भारतीय ज्ञान परंपरा

संस्कृति, दर्शन, शैक्षिक विचारधाराएँ और नवाचार

सम्पादक :
डॉ. दिनेश चन्द्र शर्मा

भारतीय ज्ञान परंपरा :

संस्कृति, दर्शन, शिक्षा विचारधाराएँ और नवाचार

सम्पादक :

डॉ. दिनेश चन्द्र शर्मा

Ph.D., D.Lit. (Sub.)

निदेशक, कॉम्पिटिशन प्लस ग्रुप ऑफ इन्स्टीट्यूशन,

अजमेर

छवि पब्लिकेशन्स

अजमेर-305001

प्रकाशक :
छवि पब्लिकेशन्स
अजमेर-305001
मो. 9660111549

संस्करण :
प्रथम 2022-2023

ISBN : 978 - 81 - 89435 - 64 - 6

मूल्य - 300/-

रचना - भारतीय ज्ञान परम्परा में शिक्षा के समाजशास्त्रीय आधार

सम्पादक - डॉ. दिनेश चन्द्र शर्मा

मुद्रक - श्रीनिवास प्रिन्टोग्राफिक्स, अजमेर

2. POLYMER - STRUCTURE & SYNTHESIS

Dr. (Smt.) S. Sharma
Assistant Professor (Deptt. of Science and Technology)
Hukumchand Noble Institute of Science and Technology, Ajmer

Polymers science and engineering deal with the chemistry, molecular structure, physical properties, the applications and processing in the useful forms and the biological significance of materials. It is the chemistry of large molecules-macromolecules each containing from thousands to millions of atoms. The atoms are typically linked in a sequence of repeating structural units, derived from certain molecules of small units, ie., monomers. The polymer is thus a long chain, in some polymer may coil, branch, cross-linked to other chains or take part in other orders or structural complexity.

The chemical and physical interactions among the atoms of polymer are governed by the same laws that describe systems of small molecules, but extreme molecular size introduces a new realm of properties. The diversity of macromolecular structure represented by a given chemical composition increases with the number of monomeric units present and statistical considerations must enter the description of even the simplest polymer chain. The extreme length of macromolecular chain inhibits their crystallization, hence diverse stable solid states occur which may be rubbery, glassy or semicrystalline. New combinations of properties emerge, such as rubbery elasticity and strength, combined with flexibility and optical clarity. Fabrication methods are found with polymers which facilitate their shaping into desired forms. Polymers made by man, and their fabrication into finished products have become the basis of a major industry world wide. Life itself is a basis of large molecules. The remarkable adaptations of collagen and cellulose to structural functions, the specificity and efficiency of enzymes as catalysts, the binding and release of oxygen by hemoglobin and myoglobin, and the encoding of specific genetic information by the nucleic acids, all

have their origins in the polymeric nature of the molecules involved."

Polymer study and research is thus interdisciplinary, with major contributions from chemistry, physics, several branches of engineering, biomedical science and molecular biology.

Polymers are essential in fulfilling a broad range of national needs, present and prospective, in such categories as energy, transportation, construction, agriculture and food processing, medicine and national defense. The history of polymer science and engineering is replete with unforeseen discoveries of major consequence, and the future of this field is bright one promising. For example, the recent break throughs in understanding the structure and invivo synthesis of biopolymers still have to make their major impact on synthetic polymers, and the theory and application of composite materials based on polymers are still in their infancy.

Enormous studies have been made in the field of biopolymers, since the discovery of the DNA double helical structure in 1953. This was followed by various advances: the determination of the detailed sequence structure of nucleic acids and proteins, the recognition of nucleic acids as the carriers of heredity and the solid-state synthesis of sizable protein molecules. Further progress has continued in many related areas, including such vital aspects as the three-dimensional structure of enzymes, its connection to binding of specific molecules, and thus its catalytic function.

The production of polymers on a volume basis now exceeds that of steel, and its growth rate (8.5% per year) is four times that of steel and nonferrous metals. Polymer industries add $ 90 billion per year of value added by manufacture and employ 3.4 million people. Polymers also have a high technology aspect which will be increasingly important in the future and may have a critical impact on fulfilling national needs.

