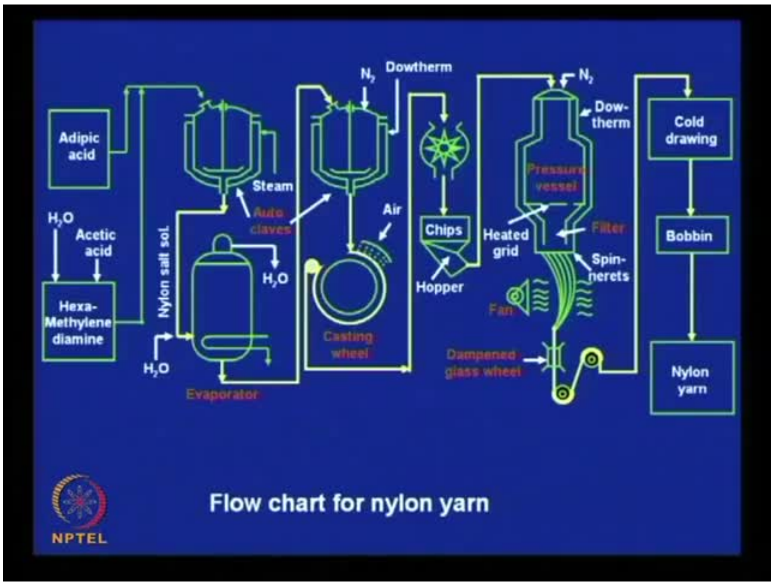
Science and Technology of Polymer
Prof. Basudam Adhikari
Science and Technology of Polymers
Indian Institute of Technology, Kharagpur

Lecture - 16
Polymerization Techniques (Contd.)

Please put your attention to the bulk polymerization, a manufacture of polymer by bulk polymerization technique.

(Refer Slide Time: 00:24)



Flow chart for nylon yarn

Here is a flow chart for nylon yarn manufacture. Here this nylon, which is manufactured by bulk polymerization technique, can be prepared in the form of granules; or in that establishment, there can be set up or units, which can lead to the final product also. Here it shows nylon yarn; from the yarn, one can make that from the fiber, one can make yarn, nylon yarns. Now, here in this flow, typical flow diagram, see these are the raw materials, raw material silos adipic acid, adipic acid and hexa methylene diamine.

Hexa methylene diamine is actually dissolved in water; adipic acid is dissolved in water. When these two are mixed in solution phase, some nylon salt is formed. Here you see this nylon salt, nylon salt is formed actually that step is not shown here separately in this flow diagram. When these two reactants are mixed immediately, a solid precipitate of hexamethylene adipamide is formed, hexa, hexamethylene adipamide. If you add acid to an amine say aniline and acetyl aniline hydrochloride is formed that is, aniline salt; likewise, in this case hexa methylene diamine, when it is mixed with adipic acid hexamethylene adipamide salt is formed.

Now, here this is a condensation polymerization, it needs strict control of stoichiometry, you have seen; in this stoichiometry control is not properly maintained one cannot lead to high molecular rate product you have seen. Even if in it you go up to 99 percent conversion you may not get high molecular rate polymer, provided you do not have this one is to one or equimolar ratios of the reactants are accurately taken. And again that is a difficult task during weighing of the raw materials, see adipic acid and hexa methylene diamine.

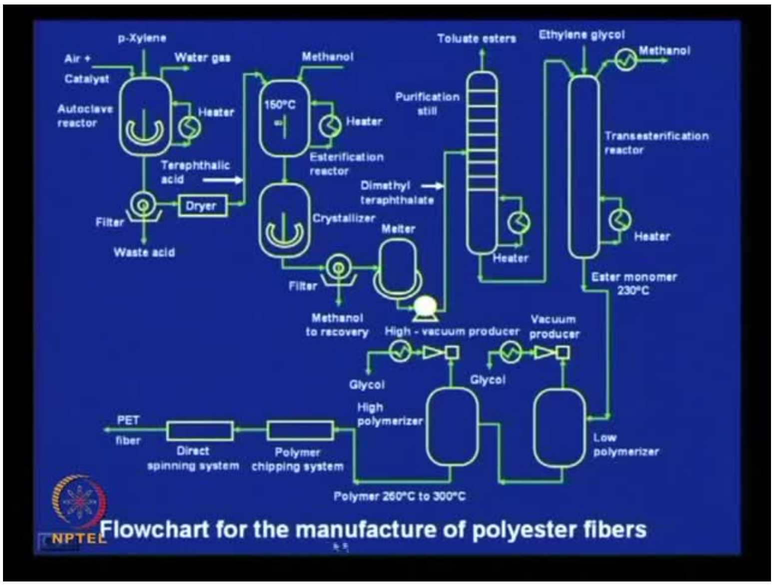
These raw materials during weighing some quantity of any of this two, maybe less or more other than equimolar mixture. But if you mix these two in solution phase a salt will be formed in one is to one molar ratio and then that salt is since adjust solid that can be filtered and worst and which can further proceed to main polymerization of that salt. Now, if you consider this as a reactor where salt is formed then that is transferred to another evaporator where water is removed from the solution or it is filtered.

