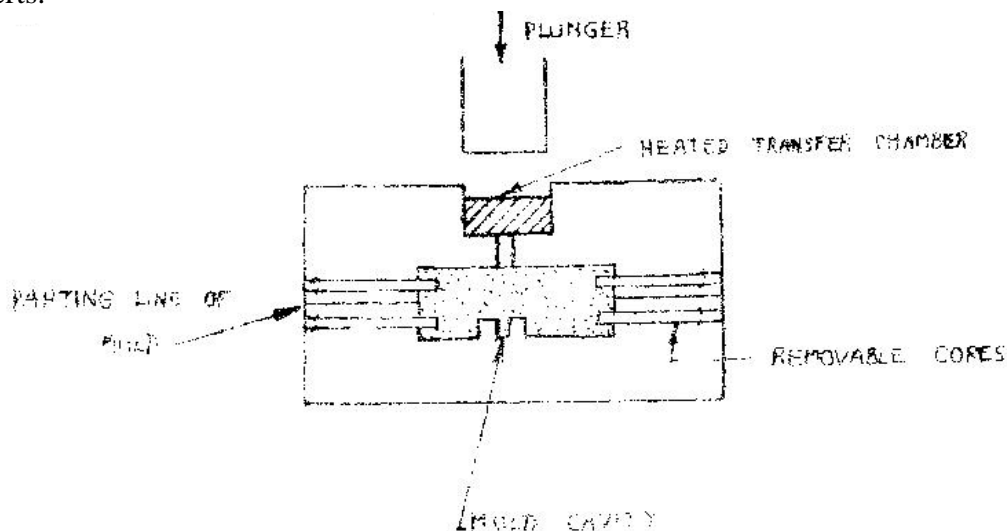


Fig 8.6.5 Diagram of transfer molding

To avoid these difficulties, the solid resin compound is first placed in a transfer pot, where it is heated until it melts. It is then forced into the heated mold cavity, distributing the pressure evenly on all surfaces and avoiding the difficulties described above. As in compression, molding pressure is maintained until the curing is complete, at which time the mold is taken apart and the object removed.

8.6.6 Extrusion molding: It is similar to hydraulic extrusion. However, a mechanical screw rather than a ram is used. The screw forces the solid thermoplastic compound

through a heating zone where melting occurs. The viscous liquid is then extruded through a shaped orifice onto a conveyor or run-off table as shown in Fig 8.6.6.

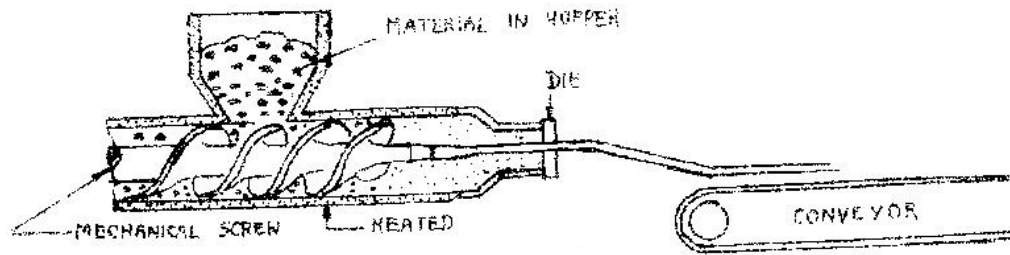


Fig 8.6.6 Diagram of extrusion molding

The length coming from the extrusion –molding machine is commonly cooled by such devices as blowers, water sprays or immersion in a water tank. Extrusion molding is useful for forming continuous thermoplastic shapes such as sheets, filaments, rods and tubes. The cross-sections of filaments, rods and tubes can be varied by changing the shape of the die. To change the internal shape of the tubing, core must be changed.

8.6.7 Casting: It is a process of fairly limited application, useful mainly for thermosetting and to some extent for thermoplastic resins. Steel mandrels having the size and shape of the finished article are dipped into molten lead. A thin shell of lead freezes on the steel. When the steel mandrel is withdrawn a thin lead mold is obtained. Plastic is poured into the mold and cured for several days at temperatures near 60⁰ C. The cured plastic is then knocked from the mold and the lead is remelted for cycling through the process again. This process is useful for making rods, tubes, cylinders and special shapes such as screw driver handles, gear and gear blanks.

