

Lecture36: Introduction To Polymerization

Technology

36. 1 Definitions and Nomenclature

Polymer: Polymers are large chain molecules having a high molecular weight in the range of 10^3 to 10^7 . These are made up of a single unit or a molecule, which is repeated several times within the chained structure.

Monomer : A monomer is the single unit or the molecule which is repeated in the polymer chain. It is the basic unit which makes up the polymer.

ThermosettingPolymer: There are some polymers which, when heated, decompose, and hence, cannot be reshaped. Such polymers have a complex 3-D network (cross-linked or branched) and are called Thermosetting Polymers. They are generally insoluble in solvents and have good heat resistance quality. Thermosetting polymers include phenol-formaldehyde, urea-aldehyde, silicones and allyls.

ThermoplasticPolymer: The polymers in this category are composed of monomers which are linear or have moderate branching. They can be melted repeatedly and casted into various shapes and structures. They are soluble in solvents, but do not have appreciable thermal resistance properties. Vinyls, cellulose derivatives, polythene and polypropylene fall into the category of thermoplastic polymers.

36.2 Polymer Classification

Polymers are generally classified on the basis of –

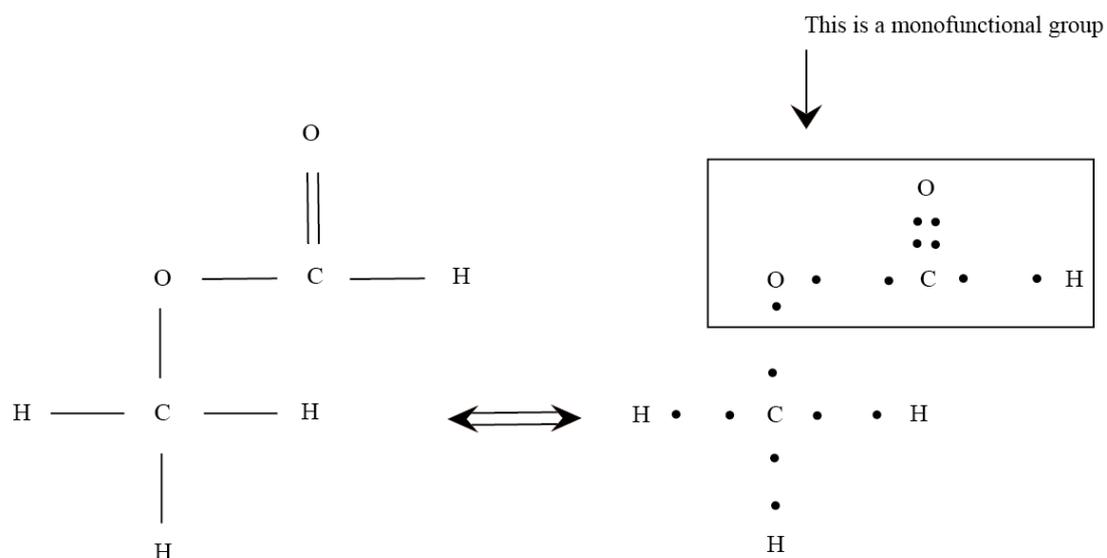
- I. Physical and chemical structures.
- II. Preparation methods.
- III. Physical properties.
- IV. Applications.

36.3 Classification According To Physical And Chemical Structures :

1. On the basis of functionality or degree of polymerization :

The functionality of a monomer or its degree of polymerization determines the final polymer that will be formed due to the combination of the monomers. The number of reactive bonds or groups that are available for coupling will determine whether the monomer will be mono-, bi-, tri-, or polyfunctional.

a .Monofunctional or unifunctional : When a single reactive group is present in the monomer molecule, then it is termed as monofunctional or unifunctional. However a monofunctional group cannot lead to the propagation of a polymer chain. For example , in carboxylic acid, CH_3COOH , the $-\text{COOH}$ group is the monofunctional group.

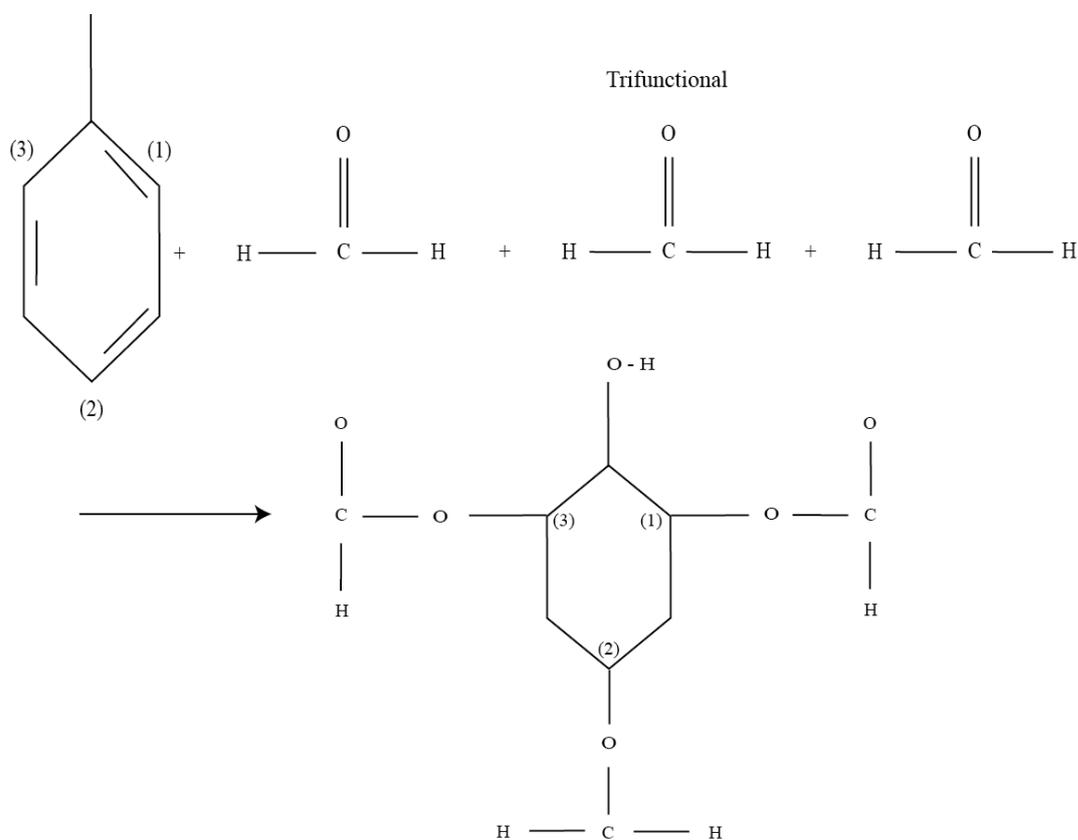


b .Bifunctional: When two reactive groups are present in the monomer molecule, then it is termed as bifunctional. More often than not, polymerization reaction with bifunctional groups occur when a double bond splits to couple with another double bonded monomer. If a double bonded molecule is present, then the polymer would be –



c .Trifunctional: When a monomer contains three groups that are reactive, then it is termed as trifunctional. It is important to note that a trifunctional polymer may be a mixture of monofunctional and bifunctional monomer structures.

Let us consider the reaction of phenol and formaldehyde to form trimethyl phenol.



In the figure, the three formaldehyde molecules contain three reactive groups in the form of -OH groups. These reactive groups get attached to the positions 1, 2 and 3 in the phenol molecule.

2. On the basis of physical structure :

a .Linear polymers: These polymers have a linear structure. Only bifunctional monomers can form linear polymers.

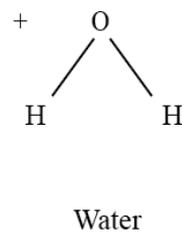
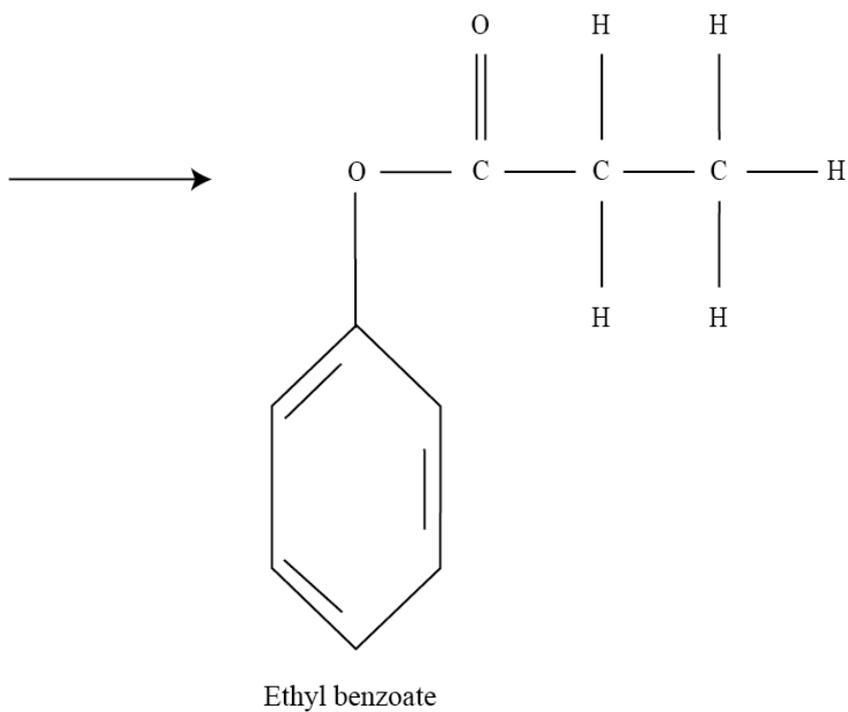
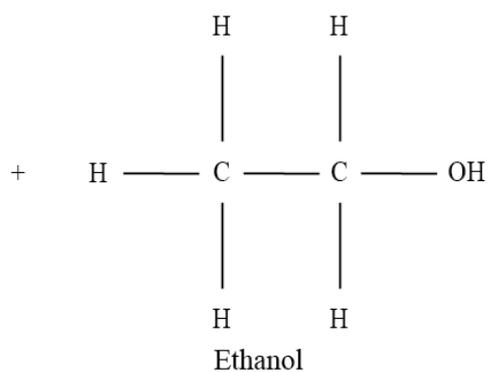
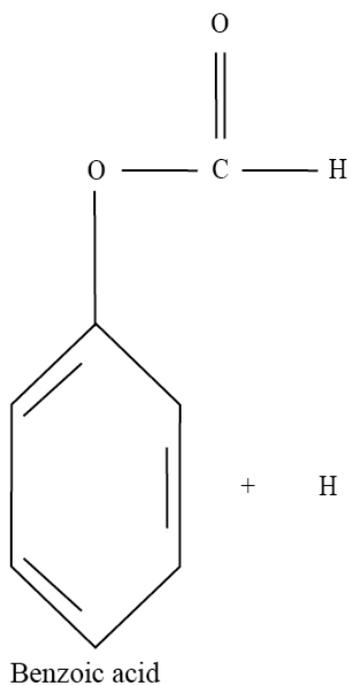


They are generally thermoplastic polymers, and except for very high molecular weight materials, they are soluble in solvents.