Most important thing is this one, reactor, main reactor where this polymer gets melted sorry mono, salt gets melted and it is maintained at high temperature usually above 250 60 degree Celsius and this is a stirrer, this is the reactor and this is the jacket, this is the dumping side, dumping side. So, this molten mass is stirred, kept stirred continuously for proper heat transfer then that pure polymer, molten polymer from this reactor is poured on to a casting wheel means nylon, fully grown nylon solid polymer is cast in the form of thin sheet over this wheel in a continuous manufacture and that is actually cooled. A casting is done by air cooling on the wheel from molten mass it becomes solid sheet over the wheel then that is actually pass through a mill, chopper mill, chopper mill which cuts or chops that sheet into small size.

So, you will get nylon chips and then that nylon chips can be used for many purpose, for product fabrication say for fiber drawing or casting of some structural items likes say gears and other things. What if there are installations for fiber drawing so that fiber it, that chips are passed through that fiber drawing units where spinnerets are there. Spinnerets are, is a device, which contains very narrow opening, narrow holes through which it is this mass, molten mass or sometimes in solution those are pressurized out of this spinneret forming very thin fiber. So, thin fibers are coming out from this spinneret that is cooled by fan, air blowing and then these are actually pass through some wheels and ultimately the yarn is formed. Yarn means is a bundle of fibers twisted, little twisted. So, nylon earned is made from this process.

The essence of these things is, is the reactor to which this nylon salt is fed, it is maintained at very high temperature and the conversation to high molecular rate occurs over here. And then that is the polymer is obtained from the bottom side of the reactor, we get the polymer product, we can get in the form of sheet, in the form of flakes, in the form of granules etcetera. Then we can imply that raw polymering material for fabrication of molded items or yarn or fiber.

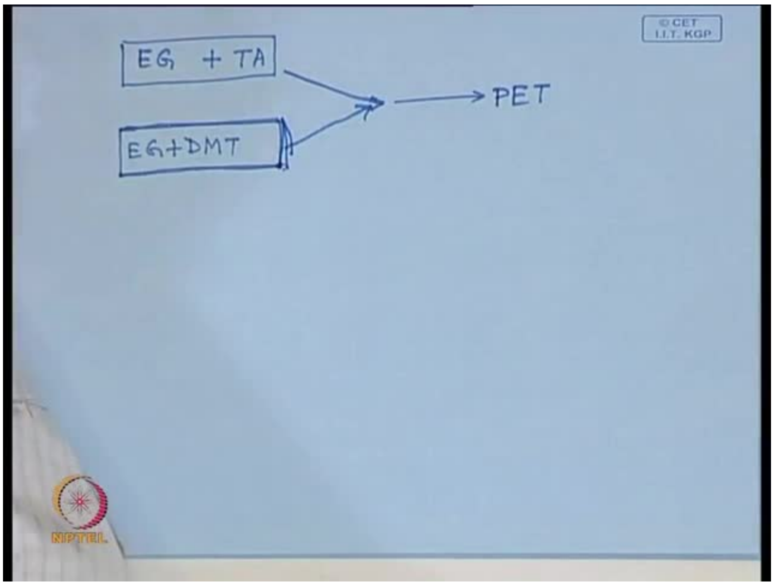
(Refer Slide Time: 09:39)



Flowchart for the manufacture of polyester fibers

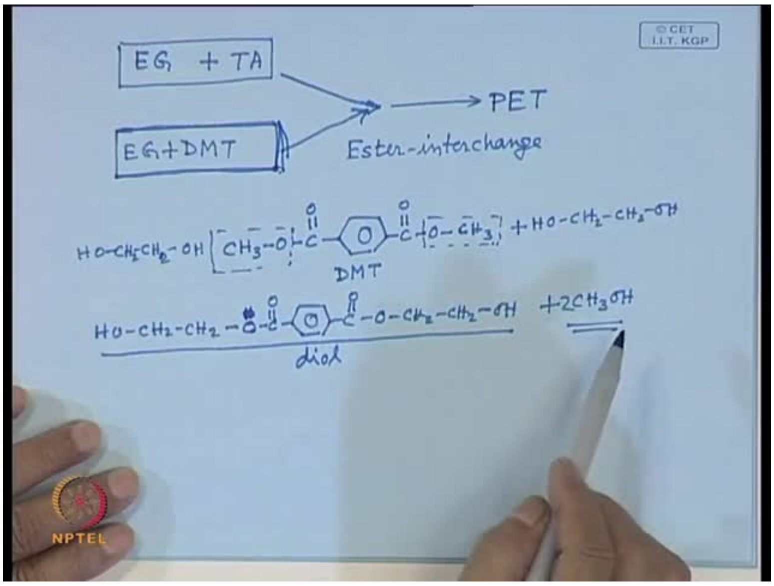
This is a flowchart for the manufacture of polyester fibers. (( )) you know, say…

(Refer Slide Time: 10:28)



As I told you this PET polyethylene terephthalate, it can be manufactured from ethylene glycol and tartaric acid or it can be made from ethylene glycol and dimethyl terephthalate. Both these can lead to polyethylene terephthalate. Now, this is, actually this is the most accepted technique this DMT root. Here this shows a DMT root. Now, till this point, till this point, actually these steps shows formation of dimethyl terephthalate. Although, in… When we study this polymerization principles we just show that this reactants like ethylene glycol and tartaric acid or ethylene glycol dimethyle terephthalate they are reacted.

