

**Organic Chemical Technology**  
**Prof. Nanda Kishore**  
**Department of Chemical Engineering**  
**Indian Institute of Technology, Guwahati**

**Lecture - 33**  
**Polymer Industry-2**

Welcome to the MOOCs course organic chemical technology. The title of today's lecture is Polymer Industry Part 2.

(Refer Slide Time: 00:53)

**Recapitulation**

- **Polymers made up of repeated basic units produced from monomers** ← *more physical chemical*
- **Classification of polymers**
  - 1) Physico-chemical structure: functionality, structure, reactions
  - 2) Mode of preparation: Polycondensation, addition polymerization methods
  - 3) Physical properties: optical properties, thermal properties, mechanical properties, electrical properties, solvent properties, chemical resistance
    - Thermoplastics
    - Thermosettings
    - Elastomers
    - Fibers ✓
  - 4) Technical applications: adhesives, coatings & films, fibers, solid shapes
- **Polymers manufacturing processes** *Pr. 3- some polymer types*
  - **Plastics (ethenic and polycondensation)**, elastomers (rubbers), polymer oils (silicones), fibers
- **Ethenic polymer processes: PE and PP manufacture** → *PVC, ABS, etc*

First, we have a recapitulation of what we have discussed in the previous lecture of this particular chapter on polymer industries. We started discussion on the basics of polymers with the definition and classification. Polymers are made up of repeated basic units produced from monomers. These monomers can be of same molecule or from the different

molecules as well. If these are from the different molecules, then we call them co-monomers and then whatever the polymer form we call them copolymers, okay? The purpose of polymers production is that they should be able to fulfill some kind of engineering material requirements. For that purpose only such kind of polymers were developed with the primary aim to have a very unique physical or very different physical and chemical properties compared to the base monomers, etc., right? So, in other words, if you want to make a comparison or a competition with the existing conventional material, they should be able to replace the existing material something like wood and metal, you know and then you can do the required engineering processing, right? Such kind of requirements are expected to be fulfilled by polymers, okay? And then we started discussions on the classification of polymers and then we realized that polymers production of methods of polymers and then reactions, then polymers type of materials produced and so many interacting features are there amongst different types of polymers.

Because of that one, classification of polymers is very difficult. However, 4 different broad ways one can commonly classify the polymers. The first one is the physicochemical structure. So, based on the physicochemical structure if you wanted to classify again based on the functionality whether the monomer is bifunctional or trifunctional or polyfunctional accordingly, you know polymers you know may be produced and then based on the structures you can see based on the physical structure you can have the linear polymers, cross linked polymers, branched chain polymers, etc. Then based on the reaction methods also how or what kind of reactions are involved to get the so called polymers.

So, based on that one also you can do a classification something like mode of preparation if you see like you know whether the condensation or addition kind of reaction going on. So, accordingly we call or we produce different types of condensation polymers or addition polymers, etc. So, other way of category or classification of polymers is based on the physical properties. So, when you consider the physical properties for a classification of polymers you should see physical properties like optical, thermal, mechanical, electrical, solvent properties along with the chemical resistance and then under this physical properties category you can have thermoplastics. That means you can melt them, remelt

them again as per the requirements and then mold them as per the requirements of the consumers that is possible.

Then thermosetting once the cross linking has been done that cannot be remelted such kind of materials are thermosetting. Then elastomers something like you know rubbers, etc. And then fibers most of the fibers are also classified based on the physical properties. Then based on the technical applications also you can classify the polymers where you can have other sieves, coatings and films, fibers and solid shapes, different types of classifications are possible. These are common but you know not exactly the way to do the classification but on a certain kind of basis these properties provide or this grouping provide certain kind of basis to do a possible classification of the polymers.

Then after that we discussed the polymer manufacture processes where we had plastics, elastomers, polymer oils and fibers are 4 categories. Under the plastic, ethenic polymers and then condensation polymers are the 2 types. Elastomers most of the rubbers comes under the elastomers and then most of the silicones or oils will come under the polymer oils and then most of the fibers like thread, etc. would be counted under the fibers. Under the ethenic, ethenic stands for ethylene, it is derived not stand for ethylene, it is derived from the ethylene.

Ethenic is derived from the ethylene because most of the polymers which are produced under ethenic category they may be having double bonds and triple bonds and then such kind of you know monomers undergo some kind of addition reaction to produce polymers, something like ethylene monomer used to produce polyethylene something like that. Under the polycondensation reactions you know when the reaction goes on some kind of small molecules like water, ammonia, formaldehyde, etc. are released to form polymers, okay? So these 2 types of polymers or you know different types of polymers falling under these 2 categories would be discussed or being discussed in the present chapter in which already we have completed polyethylene and polypropylene manufacturing under the ethenic polymer processes. Now we see PVC, ABS, etc. these kind of polymers production under the ethenic category. After that we go into the phenol formaldehyde resins, polyurethanes and then epoxies, etc. Polymers under the polycondensation processes, okay? So these things we are going to cover now in today's lecture.

(Refer Slide Time: 06:49)

## Polyvinyl chloride and copolymers

- PVC is the most widely used commodity plastic in India
- It is a versatile plastic because of its
  - Resistance to chemicals and self-extinguishing and electrical properties
- It is used in both consumer and industrial products
- It is used to make pipes, pipe-fittings, wire cables, leather cloth, sheets and films, footwear and miscellaneous

So let us start with PVC. PVC stands for polyvinyl chloride and then it is one of the most important or you know having large number of applications in the commodity market. So we start discussions on the polyvinyl chloride and their copolymers. PVC is the most widely used commodity plastic in India. Copolymers in the sense you know we will see with structures you know not only the vinyl chloride monomer, but also some other monomers may also be joining together to form the copolymers of you know polyvinyl chloride category. So the purpose of copolymerization is to enhance certain kind of properties. Let us say if you take PVC, PVC is not soluble in most of the solvents. Let us say if you wanted to improve the solubility of the PVC, then what you can do? You can have some other co-monomer and then prepare copolymers and then similarly PVC is also weak in the thermal resistance.

So if you wanted to improve the thermal resistance, what you can do? You can have some additional monomers as co-monomers and then make a modified polyvinyl chloride or

polyvinyl chloride copolymers so that thermal resistance may also improve. So basically the purpose of adding co-monomers is to improve one or other properties of the conventional polymer with a single type of monomer, right? PVC is a versatile plastic because of its resistance to chemicals and self extinguishing and electrical properties. It is used both in consumer and industrial products. It is used to make most of the pipes that we see in the household and in industry. Most of them are PVC pipes, pipe fittings, wire cables, leather cloths, sheets and films, footwear and miscellaneous, so many other types of products one can produce from the PVC or PVC copolymers.

(Refer Slide Time: 08:50)

- **Basic chemistry**
- **Addition type kinetics to produce linear polymers**
- **(a) Polyvinyl chloride**

$$n \text{CH}_2=\text{CH}\cdot\text{Cl} \rightarrow \left[ \begin{array}{cc} \text{H} & \text{H} \\ | & | \\ \text{C} & - & \text{C} \\ | & | \\ \text{H} & \text{Cl} \end{array} \right]_n$$

- **(b) Vinyl copolymer**

$$m \text{CH}_2=\text{CH}\cdot\text{Cl} + n \text{CH}_2=\text{CH}\cdot\text{X} \rightarrow \left[ \begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\ | & | & | & | \\ \text{C} & - & \text{C} & - & \text{C} & - & \text{C} \\ | & | & | & | \\ \text{H} & \text{Cl} & \text{H} & \text{X} \end{array} \right]_{m+n}$$

Basic chemistry, we start with producing the linear polymer using the vinyl chloride monomer. So this is based on the addition type kinetics where let us say you have n number of moles of vinyl chloride monomer. So it will undergo addition polymerization to produce a polymer having this kind of repeating structures CH<sub>2</sub>, CH, Cl n number of times and then this n number of times, it depends you know that will decide the final molecular weight and then other important properties, associated properties of the polymer, okay? Then vinyl copolymers if you wanted to produce rather simply polyvinyl chloride, vinyl copolymer if you wanted to produce, so there would be some other co-monomer also be present. For

example, let us say m moles of vinyl chloride monomer and n moles of this particular monomer. In general in chemistry x stands for the halogens or halides, but it is not true here, it can be some kind of functional group like it can be COOH carboxyl, it can be COOH hydroxyl, it can be COOR, these kind of things it may be having structures.