CLASSIFICATION OF POLYMERS

Polymers are classified in a number of ways:

(1) On the basis of source or origin

(2) On the basis of structure

(3) On the basis of mode of synthesis

(4) On the basis of interparticle forces.

(1) Classification of Polymers Based upon Origin or Source

On the basis of origin or source, the polymers are classified into two types:

(a) Natural Polymers

(b) Synthetic Polymers

(a) Natural Polymers: The polymers, which are isolated from natural materials, mostly plants and animal sources, are called natural polymers. A few examples are:

(i) Polysaccharides :Starch and cellulose are very common examples of polysaccharides. They are the polymers of glucose. Starch is a chief food reserve of plants while cellulose is chief structural material of plants.

(ii) Proteins: These are polymers of a-amino acids. They are building blocks of animal cells. They constitute indispensable part of our food. Natural protein, wool, leather, etc., are proteins.

(iii) Nucleic Acids: These are the polymers of various nucleotides. RNA and DNA are common examples

(iv) Natural Rubber: Substance obtained from latex is known as natural rubber. It is a polymer of 2-methyl-1, 3-butadiene (isoprene).

Biopolymers: It may be noted that polymers like polysaccharides, proteins nucleic acids, etc., which control different life processes in plants and animals are also called biopolymers.

(b) Synthetic Polymers: The polymers which are prepared in the laboratory are referred to as synthetic polymers or man-made polymers. Some examples of synthetic polymers are polyethylene, polystyrene, teflon, PVC, synthetic rubber, nylon, bakelite, orlon, polyester, terylene etc.

(2) Classification of Polymers Based on Structure

This classification of polymers is based upon how the monomeric units are linked together. Based on their structure, the polymers are classified as:

(a) Linear Polymers

(b) Branched Chain Polymers

(c) Cross-linked Polymers or Network Polymer

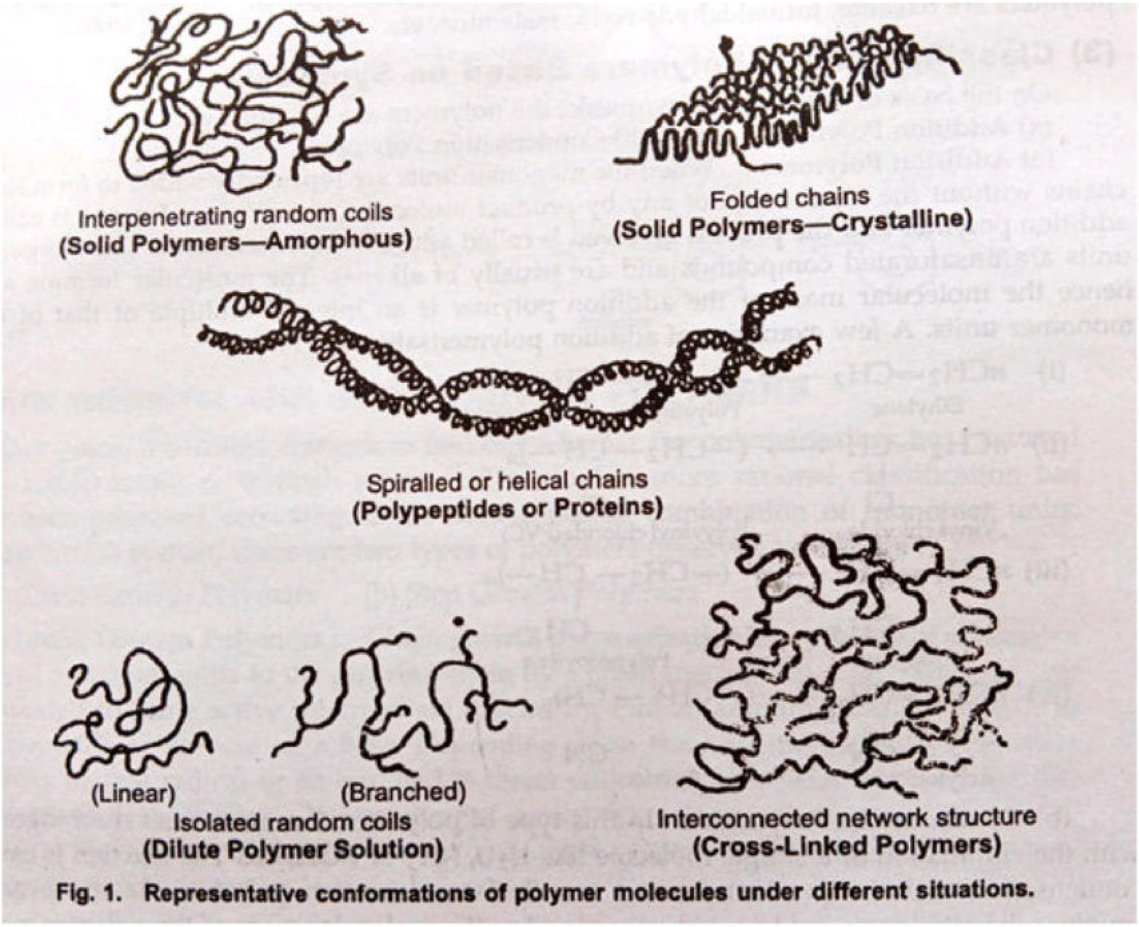


Fig. 1. Representative conformations of polymer molecules under different situations.

(a) Linear Polymers: These are the polymers where monomeric units are linked together to form long straight chains. The polymeric chains are stacked over one another to give a well packed structure. As a result of close packing, such polymers have high densities, high tensile strength and high melting points. Common examples of these type polymers are polyethylene, polyester and nylon etc.

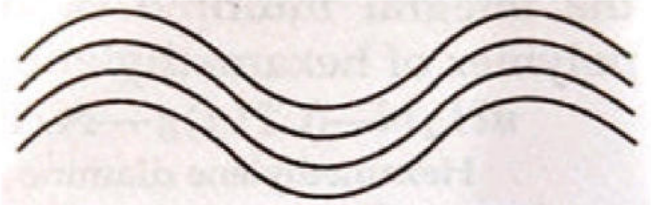


Fig. 2. Linear chain.

(b) Branched Chain Polymers: In this type of polymers, the monomeric units are linked to constitute long chains, which are also called main-chain. There are side chains of different lengths which constitute branches. Branched chain polymers are

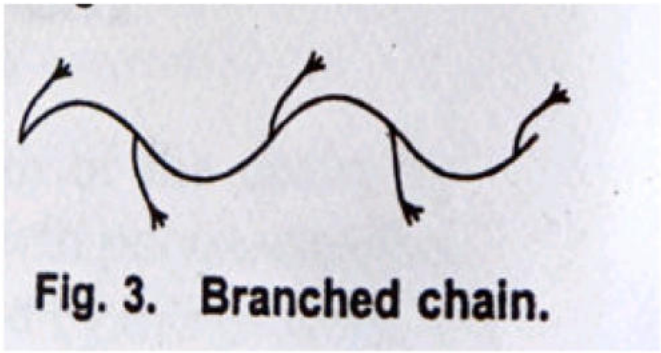


Fig. 3. Branched chain.

irregularly packed and thus, they have low density, lower tensile strength and lower melting points as compared to linear polymers. Amylopectin and glycogen are common examples of such type.

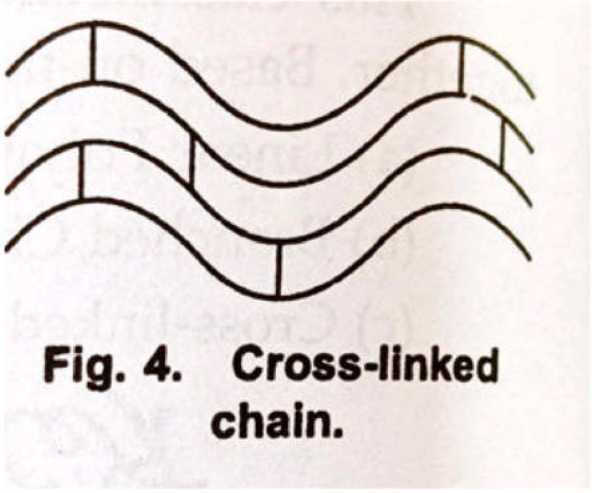


Fig. 4. Cross-linked chain.