(Refer Slide Time: 11:56)



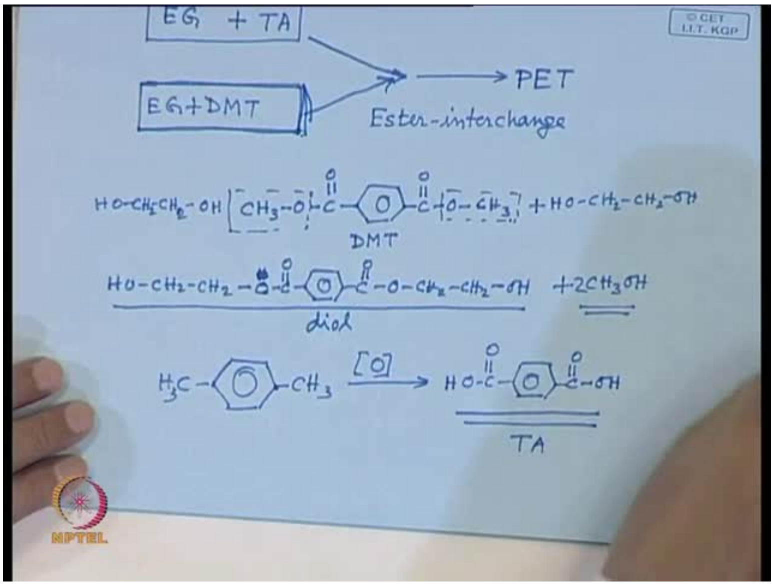
And by ester interchange process, ester interchange principle this polyethylene terephthalate is made. What is, you know what is called ester interchange reaction? Ester interchange reaction? Dimethyl terephthalate means it is already an ester. Dimethyle terephthalate in this DMT dimethyl terephthalate, this is the ester group and this part is the alcohol part. These are the two alcohol side.

Now, when these alcohol sides, alcohol parts are replaced by What happens? We get producing, here this is the byproduct, methanol is the byproduct and this entire molecule becomes say diol. It becomes a diol, intermediate diol or (( )) diol. This will further react with this kind of thing or or it can react with another DMT molecule. Ultimately what we get, gradually this unit grows bigger and bigger and bigger by which time methanol is produced. So, this is the simplest way of looking or viewing the synthesis of this polyethylene terephthalate, but in some industrial installation if you go you will find huge number of units are combined, connected to each other one after the other.

Now, in this (( )) again this is, this flow diagram which is simplified flow diagram. A real industrial installation for PET manufacture maybe further complex or complicated than this simplified flow diagram. So, what is here you see this is a reactor type where this terephthallic acid, terephthallic acid is actually synthesized. That means in that installation instead of buying DMT that manufacturer they them self manufacture this DMT in their own plant.

So, in this flow diagram it shows the productions of polyester fiber, PET fiber from xyl or xylene paraxylene and other reactants. From paraxylene they prepare this terephthallic acid. So, this is a terephthallic acid synthesize or manufacturing reactor. There is a stirring system, is autoclave type reactor, para paraxylene that as well as catalyst and here and that converts this paraxylene to terephthallic acid. What is that reaction called? Oxidation, oxidation. So, paraxylene is oxidized to terephthallic acid.

(Refer Slide Time: 18:08)



What is the formation, formulae of paraxylene? So, this product terephthallic acid, this is manufactured in this container and it passes through certain purification units, unit operations. In any chemical plant there are several unit operations, units having different functions, they are installed, and you have that productions passes through those unit operations, controlled by chemical engineers. So, as this terephthallic acid is manufactured and after it is dried then it is converted to DMT dimethyl terephthalate where this terephthallic acid is fed to this reactor, methanol is added and the temperature is maintained at 150 degree like that, DMT is made.

So, this is called esterification reactor and this DMT is crystallized in a crystallizer in another unit. So, DMT crystals are formed in methanol and methanol is separated and sent to recovery again which can be recycled to, this methanol is recycled to this step. You see here if some quantity of methanol is used at the beginning same methanol can be recycled for DMT manufacture. Otherwise what will happen if your your company buys DMT from outside then methanol will be byproduct in your unit, then that byproduct is to be sold otherwise cost computation cannot be reached. So, it is for that, those reasons it is better to manufacture DMT in the same installation.

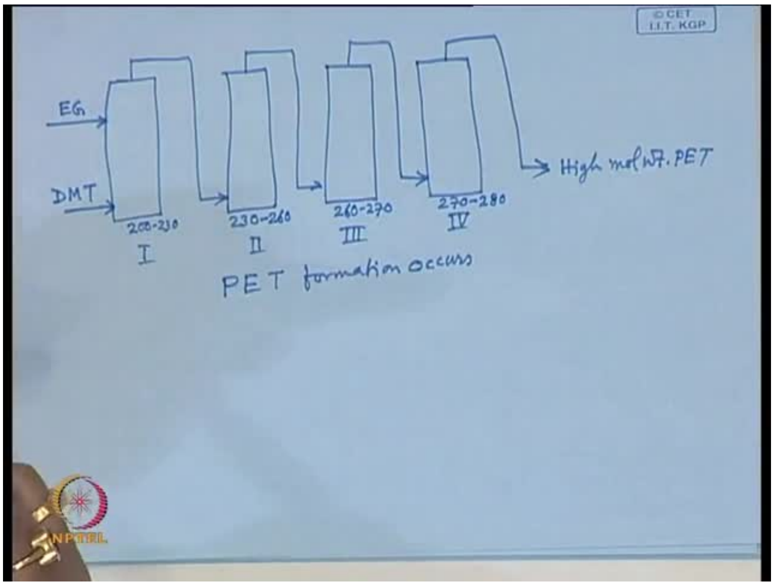
So, some quantity of methanol which is used at the beginning that can be recycled number of times. There may be little loss; there may be little loss through a operation, spillage etcetera. Barring those things if you say there is no loss then it, this process may become economic. Then it passes through a melter, where DMT is melted. Then it is pumped, molten DMT is pumped to this or for purification, because that may contain some trapped methanol, all those things because if those are not removed again that may affect the polymer molecular weight.