8.6.8 Drawing: It is a term applied to the processes analogous to what are known as deep drawing and stretching in sheet metal working. Drawing involves either stretching a sheet of thermoplastic material over a form or forcing the sheeting by means of a plunger through a die.

8.6.9 Blowing: It is similar to the process of the same name used in the glass industry. Films, sheets or extrusions of thermoplastic material are forced into hollow, closed molds by air or steam pressure. Film is the term used for flat material which is less than 0.25 mm in thickness. The process of film blowing is shown in Fig 8.6.9.

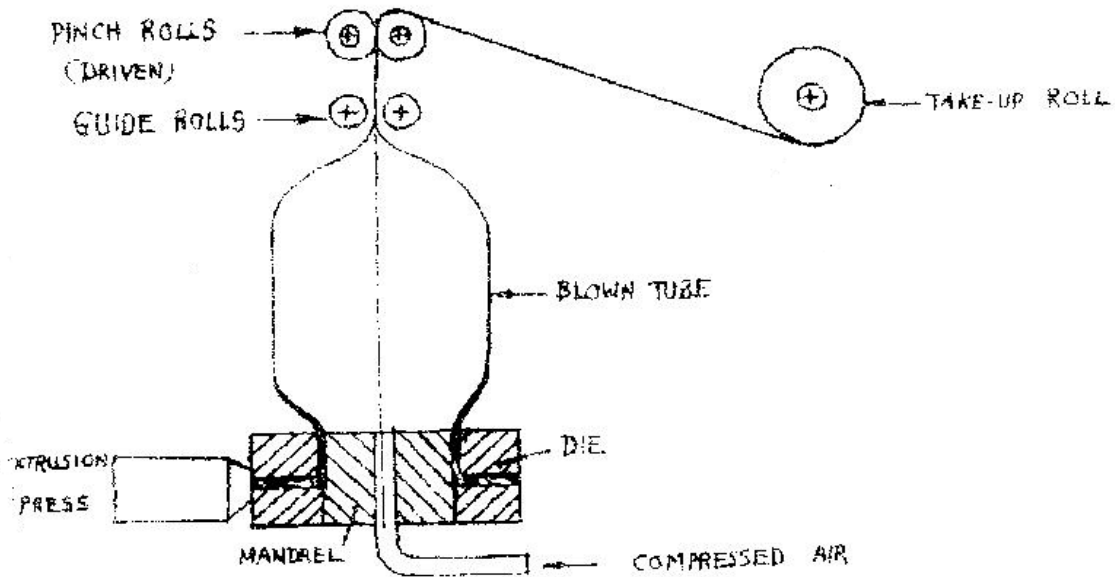


Fig 8.6.9 Film blowing

The plastic material is extruded vertically as a tube of 0.4 mm thick from an annular die. The wall thickness of the tube so produced is usually in the order of 0.4 mm to 0.6 mm. The tube is closed by pinch rolls high above the point of extrusion and air is blown into the tube through the centre of the die mandrel to inflate the tube into a thin walled bubble. The wall thickness of the bubble is the final film thickness and stretching is uniform in all directions. Usually the bubble diameter is 1.5 to 3 times the die diameter. The bubble is finally slit and opened out to make a flat film.

8.6.10 Laminating: It is used to combine sheets of materials such as paper, cloth, glass fibers and wood with plastics. In one method absorbent materials are passed into a resin-solvent solution. Upon removal the solvent is evaporated from the impregnated sheets by heating. The heat also affects a partial cure. The desired number of sheets are stacked and the stack is placed between two highly polished sheets of steel. Pressure and heat are applied so that curing is fully or partially achieved as desired. The finish on the steel surface is imparted to the laminate. Non-ferrous materials such as wood, veneer are commonly superficially coated with resin by a roll type glue spreader, brush, spray or by dipping. The plies are then stacked and cured as described above.

Plastic objects are machined and cut by methods used for shaping metals. Grinding and polishing are carried out if necessary. Thin sheets of thermo-plastics are made by solution casting or solution spraying a resin solution onto a stainless steel belt. After the solvent is evaporated, the film is cooled, peeled and wound for shipment. Thermoplastic sheet is also made by calendaring which is essentially a rolling operation to orient the polymer chains.