Principles of Polymer Synthesis
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Lecture – 37
Synthesis of Industrial Polymers (Contd.)

In the last previous several of the classes, previous several classes we have been talking about the synthesis of industrial polymers and currently we are speaking about synthesis of nylons and in fact, we have gone beyond the synthesis of nylons and we are talking about the structure property relationship of nylons. So, we will start right there.

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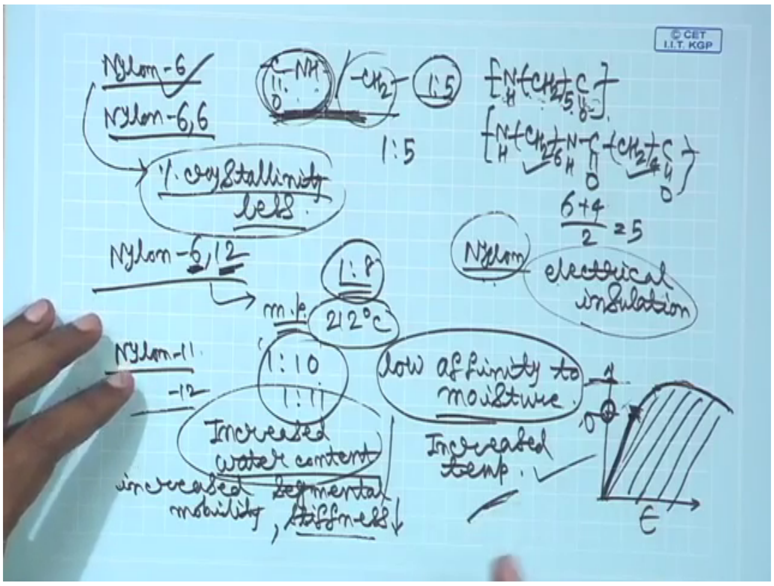

So, we had been talking about the effect of moisture content and the effect of increased temperature on nylons and we told that both of them moisture content, increased moisture content and increased temperature both will have the same effect that is it will increase the segmental motion of the material it will decrease the stiffness and the tensile strength of the material. But in turn it will increase the impact strength or the toughness of the material.

So, you would better use a nylon which actually contains less amount of water in equilibrium when it is exposed to a certain amount of moisture. Then say a lower nylon that is because I mean for electro for insulation purposes for electrical insulation purposes because for these kind of applications you do not want a lot of water to be present because otherwise the resistivity of that will decrease and insulation will not be effective. So, you go to say for example, 9 or 11 and not using nylon 6 6 for electrical insulation.

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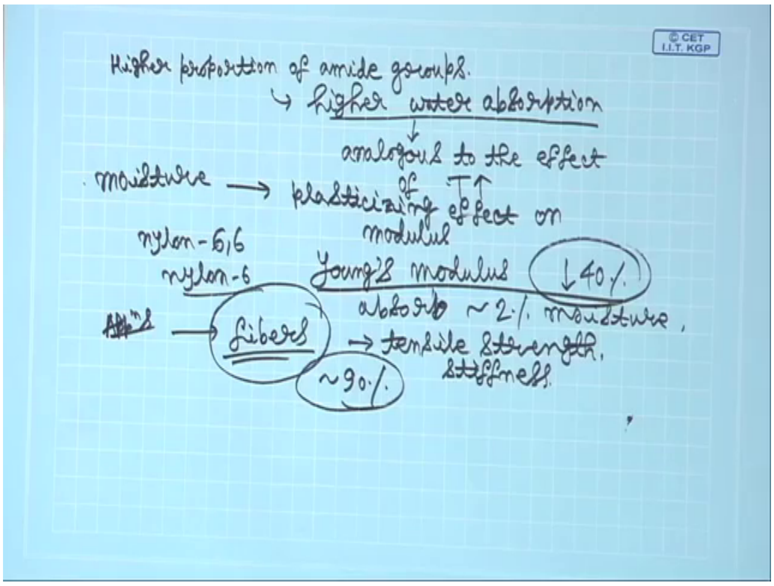

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Higher proportion of amide groups.
↳ higher water absorption
↓
analogous to the effect of $T\uparrow$
moisture → plasticizing effect on modulus
nylon-6,6
nylon-6
Young's modulus ↓40%
absorb ~2% moisture,
Appl^ns → fibers ~90%
→ tensile strength, stiffness.