So, actually basically it is a striping column. This is a stripping column or it may be called other way here it is a toluate esters. Toluate ester means it is a DMT, then that hot molten dimethyl terephthalate is passed through this polyester reactor, polyester formation reactor where ethylene glycol is fed. Here also after this methanol from this DMT after this polyesterification, this methanol, this methanol is which is produced as a byproduct, this methanol produced as a byproduct that can be recycle to this step. Now, here the methanol recovered that is the excess methanol, in this case excess methanol because this reaction is carried out taking terephthallic acid and excess methanol.

One of the reactant is taken in excess quantity, large quantity so it gives you higher production, higher conversion so that it does not set equilibrium, that is why methanol is used in excess. So, gradually there will more and more conversion to DMT here. So, here this methanol recovered that is the excess methanol. This is not the byproduct actually, the excess methanol, here is the byproduct methanol that also comes over here and whatever methanol consumed over here so that methanol is got, is got back here then polyester is synthesized.

Now, if you look in to that the flow diagram given in Polymer Chemistry by George Odian book they will find that there, these polyesterification reactors, there are only, not only one reactor there may be three or four reactors where they, reactors are maintained at different temperatures. You will see their. Please see that diagram, flow diagram. Actually, what happened I lost my assistant to draw this diagram from a book, I did not have time to examine what is this kind of diagram he made for me and I found that those reactors are not there.

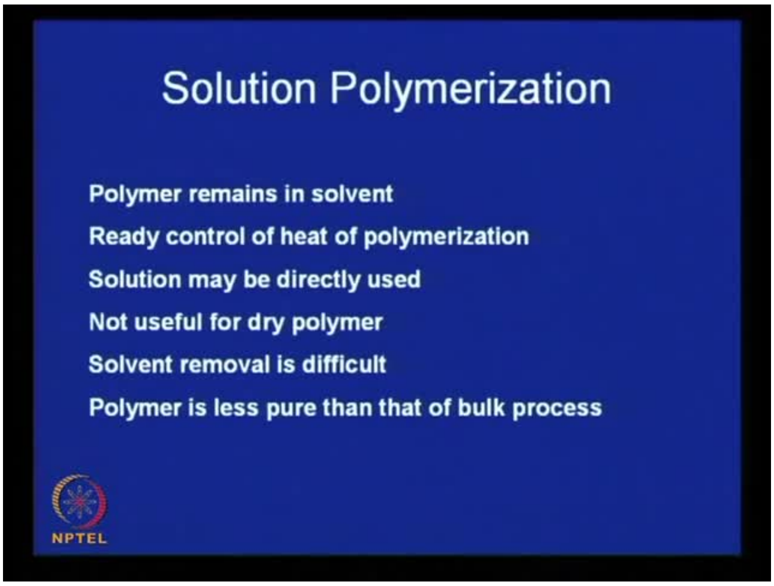
(Refer Slide Time: 25:12)



So, in that polyesterification reactor there may be more than three or four reactors. So, was this reacts, a series of reactors, in all these reactors PET formation occurs, but the temperature is different because here lower oligomers, medium oligomers, higher oligomers, high molecular rate because I told you with the growth of size there melting point changes. So, the first reactor may be kept a lower temperature then the next one is little high temperature this way finally, we get high molecular rate product from the last reactor. Then it can pass through other units, subsequent units here you see. So, this four… in this case, in this diagram all those reactors are shown in one place.

Any way here you see this is, here also shown in a different way 300, 260 to 300 degree Celsius temperature and then glycol recovery is also there, glycol recovery is also there and ultimately we get through polymer chipping system, it cuts into small flux or granules. Then if it is first directed to a spinning system we can get PET fiber. So, in one industry who are making this poly PET fiber is a huge industry because these garments which are, we are using is PET fiber polyethylene terephthalate fiber mixed with cotton, we get tiny cotton for garment manufacture. So, they are making these fibers there as well as blending or else instead of making fiber one can install some growing unit or vacuum bag molding unit. So, this PET bottles, PET bottles, PET contains are also manufacturing in the same installation directly from here.