If you have the CH<sub>2</sub>CH COOH then polyvinyl acetate you may get. If you have CH<sub>2</sub>CH OH then polyvinyl alcohol you may get, like that you know metal methacrylates you can get if x is COOR. So, now when these types of different monomers reacting together and going through addition polymerization process, then you can have a polymer with a repeating structure of this type of monomer.

(Refer Slide Time: 10:55)

- Where m is usually greater than n, and X is a group on the co-monomer such as
  - Carboxyl (-COOH): -vinyl acetate
  - Hydroxyl (-OH): -vinyl alcohol
  - Carboxyester (-COOR): -methyl methacrylate
  - Nitrile (-CN): -acrylonitrile
- Replacing HX group by chlorine atoms gives the vinylidene monomer

Now, here you have Cl, here you are having x and then m plus n number of times it is being repeated usually m is greater than the n. x is a group on the monomer such as if it is carboxyl then you can expect vinyl acetate, if it is hydroxyl you can expect vinyl alcohol, if it is carboxy ester then you may expect metal methacrylate polymers. If it is nitrile, so

acrylonitrile you can produce. Replacing HX group by chlorine atoms gives the vinylidene monomer, it is not vinyl, it is vinylidene monomer.

(Refer Slide Time: 11:28)

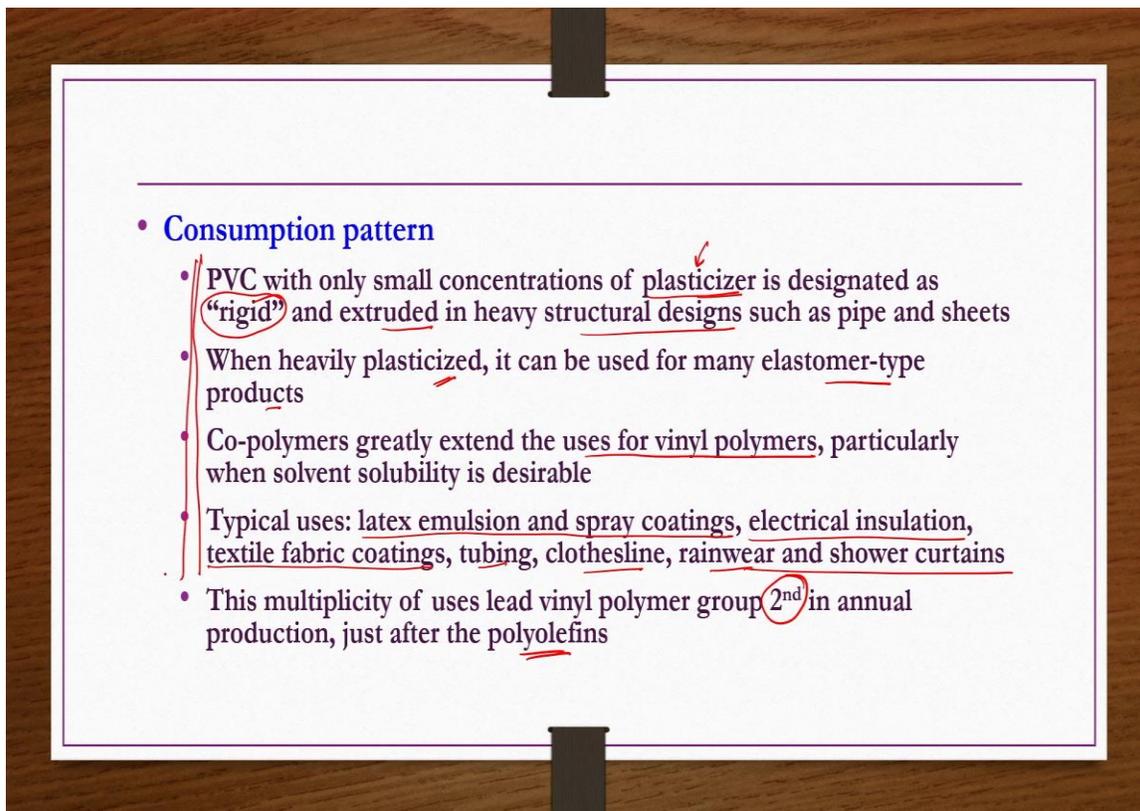
**Pertinent properties**

- PVC softening point 80 – 140°C, increasing with the degree of after-chlorination
- It decomposes rapidly at 140°C, liberating HCl; can be stabilized at lower T with acid neutralizers such as alkali metal salts
- Normal PVC is a hard, tough polymer, insoluble in most solvents
- It can be softened by plasticizers for mechanical working
- Vinyl chloride co-polymers are formulated to overcome some of disadvantages of PVC, particularly low solvent solubility and poor thermal stability

Now, some properties PVC softening point is 80 to 140 degrees centigrade and it increases with the degree of after chlorination and then after 140 degrees centigrade it immediately or rapidly decomposes liberating HCl. However, it can be stabilized at lower temperature with acid neutralizers such as alkali metal salts and the normal PVC is hard tough polymer. However, insoluble in most solvents. So, if you wanted to have the improved solubility, so then you can try to make a vinyl copolymer rather than simply making vinyl chloride polymers. So, likewise it can be softened by plasticizers for mechanical working. So, modifications can be done as per the properties, final properties that you require. Vinyl chloride copolymers are formulated to overcome some of the disadvantages of PVC. PVC let us say low solvent solubility we know, so and then another one is that also poor thermal stability. So, in order to improve the thermal stability or in order to improve the solubility in solvents, you can do or you can add different types of co-monomers and then prepare vinyl copolymers and then you get desired properties in your final polymers. So, the

polymer that you are producing from the vinyl chloride plus other kind of monomers, co-monomers.

(Refer Slide Time: 13:04)

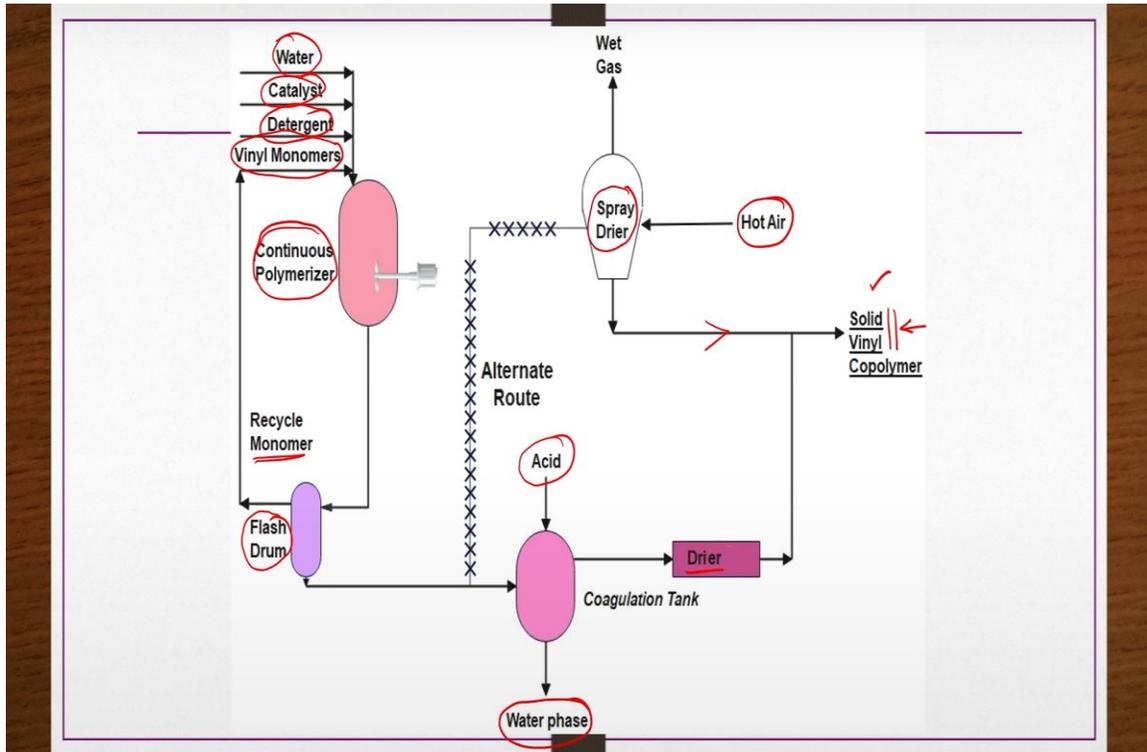


Consumption pattern, PVC with only small concentrations of plasticizers is designated as rigid very hard kind of structure you can get by adding only small concentrations of the plasticizers so and extruded in a heavy structural design such as pipe and sheets. When heavily plasticized, it can be used for many elastomer type products, for that purpose also it is used. Copolymers greatly extend the uses for vinyl copolymers, particularly when solvent solubility is desirable.

