Principles of Polymer Synthesis
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Lecture-35
Synthesis of Industrial Polymers (Contd.)

Welcome back. We are in the midst of discussion of industrial polymer synthesis at present, we are talking about injection molding process and we will continue from where we left in the in the previous class ok.

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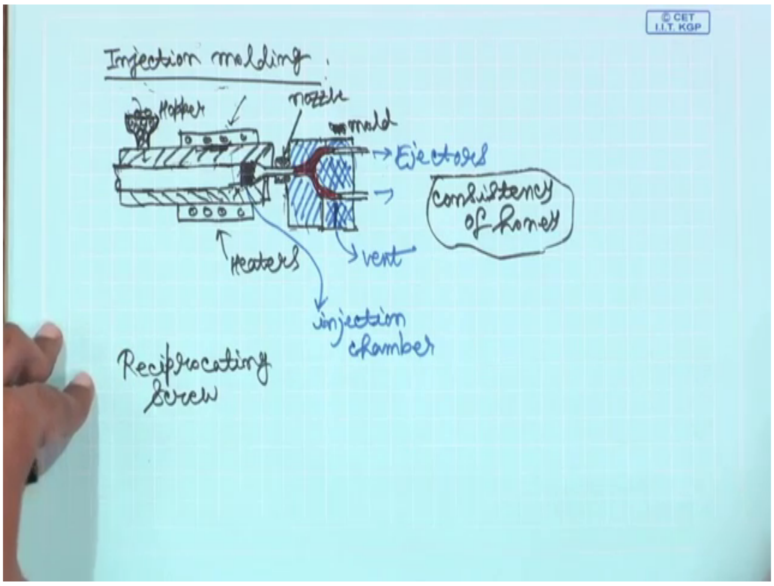

So, this was the diagram of the injection molding process a schematic diagram of the injection molding process and overall we had explained how it works, there is a moveable part. There is a immoveable part of the mold and after the product has taken the shape of the mold and has become solidified, you take out the mold the movable part and then you push the ejectors and then this polymer the mold from the mold they will be get detached so on and so forth.

Now, what are the problems of this particular process the problem here is that you are basically using a plastic that you are processing, right. So, these plastic materials typically, they are not good conductor of heat these pellets that you are putting they are plastics right now these plastics they are not good conductor of heat.

So, what will happen is that there will be an unevenness of temperature in the barrel what does that mean because you are heating through heaters the barrel and that will heat up the pellets and that will melt the pellets, but since the pellets the plastic that makes the pellets the plastic is not a good conductor of heat the temperature in the barrel will be uneven.

So, when you go from the inner wall of the barrel towards the center there will be some gradient of temperature the temperature will be highest near the wall and it will be the lowest towards the center. So, the polymer layer that is there close to the you know, surface which is you know close to the inner wall what will happen that might degrade because it may become too hot and the polymer layer which is in the central region it may be in a cooler state and it may not be fully melted also.

So, there will be this kind of in homogeneity and some part may also be destroyed so on and so forth. So, in order to get rid of this problem what we do is that instead of a piston, we use a reciprocating a reciprocating skew that is what we use a reciprocating skew and ok.

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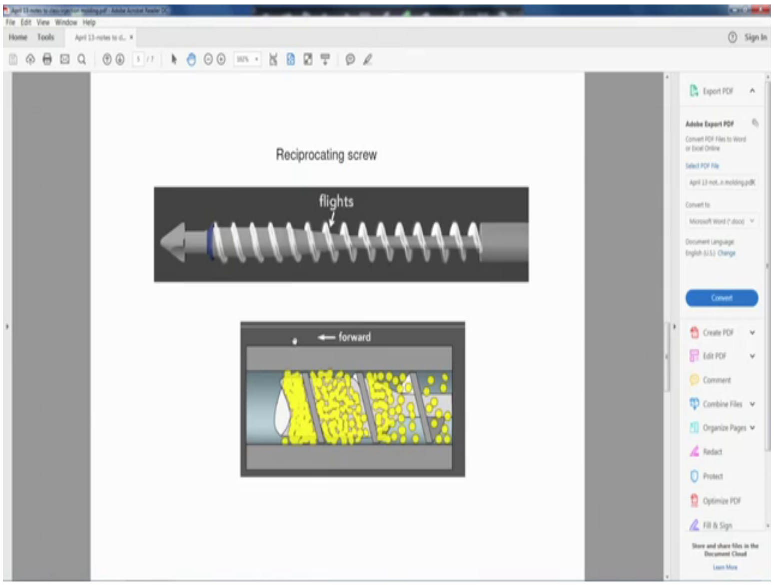
Reciprocating screw

So, this reciprocating skew, if you now look at the particular slide that I have. So, the reciprocating screw, it looks something like this and this skew has this kind of flights and this kind of flights the presence of these kind of flights that will mean that the plastic will basically fill up the region around the shaft only this is the shaft of the skew. So, the plastic is going to fill up the region around the shaft and so, there is no cooler central region to be had unlike your normal piston system. So, that way you can actually avoid that problem of heating on the side of the wall towards the wall and cooling down towards the center of the barrel this is one aspect.

