Principles of Polymer Synthesis
Prof. Rajat K Das
Material Science Centre
Indian Institute of Technology, Kharagpur

Lecture – 38
Synthesis of Industrial Polymers

Welcome back. We have been talking about synthesis of industrial polymers in general over the last several classes and the synthesis of aromatic polyamides in particular and the point at which we ended the class yesterday was the processing of aromatic polyamides specifically Kevlar parami para aramids we were talking about that. So, the topic of today continues to be the synthesis of industrial polymers and we will start right where we left in the previous class.

So, let us go back to the script directly.

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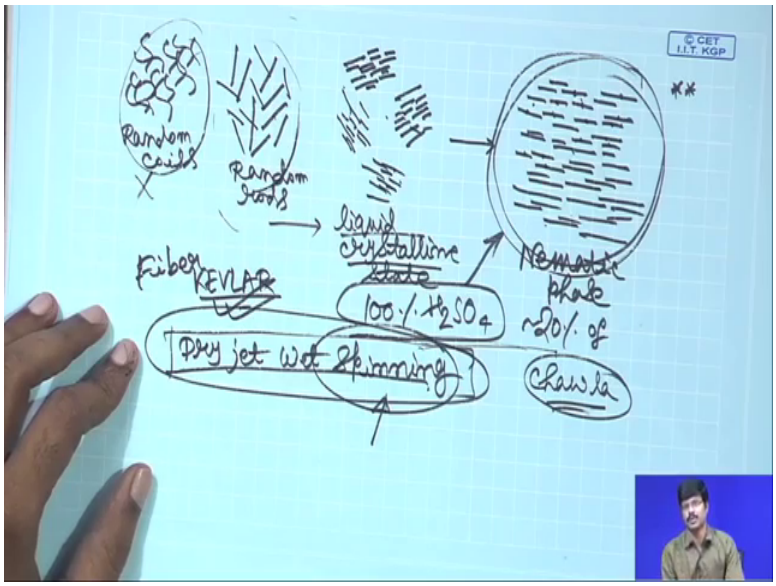

. So, we were talking about dry jet wet spinning and we told that this is the process which is used to produce Kevlar fibers highly you know Kevlar fibers with high tensile strength and the high tensile strength is a is a result of you know orientation all of all these rigid long rods along the direction along the long axis of the fibers so, that you will have very high tensile strength along the long axis of the fibers ok. And we also told that the transverse and the transverse direction you have weak hydrogen bonding interactions

which makes the properties highly anisotropic; that means, all the properties the strength the stiffness these things are enhanced along the direction of the fibers ok.

So, we promised at the end of the last class, that we will talk more about these spinning process because we told this wet spinning what is spinning I mean this is actually fiber spinning process in particular we are going to talk about that today. So, let us go right into that.

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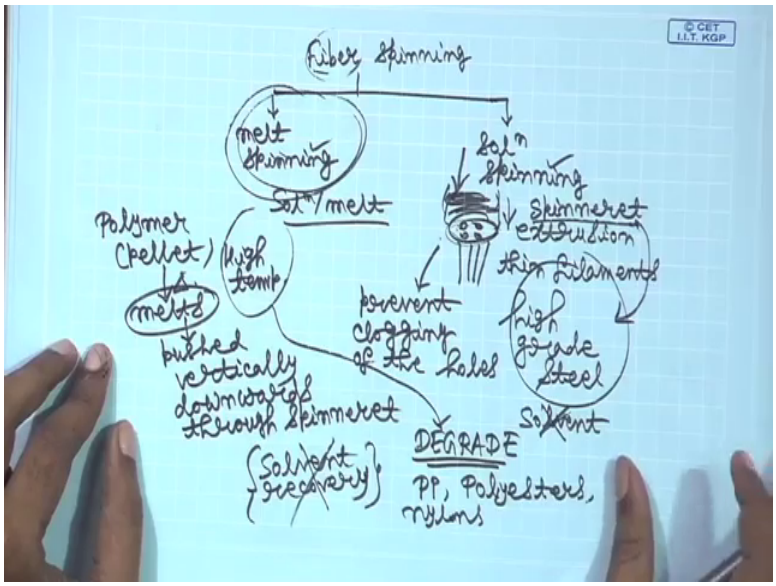

So, fiber spinning fiber spinning because in this process what you get is fibers ultimately. So, there are two ways in which you can do this kind of processing one is called melt spinning and the other is called solution spinning. So, when you are talking about melt spinning or solution skin spinning process one thing is common that you take either a solution or melt of the polymer depending on which process you are using and then you push through your spinneret. So, this is basically called extrusion. So, you have your solution or your melt on the top, and that you are pushing through this spinneret and in the process you are also achieving alignment of the fiber alignment of the polymer chains along the direction of the fibers that are going.