(Refer Slide Time: 29:35)



Solution Polymerization

Polymer remains in solvent

Ready control of heat of polymerization

Solution may be directly used

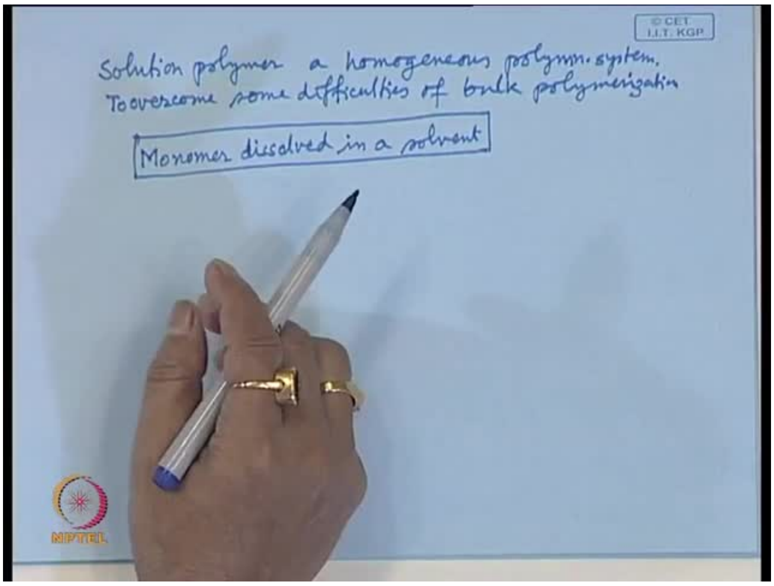
Not useful for dry polymer

Solvent removal is difficult

Polymer is less pure than that of bulk process

Next, let us see polymerization in homogenous system. So, you have seen bulk polymerization. Some installations where different units are involved for getting a polymer granules or flakes or fibers etcetera from a homogenous system and you have seen the merits and demerits of their bulk polymerization. In a heterogeneous polymerization system or a homogenous polymer sorry here will come heterogeneous polymerization system later.

(Refer Slide Time: 30:20)



Solution polymer a homogeneous polymn. system.
To overcome some difficulties of bulk polymerization

Monomer dissolved in a solvent

A solution polymerization is again a homogenous polymerization system. In order to overcome some difficulties of bulk polymerization, to overcome some difficulties of bulk polymerization a solution polymerization technique is followed. What is this? Here the monomer is dissolved in a solvent. Monomer may be a solid or a liquid. So, you take a monomer solution in a suitable solvent. Again here also the consolations of this condensation principles and addition principles come into play.

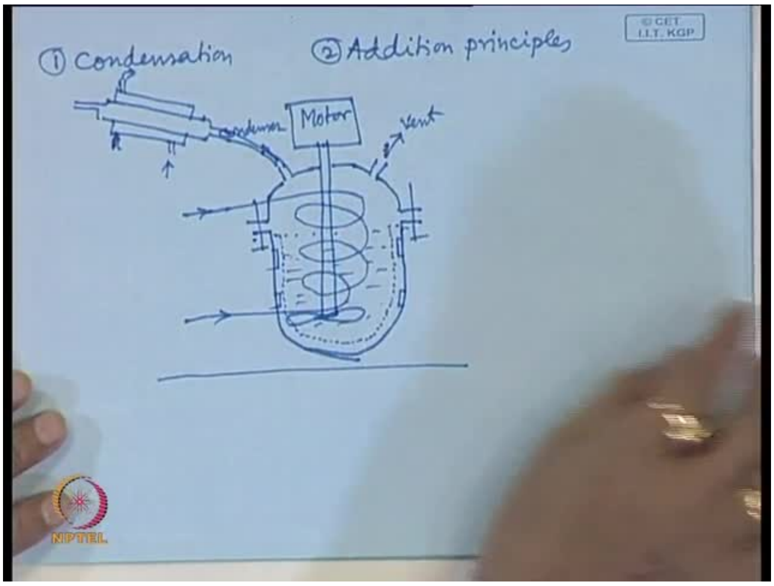
In case of condensation polymerization normally this solution polymerization technique is not followed because this condensation polymerizations needs higher temperature because their melting temperatures, melting points are higher than those of addition chain polymerizations. So, in majority of the cases, this solution polymerization is followed for addition chain polymers and characteristics of this solution polymerization. Here you see after the polymer growth that polymer remains dissolved in this same solvent.

The purpose is, in case of bulk polymerization the inter monomer, there is chance of inter monomer or some, not allow a chance it is the case that inter monomer gets converted to polymer. So, there is gradually increase in viscosity and finally, it founds a solid polymer in the solid phase. So, in order to avoid the problem of heat transfer, viscosity or to acceleration, all those things rather to control run away reactions, all those things people go through a solution polymerization.

So, even if the viscosity of the system increases due to the presence of solvent in the polymerization medium viscosity can be kept at a lowered level, say you take a polymerization; a solution polymerization batch where 70 percent or more then 70 percent or 80 percent or 90 percent even is a solvent, 10 percent is the monomer. So, 10 percent monomer, we need there is 100 percent conversion. So, 10 percent polymer will be there in the solution. So, here the 10 percent polymer remains dissolved in the solvent means it is a solution and viscosity of the system is low.

And what happens it helps easy control of the polymerization because the viscosity since the viscosity is low, the staring cannot be show big problem as is found in case of bulk polymerization. So, it can be easily controlled. Not only that if you can feed a condenser to the reactor, what happens? Due to exothermicity of the polymerization that will increase the temperature that will boil the solvent, a solvent will boil up and go to the condenser, leave the heat in the condenser and comes back after condensation in the form of liquid.