And we also, so in effect then what we talked about if we have to summarize this particular part. Then we could say something like this higher proportion higher proportion of amide groups this leads to higher water absorption and the effect of higher water content is basically analogous analogous to the effect of increase in temperature. And so your you can say that this moisture basically has a plasticizing effect because the material becomes less stiff segmental motion increases the toughness increases impact strength increases, plasticizing effect, plasticizing effect on modulus or the Young's modulus it goes down.

So, as a method of fact if you look at say nylon 6 6 or nylon 6 then the Young's modulus the Young's modulus value it goes down by as much as 40 percent when these materials they absorb around 2 percent absorb, around 2 percent moisture. So, just put around 2 percent of moisture and the Young's modulus goes down by 40 percent. So, the effect they are is basically enormous.

Now, in general if you look at the applications if you look at the applications of nylons if you look at the applications they are typically as fibers because they are having quite high tensile strength typically the materials are having quite high tensile strength and also stiffness. And I also mentioned how tensile strength and stiffness are two different stiffness are two different things and they are also resistant to attack by different solvents because of this very strong packing high crysatllinity so on and so forth and.

So, up to around 90 percent of world production of all the nylons can be accounted for by the by by its usage in fibers. So, up to around 90 percent is used for fibers and the rest of that is used for plastic applications and typically for you know because of the high cost they have not become your general purpose material like if you compare with polyethylene or polystyrene like that.

Now, because polyethylene poly styrene these things are typically available at one third of the price of nylons. So, about plastic applications nylons have not gained much ground with respect to the other you know commodity polymers this is nylons are engineering polymers with respect to commodity polymers they have not gained much ground because the cost is much higher.

However, they are used as fibers 90 percent of their production can be accounted for by their users as fibers ok. So, it because they are very optimum combination of toughness rigidity and very good heat resistance by reasonable I would tell because the melting points are quite high say on more than 200 degree Celsius so on and so forth.

Now, what we will talk about now is something else, but still the topic remains polyamides. So, until now we have been talking about mainly aliphatic polyamides which have the trade name nylon. Now, we will shift our attention to aromatic polyamides.

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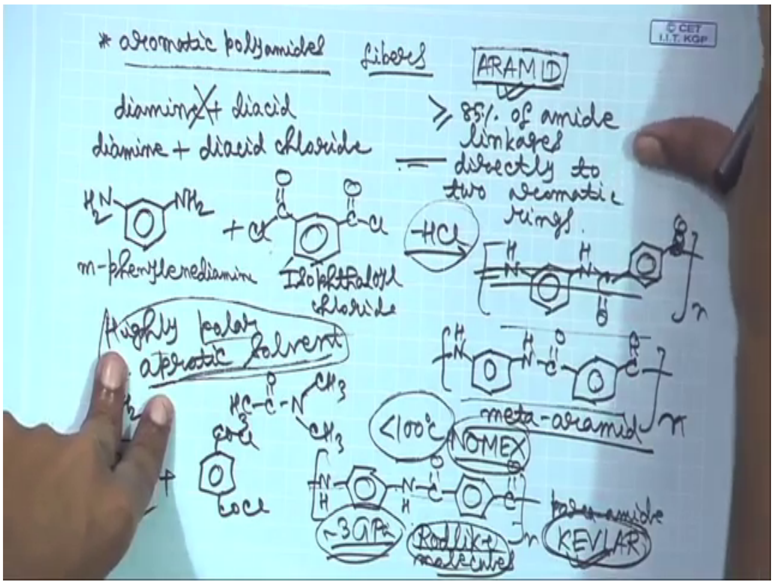