So, basically what you are going to get are thin filaments when they come out of the fiber on of the holes of the spinneret. So, thin filaments and then you can process after. Now this spinneret this is how it is called spinneret. The spinnerets are basically made of high grade steel made of high grade steel and that is because of the fact that they can be

afterwards cleaned much easily to prevent clogging of these holes prevent clogging or jamming of the holes because after you have done the reprocessing you have to clean it. So, that the polymer does not clog this holes. So, having a high grade steel actually helps.

Now, what is the situation with melt spinning? So, typically as the name suggests its a molten polymer that you are using as a processable material. So, you start with your polymer, which could be in your pellet form also and then you heat them until it melts. So, you have a molten polymer. Now this melt this is pushed vertically downwards through the spinneret. So, this is pushed vertically downwards through spinneret and so, what will happen. So, you are pushing vertically downwards through filament to the to the spinneret? This molten polymer and then when they are emerging below the spinneret outside of the spinneret when they are emerging, they are actually cooled by a flow of gas or may be in contact with air. So, that then your polymer will be solidified.

So, let us say I will show you the slide here if you look at the power point slide this is again taken from you know web this is not a picture that I had drawn.

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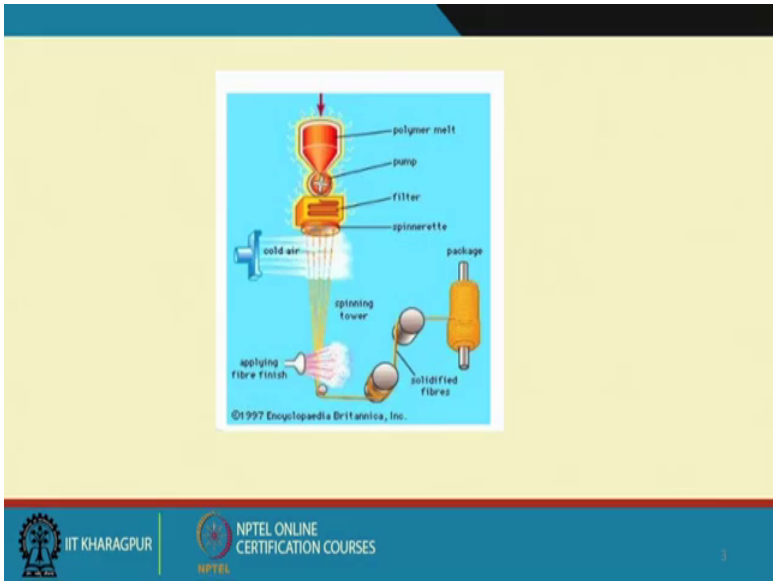

So, you see that you have the polymer melt on the top of course, it is at a high temperature because you have to reach a temperature at which the polymer has to melt and then you are pushing through say sometimes a filter because if there are some particles and all some impurity particles some you know dust particles or whatever that

you want to remove. So, the filter and then you have a spinneret through, which it has a lot of holes and it looks like you know shower air as you can see it comes out and then when it comes out it becomes cooled because you are actually pushing you know you are actually putting cold air through it or you are exposing it to a flow of cold air and then it can solidify or it can form this kind of filaments long filaments and then after that you can you can do further processing of this of this material, you can you can wash this or you can put some other things into it. So, applying fiber finish and then afterwards you can roll it like this and you have this packaged fiber roll.