Typical uses like latex, emulsion and spray coatings, electrical insulations, textile fabric coatings, tubings, clothesline, rainwater and shower curtains, etc. for that purpose copolymers mostly used. This multiplicity of uses let the vinyl polymer group second in annual production just after polyolefin, after polyethylene, polypropylene, etc. This is the

most produced polymer because of so many varieties of applications it is having as mentioned above.

(Refer Slide Time: 14:16)



Coming to the production process, it is very simple process. Here let us say 100 parts of water, 100 parts of vinyl monomer and then 1 part of the catalyst and then 1.5 parts of the detergents are taken to a continuous polymerizer or continuous reactor, it can be batch reactor also. Let us say if you have a continuous reactor, so the temperature of the reaction is something around 50 degrees centigrade and then reaction time duration is 72 hours, such a long duration is there, that is the reason mostly it is preferred to be carried out in a batch reactor though it can be done in the continuous process as well. So, after the reaction whatever the reaction mixture is there that is passed through flash drum to recover the unreacted monomer and then recycle them whereas the slurry wet polymer is there that is coagulated by using the acid coagulation in which water is being separated out then whatever the wet polymer is there that can be dried and then converted into the shapes of

requirement of the consumer whether they want pipes or connections, etc. Based on that one, this final solid shapes would be depending.

Other alternative that you do not need to go for the acid coagulation whatever the slurry after removing the monomers from the flash drum is there, that slurry directly taken into a spray dryer to which hot air is being supplied so that the drying of the wet polymer taking place and then solid polymer dried solid polymer you can get and then that dry polymer you can convert as per the final product shape whatever you want. So, most of the polymer methods production methods are straightforward like that. Let us say in the next ABS we are not going to discuss with the flow chart because there also addition of monomers along with the catalyst and fillers, etc. and then doing the reaction after the reaction separating out the unreacted monomers and then whatever the wet polymer is there that is being dried out that is the simple process followed for the most of the polymers. So, that is the reason in some of the upcoming polymers production processes we may not be having the flow chart anyway.

(Refer Slide Time: 16:42)

- **Process description**
- **Emulsion and suspension polymerization methods are used commercially; the latter is used only if high purity polymers are desired**
- **In emulsion polymerization:**
  - A typical formulation is 100 parts of water, 100 parts of vinyl monomers, 1 part of persulfate catalyst, and 1.5 parts of a detergent emulsified
  - This is fed to a pressure reactor, either continuous or batch, operating at 50°C for periods as long as 72 hrs.
  - Micellular polymer particles can be further stabilized by addition of more emulsifying agent and sold as vinyl latex
  - If solid polymer is desired, the mixture is either acid coagulated and dried or spray-dried directly

So, however, if you see the detailed text of this particular process, then we have emulsion and suspension polymerization methods are used commercially. The latter is used only if

high purity polymers are desired. In general emulsion polymerization is used, but however, if you want high purity polymer production, then suspension polymerization method is used to produce either polyvinyl chloride or vinyl copolymers. Let us say in emulsion polymerization what you do you take a typical formulation let us say in this case you know 100 parts of water, 100 parts of vinyl monomers, 1 part of the persulfate catalyst and then 1.5 parts of the detergent emulsified detergents are used are included because of emulsification.

If you wanted to do the emulsion polymerization, so emulsification is required for that purpose this detergent is being added to the reactant mixtures and then taken to the reactor where the desired polymerization reaction is taking place. This is fed to a pressure reactor either continuous or batch either way it is possible operating at approximately 50 degrees centigrade, but however, for periods as long as 72 hours and then it may be less also it may be sometimes higher also that depends on the final polymer quality and then physical properties purity etc. all those parameters comes into the picture. Micellular polymer particles can be further stabilized by addition of more emulsifying agent and sold as vinyl latex. If solid polymer is desired the mixture is either acid coagulated and dried or directly spray-dried. That is all about polyvinyl chloride polymers or vinyl copolymers production and then consumption pattern etc.

(Refer Slide Time: 18:39)

**ABS resins:**

- ABS stands for acrylonitrile, butadiene and styrene copolymer
- Internationally, there are more than hundred grades of ABS resins available
- In India, about ten grades of ABS resins are available
- It is also known as engineering plastic because it is used in various industries like
  - Refrigerator liners, automobile components,
  - Molded and thermoformed parts of telephone, intercoms,
  - Mixers, computer cabinets, cameras,
  - Vacuum cleaners, molded luggage, toys, etc.

Now, we discuss about ABS resins. Here ABS stands for A stands for acrylonitrile monomer, B stands for butadiene monomer, S stands for the styrene monomer. So different types of monomers are being added and then coupled to produce a resin kind of polymer so that is the reason this polymer is known as the copolymer. So in general what you do you take butadiene polybutadiene and then mix it with the acrylonitrile and styrene and then do the reactions as per the flowchart as just we have seen for the case of PVC kind of flowchart.

When the reaction is completed taking the reaction mixture and then separating out the you know unreacted monomers mostly it is done by the flash drums then whatever the wet resin is there that you can dry and then process as per your requirement. Coming to the ABS resins grades over 100 grades are internationally available though in India roughly 10 grades are available in the markets. It is also known as engineering plastic because it is used in various industries like refrigerator liners, automobile components, molded and

thermoformed parts of telephone, intercoms, mixers, computer cabinets, cameras, vacuum cleaners, molded luggage, toys, etc. So many types of you know products or industrial products are also being produced that is the reason it is known as the engineering plastic.

(Refer Slide Time: 20:18)

- **Preparation process**
  - Raw materials for manufacture of ABS resins are styrene, butadiene and acrylonitrile
  - A monomer-soluble polybutadiene rubber or butadiene copolymer is dissolved in styrene and acrylonitrile with initiators and modifiers
  - This mixture is polymerized through phase conversion
  - Several types of bulk polymerizers may be used interchangeably for high impact ABS
- **Advantages of ABS resins**
  - As compared to other substitutes like metals, ABS resins enjoy several advantages since it is light in weight, Easy to process and Lower maintenance
  - Current demand for ABS resins is expected to increase as a result of growth in user industries, such as automobiles and telecommunications

Preparation process raw materials for manufacture of ABS resins are obviously acrylonitrile, butadiene and then styrene copolymers. A monomer soluble polybutadiene rubber which should be soluble actually or butadiene copolymer is dissolved in styrene and acrylonitrile monomers along with the initiators and modifiers and then carry out the reaction and then after the reaction whatever the reaction mixture is there that you pass through a flash drum to separate out the unreacted monomers and then recycle them back whereas the wet polymer you can do the subsequent processing. This mixture is polymerized through phase conversion. Several types of bulk polymerization may be used interchangeably for high impact ABS as well not only the phase conversion. Advantages of ABS resins as compared to other substitutes like metals, ABS resins have several advantages since it is light in weight, easy to process and lower maintenance. Current demand for ABS resins is expected to increase as a result of growth in user industries such

as automobiles and telecommunications. So, with that we complete ethenic polymer processes under which we have discussed the production of polyethylene, polypropylene, PVC and then vinyl copolymers and ABS resins.