3. On the basis of chemical reactions :

Depending upon the basis on which monomers undergo chemical reactions to form polymers, polymers can be further subdivided.

a .Polycondensation Reaction : It is a stepwise process in which the monomers react by eliminating small molecules like H_2O , NH_3 , CH_2O and $NaCl$ in a repetitive manner . Indefinite growth of the polymer occurs at both ends. The condensation reaction terminates when one of the reacting molecules is completely consumed in the reaction. In general, bifunctional monomers with different functional groups undergo such reactions. One common example of a condensation reaction is the esterification reaction. Benzoic acid reacts with ethanol undergoing condensation reaction to give Ethyl benzoate, expelling one molecule of water (H_2O). The polymer formed after the reaction (in this case, ethyl benzoate) is called the condensation polymer.



b .Addition Reaction : These reactions occur by the formation of rapid formation of rapid chains and no elimination of small molecules occur. Such reactions generally occur among double or triple-bonded molecules, or oxo-ring compounds.

Addition reactions can be further of three types—

- i. Step Reactions
- ii. Chain Reactions
- iii. Ionic Reations

i .Step Reactions: In step reactions, a π bond is broken and two new σ bonds are formed. The substrate of an electrophilic addition reaction must have a double bond or triple bond.

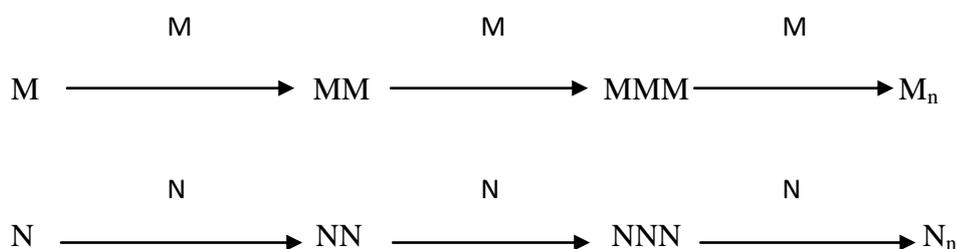
ii .Chain Reactions : In chain addition reactions, the polymer is formed in a single step and within the fraction of a second. The chain kinetics occur in 4 steps – Initiation, Propagation, Transfer and Termination.

Variations of Chain Addition Reaction :

If we consider ‘M’ and ‘N’ be two monomeric species, then the chain addition reaction can be of the following types –

Homopolymerization

If only M and N are present,



Copolymerization

If M and N are present together,

Random type



Alternating type



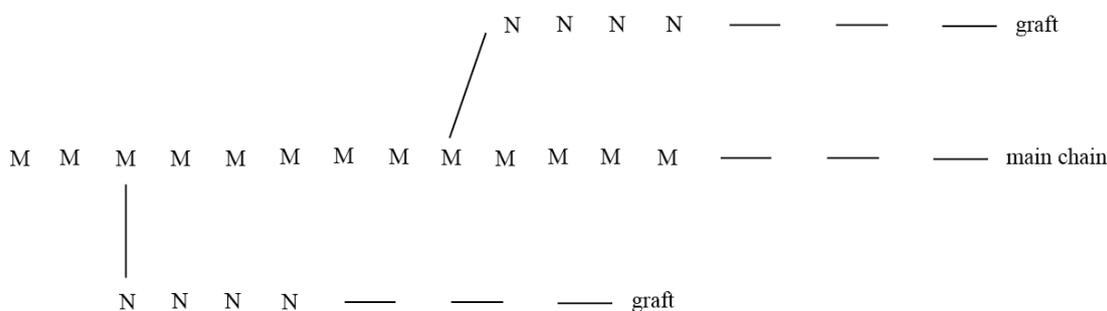
Block Polymerization

In this type, multimers resulting from straight polymerization coupled together in blocks.



Graft Polymerization

These have a structure which differs from block polymers ; and are formed from M and N multimers.



In Graft polymerization, β – or X - radiation or chemically reactive functional groups ensue the formation of reactive radicals on the main chain or on the grafted section.

Reaction Kinetics :

Let,

A – radical source

B – monomer molecule

*- activated

B_m, B_n – growing monomer molecule chain of lengths ‘m’ and ‘n’.

X – any solvent, impurity, etc. which can act as transferable energy species.

Initiation

It is the rate – controlling step in the chain Addition Reaction. This stage is relatively slow and requires energy for breaking and forming the bonds.

The energy is supplied as thermal energy or in the form of radiations (α -, β -, or γ - rays). However, by using a catalyst, the activation energy required can be substantially lowered.



Propagation

These reactions occur between the already formed free radicals and an inactive monomer. With low activation energy, there is more probability of reaction or collision between the species. As a result, rapid reactions occur to attain the given degree of polymerization.

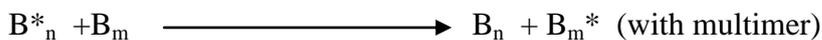
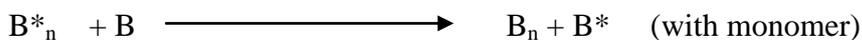


controls the degree of polymerization]

Chain Transfer Reaction

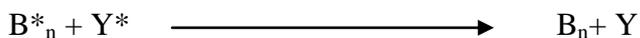
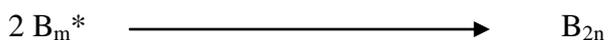
In this reaction, one radical of the multiplying chain terminates and without the loss of any number of free radicals, a new chain begins. These reactions control the degree of polymerization and the rate of branching of the polymers.

Branching usually occurs at higher temperature, with the reaction of a multimer with a dead chain, followed by lengthening of the branch due to successive monomer addition.



Chain Termination

A chain terminates with the net loss of one free radical. It may occur by the collision of growing chains with coupling or disproportionation. However, if a growing chain collides with an initiation radical, undesirable impurities or the wall of the reaction vessel, then it might also terminate.

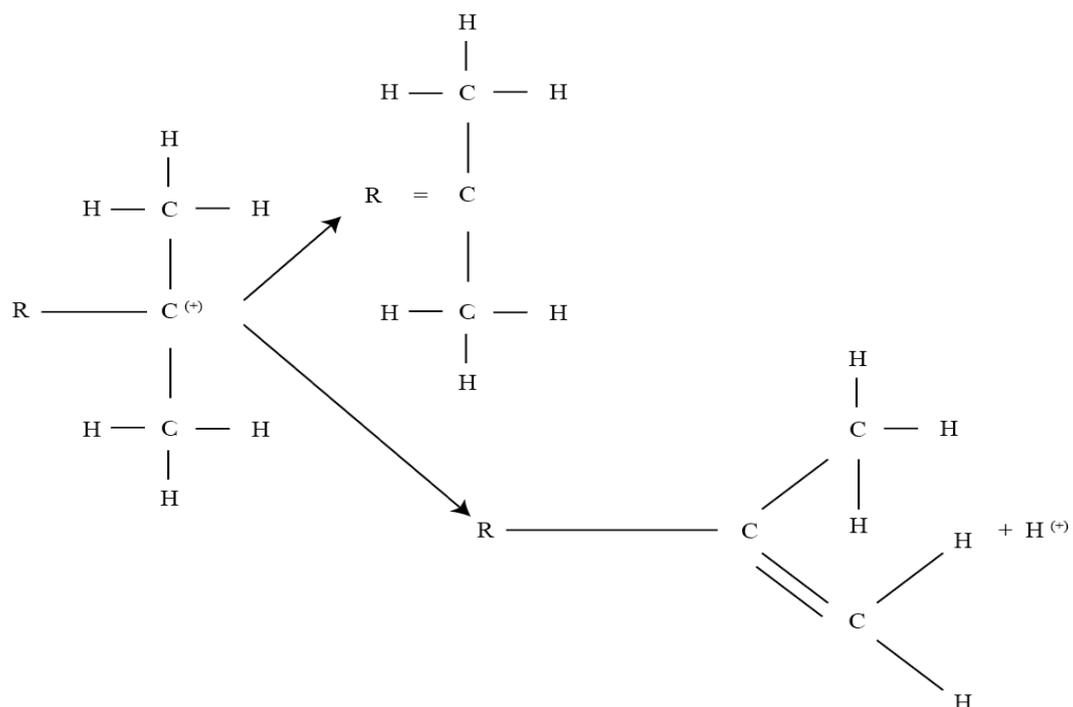


iii .Ionic Reaction :

These are similar to chain addition reaction with free radicals, however; instead of neutral, unpaired electrons, they have a positive or negative charge. A co-catalyst may be used, which is usually a trace of H₂O, which is necessary to produce ionization, as the reaction cannot occur in absolute dry conditions.

An example of ionic addition reaction is the preparation of polyisobutylene with boron trifluoride catalyst.

Termination



References :

Ullmann F., Encyclopedia of Industrial Chemistry, Wiley – VCH, 1999-2012

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

Lecture 37: Introduction to Polymerization

Technology (Contd).

37.1. Classification According To Preparation Methods :

Preparation methods for polymers may be roughly divided into two categories –

(A). Condensation Polymerization Methods.