Now, the second aspect is that as what I was telling the screw who has these kind of flights and what happens is that the screw is rotating and it is also axially retracting and in the process what happens is that these pellets it is pushing towards the injection chamber which is on this side, it is pushing the pellets towards the injection chamber.

Now, this is one thing and second thing is that when they are being pushed towards the injection chamber. They are also being sheared between the shaft between this shaft this shape of this between the shaft and the bearing barrel wall. So, they are being sheared they are being pressed and the shearing forces is also occurring on these on these pellets. So, what is happening is that they are being heated up as they are being pushed towards the injection chamber.

So, and if you look at the diameter of the shaft the diameter is smaller here and the diameter is bigger here. So, as you go towards the injection chamber which is somewhere here this diameter goes up. So, there will be more effective shearing as you go from this side to this side.

So, basically the temperature of the pellets will become higher as you go more and more towards the injection chamber and in fact, 70 to 90 percent of a heating necessary to melt the pellets can be supplied already by this reciprocating skew by the shearing force that itself will supply 70 to 90 percent of the of the temperature that is required of the heating that is required to melt these pellets and the melt is not only sheared. So, these pellets when they are getting molten. So, these pellets here they are not only sheared, but they are also being pushed towards the injection chamber.

So, a combination of these two processes ensures that the melt that is produced is homogeneous so. In fact, I can show you a video of this particular process. So, things will become little bit clearer to you that way. So, the video is coming up right here. So, this is how the reciprocating screw basically pushes the material towards the injection chamber.

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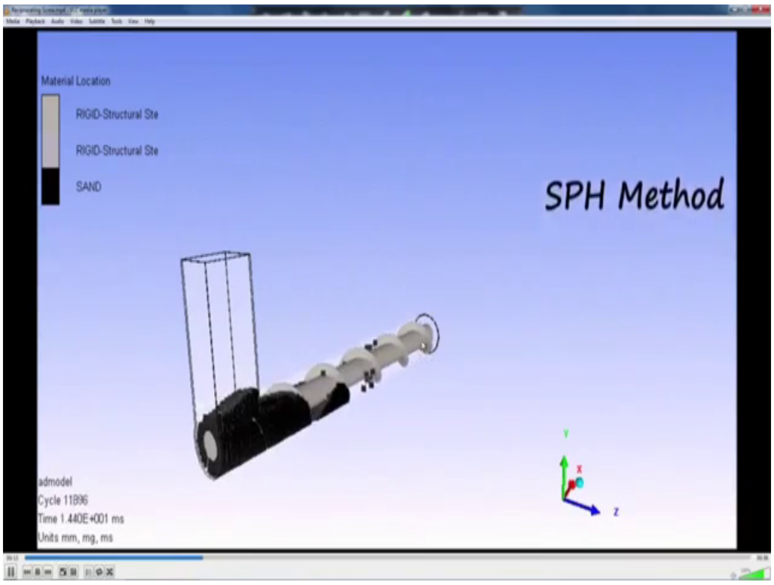

So, the material is coming from here through the hopper and then you see that the screw is basically axially retracting, it is another process.

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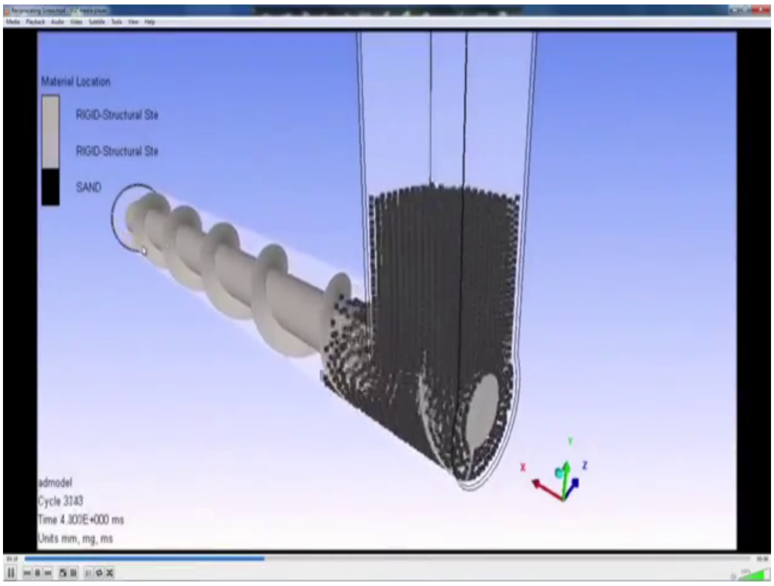

So, you see another look of it. So, you see the screw is axially retracting. So, it is retracting and in the process, it is pushing the particles towards the injection chamber here again you see. So, it is axially retracting. So, all the particles are being pushed towards the injection chamber at the same time they having sheared against the wall of the injection of the of the barrel also.