So, this is basically then your process of melt spinning. So, now, let us come back to the script to our paper ok. So, we were talking about melt spinning. So, you general then it is a very simple process all right. So, what about the advantages and disadvantages of this process? You see you are using high temperature. So, if you are using high temperature that has a possibility to degrade you polymer that is a problem that can happen this is a disadvantage, but the advantage is it requires no solvent you do not need to use any solvent, you just melt the polymer and use it. So, you do not need to use a solvent. So, that is why your solvent recovery solvent recovery, which itself is also it also takes some cost it also incurs you have to also incur some cost in order to recover the solvent this solvent recovery is not required and you can also run the process at high speeds.

So, these are the advantages and the disadvantages that you are going to high temperature. So, the polymer might degrade and typically say polypropylene polyesters or nylons these are processed by melt spinning technique now.

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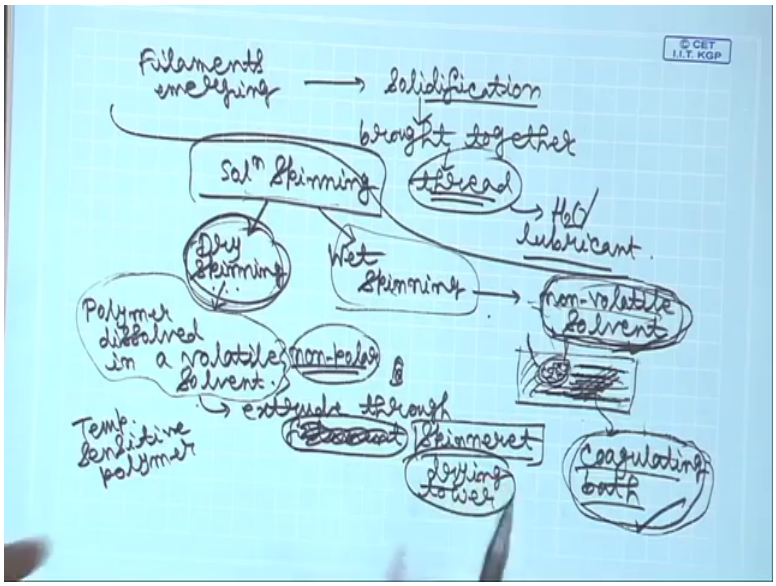

So, the filaments that have the filaments that have come out the filaments that have that have emerged through the spinneret after the after passing through the spinneret and they will then solidify because you are exposing them to a flow of cold air solidification, and they can be then all the filaments can be brought together and then they to form a thread and then you can wind this thread up so on and so forth. You can also treat this with water or you can treat this with lubricant ok. So, afterwards you can have all the kinds of you know you can roll it up so on and so forth.

Now, we are going to talk about. So, this is melt spinning the other process which you can use for spinning the fibers is solution spinning as the name suggests instead of starting with a molten polymer, you start with a solution of the polymer. Now solution spinning you would use when the polymer in question that you are going to process through this spinning technique, that polymer has a possibility to degrade near its melting temperature then you cannot use your melt spinning technique, then you rather you then you would rather use solution spinning technique.

Solution spinning technique has two classifications, I mean it can be classified into two parts either you can use dry spinning or you can use wet spinning both are solution spinning techniques. So, what you do in dry spinning is the following, you dissolve the polymer in a volatile solvent, a solvent which has a low boiling point typically you will

use non polar solvents because they will have low heats of vaporization and low boiling points.

So, what you do is that you take this polymer solution and you extrude through filament and this filament is basically I mean the sorry the spinneret sorry spinneret extrude through spinneret. So, this spinneret is basically enclosed in what you call as drying tower now by now you must have realized why it is called dry spinning technique, because you have polymer which is in solution and after you have extruded through the spinneret, the whole chamber the whole thing is in a drying tower. So, after you have extruded through the through the spinneret the fibers, that are still with the solvent they go through a drying process. So, maybe the hot air is being passed through the fibers when the fibers are in between the spinneret and in the bottom line you can pass the hot air through it.

So, that the solvent will be evaporated and so, the drying tower you are pushing putting hot air into it. So, the solvent will be evaporated and the concentration of the polymer will increase. So, ultimately you will have a solid polymer filament at the end. So, if you look at the schematic that I that I have, again taken from the web.