(B). Addition Polymerization Methods.

(A). Condensation Polymerization Methods :

These methods are usually employed for low molecular weight functional group reactions, where the stoichiometric proportions of the reactions are fixed for the desired final products. During processing, solvent addition may or may not be important. These reactants are usually mixed in a batch reactor with controlled temperature and addition of catalysts. Vacuum processing or Azeotropic Distillation may be employed to remove condensation products such as H₂O to obtain a higher degree of polymerization.

(B). Addition Polymerization Methods :

These methods are carried out with controlled thermal and catalyst conditions. They may be further classified as –

i .Bulk Polymerization : This mode of polymerization may be employed to obtain the purest form of polymer, and the greatest yield of polymer per unit volume may be obtained using this method. This method involves only the monomer molecule, an initiator and a chain transfer agent (if necessary). In a large scale batch form, the process is to be run slowly or in

continuous mode with large heat transfer area. Casting of objects of various shapes may be accomplished using the Batch Bulk Polymerization. Using continuous bulk polymerization processes, polystyrene and other thermoplastic compounds may be moulded.

ii .Solution Polymerization : An inert solvent is added to the reacting components in the reaction vessel in this process. The solvent enhances the heat capacity, thereby reducing the viscosity and facilitating heat transfer. Some of the solvent may be refluxed to remove heat from the reaction vessel. But , much of the reactor space is taken up by the solvent. As such , compared to Bulk Polymerization, Solution Polymerization reduces both the reaction rate and the molecular weight of the compounds. Additional batch and continuous processes are used to separate the final polymer product and to recover and store the solvent used.

iii .Suspension Polymerization : Inorder to control the enormous amount of heat release in Bulk Polymerization, Suspension Polymerization method was developed. The reaction mass is dispersed as minute droplets of size 0.01 – 1 mm in diameter in a continuous aqueous phase. Each of these droplets act as tiny bulk reactors. Heat transfer occurs from the droplets to the water having large heat capacity and low viscosity. Cooling jackets are used to facilitate heat removal. Agitators are used along with suspending agents in the aqueous phase inorder to maintain a specific droplet size and dispersion.

The Suspension Polymerization process cannot be run in a continuous mode , since, such a system has stagnant corners where polymer accumulation may occur. On a commercial scale, Suspension Polymerization is carried

out in jacketed, stainless steel or glass – lined stirred tanks, which may have a capacity of 20,000 gal or 75.5 m³.

Suspension Polymerization produces small, uniform polymer spheres. These are used directly, or may be extruded and chopped to form larger, moulded pellets.

iv .Emulsion Polymerization : This is the most widely used method of polymerization. This process overcomes the difficulty of heat control and low degree of polymerization. The organic reaction mass is emulsified with soap in a continuous aqueous phase. The dispersed particles are smaller in size than in Suspension Polymerization ($\leq 0.1 \mu\text{m}$) . In addition, due to stabilizing action of soap, the emulsion obtained is stable and agitation may not be necessary. In some methods, a water – soluble initiator may be used. The main product of Emulsion Polymerization is latex, which forms the basis of the popular latex paints. By coagulating the latex with ionic salts and acids, solid rubber may also be obtained.

v .Homogeneous Polymerization: In case of homogeneous bulk polymerization, the feed is a gas , liquid or solid monomer. No initiators or additives are used. For homogeneous Solution polymerization, the monomer is completely dissolved in a solvent.

vi .Heterogeneous Polymerization: In heterogeneous Emulsion polymerization, the monomer molecules are emulsified in aqueous media in the form of micelles. For heterogeneous Suspension polymerization, the monomer is suspended in an aqueous or other type of media as large droplets.

37.2.CLASSIFICATION ACCORDING TO PHYSICAL

PROPERTIES :

Polymers can also be classified according to physical properties as –

- i. Thermoplastic
- ii. Thermosetting
- iii. Elastomers
- iv. Fibers

i .Thermoplastic : The polymers in this category are composed of monomers which are linear or have moderate branching. They can be melted repeatedly and casted into various shapes and structures. They are soluble in solvents, but do not have appreciable thermal resistance properties. Vinyls, cellulose derivatives, polythene and polypropylene fall into the category of thermoplastic polymers.

ii .Thermosetting : There are some polymers which, when heated, decompose, and hence, cannot be reshaped. Such polymers have a complex 3-D network (cross-linked or branched) and are called Thermosetting Polymers. They are generally insoluble in solvents and have good heat resistance quality. Thermosetting polymers include phenol-formaldehyde, urea-aldehyde, silicones and allyls.

iii .Elastomers : These are resistant solids which have considerable flexibility. They are composed of polymers with glass transition temperature below room temperature.

One major difference between elastomers and plastics is that the elastomer is in a liquid state, while plastics are in the glassy state. Examples of

elastomers are Butadiene, Butadiene co – polymers and their derivatives, polycondensation products, silicones and thiokols.

iv .Fibers : These are solids which can form thread – like structures and have high tensile strength.

Examples of fibers are Polyamides, Polyesters, Polyurethanes, Protein derivatives.

37.3.CLASSIFICATION ACCORDING TO APPLICATIONS

On the basis of applications, polymers can be further classified as –

i .Adhesives: Some polymers can be used for bonding . They are usually of the resin type and require some water resistance . Some common adhesives are -

Cellulose adhesives ; which consist of cellulose derivatives dissolved in a solvent. Eg.Duco cement.

Vinyls ; these are rubber base type water-emulsified latex adhesives.

Apart from these, some cheap natural products such as starch, dextrans, proteins and natural rubber may also be used for adhesive formulations.

ii .Coatings and films : A large bulk of the polymers produced are used for manufacturing coatings and films. Free films of polyethylene and cellulosic types, protective and decorative coatings are the products of the polymer industry.

Coatings can be manufactured by solvent evaporation followed by polymerization. Emulsion and casting or extrusion of free films by mechanical methods can also produce coatings and films.

iii .Fibers: These are formed by extrusion or spinning of linear monomer molecules into thin sections of diameter in the range of 10 – 50 microns.

Fibers have excellent tensile strength , creep and resilience.

Fibers are extensively used in the textile industry . Cotton, wool etc. are the examples of some natural fibers.

37.4.Technical Questions

Q. 1. Mention the merits and demerits of Emulsion Polymerization w.r.t. other polymerization processes.

Ans. 1.One of the major advantages of Emulsion Polymerization is that it has good heat control over the entire polymerization process. The heat control occurs by transfer to the aqueous phase, and this enables little change in the viscosity of the emulsion medium.

Secondly, in this process, the reaction mass is emulsified with soap in a continuous aqueous medium. Soap has a stabilizing action, and hence, the emulsion obtained is stable and no agitation is necessary. Due to this, extra cost incurred in employing agitators is avoided.

Moreover, Emulsion Polymerization overcomes the difficulty of low degree of polymerization, as encountered in Solution and Bulk Polymerization. Since the degree of polymerization directly depends upon the droplet sizes, and in this process, spherical monomer particles (micelles) in the range of 1 – 10 μ , are yielded ; hence, the degree of polymerization is sufficiently higher than in the other two processes.

However, Emulsion Polymerization has certain disadvantages. It blocks the emulsifiers used in the process. In addition, the process has poor capacity and low electrical resistance , which sometimes create major problems.

Q.2. What are stereospecific Polymers ? How are they achieved?

Ans .2. Stereospecific Polymer are specially oriented polymers which have certain properties that are completely different from the usual polymers. These special properties include high density and melting points ,crystallinity and improved mechanical properties.

The reason for having these special property in the polymers is because of tailored atomic arrangements, which are achieved by the addition of catalysts like Ziegler catalysts or supported metal oxide catalysts. Even, X-ray and γ - ray radiations can bring about stereospecificity in the polymers.

The stereospecific polymers can be realized by examining the spatial arrangement of atoms on the main chain .

References :

Ullmann F., Encyclopedia of Industrial Chemistry, Wiley – VCH, 1999-2012

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

Lecture 38. Processing Technologies

38. 1. Introduction

All the processing stages between manufacture of the crude polymer and the final molding step are called the compounding processes. These include storage, transportation, metering, mixing, plastication and granulation. Sometimes additives may be added to the polymer mix to allow production on an industrial scale. Addition of plasticizers renders flexibility and ductility to rigid and brittle polymers. In a similar way, fillers can enable to enlarge the volume and also has influence upon the polymer properties.

38. 2. Processes

The various compounding processes are –

1 .Mixing: Mixing allows obtaining a homogeneous mixture of polymer and additives. The additive is distributed uniformly throughout the crude polymer, without any unnecessary stressing .Mixing can occur under the action of gravitational forces in a tumble mixer ; or in a ribbon mixer , where materials are mixed in a horizontal barrel in a spiral manner. Such mixers are collectively known as cold mixers.

Another class of mixers are the hot mixers, wherein the polymers are heated by contact with heated metal components. Such mixers are also known as high – speed or turbo mixers. This method is widely used in the plastic industry , especially in the compounding of poly vinyl chloride (PVC).

2 .Rolling and Kneading: Before processing , the plastics are compacted, melted, homogenized and modified with additives. These include rolling, in which the plastic is passed between two counterrotating , heated rolls wherein it is pressed into a thin layer. It is an open process in which

additives can be added, and other scrap materials may be reintroduced. PVC is one plastic which extensively employs this process. Moreover, the material temperature can be controlled precisely and cleaning of the machine is easy.

3 .Pelletizing : It is the method of producing granules of equal size and shape. This enables the optimum feed behaviour on the processing equipment. Pelletizing can be done in hot or cold conditions.

Using a pelletizing die, strands, ribbons or sheets are formed ; and after solidification, they are chopped into the desired shapes. This is one procedure strictly followed in cold pelletizing. However, in hot pelletizing , the plasticated material is sent through a die , and a blade that rotates on the surface of the die plate chops the exiting strands. The melt is then cooled ; and subsequently the water is removed.

4.Shredding and Grinding : In thermoplastics processing, a variety of semifinished and finished products are generated. These products, in order to be made suitable for processing, must be cut to produce a pellet form. A range of particle sizes is obtained in the process.