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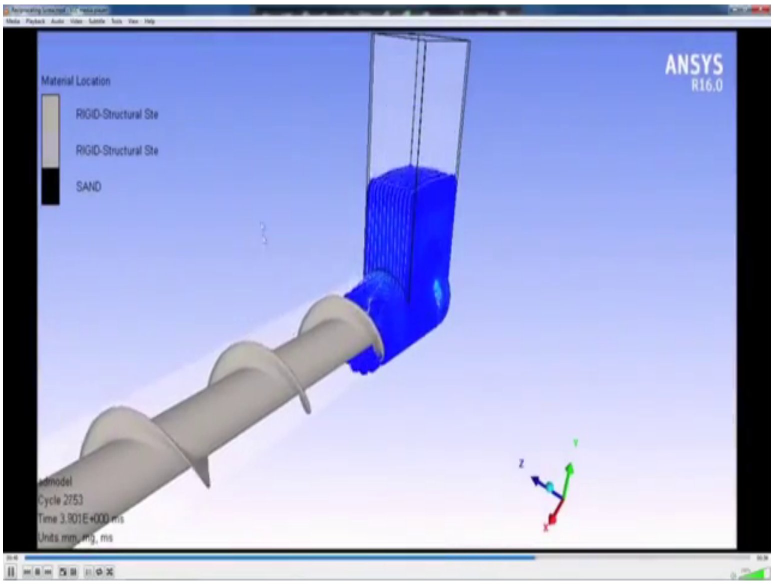

So, they are being heated up they are being heated up more as they are passing towards the injection chamber because the diameter of this is becoming higher and higher. So, this is a video that I have downloaded from the YouTube. So, of course, I hope that this gives you a better concept of the thing.

Now, something more I wanted to say here. So, if you look at you know screw little bit more closely you look at the screw here.

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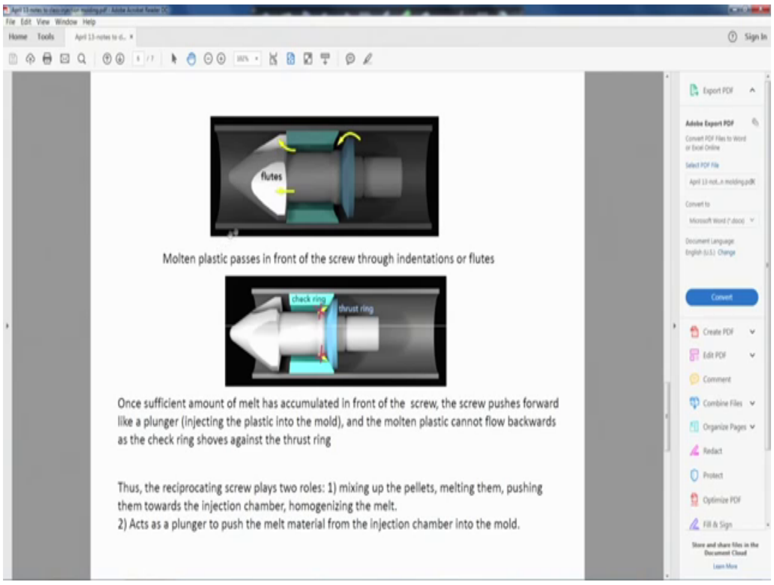

Molten plastic passes in front of the screw through indentations or flutes

Once sufficient amount of melt has accumulated in front of the screw, the screw pushes forward like a plunger (injecting the plastic into the mold), and the molten plastic cannot flow backwards as the check ring shoves against the thrust ring

Thus, the reciprocating screw plays two roles: 1) mixing up the pellets, melting them, pushing them towards the injection chamber, homogenizing the melt.
2) Acts as a plunger to push the melt material from the injection chamber into the mold.

So, there are these kind of indentations on the screw it is not completely plain you have these kind of indentations on the screw. So, so what happens is that molten plastic that is passing from this side to the front of the screw that is passing basically through these indentations or what you call as flutes and once sufficient amount of melt has accumulated in front of the screw, then what happens the screw pushes forward like a plunger and it injects the plastic into the mold.

So, it has to first accumulate sufficient amount of the of the molten material in front of the screw and then it pushes forward like a plunger and it and in the process the plastic will be injected into the mold.

Now, this molten plastic that is here it cannot flow back towards the back end of the screw and that is because there is a check ring which is basically shoved against a thrust ring. So, this molten plastic has to stay here until it is pushed by this screw into the into the mold.

So, the reciprocating screw basically plays two roles. So, one is it just it mixes. So, I have already written down here it mixes up the pellets, it melts them it pushes them towards the injection chamber and in the process it homogenizes the melt and secondly, it acts as a plunger to push the melt material from the injection chamber into the mold ok.

So, this is so, I hope then you have understood the concept of reciprocating screw and how; it is basically used in order to solve the problems of in homogeneity of the material or the temperature difference or say for example, some part of the material is not molten at the central region some part of the material is molten near the barrel wall and it may become degraded also because of high temperature so on and so forth.

Now, in fact, it is a molding process typically for thermoplastic materials which heat up beyond Tg and they become moldable they become pliable they become softer. So, that you can mold it to them into different shapes and then when you cool them down, they take those shapes as you see polyethylene terephthalate the thermoplastic poly butylene terephthalate is a thermoplastic so on and so forth.