(Refer Slide Time: 35:20)

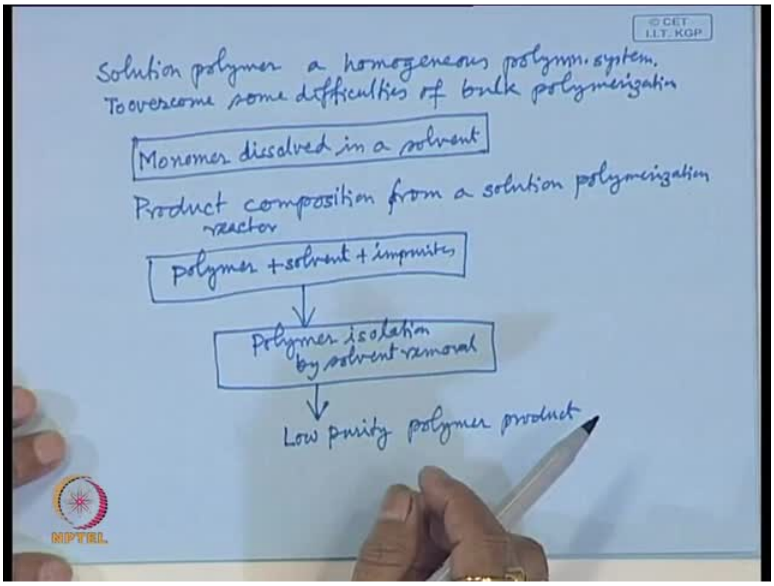


So, suppose there is a condenser like this. So, it is connected to this, this condenser is connected to this reactor. So, it contains the solvent, temperature becomes high so solvent evaporates and goes to condenser and through the condenser some, through the condenser some coolant is passed. So, solvent gets condensed over here leaving the heat in the condenser or to the condensing high or this circulating medium and it comes back.

So, it maintains the viscosity of the polymer solution which is formed over here and it provides better control of heat.

But here the heat transfer problem is solved which is a difficult situation in bulk polymerization. In this case heat transfer problem is solved, viscosity problem is managed because it is low viscous system and the stirring power consumption due to mechanical stirring for homogenization of the mass inside the reactor that huge power consumption can occur in this solution polymerization as is found in case of bulk polymerization, but there are certain problems. It is, these problems are obvious.

(Refer Slide Time: 37:30)



Solution polymer a homogeneous polymn. system.
Toovercome some difficulties of bulk polymerization

Monomer dissolved in a solvent

Product composition from a solution polymerization reactor

polymer + solvent + impurities
↓
Polymer isolation by solvent removal
↓
Low purity polymer product

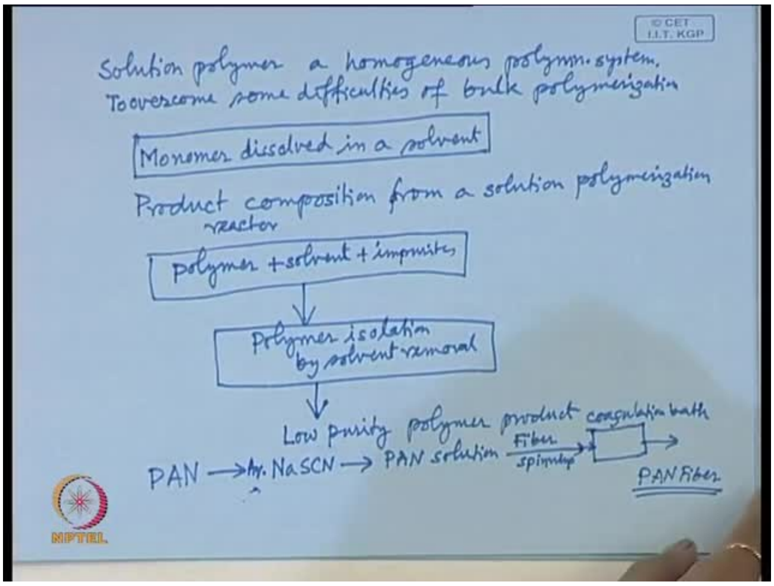
What is the product here? Product is polymer and solvent plus other impurities, then it passes through polymer isolation, polymer isolation by solvent removal. In these cases is you see the solvent which is used, these are organic solvent, you understand the problem of handling organic solvents in industry. These are highly volatile solvents sometimes low boiling solvents. Even if there is no leakage from the reactors, pipelines or (( )) system is provided, but we will find that plant area will be, will contain higher concentration of those solvents in the atmosphere beyond this acceptable limit in the environment.

Because of little bit of leakage during purification, isolation, all these things so this is not a very good tactic of polymer manufacture involving solvent. It causes environmental concern, apart from that it is not always possible to remove last process of solvent from a high viscosity solution as more and more quantity of solvent is removed by depletion, stripping or other techniques, which are available there. They being organic in nature the polymer as well as the solvent some solvent will remain trapped dissolved in the polymer. So, we cannot get a very good, a very high pure polymer, we get a low purity polymer product.