Regranulating is achieved through cutting mills. The material is added through a feed system wherein a rotor revolves with high momentum. The system is further equipped with multiple cutting heads that operate against stationary cutting edges. The rotating cutting heads are divided and displaced with respect to each other in some other machines. As soon as the desired particle size is obtained, the material is ejected through a sieve , the pores of which determine the size of the particles. The housing and rotor

may be equipped with water cooling apparatus to remove the excessive heat generated.

5.Storage and Transportation :The storage and transportation of base polymers and intermediate products are achieved through automatic equipments. These equipments have an edge over the manually operated ones as they ensure improved working conditions , lower work place , lower contamination of materials and subsequent reduction losses. Moreover, accident hazards are also reduced. Large external silos are used for the storage of polymers, either in powder form , or in the pellet form. By incorporating vibrating frames, bunker cushions, slotted shelves or similar techniques as ventilation, the formation of granule bridges is avoided.

The materials are transported via road or rail. Reserve materials and additives are transported in ships in bulk containers, drums or sacks. Pneumatic equipments are generally preferred for conveying powders and pellets. The conveyors used may be high pressure conveyors, medium pressure conveyors or low pressure conveyors. Fill level sensors help in controlling the transport interval.

Inorder to meter liquids such as plasticizers or other additives for compounding, oscillating displacement pumps are used. Metering of solids can be done using gravimetric metering equipments or volumetric metering equipments.

38. 3. TECHNIQUES FOR PRESSURELESS PROCESSING

The Pressureless Processing Techniques are used for starting materials such as monomers, plastic solutions and dispersions that can flow and that can be formed without application of external forces. The pressureless processing techniques include –

1. Casting
2. Dipping
3. Coating
4. Foaming

1 .Casting (Figure 38.1) : By polymerizing monomers in molds, thick – walled articles, embeddings, sheets and blocks can be produced. These are preferentially made up of polystyrene, polyamides and polymethylmetacrylate. Inorder to avoid thermal stresses, adequate temperature regulation is required. The mold material choice is dependent upon the use and surface quality of the moldings.

Film casting is mainly used in the photographic industry for the manufacture of cellulose acetate films. In this method of casting, polymer solution, melts or dispersions are cast directly into a metal drum or a rotating belt ; and from a slot die into precipitation bath.

Slush molding enables the production of hollow articles which are made from PVC pastes. These are made using two part metal molds, which are heated and filled with the paste. The paste gels on the outermost edges forming a skin ; and subsequently the excess paste is poured off. The remaining layer is gelled in an oven and after cooling, a hollow mold is obtained.

Slush molding can be further modified into Rotational casting for the production of hollow articles, made from PVC. The only difference is that in rotational casting, the amount of PVC paste is metered to the mold, which makes the removal of excess paste and post gelation techniques redundant. The mold is rotated about two perpendicular axes, while heating, and this enables uniform wetting of the cavity surface. Rotational casting has the advantage of low investment cost over slush molding.

In the manufacture of thick-walled, symmetrical structures such as pipes and sockets, centrifugal casting may be used. A partially filled mold is rotated rapidly about a central axis. Centrifugal force presses the material outward in the mold, and in the process, the material gets compacted.

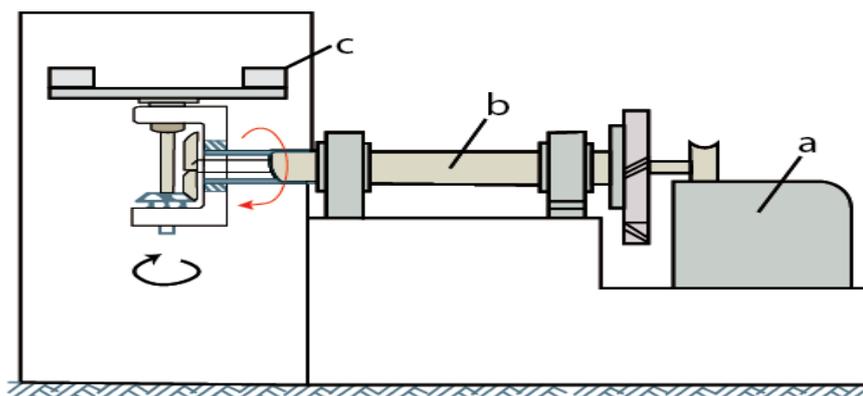


Figure 38.1 . Casting Machine

a) Motor ; b) Drive Shaft; c) Molds

2 .Dipping (Figure 38.2) : Sometimes, molds or articles are dipped into solutions, dispersions, pastes, melts or powders. Later on, the adhering material on the surface is solidified by heat treatment.

For manufacturing articles such as gloves, boots etc. in which one side remains open, a positive mold is immersed and subsequently the casting is gelled. A series of identical molds mounted on dipping frames are used for the mass production of such articles. During the dipping process, degassed

PVC paste placed in a vessel is raised and lowered. Sometimes, the dipping frame is moved, while the vessel is stationary. The immersion and removal stages are carried out slowly to allow the material to flow homogeneously from the mold and to prevent the introduction of air into the paste.

The gelation is usually carried out in circulating air oven, and during the process the paste temporarily becomes fluid. The molds containing the gelled coating are immersed in water for cooling. It is cooled to around 50 C and at this temperature, the moldings can be easily removed from the molds. Cables and wires are extensively coated using this process.

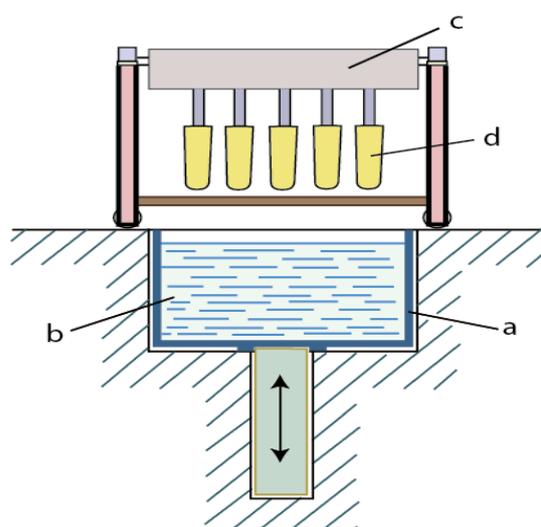


Figure38.2 .Dipping Unit.

a)Vessel; b)PVC paste; c)Dipping frame; d)Molds

3 .Coating (Figure 38.3):This process is used in the production of self-supporting films by coating sheet materials such as paper and textiles. The most important materials that are used for the production of coatings are PVC pastes.

The equipment for coating consists of an unwinding station, an expander, coating head, gelling channel, cooling system, and a rewind station. The disk brakes slows down the unwind station, and the rewind station enables

the product to be held under tension. A smooth finish to the sheet is provided by the expanders. With the help of the coating head, the PVC paste is spread upon the moving sheet manually or mechanically. Thereafter, a doctor blade is employed to spread the sheet to required thickness. A revolving roller supports the sheet, due to which an exactly defined contact area is maintained. The rolls distribute the escaping paste and form a film. The rotation speeds of the rolls can be adjusted.

Hot air or infrared dryers supply the heat required for gelation of the paste. However, circulating air heating in combination with infrared heaters is used in some cases.

The cooling effect must be high enough so that no adhesion between the individual layers occurs. The cooling is attained by two water – cooled , corrosion – resistant hollow drums.

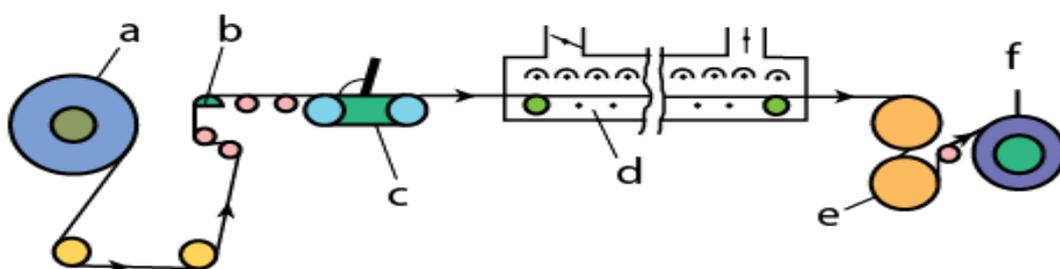


Figure 38.3 . Coating Unit

a) Unwinding Station; b) Expander; c) Coating head; d) Gelling Tunnel; e) Cooling Roll; f) Rewind Station

4 .Foaming: By adding physical or chemical blowing agents to a polymer, foams are generated. Physical blowing agents include gases and low-boiling compounds , whereas ; chemical blowing agents generally are gas – releasing compounds. Only a few materials are employed in the manufacture of foams , such as polystyrene , PVC, LDPE as well as phenolic and polyurethane resins.

The foaming process must begin when the polymer is in a flowable form and allows bubbles to develop. The conditions are fixed, once the bubbles reach the optimum size.

38. 4.Polymer Processing under pressure

Sometimes the molding process is carried under high pressure in which the solid thermoplastic materials are melted, molded and cooled subsequently.

Some of the commonly used techniques for processing under pressure are –

1. Compression molding
2. Rolling and Calendering
3. Extrusion
4. Blow Molding
5. Injection Molding

1.CompressionMolding: For the manufacture of thick – walled components and those that cannot be plasticized in extruders, compression molding is used. It plays an important role in the processing of elastomers and thermosets.

A press consisting of fixed and moving platens is used. The plunger and cavity components are mounted on these plates, and the parting plane is kept horizontal. The cavity is filled with the cold plastic and is melted by heating the mold under low pressure. When the melting is complete, the mold is closed and pressure applied. The molding is removed by releasing the press once the ejection temperature is reached.

Compression molding is uneconomical due to the fact that the process has a long cycle time ; as the material in themold is heated and cooled by conduction via the mold surface.

2.Rolling and Calendering (Figure 38.4) : The rolling mills consist of two rolls that are used exclusively for the compounding of thermoplastics. The product that results from rolling is a sheet that can be granulated after cooling or fed in plasticated form directly into the processing equipment. PVC and rubber are processed using this process.