(c) Cross-Linked Polymers or Network Polymers: In this type of polymers, the monomeric units are linked together to constitute a three dimensional network.Thelinksinvolved are called cross links. Cross-linked polymers are hard, rigid and brittle becauof their network structure. Common examples of this type of polymers are bakelite, formaldehyde,resin, melamine etc.

(3) Classification of Polymers Based on Synthesis

On the basis of the mode of synthesis, the polymers are classified as:

(a) Addition Polymers

(b) Condensation Polymers

(a) Addition Polymers: When the monomer units are repeatedly added to form lang chains without the elimination of any by-product molecules, the product formed is called addition polymer and the

process involved is called addition polymerisation. The monomer units are unsaturated compounds and are usually of alkenes. The molecular formula and hence the molecular mass of the addition polymer is an integral multiple of that of the monomer units.

(b) Condensation Polymers: In this type of polymers, the monomers react together with the elimination of a simple molecule like H2O, NH3 or ROH, etc. The reaction is called condensation and the product formed is called condensation polymer. As the process nvolves the elimination of by-product molecules, the molecular mass of the polymer is not me integral multiple of the monomer units. For example, nylon-66 is a condensation olymer of hexamethylene diamine and adipic acid.

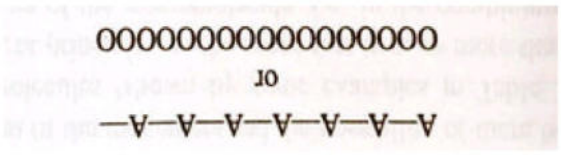
POLYMER STRUCTURE

In this section we will consider the micro-structure of the polymer ie.. the arrangement of the structural units relative to one another. Several variations are possible and thecan have pronounc effects on the properties of a polymeric material. The structural arrangements may be considered und the following headings.

Forms of polymers

A polymer may consist of monomers of identical or of different chemical structure. Polyme consisting of identical monomers are called homopolymers. Thus homopolymer is a macromolecule derived from a single monomer. Polymeric compounds containing several types of monomeric un in their chain are known as copolymers or mixed polymers. Thus a copolymer is a macromolecul derived from two or more different monomers. Monomeric units may combine with each other inte a macromolecule to form a polymer of linear, branched, or crosslinked (three-dimensional) structur

Linear polymers are polymers whose macromolecules are long chains with a high degree of asymmetn Denoting a monomeric residue by A, one would write the formula of a linear polymer as follow

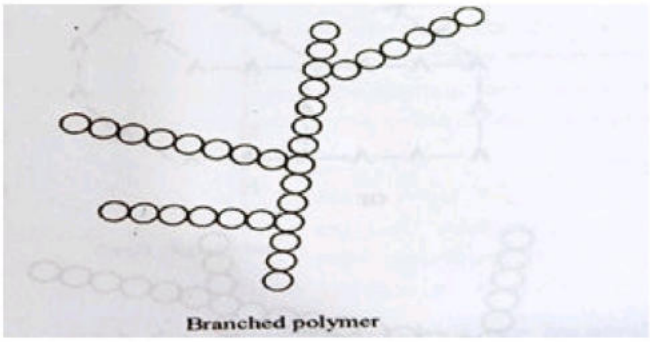


Linear Polymer

A linear polymer is one in which each repeating unit is linked only to two others. Polystyren and poly (methyl methacrylate) are

linear polymers.

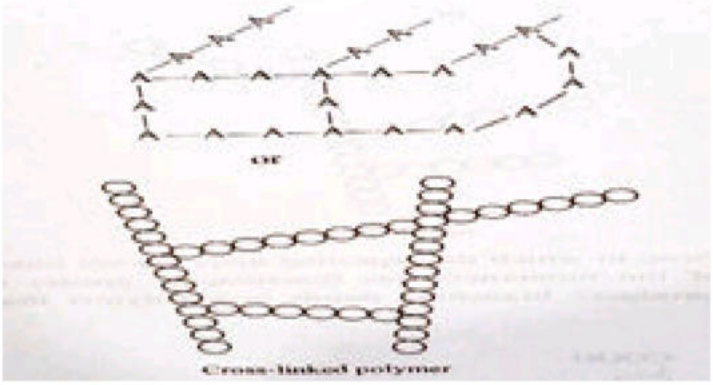
A branched polymer is a long chain (usually called the main chain or backbone chain) with sit branches (side chains), the number and length of which may vary widel



An example of the first type is the polymer made from glycerol, phthalic anhydride and linseed oil.