(Refer Slide Time: 22:03)

## Polycondensation processes

- Polycondensation has been defined as step-wise reactions of monomers with functional grouping
- This often eliminates small molecules such as H<sub>2</sub>O
- Both linear and tridimensional polymers are made; the latter are more prevalent

**\* Phenol-formaldehyde resins**

- (a) methylol monomer formation:

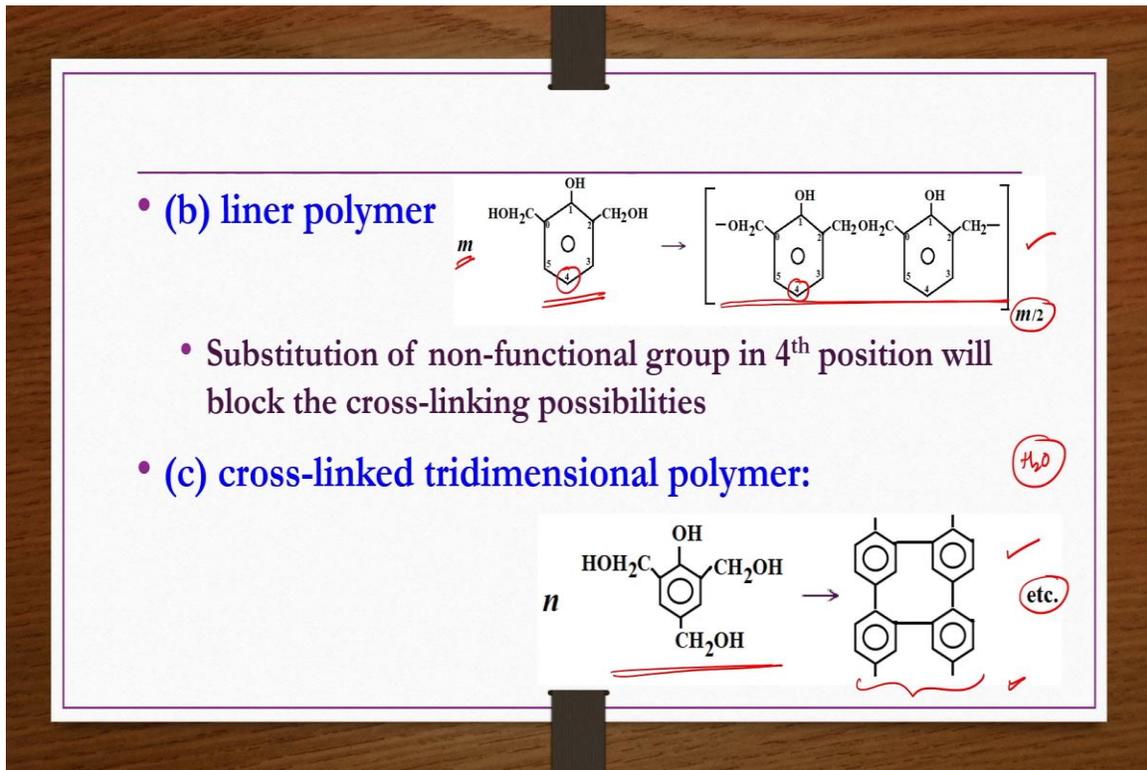
*Handwritten note:*  
Phenol + formaldehyde  
→ methylol monomer

- If  $x = 2 \rightarrow$  bi-functional ✓
- If  $x = 3 \rightarrow$  tri-functional ✓

Now we talk about the next type of plastics production or polymer production that is polycondensation processes. Polycondensation has been defined as stepwise reactions of monomers with functional grouping. In this process in general what happens small molecules like water, ammonia, formaldehyde, sodium chloride, etc. are being released and then by this polycondensation process you can produce linear polymers as well as cross linked tridimensional or 3 dimensional polymers as well you can make, okay? However, mostly polycondensation process is used for producing cross linked tridimensional polymers, okay? Under polycondensation processes different types of polymers can be produced like phenol formaldehyde is one type, then urea formaldehyde other type, then polyurethanes, epoxy resins, etc. you can produce using polycondensation process. However, first we discuss phenol formaldehyde resins, then after that epoxies and then polyurethanes we discussed. Poly formaldehyde resins first you know methylol monomer

formulation or formation is important. Here what happens phenol and then formaldehyde are reacting, phenol and formaldehyde reacting to produce methylol monomer like this. Now if  $x$  is 2, then you have only this functional and this functional, so bifunctional you have. So if  $x$  is equals to 2, it is bifunctional. If  $x$  is equals to 3, then you have this functional also would be there, so it is a trifunctional, okay? So if you wanted to produce linear polymers, then usually you take a bifunctional monomer that is dimethylol phenol monomer. If you wanted to produce tridimensional crosslinked thermosetting or thermoplastic, then you take a trifunctional monomer that is trimethylol phenol monomer you should take as a base material, okay?

(Refer Slide Time: 24:16)



So let us say liner polymer if you wanted to produce  $m$  number of monomers of this particular component that is dimethylol phenol monomer you take and then you do the polycondensation reaction. Then polymer or resin having this particular repeating unit would be produced and then  $m$  by 2 number of units would be being repeated like that, okay? So this is for the linear polymer. Substitution of non-functional group in the fourth

position, this is the fourth position if you have, then block that will lead to seizing the crosslinking possibilities, okay? So if you wanted to produce crosslinked tridimensional polymer, then what you do? You take n number of moles of trimethylol phenol monomer and do the polymerization. So water spitting will take place or releasing of water takes place and then these kind of structures or different types of structures, crosslinked structures, polymers you can produce. These are the representative structures only, okay? That is the reason etc. has been written here, okay? So now here what happens in this reaction as well as in this reaction, let us water is being removed and then that water can be dried up by heating and then vacuuming subsequently in the process.

(Refer Slide Time: 25:46)

- **Pertinent properties**
- **Based on bi- and tri-functional group, wide variety forms of phenol-formaldehyde polymers can be prepared**
- **Thus it is impossible to give specific properties in this brief outline chapter**
- **General resin characteristics can be controlled by**
  - (i) **Acid solution catalyst with excess phenol – produces linear soluble thermoplastics**
  - (ii) **Alkaline catalysts – (a) one-stage process and (b) two-stage processes**
    - In 1-stage, correct ratio of phenol to formaldehyde is reacted with proper control of time and heat to yield a thermosetting or heat reactive powder
    - This can be heated to an infusible, insoluble state via further cross-linking

Now, pertinent properties based on the bifunctional or trifunctional which group you have taken, wide variety forms of phenol formaldehyde polymers can be prepared. Thus, it is impossible to give specific properties of these phenol formaldehyde resins in general. However, general resin characteristics can be controlled by what type of catalyst are using. So whatever the phenol formaldehyde polymers are formed, they are resin in the characteristic in general. You can use the acid solution catalyst or acid catalyst H2SO4 etc.

you can use and then when you use these acid catalyst with excess phenol, then you can produce linear soluble thermoplastics. Thermoplastics if you wanted to produce that is a material which can be melted, remelted, molding anything that you can do as many number of times as you wish, the plastic behavior would be there. Such kind of phenol formaldehyde resin if you want to produce, then you should use acid solution catalyst.

Remember this phenol formaldehyde resin you can have thermoplastic form as well as the thermosetting type of things resin can also be produced. If you want to produce thermoplastic, then you have to use the acid catalyst like  $H_2SO_4$  you have to use. If you wanted to produce thermosetting type of phenol formaldehyde resin, then alkaline catalyst should be used and then it can be done in 2 stages, 1 stage process, 2 stage process. One stage process is simple, correct or specified proportions of phenols and formaldehyde should be taken in the presence of correct amount of the catalyst like NaOH etc. and then specified the temperature and time or control temperature of the reaction and time of the reaction very specifically to get the so called PF resins of thermosetting nature.

So, that is happening in 1 single step. So, this process is known as the 1 stage process. In the second stage process what happens whatever this thermoplastic that you got here, this thermoplastic would be mixed with hexamethyl ammonium kind of component which undergo decomposition to produce ammonia and then formaldehyde. This formaldehyde would be reacting with the thermoplastic that is being produced by acid solution catalyst and then undergo polymerization in the presence of ammonia catalyst to produce thermosetting PF resins. So, here 2 stages are there that is the reason this process is 2 stage process. In 1 stage, correct ratio of phenol to formaldehyde is reacted with proper control of time and heat to yield a thermosetting or heat reactive powders.

This can be heated to an infusible insoluble state via further cross linking. This resins whatever you get they are high viscous solutions, very high viscous like honey or even viscous liquids you get. If that resin is thermosetting and then if you do not store it properly with proper additives or diluents that will be undergoing some kind of cross linking on storing itself. So, usually if you based on the shape what type of form shape or form of resin that you wanted to get for based on the application after the reaction processing is to be done accordingly. We will see that one in the flowchart anyway.