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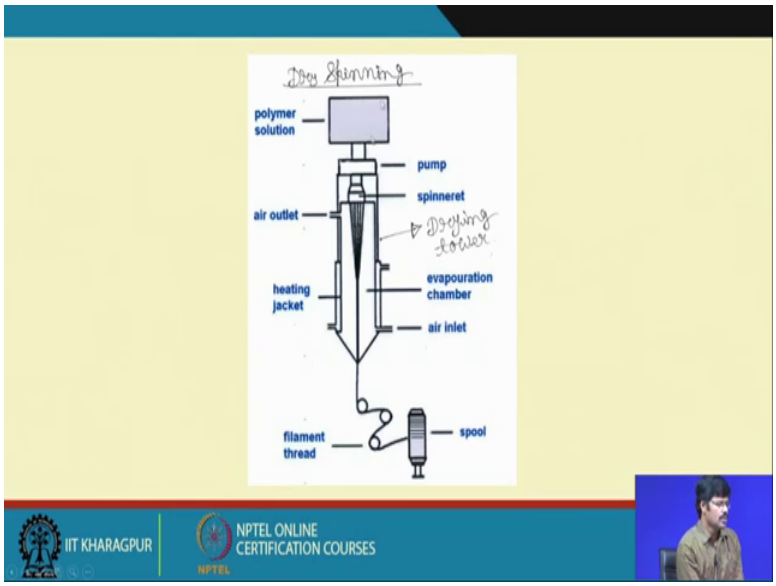

In the in the slide here; so you have the polymer solution here and you are pumping it through the spinneret this whole thing is in a drying tower. So, you are putting some hot air through it the air can go in from here and then or can come out of here. So, your

heating jacket also. So, this is also an evaporation chamber because in this situation here the solvent will evaporate leaving only the solid or the polymer. So, you will get a solid filament out of that solvent will evaporate because the solvent has a lower boiling point low boiling point volatile solvent you are using and then you are taking out the fibers and then you are having the post processing process post processing you know steps you are you are employing you are wounding it around a spool and so on and so forth you are getting ultimately the usable products like that this thread you are putting into the rolls.

So, this is your dry spinning process because ultimately you are spinning the fibers and in a situation where the solvent has already gone. But these dry spinning is a part of solution spinning because you start with a solution ok. So, what is then the wet spinning process? We already told if you look at the script now, the solution spinning there are two ways you can do the solution spinning one is dry spinning which I already talked about you are using a volatile solvent, one is wet spinning. So, for wet spinning you what you do is you dissolve the polymer in a nonvolatile solvent nonvolatile solvent. Now what you are doing here essentially different from your dry spinning is that your solvent is not evaporating.

So, how do you remove your solvent? So, what you do is that the spinneret itself through which the polymer will be extruded or the polymer solution will be extruded the spinneret itself is kept dipped in a particular solvent, which is called a coagulating bath. So, basically the spinneret through which the polymer will come out, this spinneret is already immersed in a solvent. So, basically this is a bath called coagulating bath and this particular solvent that you are choosing has to be very specific in that, this solvent this is well miscible with the nonvolatile solvent that you are using to prepare polymer solution. But the polymer that you are taking is not soluble in this solvent.

So, what is happening is that you are pushing the polymer solution through the spinneret directly into this bath. Now once it comes to this bath the polymer itself is not soluble in the solvent used in the coagulating bath. So, the polymer will precipitate out polymer will come out, but the solvent that was used to actually dissolve the polymer to start with, that is a nonvolatile solvent that cannot be evaporated that solvent itself is soluble is actually miscible with the liquid used in the coagulating bath. So, that will get miscible that will get mixed up with the coagulating bath liquid, but the polymer we will come out

because the polymer is not soluble in the coagulating bath liquid, but polymer will come out because a polymer is not soluble in the coagulating bath liquid.

So, ultimately then this precipitated polymer will form a solid filament and you can drag this filament you know through this bath using certain supports and then take it out and then you can wash these filaments with some further amount of solvent in order to remove you know in order to remove whatever was whatever the non-volatile solvent is remaining there ok. So, this is this is exactly the process that we had used for say aramid fibers the aramid fibers, where that the starting solution was constant in is to is a four.

So, in you are passing it through water ultimately, but the when you are passing it through water what is happening is that? Sulfuric acid that was used as a solvent for the fibers that gets mixed up with water, but the fibers or the polymer that is not soluble that comes out. One important difference there is that the spinneret was not dipped in the coagulating bath it was actually somewhere here if you remember the schematic there, if it was somewhere here in between the fibers started to solidify, but that was a more specific application.

