Principles of Polymer Synthesis

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Lecture - 36
Synthesis of Industrial Polymers (Contd.)

Hello and welcome back to this 8th week of the course on Principles of Polymer Synthesis. So, the topic continues to be the same as has been throughout the last week that is the synthesis of industrially important, commercial polymeric materials.

So, we have been basically our concentration will be on the preparation of step growth polymers and the we have been talking about that until now. And we have covered the polyethylene terephthalate synthesis and also we have started talking about polyamide synthesis. So, a quick recap of the of what we have talked about regarding the synthesis of polyamides.

So, I have already mentioned in the previous class that for polyamides if you are having aliphatic constituents. For example, if you are reacting an aliphatic diamine with an aliphatic diacid and you are preparing the polyamide then what you are going to get is the trade name is nylon or, so this is a you know direct amidation process we talked about that in the previous class.

Also there are two other ways in which you can prepare polyamides, one of them is you know you can have both the amine as well as the carboxylic acid function in the same molecule. Let us say you can have an amino acid and that will be then self amidation reaction. So, basically the process is the same the react reaction of an amine with a carboxylic acid. So, either the amine is on one molecule and carboxylic acid is a on another molecule or both the amino and carboxylic acid are in the same molecule.

So, when you are having both the amine and carboxylic acid the same molecules a direct you know it is a self amidation process. So, one is direct amidation one is self amidation and the third is basically your ring opening polymerization.

So, you start with an amide which is a cyclic amide the cyclic amides are called lactams and what you do is you catalyze the ring opening reaction by using water or some acid or some base. So, after opening the ring what you will basically get is one side carboxylic acid on one side and amine. So, you basically have an amino acid and this amino acid can then react with itself means in a self amidation process and and and produce a long chain of a polyamide the nylons. So, that will be also the preparation one preparation process of nylon I mean when you are doing a ring opening. So, after you have done the ring opening then one of the processes through which the polymerization can occur is through self amidation, the other process is once you have ring opened the cyclic amide and prepared the amino acid.

Now, this amino acid has one amine group on one side and carboxylic acid group on another side. Now, this amino acid itself or an oligomer of it once it has started to do self amidation and produced some oligomer so that carboxylic acid it can protonate your ring which is your cyclic amide that you are starting with it can protonate that it can activate that and then the amine of that amino acid can actually attack there and start to increase the length of the chain in the propagation step. So, that is basically the ring opening polymerization.

So, first step your ring will be open say you are using water. So, the ring will open. So, you will basically have an amine and carboxylic acid on both sides. And the second step either you will have self amidation or these particular species linear species that you have formed will basically protonate through its carboxylic acid unit it will protonate the lactam or the cyclic amide, and it will then ring open by attacking from the other side of the linear chain which is an amine and then it can continue to progress like that.

And we have talked about a situation where we are we are we are talking about preparation of nylon 6. So, we start with caprolactam in that case and if you are using caprolactam then the overall contribution of self amidation to the polymerization is only a few percent most of the polymerization actually proceeds through ring opening pathway. So, this is the point at which we stopped in the in the previous week. So, let us start from this point. So, we are talking about aliphatic polyamides the trade name being nylons. So, let us look into the systems in a little bit more detailed fashion ok.

So, let us say we are talking about nylon 6 6, nylon 6 6.

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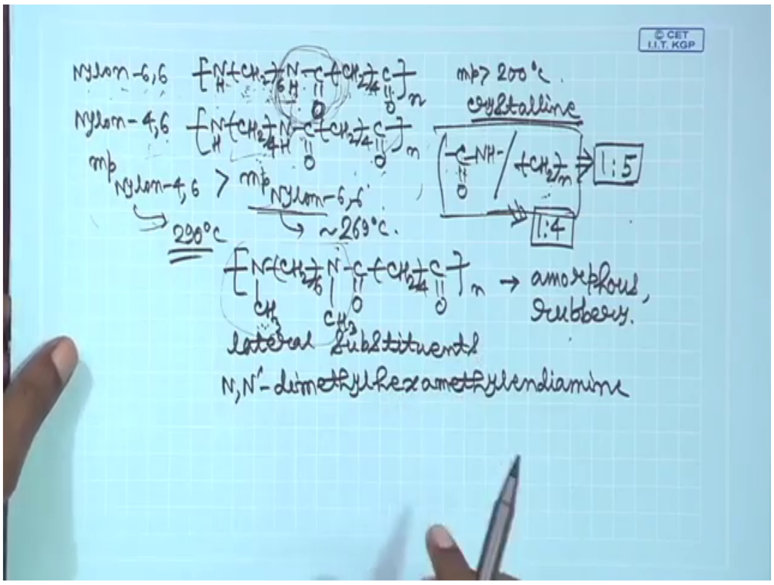

Now, this nylon 6 6 what is the formula? The repeat unit is we have talked about these things before. So, there will be 6 CH 2 units here and then you have an NH and then you have CH 2 whole 4 CO whole n. So, basically from the acid you have 6 carbons and from the amine you have 6 carbons. So, basically you name it like nylon 6 6. And let us take nylon 4 6. So, then the nylon 4 6 will be the repeat unit formula will be something like this.