(Refer Slide Time: 29:25)

- 2-stage process – thermoplastic material from acid catalysis process is mixed with hexamethylene tetramine
- This chemical is a white solid which breaks down to  $\text{HCHO}$  and  $\text{NH}_3$
- Formaldehyde combines with the resin to form a thermosetting product with ammonia as catalyst
- Both 1- and 2- stage resins are used as commercial molding materials
- Because final cross-linked polymer having good resistance to all chemicals except alkalis
- (iii) A strictly linear polymer with good heat fusion and solvent stability properties for varnishes and adhesives \*
- It is made by substituting cresol ( $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3$ ) for phenol with methyl group blocking the tri-functional position

Two stage process thermoplastic material form acid catalysis process and that is mixed with hexamethylene tetramine. This hexamethylene tetramine breaks down into the formaldehyde and ammonia during the reaction and because of the reaction temperature and then this formaldehyde would be combining with the thermoplastic resin that is formed in this process and then that formaldehyde reacting in the thermoplastic to form a thermosetting product with ammonia as catalyst. So here the process is taking place in two stages that is the reason it is known as the two stage process. Both one and two stage resins are used as commercial molding materials because of final cross linked polymer having good resistance to all chemicals except the alkalis. So these are having so many applications. Third one is strictly linear polymer that you can get with good heat fusion and solvent stability properties used for varnishes and then adhesives purposes. But however here how you get this one simply replace the phenol with the cresol then you can get the linear polymers suitable for varnishes and adhesives.

(Refer Slide Time: 30:56)

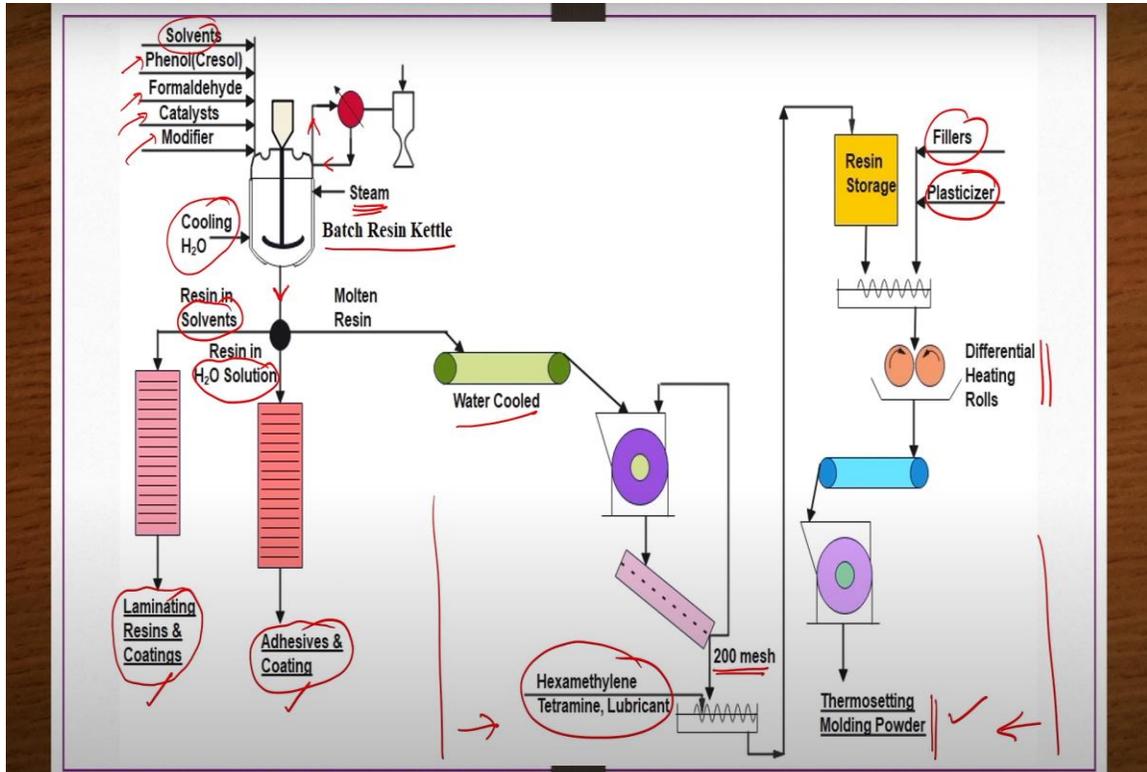
- Consumption pattern:
- Phenolic resins are low-cost polymers with excellent physical and electrical properties and fast curing characteristics ✓
- Their poor color characteristic can be partially overcome by adding pigments, dyes and fillers ✓
- Main uses fall into three classes:
  - Resins in solvents: coatings, varnishes and laminated structures ✓
  - Resins in water solutions: adhesive bonding ✓
  - Solid resin: all types of thermoset molded solid forms ✓
- For a no. of years phenolic resins ranked 1<sup>st</sup> in USA production as they were first commercial polymers ✓
- They have decreased in relative importance as thermoplastics have forged ahead ✓

Consumption pattern phenolic resins or phenol formaldehyde resins are also known as phenolic resins are low cost polymers with excellent physical and electrical properties and fast curing characteristics that is very important. However they have very poor color so their color can be improved by adding some kind of pigments, dyes and fillers. Usually they would be having under high viscous resin form that would be having like light brownish color as the degree of cross linking increases the color becomes dark brown and then very dark brown and then once it is completely cross linked it resembles like almost like a black color solid material.

So the color can be improved by adding pigments, dyes and fillers in general. Main uses fall into 3 classes if you wanted to use like in coatings, varnishes and laminated structures then what you do whatever the high viscous phenolic resins are there that you dissolve in appropriate solvent and then use for these application that is one type. If you wanted to use for the adhesives then what you do the same resin you dissolve in some water solutions and then use for the adhesive bonding purpose. If you wanted to use them for thermoset

molded solid forms then completely do the cross linking, do the fusioning and then you get a completely cross linked cured solid resin that you can use for this purpose. For a number of years phenolics ranked first in USA because of their application however nowadays you know thermoplastics are taken over.

(Refer Slide Time: 32:50)



So coming to the flowchart simple process here what you do monomers, phenol, formaldehyde along with the catalyst. Let us say if you wanted to have a thermosetting then NaOH catalyst should be used and then there should be some modifiers and then solvents also as per the requirement they are taken to a batch resin kettle and then reaction is allowed to undergo. For the reaction to undergo energy is required that is supplied through the steam. In order to control the energy of the reaction cooling water is supplied along the outside surface of the reactor. Sometimes what happened, total refluxing is done so that to control the temperature of the reactant mixtures as well.

After the completion of the reaction you know reaction temperature varies usually 70 to 130 degrees centigrade depending on the catalyst and catalyst concentration etc. So this high viscous solution whatever you get that if you dissolve in appropriate solvents and then store it that can be used for the laminating resins and coatings purpose. If you dissolve in water solutions then that solution you can use for the adhesives and coatings purpose. Otherwise this molten resin can be water cooled then dried and then crushed and then screening has been done to take the particles of 200 mesh as a final product. Others are sent back for the resizing purpose and then after this point you know you can add different types of lubricants, fillers, plasticizers as per your requirement and then finally it passes through after adding the fillers, plasticizers and then lubricants as per requirement that mixture is passed through differential heating rolls which are nothing but the you know 2 rolls are there which are heated up as per the temperature required for the molding purpose and then between these heated rolls the material passes through and then you get the desired structure that would be conveyed back and then you get do the crushing etc. to get the thermosetting molding powder. If you wanted to get solid form so this process you have to follow. Otherwise you are doing this or producing phenolics for this application so you do not need to do the drying process all this process cross linking process is not required.