When the rolls are more than two in number, and the polymer is to be shaped using these rolls; then the machine is called a calendar. The number of rolls in a calendar can be up to seven ; however, most commonly , four rolls are used. The rolls are made of polished cast iron, and are driven individually and heated. The heating medium is usually oil or water. The temperature and speed increases from one roll to the next. The roll mill must be able to withstand the extreme forces to which it is exposed, and hence, be made extremely rigid.

The calendars are one of the most expensive types of processing equipments and are employed for the manufacture of a few special products like floor coverings and films made of plasticised PVC.

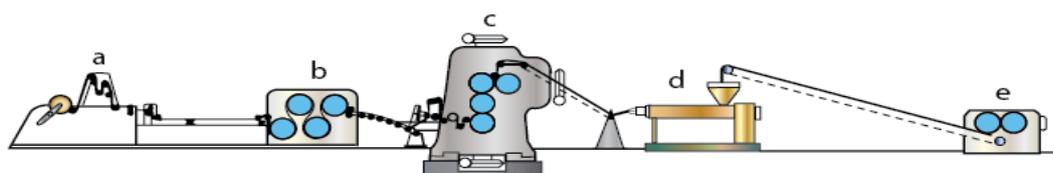


Figure 38.4 .Calendering line

a) Winder and Edge Cutter; b)Cooling Rolls; c)Four-roll calendar; d)Extruder; e)Mixing Roll Mill.

3.Extrusion (Figure 38.5):This method enables the attainment of a wide range of film thickness, and large scaling processing. Moreover, there is no necessity for expensive solvents in the recovery systems.

A device known as extruder is used to melt the polymer, which is given the specific shape by a die. Later on, a cooling system is used to solidify it.

At the onset, the raw material is dried using heated air or vacuum, before it is melted in the extruder. The extruders may be single – screw extruders, or twin screw extruders, the single screw extruder being the most common. The melt is filtered depending upon the desired purity, and then the filtered raw materials are sent through the slot die. The width and thickness of the film are determined by the width of the die and the die gap respectively. The die gap can be further adjusted during production.

The melt film emerging from the die is cast on to a highly polished roll. A vacuum device prevents the entrapment of air between the melt and the roller surface. The final film that is obtained is wound onto a roll after trimming off the edges. In a separate process, the film is cut into the designate width.

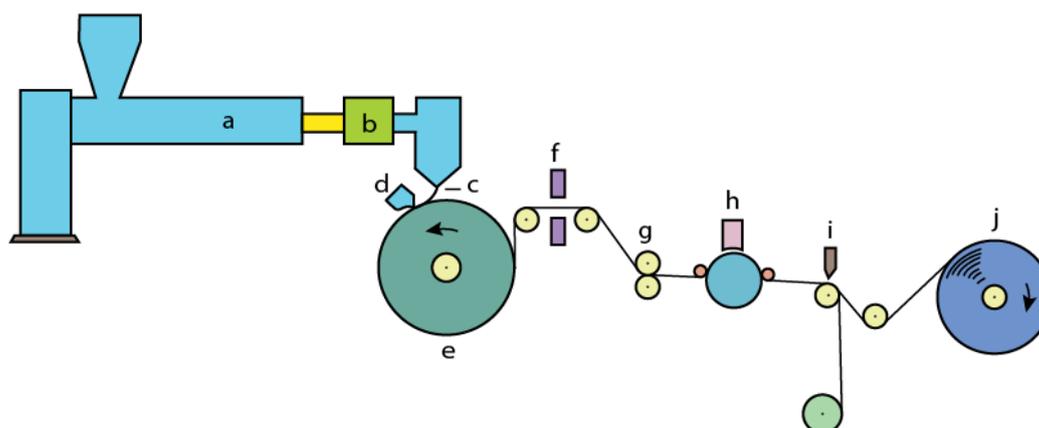


Figure 38.5 . Extrusion Molding

- a) Extruder; b) Filter; c) Slot Die; d) Air Knife; e) Cooling Roll; f) Device for measuring film thickness; g) Tension rolls; h) Corona Treatment; i) Edge Treatment; j) Winding

4. Blow Molding (Figure 38.6): This is the most common method for manufacturing hollow articles from thermoplastics. The most simple products and articles that are made by blow molding are bottles, ventilation

ducts, suit cases and fuel tanks for automobiles. Two processes are generally followed for blow molding –

a .Extrusion Blow Molding : An extruded tube or parison is elongated to reach the required length . The parison is then enclosed by the mold , which is then cut by a blade. It is then conveyed to the blowing station. In the blowing station, a blow mandrel is inserted into the mold and the actual process is subsequently carried out. It is then cooled and the finished product is removed by opening the mold. The open mold is then transferred to the position below the extrusion die in order to receive a new parison. The process then continues.

b .Stretch Blow Molding : This is a special form of blow molding in which the mechanical properties are considerably improved. A high degree of orientation is introduced in the plastics by drawing near the glass transition temperature or crystalline melting points. The molding material is drawn not only in the circumferential direction, but also in the machine direction. A mechanical ram is used for drawing in the longitudinal direction. The process is carried out under low temperature with the application of high deformation forces.

PVC, polypropylene and poly ethyl terephthalate are some of the materials for use with this process.

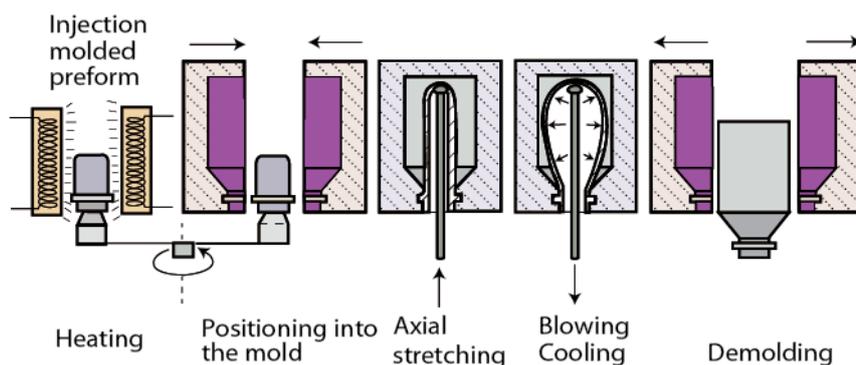


Figure 38.6 . Blow Molding Process

5 .Injection Molding (Figure 38.7) : The Injection Molding technique is significant because of its ability to manufacture complex molding geometries in a single stage operation. The process is often suitable for mass production operations because of the high degree of automation.

The Injection molding technique is a discontinuous process . The plastic pellets or granules are melted and injected under pressure into the mold cavity , wherein it is thermally cross-linked or solidified by cooling.

Through a runner system the hot melt prepared in the injection cylinder is injected into the cavity of the mold. The pressure is increased towards the end of the filling stage because of the increasing length of the flow path. After the injection phase, the holding pressure stage follows. It reduces the volume losses due to cooling of the melt , and thus, avoids marks and voids in the molding. After this , the molding is cooled sufficiently so that it is dimensionally stable for ejection. When the holding pressure phase is finished, the plastic is prepared for the next cycle by the plastication unit by rotating the screw. The melt is transported to the area in the front of the screw by the helical backward movement of the screw in the plastication

cylinder against a back pressure. After this the molding is cooled and is mechanically removed from the mold via a handling equipment.

The entire process is fully automated and is coordinated by a control unit.

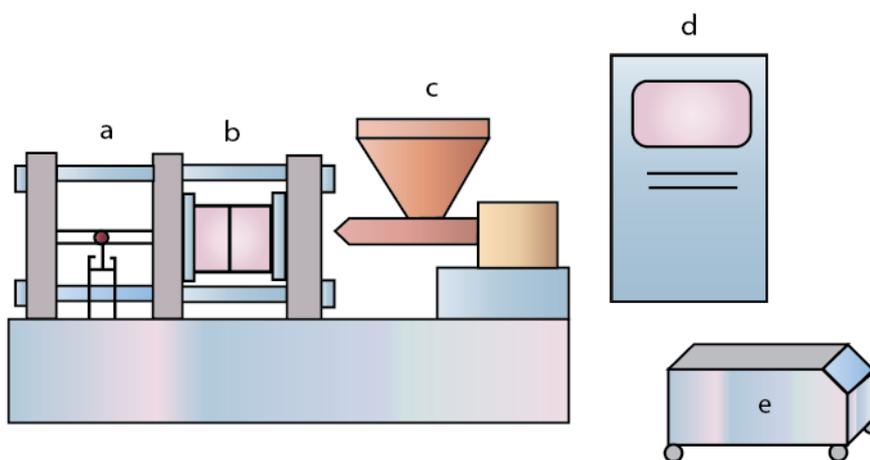


Figure 38.7 . Injection Molding Machine

a) Clamping unit; b) Mold; c)Plastication Unit; d) Control Unit; e)Temperature Control Unit

38.5 Technical Questions

Q. 1. What are the typical additives used in polymer products ?

Ans. 1. Polymer additives include materials which make and modify polymers. These include surfactants, chain transfer agents, modifiers, plasticizers, stabilizers, initiators and cross – linking agents.

Q. 2. Explain Glass Transition Temperature

Ans.2. Glass Transition Temperature of a non – crystalline material is the temperature at which the material changes its behaviour from its glassy state to a rubbery state. Glassy state refers to the state at which a material is hard and brittle; whereas , rubbery state refers to the state at which the material is flexible and elastic.

Q. 3. Apply your knowledge in Chemical Engineering and outline one problem one may encounter in polymerization processes.

Ans. 3. There are certain compounds like styrene, which are used in the polymerization process. Styrene is an olefin, and is unstable as a pure liquid. Such compounds may explode, even in the absence of oxygen.

Many polymers can be recycled, which reduces the disposal problems. But in order to do so, the polymers must be separated from each other at first, and this process may be very difficult and expensive.

Incineration is a process which is used in many polymerization processes. But this leads to release of high amount of heat energy, which could otherwise be used for various useful purposes. Moreover, carbon dioxide is produced during incineration, which leads to global warming.