In general your spinneret will be dipped in a coagulating bath and the and the liquid that you choose in the coagulating bath will be miscible with the solvent used for the polymer to make the polymer solution, but the liquid will not be solubilise in the polymer itself. So, the polymer just comes out in the form of filaments which you can afterwards collect. So, if you look at the power point slide here, this will explain further again this is taken from the web.

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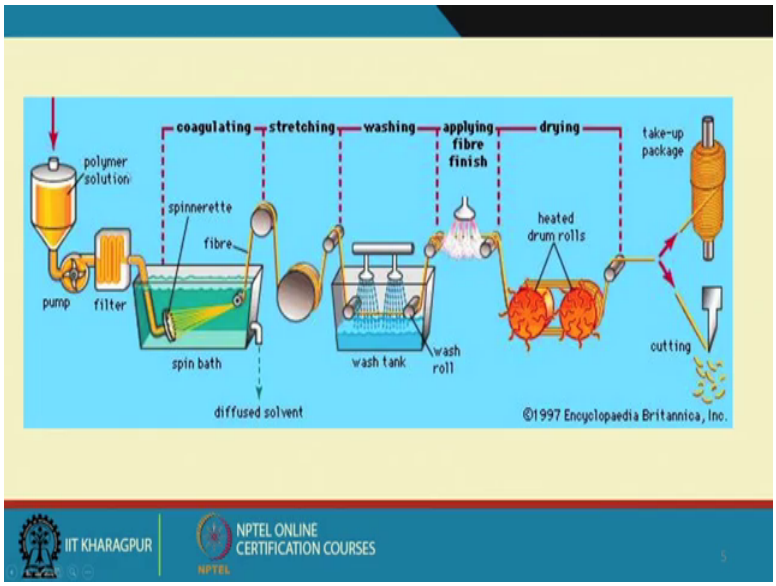

So, you are starting with a polymer solution and then you are push pushing it through a filter of course, because it has to remove all the foreign particles so on and so forth and whatnot now and then you are pushing it twist through a what it looks like you know your shower head, which is your spinneret basically. This spinneret is dipped in a in a bath of liquid and this liquid is miscible with the solvent used to make the polymer solution, but the polymer itself is not soluble in this liquid.

So, the polymer starts to precipitate out in the form of fibers then you can draw it out like this and then you can apply further washing step, in case there was some of the solvents remaining stuck to the polymer and then you can apply some other finishes and ultimately you get it out as a packaged product. So, that is what you can do. So, this is basically your wet spinning because your solvent is not evaporated, but rather removed in a coagulating bath.

Now, if you look at the advantages and disadvantages of this process lets go back to the script again. So, if you look at the advantages. So, this dry spinning process is actually advantageous over your melt spinning process, because melt spinning process is done at the high temperature dry spinning you can get a lower temperature. So, if you are using temperature sensitive polymers, then you would rather use a dry spinning process and do not use a melt spinning process this is one thing. Secondly, it has a faster production rates than melt spinning process and it has actually a faster production rate than wet

spinning process also. We will explain it after, but the flip side here is that in dry spinning you have a solvent. So, these solvent recovery is costly ok.

Now, what about the wet spinning process? The wet spinning process the disadvantage of the wet spinning process is that the production rate is basically lower than dry spinning process why? Because the filaments of the polymer that are produced there produced in the coagulating bath you have to actually drag these filaments through this viscous liquid and then take them out. So, that makes the process slower. So, overall then this is these are some of the advantages and disadvantages of different spinning processes. So, to make the long story short, you have two kinds of fiber spinning processes either melt spinning or solution spinning as the name suggests when you are talking about melt spinning process its the polymer melt that is being pushed through the spinneret, when you are talking about solution spinning process its a solution that is being pushed to the spinneret.

Now, for solution spinning process either you have a you are using a solvent which is low boiling which then gets evaporated in the drying tower after it has come out of the spinneret leaving only the solid filaments or you can use a wet spinning process in which you are using a non-volatile solvent so that the solution. So, that the solution that comes out of the spinneret, that will ultimately lead to polymer precipitation because the spinneret itself is dipped in a coagulating bath and the liquid used in the coagulating bath does not solubilize your polymer.