So, and also you can make fiber reinforced polymer polymer composites. So, you have the polymer that is coming in along with that if you put fibers into the system. So, the fibers could be actually pre blended with the polymer or they could be mixed manually and fed into the hopper.

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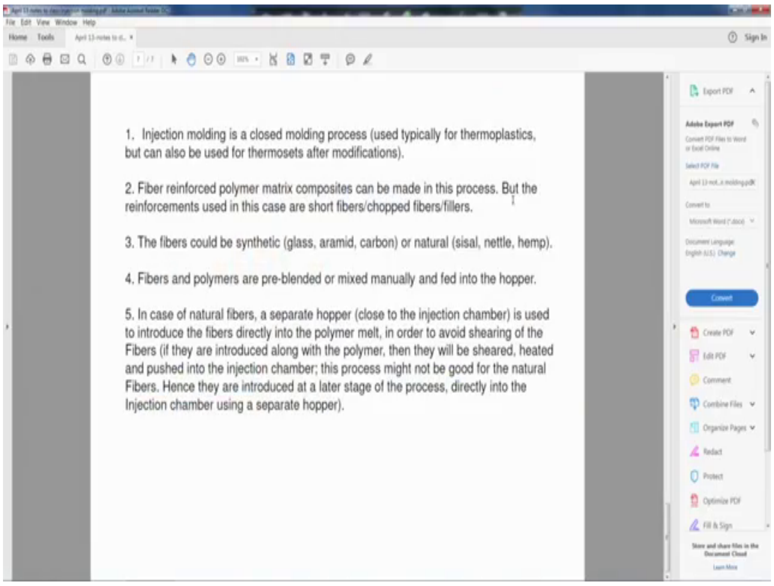

1. Injection molding is a closed molding process (used typically for thermoplastics, but can also be used for thermosets after modifications).

2. Fiber reinforced polymer matrix composites can be made in this process. But the reinforcements used in this case are short fibers/chopped fibers/fillers.

3. The fibers could be synthetic (glass, aramid, carbon) or natural (sisal, nettle, hemp).

4. Fibers and polymers are pre-blended or mixed manually and fed into the hopper.

5. In case of natural fibers, a separate hopper (close to the injection chamber) is used to introduce the fibers directly into the polymer melt, in order to avoid shearing of the Fibers (if they are introduced along with the polymer, then they will be sheared, heated and pushed into the injection chamber; this process might not be good for the natural Fibers. Hence they are introduced at a later stage of the process, directly into the Injection chamber using a separate hopper).

So, you see here I have made some points. So, the fibers could be synthetic as well as they could be natural material and something very important, I wanted to mention here when you have natural fibers, you typically will use a separate hopper or a place through which you put the fibers inside the barrel which is close to the injection chamber because when you have come close to the injection chamber inside the barrel already the polymer, melt has been produced and at that point if you are introducing the fibers they will go directly into the polymer melt and that is because if you already put the fibers at the start, it will undergo a lot of shearing because they along with the polymer pellets they are pushed towards the injection chamber so on and so forth.

So, they will be sheared they will be heated they will be pushed into the injection chamber and this process for natural fibers that is not very good that is why you want to introduce those natural fibers at the later stage of the process already close to the injection chamber using a separate hopper. So, that they can directly be added to the polymer melt and then they go into the mold ok.

So, that completes our discussion on injection molding process of course that was an off shoot of discussion because we are talking so much about injection molding and all when we are talking about processing differences between PET and PBT. So, if we have to obligated that we should have a brief and elevate a condensed discussion on injection molding process ok.

So, next what we will do is that. So, we have talked then about a couple of polyesters. So, let us talk about now polyamides.

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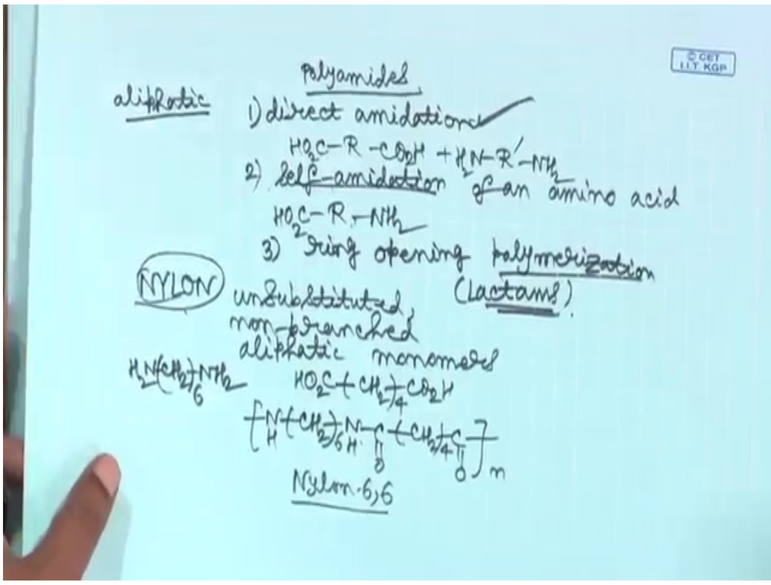

Polyamides

aliphatic

1) direct amidation

$HO_2C-R-CO_2H + H_2N-R'-NH_2$

2) self-amidation of an amino acid

$HO_2C-R-NH_2$

3) ring opening polymerization (lactams)

NYLON unsubstituted, non-branched aliphatic monomers

$H_2N(CH_2)_6NH_2$ $HO_2C(CH_2)_4CO_2H$

$$\left[\underset{H}{N}(CH_2)_6\underset{H}{N}-\underset{\underset{O}{\|}}{C}(CH_2)_4\underset{\underset{O}{\|}}{C} \right]_n$$

Nylon-6,6

So, let us start a discussion on poly amides now polyamides basically let us say we talk about aliphatic polyamides first.