Q. 4. Match the polymer processing techniques for making various products.

Group 1	Group
2	
a. Rubber sheet	1. Rotational
Molding	
b. HDPE water storage tanks	2. Compression
Molding	
c. Bicycle paddle	3. Calendering
d. Glass reinforced thermosetting plastics	4. Injection
molding	

Ans .4.a-3

b-1

c-4

d-2

Q.5 Mention some of the advantages of blow molding as compared to injection molding.

Ans.5 Some of the advantages of blow molding as compared to injection molding are-

1. Possibility of variable wall thickness.
2. Low stresses and favorable cost factor.

Q.6 What are the different types of injection molding machines that may be used?

Ans.6

1. Plunger type
2. Piston type
3. Reciprocating Screw

Q.7 What are the different types of screw zones in a extrusion machine ?

Ans.7

1. Feed zone
2. Metering zone
3. Transition zone

Q. 8 In molding process, the polymer material will try to stick to the wall of the mold (container). How can you prevent it?

Ans. 8 The polymeric material can be prevented from sticking to the walls of the mold by changing the viscosity of the polymer. This can be achieved by selecting the MOC of the container (mold) in such a way that it will create substantial viscosity gradient between the walls and the polymeric material. It can also be done by heating the walls of the mold externally.

References :

Ullmann F., Encyclopedia of Industrial Chemistry, Wiley – VCH, 1999-2012

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

Lecture 39. Polymer Manufacturing Processes

39.1. Polythene (PE)

Polymer Chemistry: The manufacture of polyethylene follows addition polymerization kinetics involving catalysis of purified ethylene. Its molecular formula is $-(\text{CH}_2-\text{CH}_2)_n-$ with a molecular weight of 1,500 to 100,000. Its melting point is $85 - 110^\circ\text{C}$. its density is 0.91 - 0.93 , when produced by high pressure process and 0.96, when produced by low pressure process.

Technology:

There are three processes by which polyethylene is manufactured –

a. High Pressure Process : This process was developed in the UK by ICI. It uses peroxide catalyst at $100-300^\circ\text{C}$ and produces low density randomly oriented polymer which have a low melting point. The process is run at pressure of 1000 – 2500 atms. This process yields Low Density Polyethylene (LDPE).

b. Intermediate Pressure Process : This process was developed in the USA by Phillips Petroleum Co. for preparing high density polymer with increased rigidity, crystallinity, tensile strength and softening point. The process uses MoO_3 and Cr_2O_3 on alumina as catalyst and is operated at 30 – 100 atms.

c. Low Pressure Process : This process was originally developed in Germany for preparing high density polyethylene (HDPE). The catalyst used in this process consists of aluminium triethylactivated with heavy metal derivatives such as TiCl_4 .

In the process flow sheet (Figure 39.1), is the description of Low Pressure Ziegler Process to produce polyethylene.

At the very onset, through the process of desulphurization and removal of light ends, high purity ethylene is prepared. The ethylene is further treated to remove traces of oxygen and its compounds which can possibly deactivate the catalyst.

The ethylene is first pumped into a reactor where it is mixed with catalyst diluents stream. The optimum temperature and pressure maintained should be 70°C and 7 atms gage. The effluent stream then follows across a series of flash drums in order to remove the solvent from the catalyst. The residual catalyst at this point is removed by adding water.

The flashed solvent is thereafter recycled to the catalyst make –up unit after appropriate drying and redistillation. The slurry which results is then centrifuged to remove the water, and the water is treated to remove the catalyst before recycle. The final products of polyethylene solids are then dried, extruded and given the required final forms.

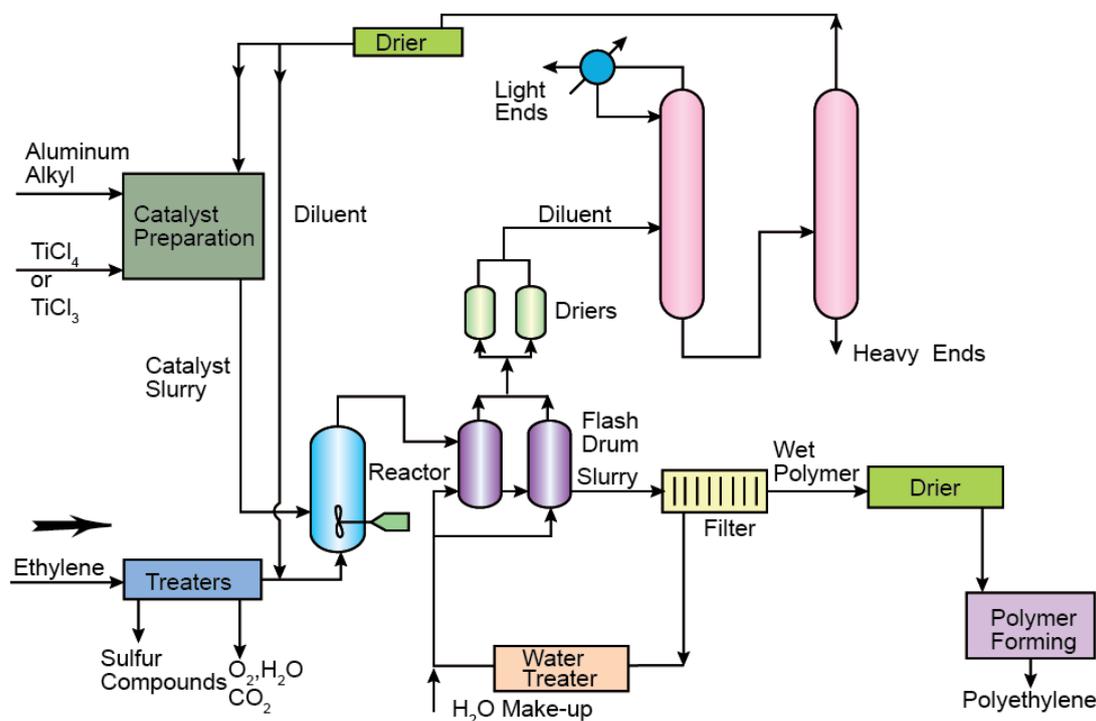
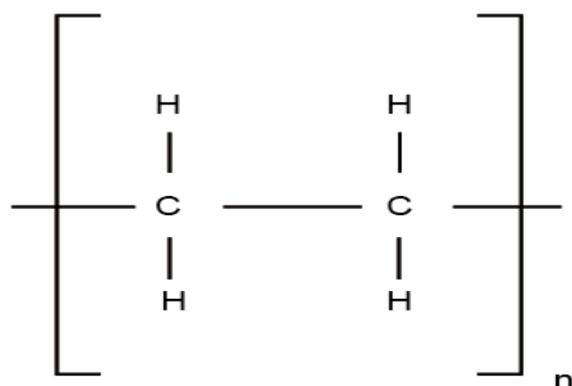


Figure 39.1 Manufacture of Polythene.

39.2 .POLYVINYL CHLORIDE (PVC)

Polymer Chemistry : The manufacture of Polyvinyl Chloride (PVC) follows addition type kinetics and produces linear polymers. Its molecular formula is given as –



where $n = 700 - 1500$

The vinyl chloride monomer (VCM) has a boiling point of 13.4°C and is a gas at room temperature and pressure. The vapor pressure of VCM over the typical polymerization temperature range of 50°C to 70°C is 800 – 1250 KPa.

Technology (Figure 39.2):

The two most commercially use methods for the manufacture of PVC are Emulsion Polymerization and Suspension Polymerization. The Suspension Polymerization process provides 80 % of the world production.

The Suspension Polymerization process is actually a bulk polymerization process which is carried out in millions of droplets . Each of these droplets act as small reactors. The liquid vinyl chloride is dispersed in water by vigorous stirring in a reactor. The reactor is fitted with baffles for optimum agitation and also has a condenser for heat removal. In the reactor , small droplets of size 30 - 40µm diameter are formed.

A monomer soluble free radical initiator is charged into the reactors. After charging, the reactor temperature is increased to $45 - 75^{\circ}\text{C}$. The heat decomposes some of the initiators to free radicals, and the monomers in these droplets begin to polymerize. The reaction is highly exothermic and the heat is removed via cooling jackets or by boil-off to the condenser. Thereafter, the condensed monomer is returned to the reactor. Although the PVC is insoluble in its monomer, it is swollen by VCM to form a coherent gel. Even in the gel phase, the polymerization continues. The polymerization is rapid at first, but slowly, as the conversion reaches 80 – 85 %, the rate is reduced due to monomer starvation.

At a predetermined pressure, the reaction is ended by adding a chain terminator or by venting the unreacted monomer to a recovery plant. Even after venting, the aqueous slurry contains 2 – 3 % unreacted monomer, which is then removed by stripping in a Stripping Column. The unreacted monomer is recovered and stored for later polymerization stages. The slurry is then passed through a heat exchanger and is passed through a continuous centrifuge to give a wet cake with 20 – 30 % moisture.

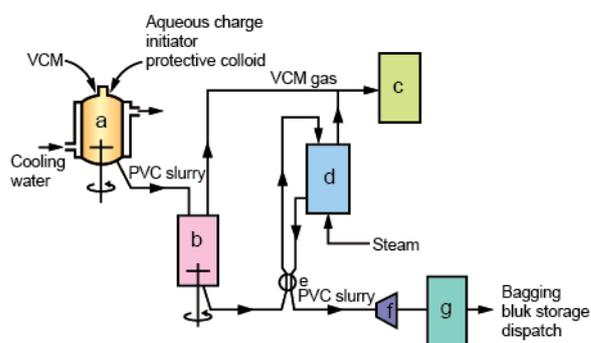


Figure 39.2. Manufacture of Poly(Vinyl Chloride).

a) Reactor; b) Blowdown Vessel; c) VCM Recovery Plant; d) Stripping Column; e) Heat Exchanger;
f) Centrifuge; g) Driers

39. 3. STYRENE BUTADIENE RUBBER (SBR)

Polymer Chemistry : The production of Styrene Butadiene Rubber (SBR) follows addition polymerization. Its glass transition temperature is approximately -55°C , but may vary with the Styrene content. It can be used extensively within the temperature range of -40 to 100°C . It may be blended with natural rubber or can be used by itself. It has good abrasion resistance properties and the addition of additives may endow it with aging stability.