(Refer Slide Time: 35:30)

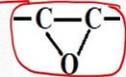
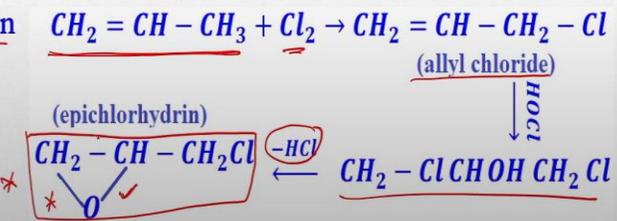
---

- **Process description:**

- Polymerization is an exothermic reaction which must be controlled by batch reaction as the material rapidly changes viscosity
- Phenol, formaldehyde and catalyst are mixed together in a jacketed autoclave (resin kettle) and heated with steam
- After reaction starts, heat of reaction is removed by refluxing and water cooling
- In the early stages of reaction, heavier viscous resin separates as a bottom layer with an aq. layer at the top
- Dehydration is next completed in the kettle by a combination of heat and vacuum
- Fused resin at 130 – 150°C is removed from the kettle, cooled and ground to a fine powder
- Heat reactive molding powder prepared above can be mixed with fillers, coloring agent, lubricants and catalyst in a ribbon blender or ball mill
- It is then heated further on a pair of differential heating rolls to prepare fast curing commercial phenolic molding powder

Now process description, polymerization is an exothermic reaction which must be controlled by batch reaction as the material rapidly changes viscosity. Phenol formaldehyde and catalyst are mixed together in a jacketed autoclave or resin kettle and heated with the steam. After reaction starts heat of reaction is removed by refluxing and water cooling. In the early stages of reaction heavier viscous resin separates as a bottom layer with an aqueous layer at the top. This aqueous layer would be dried up because of the supplied steam and then vacuum applied. Then fused resin at 130 to 150 degrees centigrade is removed from the kettle, cooled, ground to fine powder. Heat reactive molding powder prepared above can be mixed with fillers, coloring agents, lubricants, catalyst in a ribbon blender or ball mill. It is then heated further on a pair of differential heating rolls to prepare fast curing commercial phenolic molding powders. So that is all about phenol formaldehyde polymers prepared by polycondensation process.

(Refer Slide Time: 37:02)

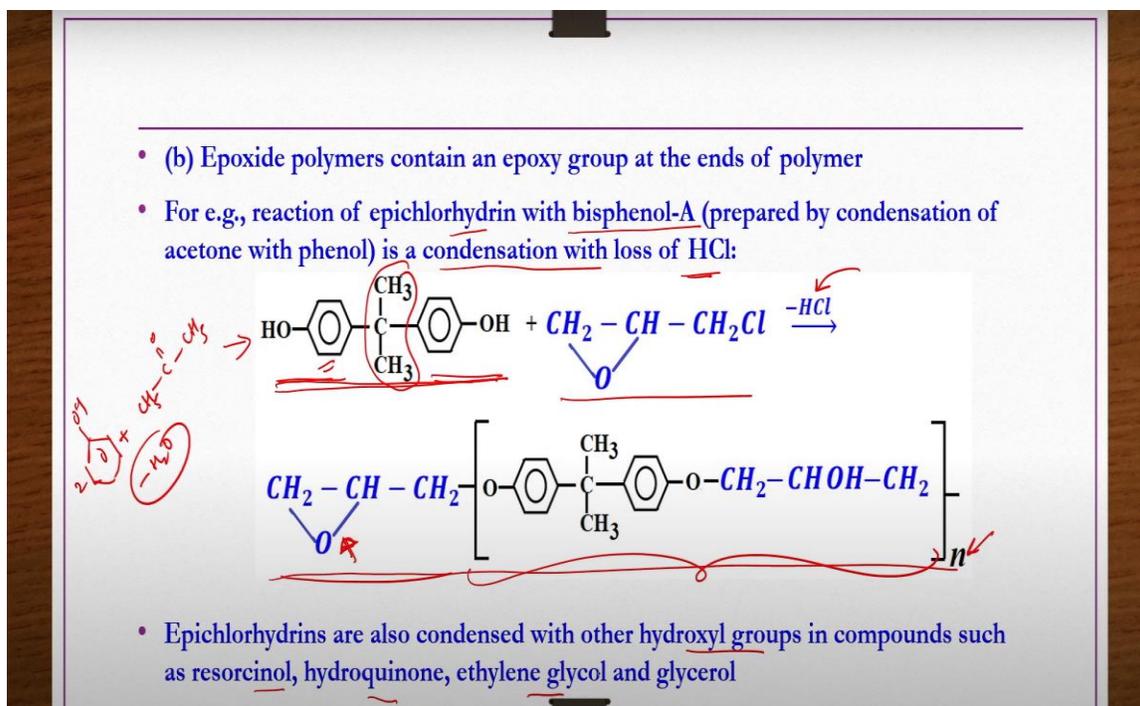
- **Epoxy polymers**
- **Basic chemistry**
- (a) Epoxidation is the addition of an oxygen atom across C=C to give
- Oxygen transfer agent can be peracids such as 
  - Peracetic acid (CH<sub>3</sub>COO·OOCCH<sub>3</sub>), hydrogen peroxide or chlorhydrin (HOCl) followed by HCl removal
- Latter gives epichlorhydrin  $CH_2 = CH - CH_3 + Cl_2 \rightarrow CH_2 = CH - CH_2 - Cl$  (allyl chloride)  


Now the same polycondensation process would be applied to produce epoxy resins. So let us start discussion on epoxy polymers. Basic chemistry different ways it is possible and then even nowadays also more and more research is going on to produce different types of epoxides. However, we take 4 important ones which are commercially viable in India. The first one is the epoxidation which is nothing but the addition of an oxygen atom across the C double bond C to give a epoxy functional group like this. Oxygen transfer agent can be peracid such as the peracetic acid, hydrogen peroxide or chlorhydrin followed by HCl removal. Whereas the latter gives the epichlorhydrin that reaction we will see. This reaction we have already seen 2, 3 times. One time we have seen like when we are discussing about the natural glycerol production, then synthetic glycerol production.

So both the chapters we have seen this reaction. So in that reaction we already realized that epichlorhydrin we get it as a kind of intermediate. So up to that part only we are discussing after that getting glycerol part we are not discussing here anyway. So in the synthetic glycerol manufacturing what happens actually propylene reacts with the chlorine to get allyl chloride which further reacts with HOCl to give the allyl alcohol which undergoes a

reaction or polycondensation reaction by removing the HCl where it forms epichlorhydrin of this particular structure. This kind of structure you will be having in epoxies. C C O are connected in a triangular form like this. So that is very common structure in epoxies. So this epichlorhydrin you get it here.

(Refer Slide Time: 38:54)



So other one is the epoxide polymers contain an epoxy group at the ends of polymer. For example, reaction of epichlorhydrin whatever we have taken or produced just now that reacts with bisphenol A so that the condensation reaction undergoes with the loss of HCl then you get the epoxides. How this is nothing but your bisphenol A, this particular component it is obtained by condensation of acetone and then phenol. So actually 2 moles of phenols reacts with the acetone and then it undergoes the condensation reaction. So where H<sub>2</sub>O is being released and then this particular bisphenol A is forming. So this bisphenol A would react with the epichlorhydrin and then this again undergo condensation reaction and then we know whenever there is a condensation reaction small molecules like water, ammonia, HCl, NaCl, etc. are being released. So here HCl is being released and a polymer would be formed or epoxide should be formed in

which whatever this within the black parenthesis shown that structure is only repeating structure whereas this is not. Now this component or this functional we call it epoxy. So this is one method. Epichlorhydrins are also condensed with other hydroxyl groups in compounds such as resorcinol, hydroquinone, ethylene glycol and glycerol as well.

(Refer Slide Time: 40:47)

- (c) Epoxy monomers can be obtained from unsaturated natural products such as vegetable oils, particularly soybean oil, and tall oil from wood pulping
- Molecular structure of polymers from epoxidized natural product monomers is extremely complex
- Both linear and cross-linked polymers are possible
- (d) synthetic epoxy monomers are obtained via butadiene cyclization and peroxidation

$2 \text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 \rightarrow \text{C}_6\text{H}_{11} - \text{CH} = \text{CH}_2 \xrightarrow{\text{H}_2\text{O}_2 \text{ or peracetic acid}} \text{C}_6\text{H}_{11} - \text{CH} - \text{CH}_2$

(vinylcyclohexane)

So third type of epoxy monomers preparation if you see that can be obtained from unsaturated natural products such as vegetable oils particularly soybean oil and tall oil from wood pulping. Molecular structure of polymers from epoxidized natural product monomers is extremely complex. Both linear and cross linked polymers are possible. The fourth way of getting epoxy monomers is the synthetic way like in obtained via butadiene cyclization and peroxidation reaction. If you see the reaction 2 moles of the butadiene undergo cyclization reaction to produce vinyl cyclohexane. This vinyl cyclohexane react with the hydrogen peroxide or peracetic acid to produce this epoxy monomer.