Now, they can be produced by a direct amidation process you know you take a diacid and you take a diamine and then you can create a polyamide. So, this is a direct or direct emulation process or what you could do is you could produce the polyamides by self amidation self a mutation of an amino acid, I mean you can take a monomer which has both carboxylic acid as well as an amine.

So, this is your amino acid. So, this molecule can react with another molecule of the same nature because it is a bi functional and both the functions are not the same. So, you do not need another monomer. So, it is self amidation. So, either you can use a direct amidation process or you can use self amidation process or thirdly you can use ring opening ring opening polymerization.

You can use a ring opening polymerization process of cyclic amides which are called lactams ok. Now, we have heard this name nylon a lot nylons what are these nylons nylon is basically trade name for polyamides which are made from unsubstituted non branched aliphatic monomers.

So, nylon is typically not only one material it is a class of materials which is made from. So, of course, these are polyamides unsubstituted non branched does not have any branch aliphatic monomers.

So, the polyamides which are based on aromatic monomers, they are not nylons polyamides which are based on aliphatic monomers, they are called nylons the trade name. Now certain seem certain you know nomanclatures that I should tell you here. So, let us say you are doing you are preparing a nylon through direct or direct amidation process, let us say you have taken a diamine hexamethylene diamine and then you take hexamethylenediamine and the acid is let us say you take adibic acid ok.

So, what will be the resultant polyamide the polyamide that you produce has a structure a repeating unit like this ok. Now these particular nylon that you have produced this is nylon because these are aliphatic monomers that you are using this nylon is termed as nylon 6 6; this is nylon 6 6.

So, basically these nylons that are made from the direct amidation or direct amidation process, they are designated by two numbers the first number it represents the number of carbon atoms in the diamine chain.

So, the number of carbon atoms in the diamine chain 6 number of carbon atoms. So, the first number designates that the second number represents the number of carbon atoms in the acid. So, it is 1 plus 1; 2 plus 4; 6; that is why it is nylon 6 6, ok.

So, when you are producing nylons through direct amidation basically, they are designated by these kind of numbers. So, there will be two numbers. So, you could have 9, 4, 6. So, if it is nylon four 6 then it will be instead of hexamethylene diamine, it will be tetra methylene diamine so on and so forth.

So, those kind of things you should keep in mind. Now, since we talked about nylon 6 6, let us talk about the preparation of this nylon 6 6, now of course, we are going to look at the process of direct amidation for for the preparation of nylon 6 6.

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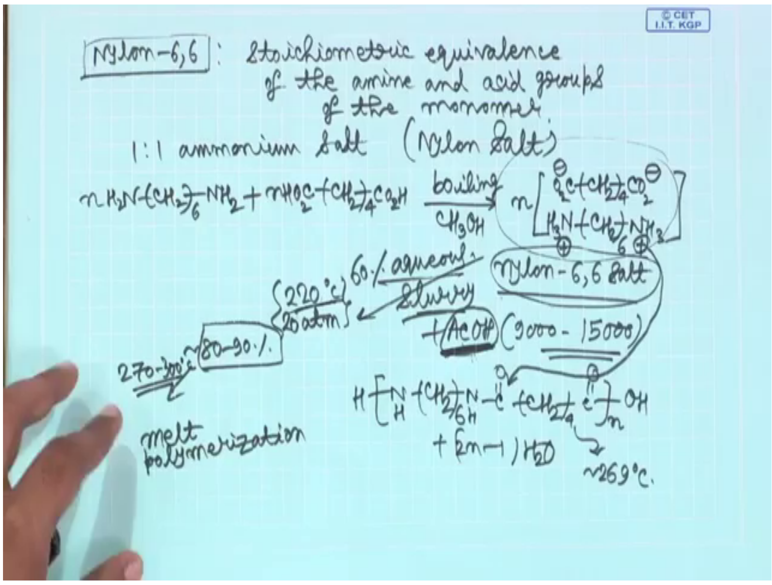

Nylon-6,6 : Stoichiometric equivalence of the amine and acid groups of the monomer.

1:1 ammonium salt (Nylon salt)

So, what we do; how do you prepare nylon 6 6? So, to obtain polymers of high molecular weights; what we do is that we ensure stoichiometric equivalence of the amine and acid groups of the monomers stoichiometry equivalent we are trying to ensure.