So, aromatic polyamides, now aromatic polyamide fibers are generally known as aramid fibers. Now, you will you will tell they are aramid fibers and how do you define this term aramid. So, it is defined as a long chain of synthetic polyamide a long chain of synthetic poly polyamide in which at least 80, 85 percent of the amide linkage, at least 85 percent of the amide linkage they are attached directly they are attached directly to two aromatic rings then you call them as aramid fibers two aromatic rings. Now, synthesis wise it is quite different from how do you how you approach the synthesis of aliphatic polyamides because you know if you are using a diamine and a diacid for the synthesis of the polyamide.

So, it is basically an amide formation reaction now in this case you have to then use a diamine, diamine which is an aromatic diamine and you have to use a diacid aromatic diacid the thing is the reactivity of aromatic diamine is significantly lower with respect to their aliphatic counterparts, because the lone pair on the nitrogen you see that nitrogen lone pair has to attack to the carboxylic acid unit. So, this lone pair of nitrogen is less available because of the resonance stabilization with respect to the aromatic ring you can displace them into the aromatic ring in a in a in trying different resonance structures.

So, they are not as easily available. So, the reactivity of these aromatic amines is lower and that is why what you do is that in this case if you used just a diamine and a diacid an aromatic diamine and aromatic diacid because of the lower the activity of a of the aromatic diamine you would require I mean significantly higher temperature in order for the reaction to proceed which is not practical because have those high temperatures your material might degrade. So, you want to still do at a lower temperature and that is why what you do is you take the diamine aromatic diamine you take the aromatic diacid, but you activate the aromatic diacid. So, what you do instead of using aromatic diacid you use aromatic diacid chloride ok.

So, diamine plus diacid this reaction is not used. So, what you do is that you use a diamine and you use an activated diacid the derivative of that that is diacid chloride diacid chloride. So, an example could be let us say you react this diamine this is actually meta phenylene diamine. You react that with this diacid chloride, now this is isotalic acid if you have CO 2 H on both sides. So, this is isolohthaloyl chloride.

So, this is already an activated material. So, the electrophilicity of this carbon is increased because of the electron withdrawing effect of chlorine that compensates for the reduced reactivity of the amine and what you get is liberation of HCl and a polyamide of this kind of structure NH, NH, CO ok, CO this is a polyamide.

So, basically this is a sorry I have drawn the structure wrong because this is in meta position. So, this will be not here actually let us draw the structure in a different way. So, this is not a right structure because here I have drawn in the para position this should be the structure here. So, you have NH and then NH CO CO. So, this is meta position ok. So, this is called a meta aramid, this is a meta aramid meta aramid. So, this is poly meta phenylene isothelamide ok.

So, this is poly meta phenylene isothelamide and the trade name of this compound is no mix and the polymerization these polymerization these polymerizations are typically they are carried out in solution and the solvent that you are using is a is a highly polar solvent. But this is aprotic solvent also unlike water can donate protons polar aprotic solvents you are going to use here. Say for example, you have I mean just an example d m a. So, dimethyl sulphoxide is a polar aprotic solvent that you are not going to use here , but in general that work I mean polar aprotic solvents are solvents which are polar, but which do not have the ability to donate protons.

So, in this case what you use is dimethylacetamide. So, this is acetamide CH 3 CO NH 2. So, instead of two hydrogens if you have two CH 3 units it is dimethylacetamide. This is a polar material polar solvent, but these cannot donate protons. So, polar aprotic solvent. Temperatures are typically less than 100 degree Celsius compare that with the temperatures that we use for your aliphatic polyamides preparation upwards of 200 degree Celsius there and here because this is activated you do not need very high temperature.