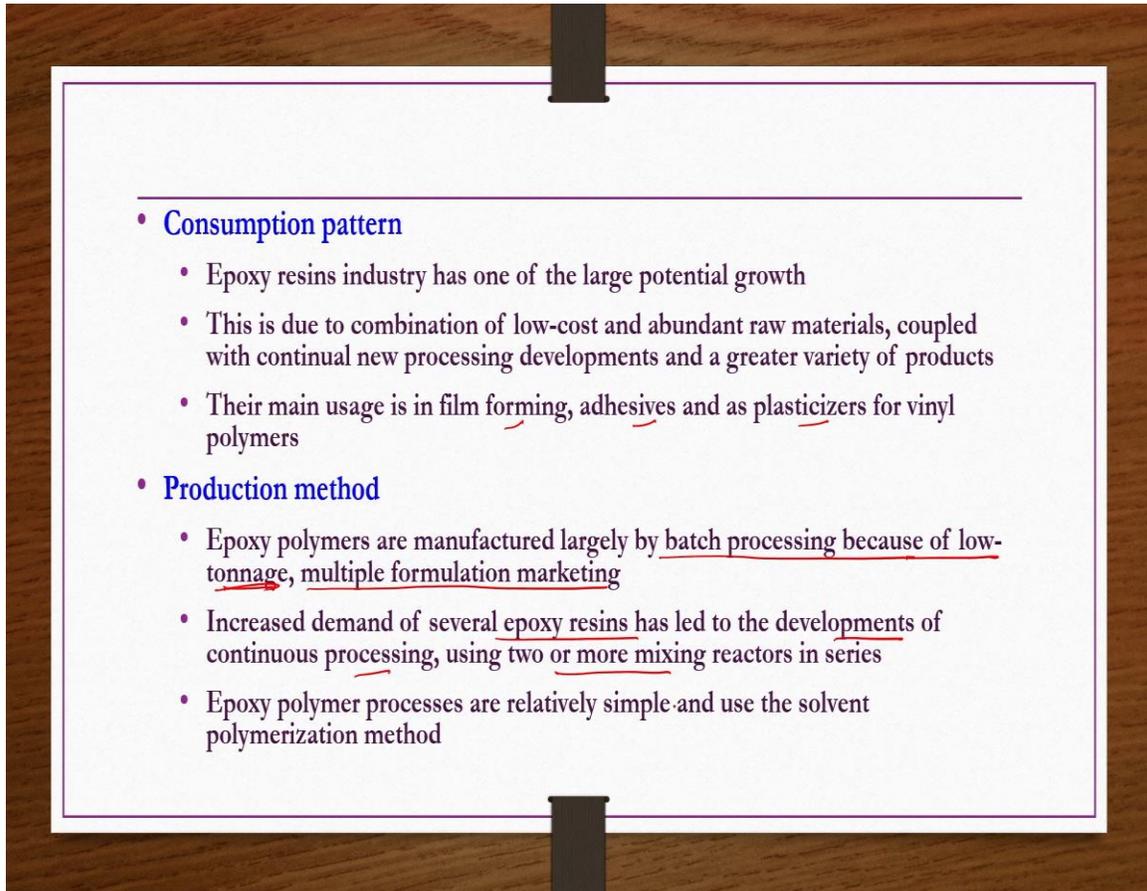
(Refer Slide Time: 41:41)

- **Pertinent properties:**
- **Epoxy resins exhibit extreme versatility because of possible combinations of properties such as**
  - Chemical stability from ether linkages ✓
  - Chemical reactivity from residual epoxy and hydroxy groups ✓
  - Excellent adhesion to a variety of surfaces ✓
  - Good abrasion resistance ✓
  - Curing and molding without evolution of gas and with low shrinkage ✓
  - Outstanding electrical properties ✓
  - Ability to form copolymers with unusual properties ✓
- **Molecular structure, purity and residual saturation in the product are the main criteria for suitability in most applications**

So pertinent properties epoxy resins exhibit extreme versatility because of possible combinations of properties such as chemical stability from ether linkages, then chemical reactivity from residual epoxy and hydroxyl groups, excellent addition to a variety of surfaces, good abrasion resistance curing and molding without evolution of gas with low shrinkage, outstanding electrical properties ability to form copolymers with unusual properties so and so many properties it can exhibit. Molecular structure purity and residual saturation in the product are main criteria for the suitability in most of the applications as per the applications as per the properties that you are designing in final epoxy resins

accordingly molecular structure and then corresponding purity and residual saturation one has to see.

(Refer Slide Time: 42:45)



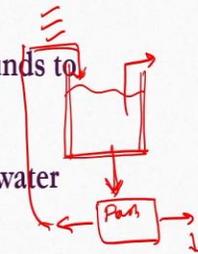
- **Consumption pattern**
  - Epoxy resins industry has one of the large potential growth
  - This is due to combination of low-cost and abundant raw materials, coupled with continual new processing developments and a greater variety of products
  - Their main usage is in film forming, adhesives and as plasticizers for vinyl polymers
- **Production method**
  - Epoxy polymers are manufactured largely by batch processing because of low-tonnage, multiple formulation marketing
  - Increased demand of several epoxy resins has led to the developments of continuous processing, using two or more mixing reactors in series
  - Epoxy polymer processes are relatively simple and use the solvent polymerization method

Consumption pattern epoxy resins industry has one of the large potential growth. This is due to combination of low cost and abundant raw materials coupled with continual new processing developments and a greater variety of products. Their main uses in film forming are the sieves and as plasticizers for vinyl polymers. Coming to the production methods, epoxy polymers are manufactured largely by batch processing because of a low tonnage you produce in low tonnages and multiple formulation marketing as well as the reaction time is also very large. Increased demand of several epoxy resins has led to the

developments of continuous processing using 2 or more mixing reactors in series. Epoxy polymer processes are relatively simple and use the solvent polymerization method.

(Refer Slide Time: 43:42)

- Unsaturates, epoxidizing agent, and solvent are contacted on a programmed addition schedule for given  $t$ - $T$  conditions
- Water or other condensibles and solvents are removed and the solid or oil resin fraction is given a final purification and drying
- Unusual engineering design features are:
  - Safety precautions in handling the peroxidizing compounds to avoid detonating conditions
  - Exact  $T$  control with provisions for rapid dumping and water flushing for a runaway reaction



Unsaturates epoxidizing agent and solvent are contacted on a programmed addition schedule for a given temperature and time conditions. Water or other condensibles and solvents are removed and the solid or oil resin fraction is given a final purification and drying. Simple straightforward as we have seen other flowcharts just now for other polymers like PVC and then phenol formaldehyde kind of reactors are suitable here. You can take a batch reactor or continuous reactor, mostly batch reactors are there.

So here epoxidizing agent, any unsaturated solvents etc., catalyst etc. are taken to the reactor, allowed to undergo the polymerization reaction whatever the water is there that is dried off by the heat or vacuum and then mixture whatever is there that you take to the flash drum to separate out the monomers and then recycle back. Whereas the wet polymer

you can take and then dry it, purify it and dry it as per the requirements. Unusual engineering design features are safety precautions in handling the peroxidizing components to avoid detonating conditions, exact temperature control with provisions for rapid dumping and water flushing for a runaway reaction is very essential to carefully design. So that is all about epoxy resins, their basic chemistry, manufacturing process, applications, properties etc.

(Refer Slide Time: 45:28)