Cost of this product, cost of this polymer will be higher because the solvent removal step becomes expensive. If somebody needs very high purity polymer from the solution polymerization technique, that will incur very high cost for purification of the polymer from the solvent. So, cost will be more. Apart from this thing, if you do not need to isolate the polymer from the solution we can directly use it, say polymer is manufactured for the purpose of surface coating paint industry. For paint industry, we can synthesize the polymer by solution technique.

So, we will get a polymer solution in a solvent. So, we can avoid the solvent removable step if we can directly use that polymer solution for surface coating or for other purpose or direct fabrication of the product from the polymer solution. So, it is written here, it, this technique is not useful for making in dry polymer granules or fibers or flex or sometimes it can be used for fiber manufacture, direct. In in that case, it is advantageous.

(Refer Slide Time: 43:20)



Solution polymer a homogeneous polymn. system.
To overcome some difficulties of bulk polymerization

Monomer dissolved in a solvent

Product composition from a solution polymerization reactor

polymer + solvent + impurities

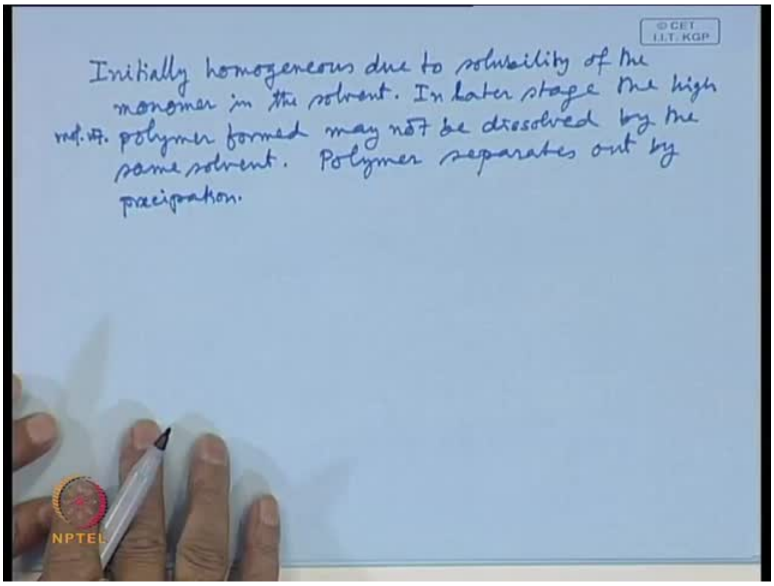
Polymer isolation by solvent removal

Low purity polymer product

PAN → Aq. NaSCN → PAN solution $\xrightarrow[\text{spinning}]{\text{Fiber}}$ coagulation bath → PAN Fiber

Say, for PAN polyacrylonitrile. For polyacrylonitrile, for polyacrylonitrile, it is a tough houdini polymer and for this polymer there is a good solvent, good organic solvent which can dissolve it. For this PAN, people use sodium thiocyanate. So, what is done? This PAN is dissolved in aqueous sodium thiocyanate is a very good solvent for this PAN, it get dissolved, then this PAN solution in sodium thiocyanate solution solvent, this, this is passed through a spinneret for fiber spinning. Actually, it passes through a coagulation bath. This is a coagulation bath, the fiber gets coagulated and you get PAN fiber. So, except these cases of direct product manufacture, this solution polymerization technique is not suitable and in some cases what happens although the polymer is synthesized in solution phase, in homogenous phase.

(Refer Slide Time: 45:33)



Initially homogeneous due to solubility of the monomer in the solvent. In later stage the high mol. wt. polymer formed may not be dissolved by the same solvent. Polymer separates out by precipitation.

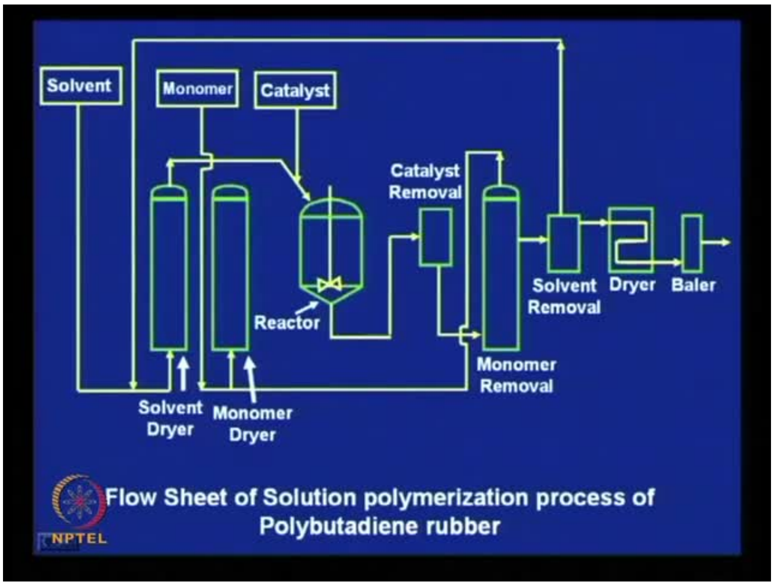
It can show initial homogeneity due to solubility of the monomer in the solvent. In later stage, what happens the polymer, the high molecular rate polymer formed may not be dissolved by the same solvent. In that case, polymer separates out by precipitation. That is a good technical. Initially, it is homogenous system. So, long it remains in the soluble phase polymer growth occurs. After certain growth when the polymer is of very adequate molecular size, it comes out of the soluble phase, polymer phase, which is out.