And you typically use a base in order to scavenge the liberated HCl the acid and the choice of the solvent is dictated by the fact that the growing polymer chains should not precipitate out before the polymerization has not reached the intended molecular weight remember that your temperature here is low.

So, the solubility of this material might be lower in the solvent. So, if there is the case then it it have can prematurely precipitate out before the high molecular weight is reached in order to stop that situation you are using a highly polar aprotic solvent in which it has good solubility. And that is why it does not prematurely precipitate out before you have reached a chain which is of long enough length; that means, high enough molecular weight.

So, because the temperature that we are using here is much lower than the temperatures that we use for your aliphatic polyamide synthesis. Now, this is a metadiamine you are reacting with a meta diacid chloride if you start with the para version of these; that means, paraffin in diamine if you react with what is that compound if you have CO 2 H here and CO 2 H here there will be terephthalic acid that will be then you will be then reacting this para amine which is your paraffin in diamine with COC l, COC l terephthal chloride. If you react that and then what you will get is a para version of this material, the para version of this material will be para amaide that is this NH NH CO this is your para amide ok.

Now, this pair amide that you have here the trade name of this para amaide. So, this is a para amide trade name of this para amide is Kevlar. So, already now we have described the synthesis of nomex and Kevlar. Now, if you compare between nomex and Kevlar you see that Kevlar has all these para orientation. So, ultimately the chains they can pack better than your meta aramid. So, and typically the Kevlar is the most well studied material and when you are making fibers out of this you will see since this is para orientation. So, this molecule the extent in the extended form it can orient along the direction along the long axis of the fiber all these molecules will orient along the long axis of the fiber that will give the fibers enormous tensile strength up to 3 giga Pascal up to 3 giga Pascal approximately and you will have all these hydrogen bonding interactions in the transverse direction ok.

So, you will have hydrogen bonding interactions in the transverse direction and in the longitudinal direction they will just pack nicely they will be just parallel like that, and also you will have these pi pi stucking interactions between the aromatic units of the subsequent subsequent layers. So, all these things will make the material highly anisotropic because along the length of the fibers because they are all oriented along the length of the fibers you will have enormous tensile strength and on the transverse direction of the, so along the, so this is the length of the fiber.

So, along the transverse direction you will have the hydrogen bonding interactions which is definitely weaker because along these length you have the polymer chain itself which has covalent bond between the molecular units the covalently bonded compound the chain is extended along these length. So, the tensile strength is quite high, but if you see the transverse direction which is these direction these direction in this direction you will have hydrogen bonding interactions and so that is weaker.

So, that is why you will have the properties that will be enhanced your mechanical properties will be enhanced along the length of the chain and they will not be that much enhanced along the transverse direction that is why it will be an anisotropic. It will have highly anisotropic property you have para aramid fibers or Kevlar it will have highly anisotropic property.

Now, something also you should remember these these are all rod like molecules, these are all rod like molecules and these kind of efficient packing of these molecules not only make them very highly crystalline, but also it makes it difficult to solubilize in many different solvents. So, the processability is also you have to adopt different ways for processability.

So, normal drawing of the fibers may not work what you have to do is you have to use something called a spinning techniques will come to this.