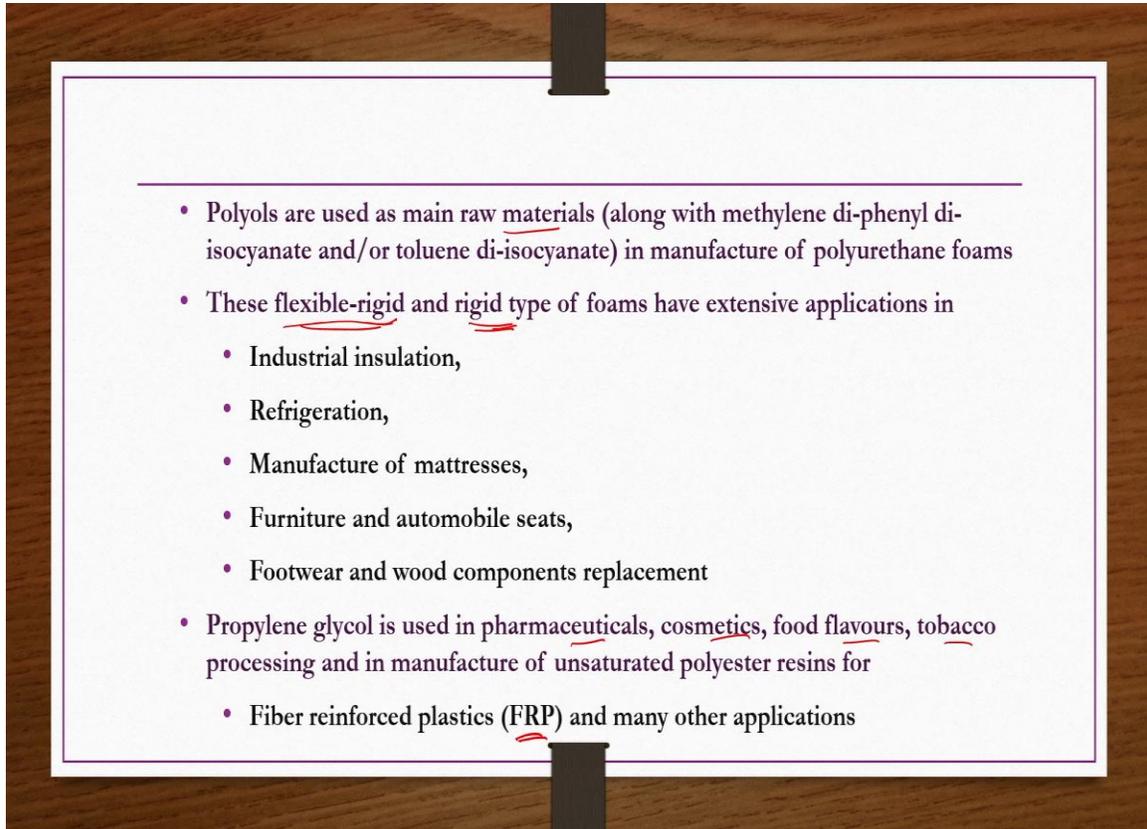
**Polyurethanes:**

- This is one another type of condensation polymer
- Organic isocyanate compounds have been known for a long time
- But first became commercially interesting in the last two to three decades based on work by O. Bayer
- It was shown that reaction of di- and polyisocyanates with di- and polyols formed polyurethanes with many uses
- Considerable increase in production capacity for di-isocyanate feedstock increased because of its use in production of polyurethanes which are used in
  - Automobile industry, ✓
  - Construction ✓
  - Refrigeration technology ✓

Now finally we discuss about polyurethanes and then we conclude this particular chapter. Polyurethanes, this is one another type of condensation polymer, both thermosetting and thermoplastics can be produced by this kind of condensation polymer to get different types of polyurethanes. Organic isocyanate compounds have been known for long time, but first became commercially interesting in the last 2 to 3 decades based on the work of Bayer where it was shown that dye and poly isocyanates with dye and polyols formed polyurethanes with many uses. Considerable increase in production capacity for dye

isocyanate feedstock increased because of its use in production of polyurethanes which are used in automobiles, constructions, refrigeration technology, etc. Actually we are first talking about the raw materials. Raw materials are diisocyanates and then diisocyanates or polyols. So about the importance of diisocyanates, we have seen here.

(Refer Slide Time: 46:38)



Now about the other raw material, polyols are used as main raw materials along with methylene diphenyl-diisocyanate that is MDI and R, toluene diisocyanate that is TDI in manufacturing of polyurethane forms. These flexible, rigid and rigid type of forms, they are rigid and flexible as well or only rigid as well. So, the either of them you can produce. They have extensive applications in industrial insulation, refrigeration, manufacture of mattresses, furniture and automobile seats, footwear and then wood components replacement, etc. Propylene glycol is used in pharmaceuticals, cosmetics, food flavors, tobacco processing and in manufacturing of unsaturated polyester resins for fiber reinforced plastics and many other applications.

(Refer Slide Time: 47:35)

- Toluene di-isocyanate (TDI), in the form of its 2,4- and 2,6-isomers, has been the most significant di-isocyanate
- However, recently 4,4'-diphenylmethane di-isocyanate (i.e., methane diphenyl di-isocyanate, MDI) has overtaken TDI
- Another important component of polyurethanes is hexamethylene-1,6-di-isocyanate (HDI)
- TDI is generally manufactured in a continuous process involving three steps as below:
  - Nitration of toluene to di-nitrotoluene ✓
  - Hydrogenation of di-nitrotoluene to toluenediamine
  - Phosgenation to toluene di-isocyanate
- **Manufacturing process**
  - MDI is produced by reacting aniline with formaldehyde to get methylene bis-dianiline
  - Diamine is reacted with phosgene to yield MDI
  - TDI is manufactured by reduction of di-nitrotoluene to diamine with hydrogen and reacting the diamine with phosgene to yield TDI

Coming to the raw material, toluene diisocyanate which is important from the polyurethane manufacturing point of view. It can be used in its isomers 2, 4 and 2, 6 isomers form. It is the most significant diisocyanate from the polyurethane manufacturing point. However, recently 4, 4-diphenylmethane diisocyanate that is methane diphenyl diisocyanate nothing but MDI has overtaken TDI. Another important component of polyurethane is hexamethylene 1, 6 diisocyanate which is HDI. TDI is generally manufactured in a continuous process involving 3 important steps. First one is the nitration of toluene to get the dinitrotoluene, then this dinitrotoluene would be undergoing hydrogenation to produce toluene diamine, then this toluene diamine would be undergoing phosgenation reaction to produce TDI, toluene diisocyanate. If you see the manufacturing process of MDI, MDI is produced by reacting aniline with formaldehyde to get methylene, bis-dianiline. This dianiline or nothing but diamine is reacted with phosgene to yield MDI. TDI methods or production method is already discussed here. The same thing is shown here again.

(Refer Slide Time: 49:07)

- **Manufacturing process for polyurethanes**
  - Thermoplastic polyurethanes are formed by linking three basic components as mentioned below:
    - i) A linear hydroxyl terminated polyol with mol. wt. of 500 – 3500
    - ii) A di-isocyanate, which may be aromatic such as MDI, TDI or non-aromatic, as dicyclo hexyl methane di-isocyanate
      - However, MDI is preferred in general
    - iii) A low mol. wt. glycol such as 1,4 butanediol, ethylene glycol, or 1,4 phenylene bis b-hydroxyl ethyl ether to serve as chain extender

Manufacturing process for polyurethanes we see. The previous one is that diisocyanates TDI, MDI manufacturing we have seen because they are most important raw materials to produce polyurethanes because this TDI or MDI are reacting with the diols or polyols to produce polyurethanes. So how these polyurethanes are being produced from these TDI, MDI and then polyols that we are going to see now. Thermoplastic polyurethanes are formed by linking 3 basic components as mentioned below. First one is a linear hydroxyl terminated polyol with molecular weight 500 to 3500. Second one is a diisocyanate which may be aromatic such as MDI, TDI or non-aromatic such as dicyclohexyl methane diisocyanate. However MDI is preferred in general and then third one is low molecular weight glycol such as 1, 4 butanediol ethylene glycol or 1, 4 phenylene bis-B-hydroxyl ethyl ether to serve as chain extenders. By either of these 3 methods you can produce thermoplastic polyurethanes.

(Refer Slide Time: 50:36)

## References

- C.L. Dryden, *Outlines of Chemical Technology*, Edited and Revised by M. Gopala Rao and S. Marshall, 3<sup>rd</sup> Edition, Affiliated East West, New Delhi, 1997.
- T.G. Austin and S. Shreve, *Chemical Process Industries*, 5<sup>th</sup> Edition, McGraw Hill, New Delhi, 1984.
- R.E. Kirk and D.F. Othmer, *Encyclopaedia of Chemical Technology*, 4<sup>th</sup> Edition, Interscience, New York, 1991.
- P.H. Groggins, *Unit Processes in Organic Synthesis*, 5<sup>th</sup> Edition, McGraw Hill, 1984.

References for today's lecture. In fact the references for the today's and then previous lecture on polymer industry are presented here.

Outlines of Chemical Technology by Dryden edited and revised by Gopala Rao and Marshall third edition. Chemical Process Industries by Austin and Shreve fifth edition. Encyclopedia of Chemical Technology by Kirk and Othmer fourth edition and then Unit Processes in Organic Synthesis by Groggins fifth edition. However the entire lecture notes of today's lecture as well as the previous lecture on polymer industry can be found from this reference book. With this we complete our lectures on polymer industries as well. Thank you.