The major example of the second branched polymer type is the polyethylene that is made by free radical polymerisation at 100-300°C and pressure of 1000-3000 atm. Depending on reaction conditions, these polymers will contain 20 to 30 ethyl and butyl branches per 1000 carbon atoms. They differ sufficiently from linear polyethylene.

Crosslinked or three-dimensional polymers consist of long chains connected up into three-dimensional network by chemical crosslinks:



POLYMER PROCESSING

Processing of polymer' is an important branch of polymer chemistry and technology. Polymer processing is an engineering speciality which is used to polymeric materials into useful products. To prepare a toy, household products, comen have to convert a polymer into elegance and better finished shapes and structures. In he artificial heart, kidney, blood cells, wall tiles, combs, helmets and several other

produc polymer-processing technology makes possible to convert refined and finer form conventional materials.

A large number of synthetic polymers now exist which cover a wide range properties. These can be grouped into three major classes:

(a) plastics (b) elastomers (c) fibres

PLASTICS

Plastic is a material in which a stress produces a non-reversible strain. Plastic is define as an organic high polymer which is capable of changing its shape on the application force and retaining this shape on removal of this force.

The plastic is a Greek word, which means a material that can be moulded and forme any shape of choice. Plastic is a synthetic polymer, which can be converted into compie shapes by the application of heat and pressure. It is sub-divided into (i) thermosetting plast and (ii) thermoplastics.

The thermosetting materials become permanently hard when they are heated abo the critical temperature and will not soften again on reheating. They are genen cross-linked in this state.

A thermoplastic polymer will soften when heated above glass transition temperature, again and can be reshaped if required before hardening T. It can then be shaped and on cooling will harden in this form. On heating it will soften cycle can be carried out repeatedly.

when the temperature drops. This There are various classes of plastics available, however, few of main types are as follows:

Plastics

Name of Plastics

(1) Acrylic plastics

(2) Amino plastics

(3) Cellulosic plastics

(4) Epoxide plastics

(5) Fluoro plastics

(6) Phenol plastic

(7) Polyamide plastics

(8) Polyesters

(9) Polyolefines

10) Styrene plastics

(11) Vinyl plastics

Major Examples

Polyacrylonitrile Polymethyl methacrylate

Melamine-formaldehyde resin Urea-formaldehyde resin

Cellulose nitrile Cellulose Acetate Ethyl Cellulose

Epoxy resins Epoxy novalac resins

Polyvinylidene fluoride Polytetrafluoro ethylene

Phenol-formaldehyde resin Phenol-furfural resin

Polycaprolactam (Nylon 6) Polyhexamethylene adipamide (Nylon 66)

Polyethylene Terephthalate Polyethylene adipate Unsaturated polyester resins

Polyethylene Polypropylene

Polystyrene Styrene-acrylonitrile copolymer

Poly vinyl chloride (PVC) Poly vinyl butyral

Thermosetting Plastics

The thermoset plastics are more superior and have dimensional stability chans as compared with the thermoplastics which have better impact properti thermosetting plastics are alr ady changed irreversibly from fusible, soluble produs highly intractable cross-linked resins which cannot be moulded by flow.

In actual sense, the plastic materials have properties in between elastomeric and fibre-forming polymers. They consist of good rigidity and tensile strength. Plastics can either be fully amorphous or partially crystalline in nature. A fully amorphous polymer will be a plastic material, when its glass transition temperature (1) is above the 'use temperature. Polystyrene with Te 100°C is a good example. Amorphous plastics are brittle the rubbery state and existing in

Partially crystalline polymers are tough plastics above Ty and below melting temperature, Tm. Suitable example of this type of plastic is polyethylene. It possesses a Ty of -125°C and a Tm of 146°C. The crystalline component in these polymers gives good strength and rigidity.