So, we are using this say you are using a diamine and the diacid, we want to ensure stoichiometry equivalence of the 2, when you are starting the reaction how do you do that this is readily obtained by a preliminary formation of a 1 is to 1 ammonium salt ammonium salt and this is often called as a nylon salt, I will I will go into the details little bit more.

Now, let us say we are talking about this particular thing because nylon 6 6, right. So, you are talking about this molecule which is hexamethylenediamine and adibic acid. So, first you have to prepare a an ammonium salt one is to one ammonium salt which is nylon salt from these two. So, you react your hexamethylenediamine you react to your hexamethylenediamine with your adipic acid the solvent that you use is boiling methanol and then the salt is produced because of the you know acid base reaction that happens.

So, this proton is abstracted it goes here it becomes NH3 plus and it becomes Co 2 minus and same is the fate for both the sides. So, basically it is an acid base reaction that will happen and you will get a nylon salt or an ammonium salt of this composition you would have a Co2 minus Co2 minus Ch 2 whole 4 Co 2 minus and then you have NH 3 plus CH 3 whole 6 NH 3 plus.

So, this is your nylon 6 6 salt one of the nylon; nylon salts and what happens is that if you are boiling these two in methanol a comparatively. So, this material is comparatively insoluble. So, it just precipitates out and then what you do is that you take. So, nylon salt is prepared. So, you have you have a sheared stoichiometric equivalents of the acid and the amine group.

So, you take a sixty percent aqueous slurry of this material and you add a trace of acetic acid basically acetic acid is added as a mono functional impurity, it can limit the molecular weight if you remember the principle that we talked about when you are talking about the step polymers how to limit the molecular weight so on and so forth.

So, this can limit the molecular weight this actually limits the molecular weight desired level which is somewhere between 9000 and 15000. So, you take a 60 percent aqueous slurry and you heat it up to so around 220 degree Celsius. So, this is basically a high temperature reaction, if you do not even if you do not remember these specific values you should remember, it is a high temperature reaction, it is a high pressure reaction also around 20 atmosphere to 20 degree Celsius and this reaction.

So, you take these 60 percent aqueous slurry you heat it, you under high pressure at a trace amount of acetic acid to control or regulate the molecular weight and do the reaction under nitrogen and the polymerization then will proceed up to 80 to 90 percent remember that in this reaction some water is also produced.

So, initially when you are doing the reaction you are not removing water even without removing water, you can go to 80 to 90 percent of conversion under this high pressure high temperature and once you have reached this kind of conversion what you do is you raise the temperature further.

So, from 220 degrees; you now raise the temperature to 270 to 300 degree Celsius; so, higher temperature and the steam or the water that is produced that is now continuously driven off to drive the polymerization to completion.

So, basically if you take this thing your nylon salt the product that you will have when you are heating it up under high pressure; so on and so forth is this product which is nothing, but your nylon 6 6; whole in oh and then you will have 2 n minus 1 number of water molecules released and basically at the later stages you see the temperature has gone towards 280 to 290 degree Celsius.

The later stages basically constitutes a melt polymerization, this is basically a melt polymerization the later stages and that is because of the fact that the nylon 6 6 by itself, it is melting point is around 269 degree Celsius.

So, the temperature for the final step; so, you have eighty to 90 percent conversion initially and then you are increasing the temperature further and you are now starting to remove the water that is produced in order to drive the reaction to completion and in the process; what is happening is that you have gone to higher temperature and whatever nylon 6 6 has already been produced, it has a melting point which is around 270. So, when you are close to three hundred degrees it has molten. So, the final stages of this reaction is basically a melt polymerization.

So, these things you should you should keep in mind. So, there are then several interesting characteristics of this particular reaction you just do not directly do the reaction, you first prepare one is to one ammonium salt in order to ensure stoichiometric equivalence of the acid and amine group and then, what you do you take a an aqueous slurry and under high pressure high temperature you drive the reaction forward up to 80 to 90 percent and then you can drive to completion by removing the water and basically, it is a melt polymerization towards the later stages because the temperature is very high and at this temperature the product that is produced or the product that was already produced at 80 to 90 percent conversion of the oligomers or whatever.

So, the product the product has a lower melting temperature than your reaction temperature ok. So, this is your direct emulation process typically you will prepare your nylon salt and then you will proceed for the final reaction. So, we will now talk about self; In fact, we will now talk about self amidation as well as ring opening polymerization of lactams together and there is a reason why we will talk about them together ok.

So, we told already that what kind of numbers we use for making nylons for symbolizing for naming the nylons that have been prepared by a direct amidation how do we number them when we prepare them by self amidation or when we prepare them by ring opening polymerization of electron.