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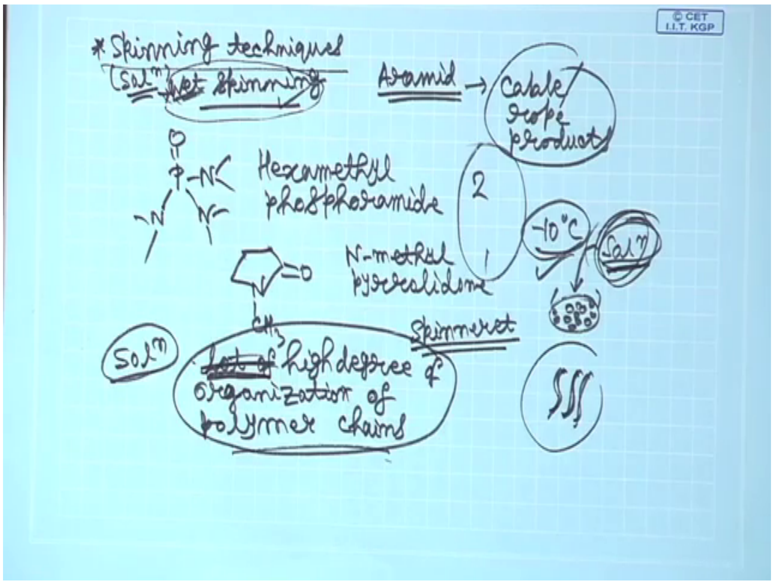

You have to use spinning techniques say in this case it is solution solution spinning technique or where or wet spinning technique. In fact, this is wet spinning technique or wet spinning process that you are going to use in order to process these materials into into fibers. Now and of course, these aramid this para aramid fibers that you are going to produce they are used as you know cable or you know rope products so on and so forth, and the production is expensive because the you know processability processing is also expensive.

So, we will come to that now. So, typically what you do for processing of aramities are aramid fibers because we are not going to talk about meta aramid fibers anymore we are going to talk about para aramid fibers. So, before you come to processing you should also have a another look at this particular reaction by itself.

If you compare these two reactions this reaction is done in dimethyl acetamide temperature is somewhat less than 100 degree and if you are talking about the preparation of the para arami aramid which is Kevlar then typically for this preparation what you do is these are your starting materials and the solvent that you are using is a a mixture of hexamethyl phosphor amide.

So, this is your hexamethyl, hexamethyl phosphor amide you are using and along with that you are using N methyl pyrolidrone which is this molecule in methyl pyrolidrone and you are taking that in 2 is to 1. So, this is 2, this is 1, 2 is to 1 ratio the temperature is minus 10 degree Celsius. So, you do it quite a low temperature this particular reaction.

Now, let us come to the processing of this material. So, what you typically do as I already told you that this is a wet spinning technique we will come to what a spinning technique is slowly. So, the point here is that you start with a solution of the material, you start with a solution of the material with a specifics with specific properties and you see that you have to have fibers that have come out ultimately after processing those fibers are in the solid state and they have a long range strong orientation along the length of the fibers that is what you have to achieve. So, what you start with is a highly concentrated solution of this para aramid that you have prepared.

So, because, ultimately what you will get after the reaction you get pellet us of this material and then you polymerize this material and then you dissolve in a suitable solvent I will come to what solvent you are going to use for para aramids, but let us look at the properties that you would like to have in this precursor solution. So, you start with this solution and the idea is you will force it through something which is called a spinneret.

These spinnerets if you look at the script here, these spinneret are nothing, but they look like you know the shower heads. So, this shower heads will have lot of holes in it. So, what you do is push your polymer solution through this you put lot of pressure and you push it through this and that way you are actually orienting the material the first thing. And the second thing is also your starting solution should have lot of organization of the chains the chain should have as much organization as possible in the starting solution.

So, that ultimately it helps in the final organization of the fibers ultimately will get the fibers. So, if already in your solution it is organized and then when you are forcing through the spinneret there is a little bit more organization that is happening. So, this actually is augmenting the final system; that means, in the final fibers that you are getting you have a lot of orientation of these chains along the length of the fibers and that will give it a the tensile strength that you want.

So, in order to do that you have to start with a highly concentrated solution in which there is a lot of organization a lot of organization organization or a let say this is not a very right term here. Let us say high degree high degree of organization of polymer chains polymer chains is required in your starting solution for the processing ok.

Now, something that you need to keep in mind here is the following. We are talking about rigid chains here. Normally polymers are flexible chains. So, when you dissolve in a solvent they will have this kind of random, they will be like random coils you know flexible chains. So, you may have this kind of random coils when you dissolve them in a solvent.