The drawback of fully amorphous plastic is its brittleness. This can be removed by adding some elastomers during the reaction. If a small percentage of butadiene rubber is dissolved with styrene monomer at the time of polymerisation, the polystyrene is formed. This product contains reduced brittleness, and improved strength and impact properties. Such polymer is known as 'high impact polystyrene'.

Cross-linking of plastic materials improves the structural rigidity and the resistance to swelling by solvents and also increases the upper range of the 'use' temperature. Generally, the thermoplastic materials are uncross-linked and the thermosetting plastics are cross-linked systems. For example, phenol-formaldehyde, urea-formaldehyde and epoxy systems involve cross-linking, while polyethylene and polystyrene are uncross-linked systems.

Thus, the cross-linking or plasticisation is required when (i) the Tm is low (ii) the material can be melted and moulded without decomposition (iii) the uncross-linked material itself can show the properties of the end product.

If the Te is very high, e.g., as in PVC, which consists of too high Tm, 310°C. The processing cessing of PVC is very difficult, therefore, its flexibility and softness can be improved by cross-linking it. Consequently, the improved PVC is used to make the various products ranging from rigid tubes to soft flexible toys.

PROCESSING TECHNIQUES

There are various techniques in which the compounded polymers or resi processed and converted into finished products. Polymeric materials are used forms such as sheets, rods, tubes, coatings or adhesives and also as moulded and ti

(1) Calendering

The calendering is a process, which is employed to prepare continuous sheets and films from a compounded polymeric material.

The main polymers which are usually calendered sheets are polyvinyl chloride (PVC), styrene copolymer (ABS).

In this process, a calendering machine is used which consists of a set of highly polished metal rollers rotating in opposite directions. These rollers involve precise adjustment of the gap between them. This gap determines the thickness of the sheet which has to be calendered out. Instead of a sheet, if thin film is required, a series of rollers with a diminishing gap between them is used. In the calendering machine, the compounded polymeric material is placed between hot rollers. The sheet emerging the rollers is cooled by passing through cold rollers. The sheets are finally wound up in rolls. The schematic diagram of a calendering machine is shown in fig. 1

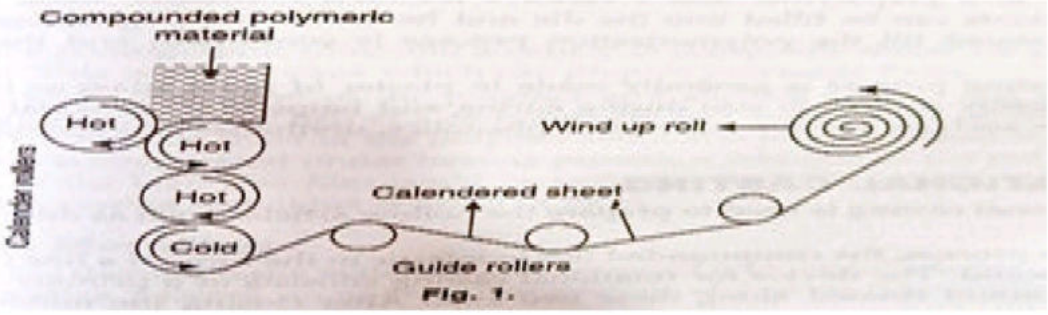


Fig. 1.

2) Die Casting

Liquid prepolymer can be converted into solid object in a required shape by da process. Die casting is an inexpensive and simple process; where a petri-dish is prepolymer compounded suitably with a curative and essential ingredients are fl petri-dish. This dish is then placed in an hot oven for few hours to complete reaction. After heating, it is kept for cooling at room temperature. The solid produd petri-dish is pulled out. Here the petri-dish is known as a die. The solid thus cast wi shape similar to the interior of the petri-dish. A simple illustration demonstrating the process is shown in fig.