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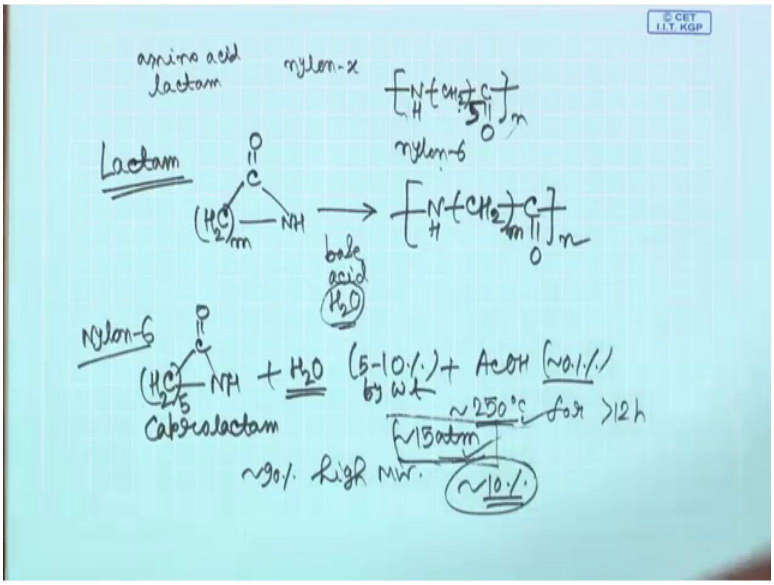

So, an aliphatic polyamides that you that you that you make either from an amino acid which means self amidation or when you make from a lactam which means in an opening polymerization that nylon that you prepare is called nylon x this x is basically the number of carbon atoms in the repeating units as simple as that.

So, if you are looking at this particular nylon of course, this can be prepared for from the corresponding aminos, you see the structure the repeating unit of the structure is different when you are preparing from the nylon when you are preparing from direct amidation the structure is like this when you are preparing from self amidation or ring opening polymerization the structure is like this.

So, the number of carbon atoms in the repeating unit will come into the picture when you are raising it in this nylon. So, this will be nylon 6 because there are 5 carbon atoms here and one carbon atom here. So, this is nylon 6. Now when you are looking at the polymerization ring opening polymerization as I told we will talk about the ring opening polymerization and the self amidation together.

So, when we are talking about ring opening polymerization. So, let us say we are starting with a lactam, it is a cyclic amide I already told. So, the cyclic amide could be of this form m number of units and then this is your cyclic amide. Now this cyclic amide can ring open and then it can polymerize and it will produce a polymer of this particular form.

Now, this kind of ring opening polymerization that could be initiated by the presence of base or the presence of acid or even by just present of presence of water when water is used to do this polymerization basically this is called hydrolytic polymerization so, for so, so the initiation of the reaction by water is most often used in the industrial polymerization starting from reactants.

So, how do you prepare nylon 6; how do you prepare nylon 6; so, what you do basically you start with what you call as caprolactam capro lactam. So, you start with caprolactam. So, it is a basically a batch process you are doing in a batch reactor, let us say and you mix this caprolactam with water say typically 5 to 10 percent by weight this water acts as a catalyst and you use a molecular weight regulator also acetic acid, let us say around point one percent very small amount of acetic acid and this mixture is heated in a reactor of course, on the nitrogen at around 250 degree Celsius for greater than 12 hours.

So, to make a long story short basically you are using water in order to initiate the reaction it is a catalyst. So, it is ring opening polymerization ring opens and then polymerizes and you are using acetic acid as a molecular regulator and typically you are doing at a high temperature and high pressure also around fifteen atmosphere.

So, overall even if you do not remember the specific temperatures as long as you know it is a high pressure high temperature; that is and this pressure is basically maintained by venting off steam and the product that ultimately you will get you will get around 90 percent of I mean this is experimental result that I am talking about around 90 percent of high molecular weight polymer, you will get and around 10 percent, you will get low molecular weight material which will be mainly your monomer and you can remove the low molecular weight materials by vacuum distillation after.

Now, if you look at this particular process in little bit more detail let us let us let me look at this particular process in little bit more detail.

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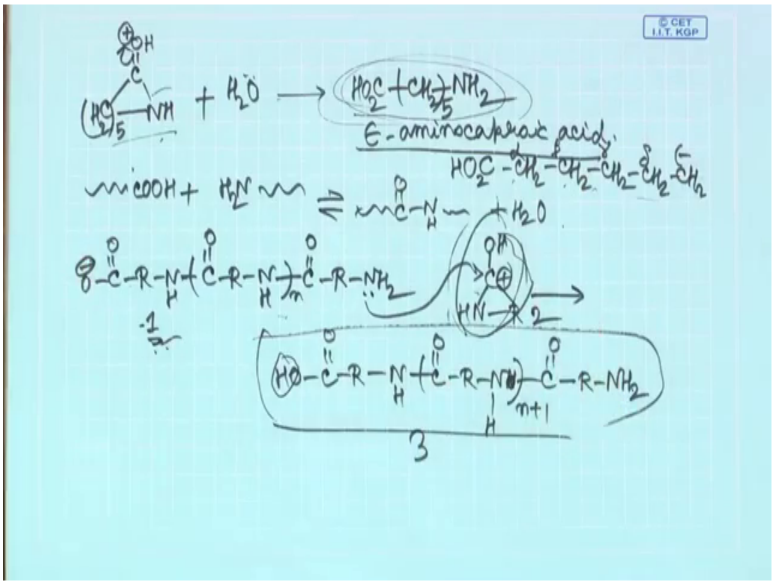

So, you have your lactam here. So, basically it reacts with water. So, of course, if it reacts with water you know the water can attack here and it can open up this amine bond. So, basically you will have an amino acid that is produced. So, you will have an amino acid which is of this form. So, this kind of amino acid is generated this is epsilon amino caproic acid because if you have CO2H and then CH2 alpha, this is beta this is gamma, then this is delta and then this is epsilon.