So, that is also a solution polymerization, but you are getting polymer isolated. This is easy technique, simple technique and you can avoid the polymer isolation step by solvent evaporation, distillation, stripping etcetera. In that case it is advantages at the same time you are having already the advantages of heat removable thermal control, control of the polymerization kinetics etcetera.

Student: (( ))

If a polymerization is carried out in liquid phase say here in this case solution phase since the monomer is dissolved in a solvent, dissolved in a solvent so heat transfer becomes easy and the polymerization kinetics is good, it leads to high molecular weight avoiding unwanted reactions. If it would have been carried out in bulk, it had to pass through that high viscosity mass leading to various side reactions. So, including all these things if you say it gives you good polymerization kinetics we are not wrong. That means we can have a better control on polymerization kinetics in this solution polymerization technique. If you have a thermal control you will have a better control on polymerization kinetics, but the problem is if we need to isolate the polymer from this solvent the polymer is less pure than that of bulk process.

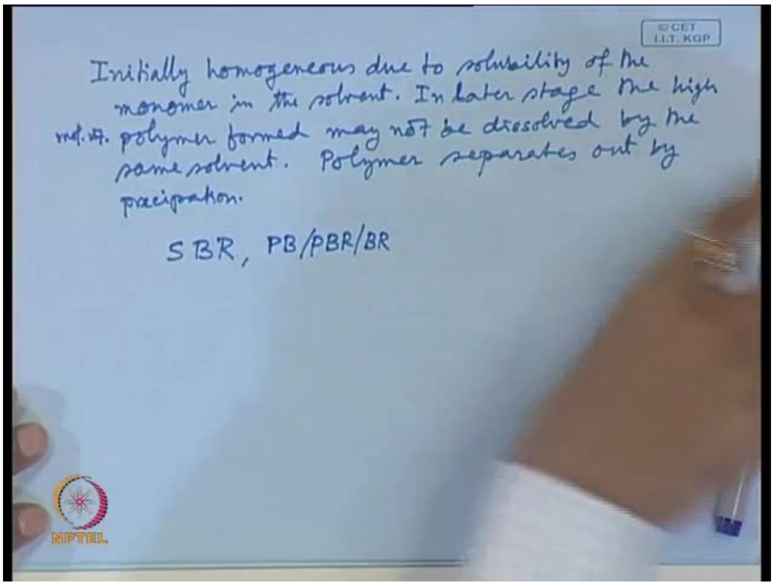
(Refer Slide Time: 49:54)



Flow Sheet of Solution polymerization process of Polybutadiene rubber

Here you look at the flow sheet of solution polymerization process of say polybutadiene rubber.

(Refer Slide Time: 50:09)



Initially homogeneous due to solubility of the monomer in the solvent. In later stage the high mol. wt. polymer formed may not be dissolved by the same solvent. Polymer separates out by precipitation.

SBR, PB/PBR/BR

Now, this SBR styrene butadiene, polybutadiene PB sometimes PB or PBR or sometimes BR, same you will find at these abbreviations for the same polymer, same polymer in different books. Either it is called polybuted PB or PBR or BR. The polymer is same polybutadiene rubber. Now, that this styrene butadiene, polybutadine or other polymers they are made by (( )) process or suspension process. Normally, normally these polymers are not synthesized by bulk technique. They are polymerized by solution technique, solution technique, solution SBR, solution BR etcetera. Their grades are mentioned as solution SBR, solution BR like this.

Now, here you look at this flow diagram. Solvent as a solvent, now this solvent be contain some moisture or other thing. So, that moisture or water (( )) so, some solver it has to pass through a solvent drying unit, solvent dryer. Then monomer is fed to the through another to another dryer dryer. So, monomer and solvent are first dried to remove water because you have seen if this polymerization is carried out by an anionic polymerization, an anionic polymerization so they need this solvents and the monomers need to be perfectly dried, trace of water will cause problems in anionic polymerization.

So, after this solvent drying, solvent drying that is fed to the reactor. Here this schematic of a starring unit is required for homogenization of the mass in a solution polymerization for proper heat transfer and details are not shown over here, it can have jacketed cooling or cooling coil in side. In side there will be vapors, all those things. Then the polymer ((

)) a monomer is converted to polymer containing the catalyst say sodium polybutadiene, sodium amide sodium amide or other. Those catalysts are used for polymerization.

Then that catalyst needs removal, after removing the catalyst from the polymer this monomer is removed, solvent is removed and both this monomers and solvents all are recycled to the silos, recycled to the silos. Silos are not shown over here. So, this monomer unreacted monomer and solvent, they are collected from the polymer and recycled or reused. Then polymer is there after removing the solvent it is dried and then it is obtained in this form of sheet and then those sheets are piled together, piled together, large number of sheets pile together in the form of a bale like bale of cotton layers like this, bale of garment layers, big bale. So, bales of 50 kg size or 25 kg bales of this polybutadiene rubber that is collected from this end unit, set passes through a baler. So, we get polybutadiene rubber. So, over all this shows the flow sheet of solution polymerization process of polybutadiene rubber.

Thank you.