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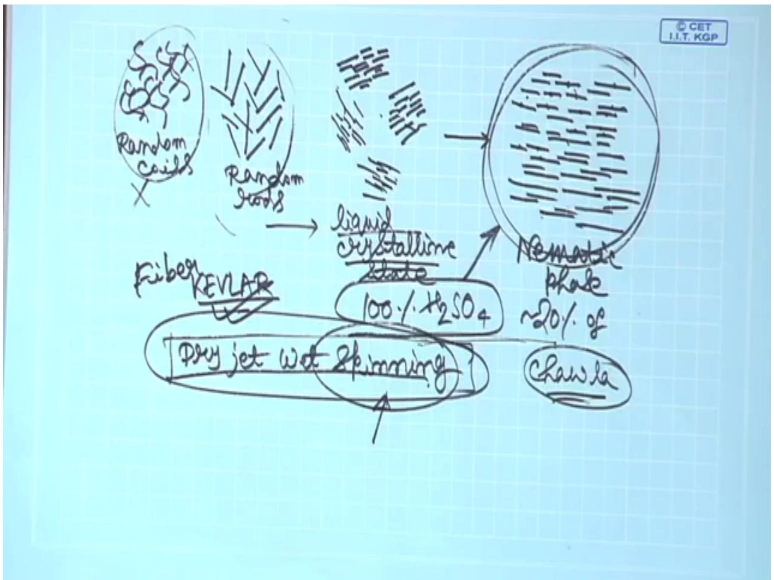

In our case we are talking about para aramid molecules which are like random rods then when you dissolve then in a particular solvent they will be like the rigid rods. So, this is a random rod configuration when you increase the concentration. So, this is in dilute solution you dissolve in the solvent I am not I am not here talking about what solvent we are using. Let say we have the right kind of solvent that we want to use; So, at a low concentration you will have all these random rods that are there why you increase the concentration what will happen there will be regional organization like this.

So, in different regions you will have the chains organized like this. So, you will have this kind of domains of organized chains. These is what you have this is what you call as a liquid crystalline state. So, the material is still liquid, but it is starting to have this kind of organization in the material. So, it will have a liquid crystalline state so obviously, obviously in all kinds of solvents the same polymer when you dissolve it will not from this kind of state. So, it depends on which solvent you are using. So, that I have to standardize first. So, you have gone to higher concentration this situation is not existing here because we are talking about para aramid fibers which are rigid rods, you know in para direct in the para position you have all the functionalities of the aromatic rings and this is also rigid because you have lot of aromatic units. So, that also it provides lot of stiffness to the material. As I already told before, the aromatic units provide rigidity, so liquid crystalline state.

If you increase the concentration further then what you will have is this kind of system. You will have a long range order throughout the material. So, all these chains are oriented along a certain direction however, if you if you look at the center of these chains the center of these chains. The center of these chains are arranged randomly. So, all the chains are oriented along a certain direction we have, but if you look at all the centers just take the centers of all these rods. If you just see this particular diagram how are these centers arranged the centers are arranged randomly.

So, this particular situation where you have a long range order, but the centers are arranged randomly this is going to give you a state which is called nematic phase nematic nematic liquid crystalline phase this is the phase that you are looking for. If you start with this kind of phase, that means, a solution of the polymer which where the polymer is at least oriented like this.

So, you now already have a lot of organization a very high degree of organization of polymer chains in the solution and after this through spinning process which I am going to describe afterwards you further align these materials. So, it helps if it is already aligned that is the point and then you will ultimately remove the solvent and you will get your fiber, that is the idea. So, it turns out that for this Kevlar or para aramid you have to use hundred percent H 2 SO 4 sulfuric acid and if you dissolved in 100 percent H 2 SO 4 around 20 percent of this material then what you will get is this nematic phase.