So, your polymer comes out and then you can draw that polymer through the viscous liquid and it comes out you take it out as a fibers after of course, this process the production rate is slower as I told because the fibers have to be dragged through the through the viscous liquid.

Now, let me show you maybe a couple of videos, so which you may find interesting again it is downloaded from YouTube. So, I will show you a couple of videos here.

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So, the first video will be the video of the polymer melt spinning. So, you see this is your this is in general how it looks the machine, polymer pelletes that were pushing fitting here this is your starting material and then your full process is automated.

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You fix the temperature because you have to melt your polymer. So, this is your spinneret here.

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So, you can see that the fibers are coming out and the fibers are being solidified in the air and it is being dragged and you can actually pull it, this kind of shapes if you if you pass it over them and then again you do like this actually helps you to have more and more orientation after.

So, this is a in a nutshell your melt spinning process of course, you are doing it at a high temperature. Now what I will show you after is a wet spinning process and this is a wet spinning process of what you call as nano cellulose. So, basically nano cellulose is nothing, but the fibers of cellulose which has nanometric dimension which has diameter in the nanometer range. So, you know if you look at the wood basically is a composite material and it has a matrix and then it has fibers also. So, matrix is basically lignin matrix, which is strengthened by the presence of these collagen fibers the overall system is strengthened because its a composite material.

So, what you do is that when you extract out these collagen fibers. So, you basically start with a wood pulp and then you use a homogenizer, what we call as a homogenizer at high speed and high pressure. So, that you extract out these nano nanometric fibrils out of these pulp and. So, ultimately what you will get is a nano cellulose suspension in water and this particular system afterwards you can do a wet spinning process in order to get your fibers out. So, I am going to play this video now. So, again this is downloaded from the YouTube. So, I have already described the preparation of nano cellulose. So, the

raw material is basically wood and which has lignin in the lignin matrix you have cellulose nano fibers and so, the product after pulping, you have these wood fibers.

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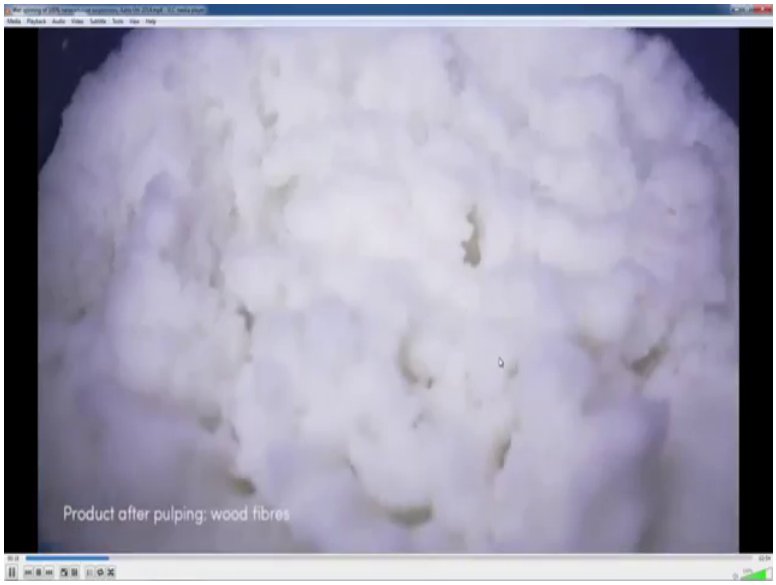

And then what you do is what you call as micro fluidization. So, you put high pressure and after this process is complete what you get is a suspension of nano cellulose in water and then in order to adjust the concentration you apply centrifugation.

So, with equal weights on both sides you will rotate it fast so, that your solid will precipitate out.