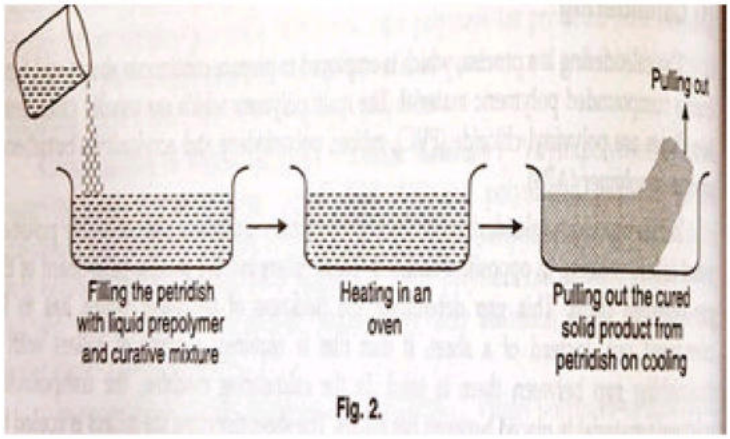


Fig. 2.

Rods, tubes and the sheets of limited lengths can be produced by the casting Instead of a prepolymer and a curative mixture, monomer along with cataly other ingredients can be filled into the die and heated to the polymerisation temp The die is heated till the polymerisation process is continued, and the solid pre formed.

The casting process is generally made in plaster of paris, glass or lead die. The blocks can easily shrinks in size during curing and helps in its removal from the de prepolymers such as, polyesters, acrylics, phenolics, urethanes and epoxides are su die casting.

(3) ROTATIONAL CASTING

Rotational casting is used to prepare the hollow articles such as dolls, rainboots, hi balls etc.

In this process, the compounded thermoplastic in the form of a fine powder is pa a hollow mould. The device for rotational casting consists of a primary and the se axes. The mould rotated along these two axes. After closing the mould, it is heat

rotated. Due to rotation, the molten plastic distributes uniformly along the entire surface of surface. After this mould can be opened and the desired product is removed. The rotating process is continued. Now the thermoplastic material solidifies in the shape of that thermosetting material along with curative mixture can also be taken in liquid form in mould and casting is made under elevated

temperature to get a desired shaped product When a liquid material is used for rotational casting process, it is known as 'slust. moulding'. The apparatus used for rotational casting is demonstrated in fig. 3.

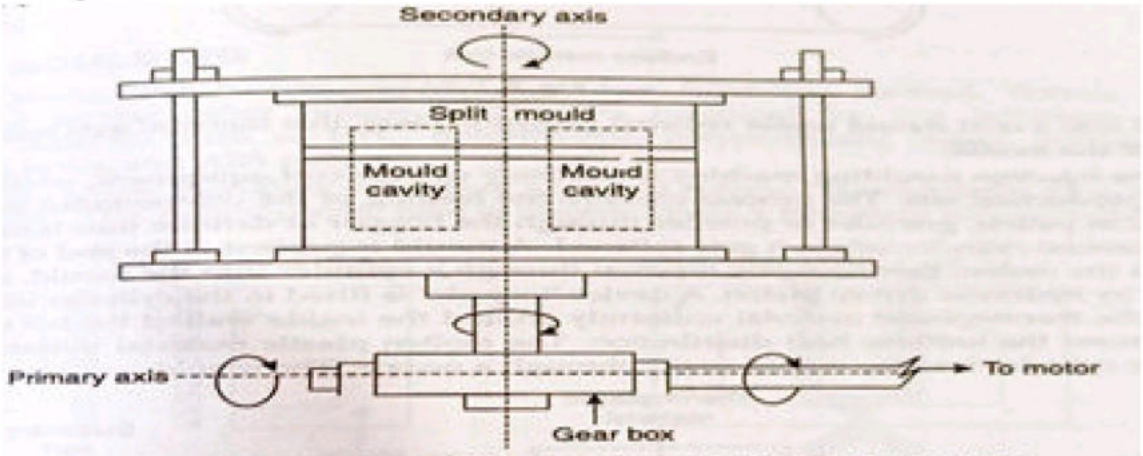


Fig. 3. Apparatus for rotational casting showing hollow moulds, alongwith primary and secondary axis.

(4) Film Casting

Most of the photographic films and a variety of cellophane sheets are prepared by film casting process. This is a technique which can prepare polymeric films.