Of course, you have to standardize this because in all solvents this kind of phase may not generate. So, once you get this particular phase what you do is that you pass it through a spinneret. So, if you now see the corresponding you know diagram in the power point slide. So, you will see that for example, so, this is this is your spinneret the this has all these holes in it this exactly looks like your showerhead in the bathroom.

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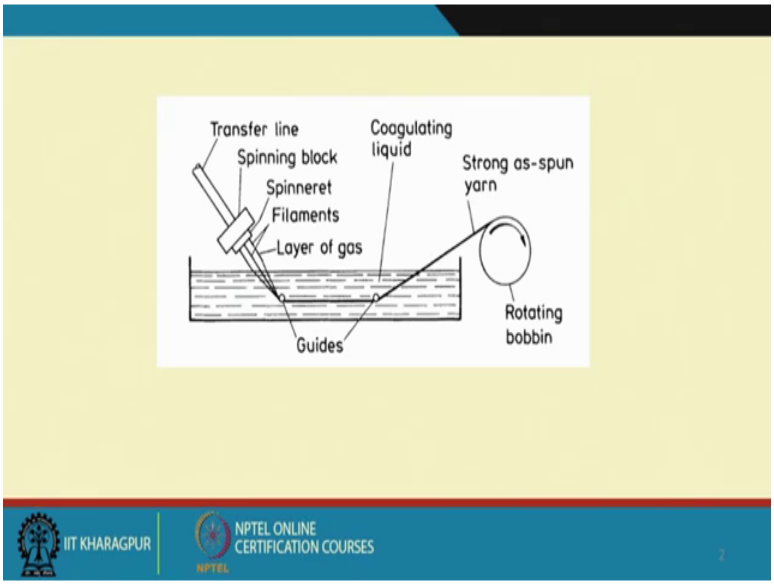

So, you are putting your polymer solution which is highly concentrated solution in sulfuric acid 20 percent solution, and it is basically nematic liquid crystalline phase it has all these orientations of these chains so on and so forth blah blah. And then what you are doing you push through these spinnerets and the polymer comes out to this little holes and so you start to get the fibers already and there is a r in between and then what you do is that you are passing this particular system through the water. So, this is water here.

So, the fibers already the filaments let say the filaments they have already started to generate and when you are you know having this coagulation bath here it can actually remove the sulfuric acid that was there in the system. So, and then you are getting all these fibers and you are using these guides that will guide them out of the coagulate coagulating liquid and then you have a rotating bobbin on which you can have the as spun yarn, I mean you can spin this material like this and you can have these rolls of these fibers so on and so forth.

So, this is a process which is called dry jet wet spinning wet spinning I have already mentioned the name. I did not mention I mean as far as the concept is concerned I have I not still gotten into the details of that, but this is the overall process. So, you do what you call as dry jet wet spinning and you have a coagulating liquid in this case typically you can use you know water and in fact, the fiber here it starts to solidify already in between when you have the air. So, it was sulfuric acid solution and it is coming here and in between. So, basically what you are doing is the solution that we are starting with you are keeping at a very high temperature in this case it is at 100 degree Celsius. So, it is just coming out here it is getting cooled down. So, it starts to solidify the filaments start to appear and then you are pushing the filaments through the water and the water can take away the sulfuric acid that was stuck to the filaments and then you take it out so on and so forth. So, this is your dry jet wet spinning process.

Now, let us come back to our script here. So, we will try to explain this particular situation a little further. Now, we were talking about spinning process, we were talking about spinning process and we already talked about what you call as dry jet wet spinning.

We showed you the schematic the schematic is actually taken from the book of Chawla. I will attach that as the of course, when I send you the study materials. So, dry jet wet spinning process this is what you use for Kevlar fiber preparation which prompts me to come to talking about in general what is a spinning process.

So, what we will do is because we are running out of time today we will stop here and we will start right in the next class with a concept of fiber spinning process.

So, until then thank you and see you in the next class.