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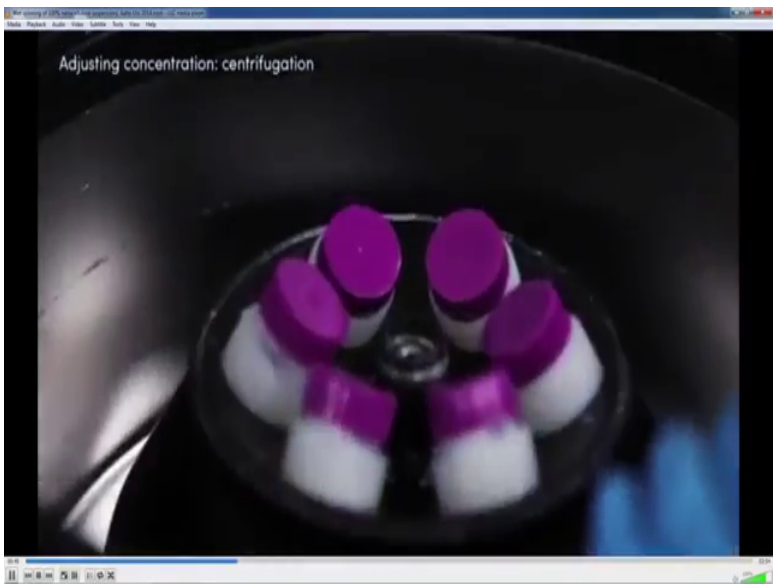

So, that is the process being shown here as very high speed you rotate this material. So, concentration ultimately that you will get is 2 to 4 percent. So, the centrifugation is already done you take this material out and remove the top layer of solvent and now you get this product which also will contain little bit of liquid. So, now, is the wet spinning process take this out and you load it in the container and then you load this in the machine. So, basically on the left you can see the syringe and it is certain rate you can push it through with a syringe pump.

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So, you see this is an acetone bath being prepared because the polymer is not soluble in acetone and then when you are pushing it through basically it is in water suspension. So, water is miscible with acetone, but nano cellulose just comes out because it is not miscible with acetone and then you can just drag out these fibers like this. So, you have all these fibers that has been produced and you can dry them up by suspending them like this in the air.

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These nano cellulose fibers have a lot of orientation basically they are quite strong.

So, you have a 100 percent nano cellulose fiber that you have got from the water suspension using acetone as the coagulating bath, now you can see that they can lift actually quite a bit of weight. So, they are quite strong because they have lot of orientation in the material.

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So, this is your wet spinning process you can see this heavy weight also can be lifted and the and the and the fibers are not broken.

So, I hope this has given you in a nutshell an overall idea of how the spinning processes are done. So in fact, I have shown you a couple of videos one is for the male spinning technique and one is for the weight spinning technique and you see that always you are using a spinneret and the general concept is that to the spinneret, when the fiber comes out maybe it is a molten polymer or maybe it is a solution after it comes out if it is molten then what will happen is that it will start to get solidify because of presence of cold air and if it is say for example, in a solution and if you are using a dry spinning technique, then you are using a solvent which is low, which has you know high volatility which is low boiling solvent typically nonpolar solvent.

So, when it comes out to the spinneret after pushing already alignment has started to occur and then your solvent evaporates you get the fibers and if it is a wet spinning process then basically the spinneret is dipped in a coagulating bath, the fibers will come out inside the collaborating bath so on and so forth.

One important thing to keep in mind here is that, depending on the you know shape of the holes you can get different shapes of the fibers also that is very important because it is through the holes of the spinneret that we are pushing the material through. So, with this we will fit we will stop what we wanted to talk about polyamides we have already finished. So, we will stop at this juncture as far as our discussion on polyamides is concerned and what we will do now is, we will start talking about another class of materials. So, until now we have been talking about engineering some of the engineering polymers, we have talked about we have talked about polyesters, we have talked about polyamides in polyesters, we have talked about polyethylene terephthalate or poly butylene terephthalate and for polyamides we have talked about aromatic polyamides aliphatic polyamides. So, we were saying how to process aromatic polyamides, from there the concept of speeding came and then we just went into this concept of spinning techniques so on and so forth.

So, what we will now talk about is polyamides. Polyamides is a is basically a specialty polymer its quite costly to prepare polyamides and also they are they can withstand quite high temperature. If you remember the discussion that we had right at the start of this these sessions of the synthetic synthesis of the polymers, we talked about commodity polymers, engineering polymers, then specialty polymers. So, polyamide is a class of polymers which goes into the specialty polymers category.

So, what we will do in the next class is we will start talking about polyamides the synthesis of that the structure property relationship of that. So, we will stop here today.

Thank you for your attention and see you in the next class.