In this process, a solution of the polymer in a suitable solvent and concentration is poured on an endless metallic belt at a constant rate and speed. Thus on the surface of the metallic belt, a continuous sheet of the polymer solution is formed. When the solvent of the polymer solution is evaporated under heating process, a thin film of the polymer is formed on the surface of the belt. The film could be removed easily by stripping

(5) Injection Moulding

Generally the thermoplastic materials are converted into useful articles by this method. In injection moulding process, an appropriate amount of molten thermoplastic material isinjected into a cold mould under reduced pressure. Here, this material gets solidified to shape of the mould.

The injection moulding machine is relatively of high cost equipment, which consis a high production rate. The process contains the feeding of the compounded thermoplas material as pellets, granules or powder through the hopper at definite time interval into 6 hot horizontal cylinder where it gets softened. A mould is present at the end of the cylinde To push the molten thermoplastic material through a cylinder into the mould, a pressum applied by hydraulic driven piston. A device 'torpedo' is fitted in the cylinder which helps spread the thermoplastic material uniformly around the inside wall of the hot cylindern thus ensures the uniform heat distribution. The molten plastic material ultimately injec From the cylinder into the mould cavity through a nozzle. The mould consists of two partmovable part and (b) a stationary part. The movable part can be opened or locked on th estationary part, while stationary part remains fixed to end of the cylinder. A mechanical locking device is used which helps the mould to properly held in position as the molten plastic material is injected under a pressure as high as 1500 kg/cm^2. In order to stand at high pressure conditions, the locking device is designed very skillfully. After filling the molten material in mould, it is allowed to cool in

cold water and then either manually or by automated procedure. The schematic diagram of whole process is pened to remove the desired article. Thewhole process could be repeated many times described in fig. 5.

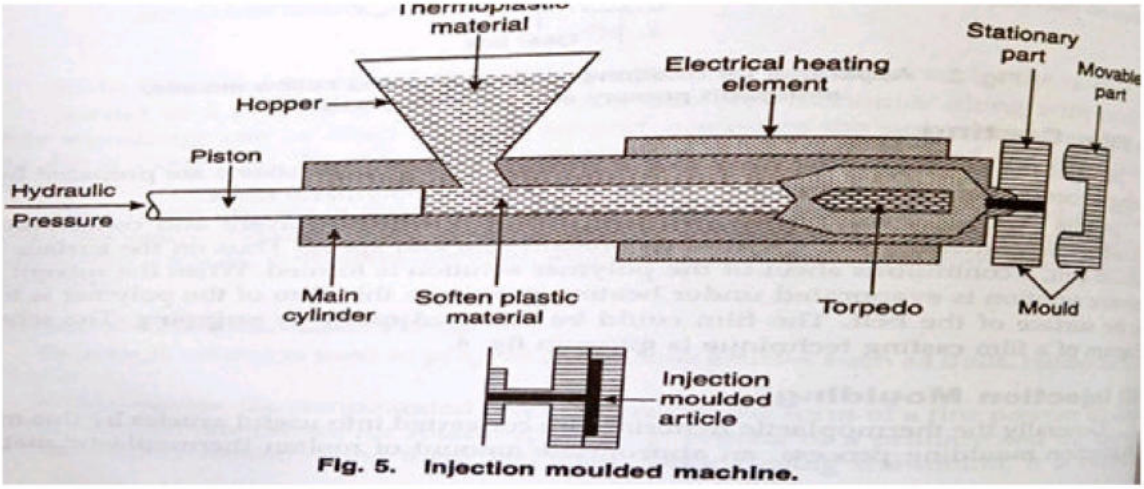


Fig. 5. Injection moulded machine.

Post Treatment of Fibres

To make more useful, the fibres are subjected to post treatments. The treat methods are scouring, lubricating, sizing, dyeing etc.

For scouring, soap and detergents are employed. Scouring means removal of dirte other impurities from the surface of the fibres.

For lubrication, vegetable oils are used. Lubrication, means to protect fibris external friction which may be resulted on the fibres by neighbouring fibres on m metallic surface during processing. Lubrication also reduce static electricity formed on fibres.

Sizing is a process, which helps to give a protective coating to the fibres.

Dyeing means to impart colours to the fibres. This process is done by immersing fi into a dye solution till the dye penetrates into the fibres. Penetration takes place particle at the amorphous regions of the fibre. Hydrogen bonds or Vander Waals' bonds play a significant role in the absorption of the dye by the fibre.

❑❑❑