Technology (Figure 39.3):

SBR is produced by the copolymerization of Butadiene and Styrene by emulsion polymerization in 3 : 1 weight ratio.

The fresh and recycle monomers are purified by 20 % aqueous caustic purification. Then the stream is continuously passed through 6 to 12 glass – lined or stainless steel reactors. The residence time in these reactors ranges from 5 to 15 hours. Steam heating, water cooling and refrigeration are carried out in these reactors. These reactors are equipped for producing both cold and hot SBR. Cold SBR is produced at 5°C and 1 atm gage by refrigeration techniques ; whereas hot SBR is manufactured at 50°C , and 3-4 atm gage.

The polymerization product is then stripped with chemical inhibitors and the latex resulting from the reactors are collected in blow down tanks. The latex is then sent to a falling film stripper to remove the butadiene ; and the bottoms are fed to a perforated plate column where styrene is stripped out.

The monomer – free emulsion is then added with certain compounding ingredients in blend tanks. The latex is coagulated to rubber. The crumbs of

rubber float onto shaker screens where the catalyst, emulsifiers and other solubles are removed by the action with wash water. The crumbs are dried in continuous belt dryers with hot air and are subsequently pressed into bales.

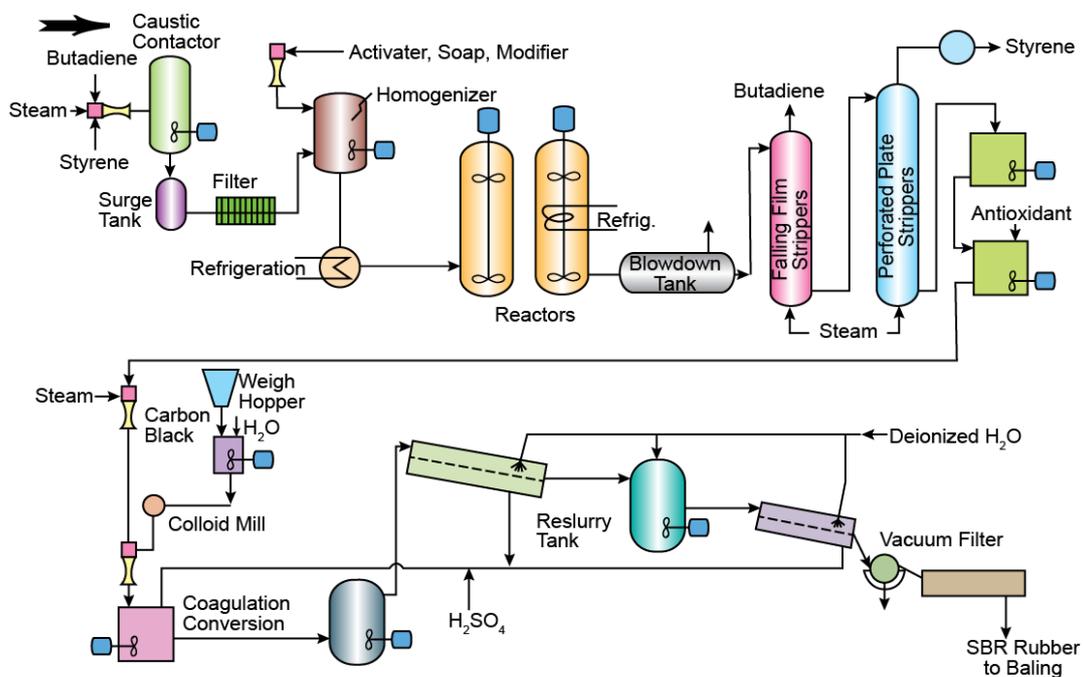


Figure 39.3 Manufacture of Styrene Butadiene Rubber

References :

Ullmann F., Encyclopedia of Industrial Chemistry, Wiley – VCH, 1999-2012

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

Lecture 40: Manufacture of Phenol Formaldehyde, Viscose Rayon and Nylon

40.1: Phenol Formaldehyde

Polymer Chemistry : The formation of phenol formaldehyde follows step – growth polymerization. The process can be either acid – catalysed or base – catalysed.

Base-catalysed phenol formaldehyde resins are made with formaldehyde to phenol ratio of around 1.5. Such resins are sometimes called resols, and are found in varied industrial products. Laminates are made by impregnating one or more layers of base materials like paper or cotton with phenolic resin with the application of temperature and pressure. Moreover the resins act as binding agents in brake pads, brake shoes and various other applications.

Technology (Figure 40.1) :

The polymerization process for the manufacture of phenol formaldehyde is an exothermic one and is controlled by a batch reactor as the viscosity of the material changes rapidly.

The raw materials for the process – phenol, formaldehyde and the catalyst are mixed in a jacketed autoclave, which is also termed as a resin kettle. Inside the autoclave, the mixture is heated with steam. Water cooling and refluxing remove the excess heat of reaction. During the initial stages of the reaction, the heavy viscous resins settle as the bottom layer, with an aqueous layer on top. A combination of heat and vacuum in the resin kettle (autoclave) enables the dehydration of the reaction mixture.

At around 130-150°C, the resin fuses and is removed from the kettle. Then product is then cooled and is ground to form fine powders. This molding powder which forms can be mixed with fillers, coloring agents, lubricants and catalysts in a ball mill. In order to prepare the commercial phenolic molding powder, the final product may be further heated on a pair of differential heating rolls.

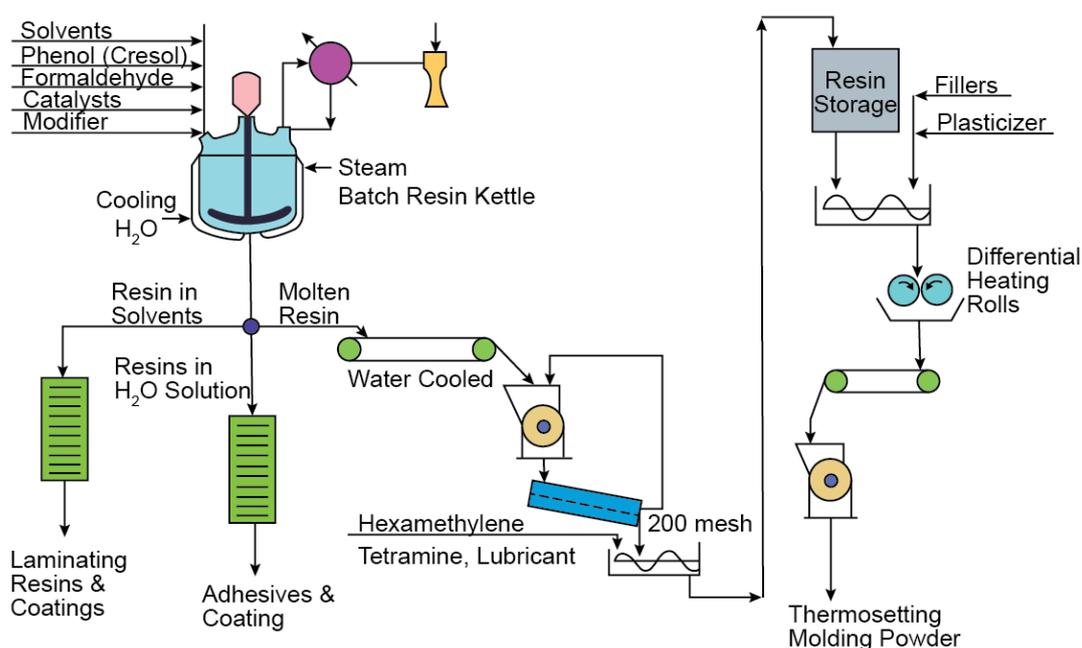


Figure 40.1 Manufacture of Phenol Formaldehyde.

40.2 VISCOSE RAYON

Polymer Chemistry: The raw material for the production of Viscose rayon is wood pulp. However, the manufacturing process emits toxic effluents which have adverse environmental effects. Because of its cellulosic base, it has some properties which are similar to those of cotton and any other natural cellulosic fibres. It has moderate resistance to acids and alkalis. However, it may be damaged by relatively weak acids. Moreover, due to the inelasticity of fibers, it has poor abrasion resistance.

Technology (Figure 40.2):

The raw materials used in this process are cellulose wood pulp sheets or cotton linters. These are placed in a steeping press with contact in aqueous NaOH Solution for a period of 2 – 4 hours at normal room temperature. A hydraulic ram presses out the excess alkali and the sheets are shredded to crumbs and aged for 2 – 3 days. The aging process has its direct consequence on the viscosity of the solution.

Later CS₂ is added in a rotating drum mixer over a period of 3 hours. The orange cellulose xanthate which forms is transferred to a solubilizer, wherein it is mixed into dilute caustic. The mixing of cellulose xanthate and dilute caustic yields a orange colored viscous solution which contains 7 – 8 % cellulose and 6.5 – 7 % NaOH. It is digested at room temperature for 4-5 days. Thereafter, the solution is filtered and fed to spinning machines.

The spinning is carried out in extrusion spinnerettes, which are made up of platinum or gold alloys. The orifices of these spinnerets have a diameter of 0.1 – 0.2 mm. for continuous filament yarns and of diameter 0.05 – 0.1 mm for short fibre shapes. The solution extruded from the spinnerette is contacted with an acid bath which precipitates the filaments without causing them to break or stick together. The processing treatments of washing, desulphurizing, bleaching and conditioning takes place continuously and in order after the filaments are wound on a series of plastic rolls.