So, that is why it is epsilon amino caproic acid from caprolactam, you are getting caproic acid. So, it can open up like this with water and now you can have a self amidation if you want so self amidation. So, self polymerization, let us say at the end of a chain you have CO2H I mean at the end of a growing chain it can react to it an NH 2 at the end of a growing chain just a generic way in a reversible way and it can produce your polymer that can happen or what can happen is that this particular amino acid this particular amino acid can initiate the ring opening polymerization of lactam.

So, let us say you have. So, you have an acid group on one side and amine group on another side, I mean, it is polymerizing say through self amidation, if it is polymerizing and all or it could be this particular material also you know it could be this particular material also.

So, one side you have CO2H the CO2H can become oh minus and that proton can go and attach to your lactam. So, I am just putting R here it can be CH2 whole 5. So, basically the lactum will be activated by a proton exchange reaction with this acid and this is a generic way to represent this chain is growing you know R CO2H and then there was an H 2 and that reacted with another CO2H unit and then it made an amide unit.

So, like that it grows. So, this is the repeat unit at the end there you have an amine, it can again react with another acid so on and so forth. So, this is growing now this can actually initiate a ring opening polymerization, here how this lone pair here can attack and open up this and then what you will get. So, this is let us say, this is the number one species and then what you will get is this and then this proton exchange proton again you put back here.

So, what you will get is COR NH. So, this will be COR NH. Now COR NH and this also will now be a part of the amide. So, this unit can come in here because this will become a repeat unit. So, this will be added to this repeat unit. So, this will be NHN plus 1 number of units and then at the end you will have again CO R NH 2 that you understand because it will be COR NH and then again it will be CO and then this bond breaks. So, this bond breaks up and then at the end you will have R NH 2.

So, basically if you have these species this can react with your lactam and it can add another of these amide units here to grow the chain by one more unit. So, this is a propagation step and this kind of propagation step could occur these also you see this particular material has an acid on one side and an amine on another side. Now if this amino acid through self amidation has increased the length of the chain.

This R maybe the CH2 whole 5, let us say these R is the CH2 whole 5, this amino acid can increase its length, then this will be of generic structure this or it could be this, then you can just say CO2H NH 2. So, basically what you need to keep in mind the principle is that you have an acid that has been produced now this acid is going to catalyze this particular reaction.

So, what will happen there will be proton exchange reaction? So, this proton can attach here. So, once the proton attaches here once the proton attaches here you will have a positive charge here and then you can draw a resonance structure in which these electrons move here. So, ultimately your c single bond oxygen oh and then it will be C plus. So, this will become electrophilic and then this amine can attack and it can open it.

Now, once you have this chain one unit more this NH 2 can attack again another electron molecule and that lactam molecule can be protonated by this proton. So, like this it can continue. So, this is your propagation step. So, the CO2H group in the amino acid. So, this is also an amino acid one side amine one side acid this is the long amino acid this is short amino acid.

If it has been allowed to self amidate more, then it will be a longer chain if you just talk about this then it will be just this part, but the principle is the same one side amine one side acid. So, this CO2H group, it protonates the lactam and it will form. So, it will form to the CO2H group has protonated the lactam and so, this becomes CO minus OH that is species one; let us say this is species two and then a nucleophilic attack of the amine will produce species three and this can subsequently protonate another molecule of lactam and the process can go on.

So, this; so, you can think about it that this polymerization reaction could proceed both ways either this could self amidate and go on to form a long chain or at some middle stage whatever self amidate oligomer is there maybe not a long chain that can actually open up this and then through a ring opening polymerization this could elongate.

So, both ways either self amidation could occur or ring opening polymerization could occur in this particular process. Now it turns out that this self amidation reaction this only accounts for a few percent of the total polymerization in this caprolactam ring opening polymerization system.

So, if you start with caprolactam you are trying to get nylon 6 as the product only a few percent of the reaction occurs through self amidation mostly it passes through ring opening polymerization. So, basically it will only produce a an oligomer and then it will directly go and it will activate this lactam and react further instead of just increasing the chain all by itself.

So, we will stop here today and we are not yet done with polyamides because we have talked about aliphatic polyamides until now and we have talked about self amidation process we have talked about ring opening polymerization process and both we have talked about together because self amidation is one part of the whole polymerization process when you are doing a ring opening polymerization and we told that especially for caprolactam.

If we are trying to prepare nylon 6 by ring opening caprolactam, then basically self amidation accounts for only few percent of the polymer product mostly it goes through ring opening polymerization and we also talked about the preparation of nylon 6 6, where we are doing direct amidation of a diamine reaction with a diacid and in that process we prepare a nylon salt initially 1 is to 1 ammonium salt in order to make sure that stoichiometry is maintained and in both the cases we are using molecular regulator like acetic acid ok. So, we will continue with this in the next class until then.

Thank you and goodbye.