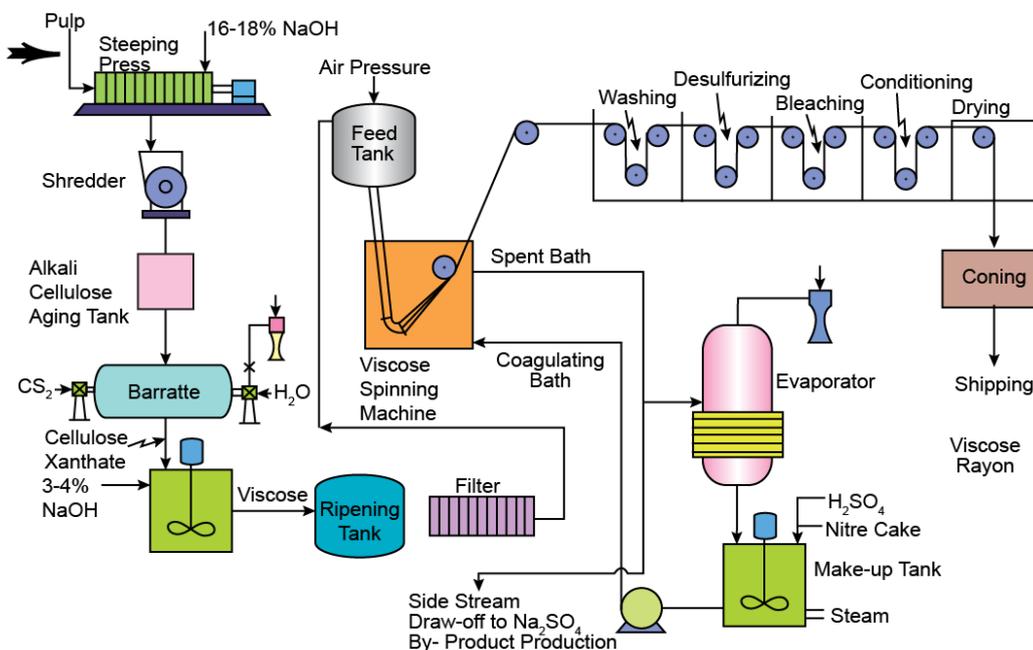


Figure 40.2 Manufacture of Viscose Rayon

40.3 NYLON

Polymer Chemistry: Nylon 66 (or 6,6 - Nylon) is a condensation polymer formed by the condensation polymerization of Adipic acid (a dibasic acid) and hexamethylenediamine (a diamine). In the nomenclature, the first number refers to the number of carbon atoms in the diamine and the second number designates the number of carbon atoms in the dibasic acid.

Nylon – 6 is a polymer of caprolactum . The number refers to the total carbon atoms in the ring, which can vary from 5 to 12.

Both Nylon – 6 and Nylon – 66 have similar properties and can be used as thin films and fibres; and for extrusion and injection molding in plastics.

The major difference in the physical properties of these two nylons is that the melting point of Nylon – 66 is 40 – 45°C higher than Nylon – 6.

Moreover, Nylon – 66 is harder, rigid and its abrasive – resistance is lower than that of Nylon – 6.

Technology (Figure 40.3):

In the production of Nylon – 66, first, the amine and acid is mixed in an aqueous solution, with the pH adjusted at 7.8 to form Nylon salt. The salt is then concentrated under vacuum. It is thereafter charged to an autoclave where the rest of the water is removed. The temperature is gradually increased to 280°C in the autoclave to complete the polymerization and the water of condensation is removed.

The final product has a molecular weight of 12000 – 16000. It is extruded as ribbons onto chilling rolls. Then, it is sent to a chipper which produces small chips, which possess the convenience of storage and rehandling. These chips are melted, metered through high pressure pumps. After filtration, these are passed via a melt spinnerette to produce nylon fibers. Upon cooling, these filaments harden and are wound on bobbins at a rate of 750 metres per minute or even higher. In order to give the fibre desirable textile properties, the threads are stretched to about 4 times its original length.

The production of Nylon – 6 is similar to that of Nylon – 66, the only difference being the nature of polymerization. Nylon – 6 is manufactured by the step – wise condensation of caprolactum with no net water removal. However, to maintain the thermal equilibrium between monomer and polymer at the melting and spinning temperatures is the only difficult task. Monomer retained on the fibres accounts upto 10%, so the fibres are water – washed to remove the soluble caprolactum retained.

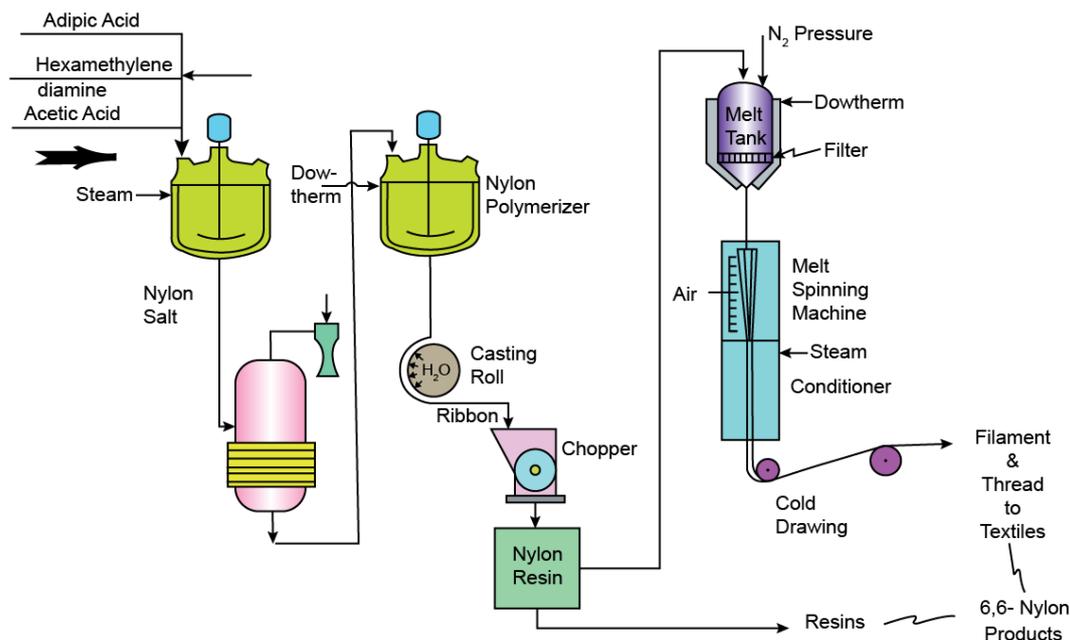


Figure 40.3 Manufacture of Nylon.

40.4 .Technical Questions

Q. 1. What is the Spherilene process ? Explain how spherilines are developed.

Ans .1. The Spherilene process is a new, gas – phase Polyethylene ‘swing’ technology. It is based on a well – established technology, known as the Reactor Granule Technology (RGT), which is basically a refinement of gas – phase and bulk – polymerization reactors.

In the Spherilene process, Zeigler spherical – form – supported catalyst particles act as microreactors. In the first and second gas – phase reactors, the polymerizing particles grows on itself in a gradual manner. However, during the whole growing process , the particles retain their original spherical form, and allows for perfect control of the final morphology of the polymer.

Q.2. What are General – purpose Polystyrene (GPPS) and High – impact Polystyrene (HIPS) ? How are they different ?

Ans.2. GPPS is also known as crystal polystyrene. It has good clarity and fairly good mechanical properties. Although GPPS can be processed into most types of objects, it is relatively brittle. It is used in applications where light transmission properties are important.

On the other hand, HIPS contains an elastomer like polybutadiene rubber, which improves its mechanical properties. It has appreciable impact strength and hence, is milky or opaque in appearance. HIPS is tougher than GPPS, and also has good processing properties.

Q.3. In high pressure technology, which one is more advantageous – Centrifugal Compressors or Reciprocating Compressors? Why?

Ans.3. In high pressure technologies, centrifugal compressors are more advantageous than reciprocating compressors. This is because centrifugal compressors have low investment and maintenance costs, and ensures more reliability than the formerly used reciprocating compressors. Moreover, they require less space and provide high efficiencies even at high flow rates.

Q. 4. What are the problems that may be encountered when the reactor walls are contaminated with polymer materials? How can this problem be mitigated ?

Ans. 4. If the polymer material builds up on the reactor walls, then it can lower the rate of heat transfer considerably. Moreover, it can also have detrimental effects on the quality of the product. This problem is very much encountered in the Poly vinyl chloride manufacture process.

The reactor walls can be kept free of the polymer material by using certain build – up suppressing agents or anti – fouling agents. In addition, cleaning of the reactors with high pressure water after a certain number of batches ensures the reactor walls free from polymer materials.

Q. 5. In conventional drying processes, why is the method of selective drying so important ?

Ans. 5. Selective drying is important in most drying processes, because , it ensures the prevention of thermal degradation of the material being processed. Moreover, the overdrying of the drying goods is avoided using this method.

Q. 6. Match the product in group 1 with the nature of reaction in group

2 :

Group 1

- a. Polyethylene**
- b. Nylon**
- c. Polystyrene**

Group 2

- 1. Condensation Polymerization**
- 2. Addition Polymerization**

Ans 6.a-2

b-2

c-1

Q.7. What kind of catalyst in the Low Pressure Zeigler Process for the manufacture of polyethylene ?

Ans . 7. Aluminium triethyl combined with titanium tetrachloride.

Q. 8. Match the processes used for producing various products from PVC.

Group 1

Group 2

- | | |
|------------------------------|--------------------------------------|
| a. Extrusion | 1. Rexin / Leather cloth |
| b. Injection Moulding | 2. Rigid containers / bottles |
| c. Blow Moulding | 3. Pipe fittings |
| d. Calendering | 4. Rigid pipes |

Ans 8.a-4

b-3

c-2

d-1

Q.9 What does the Ziegler – Natta catalyst consist of ?

Ans9. The Ziegler Natta catalyst consists of a combination of HF and BF_3

Q.10 Which two polymerization methods are commonly used for the manufacture of polyvinyl chloride ? Mention some of the disadvantages of using PVC as a polymer.

Ans10. Two methods for manufacture of PVC are Emulsion Polymerization and Suspension Polymerization.

Disadvantage of PVC is that it has low solvent solubility. In addition to this, the heat stability of PVC is poor.

Q11. What is the main criteria based upon which Polyethylene is classified ?

Ans11. Based upon its density and molecular bonding.

Q12. Which of the following has a higher melting point – Nylon -6,6 or Nylon -6 ?

Ans12. Nylon – 6,6 has a higher melting point than Nylon -6 (about 40 – 45 ° higher).

References :

Ullmann F., Encyclopedia of Industrial Chemistry, Wiley – VCH, 1999-2012

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012