So, this is nylon 4 6 the first number indicates the number of carbon atoms in the in the amine, second number indicates the number of carbon atoms in the acid. Now, if you have to compare between these two now both of them are quite crystalline in nature. So, typically nylons are having crystallinity. So, they are crystalline in nature and typically nylons have melting point which is higher than 200 degree Celsius.

Now, if you have to compare between these two molecules say nylon 6 6 and nylon 4 6, you can see one important difference between the two is that the ratio of the amide two methylene units is basically higher in nylon 4 6. Let us I mean I will explain this little bit more here. So, the ratio of your CO NH that is your amide unit amide unit to your methylene units ok. So, this ratio is basically higher in nylon 4 6, I mean how do you know that this is higher. Say for example, if you have nylon 6 6 an amide unit comes either every 6 CH after every 6 CH 2 units or after every 4 CH 2 units your amide unit in a repeating unit that is coming either after every 6 units of CH 2 or every 4 units of CH

2. So, on an average one amide unit is coming after how many number of CH 2 units that will be 6 plus 4 divided by 2. So, basically that ratio for nylon 6 6 is basically 1 is to 5.

So, on an average you have 5 CH 2 units and then you have one amide unit again another 5 CH 2 units on an average. Actually there is 6 and 4, but you have to take the average. So, this is 1 is to 5. If you compare that with nylon 4 6, what is this ratio for nylon 4 6? It is basically 4 here and 4 here, so on an average it is 4. So, the nylon 4 6 this is 1 to 4.

So, the ratio of CO NH two CH 2 groups the ratio of CO NH to CH 2 groups that ratio is higher for nylon 4 6 than nylon 6 6. So, what is the effect on the properties then? The effect is that the melting point of nylon 4 6, the melting point of nylon 4 6 is higher than the melting point of nylon 6 6, and also the crystallinity of nylon 4 6 is higher than the crystallinity in nylon 6 6. Why is that so? Because you see here you have this amide units.

Now, these amide units are very good hydrogen bonding units. So, this NH it can donate one hydrogen and in the next chain we will explain this in more detail after. In the next chain the carbonyl of the next chain that carbonyl oxygen which is electronegative it can accept the hydrogen from the other chain. I mean so there will be an interaction between the carbonyl of the next chain and the NH of this chain.

So, basically then this is hydrogen bonding interaction and this kind of hydrogen bonding interaction is very strong for nylons because you have all these amide units and the strength of these hydrogen bonding interactions ensures that there is a very good packing that is why typically the melting points are quite high and they are quite crystalline in nature the materials. So, of course, if your amide 2 CH 2 unit that ratio is higher; that means, the extent of hydrogen bonding interaction will also be higher.

So, that will be a better packing the situation will be a better packing it leads to a better packing so; that means, in nylon 4 6 the crystallinity will be higher and for the same reason the melting point also will be higher. So, some of these things directly relate to your your structure. So, you see that how the property evolves on the basis of structure.

Let us delve into a little more detail on this. So, the melting point of nylon 6 6 is approximately I think 269 degree Celsius and this will be close to two ninety degree Celsius ok. So, you see that he says higher melting point this also has higher percent crystallinity. Now, let us say we have another nylon say we had nylon 6 6 right let us write down this thing nylon 6 6 CH 2 whole 4 CO whole n now instead of having hydrogens in the nitrogen let us replace the hydrogens with CH 3 units.

So, what happens? If you replace the hydrogens with CH 3 units; So, these are basically your you are putting some lateral substituents on the nitrogen of the amides substituents. Now, this lateral substituents if you are putting; that means, that that will destroy the possibility of hydrogen bonding because you know this for the amide unit NH this hydrogen can be donated to the carbonyl of another amide another link. So, if you have one chain which has this amide unit if you have another chain which has amide unit there will be hydrogen bonding between the carbonyl oxygen of the other unit and the hydrogen of this unit.

So, if this hydrogen, so there basically this is this you these group is hydrogen bond donor the traditional name is like and this is your hydrogen bond except of the carbonyl oxygen. So, if this hydrogen is being replaced then you are actually stopping the hydrogen bonding from occurring. So, hydrogen bonding is at the heart of crystellinity of these materials it is at the heart of high melting point of these materials and this is also the reason normally why the nylons are typically also very stiff materials.

So, you will see that many for fiber applications and all you can use nylons nylon ropes so on and so forth. So, that is why I mean you will get those kind of stiff stiff materials because you have you know aligned hydrogen bonding interactions, but if you now destroy this hydrogen bonding interaction then your will also destroy crystallinity.

So, if you have this material how can you prepare this material, you start with an amine which corresponds to this which is basically n n prime dimethyl hexa methylene diamine, and then you react that with adipic acid and then you get. This product this product is not crystalline it is actually amorphous and rubbery. So, you now see how the structure directly dictates the property ok.

So, typically if you are looking at nylons where your lateral substituents are not there, they are quite resistant to oil and solvent and they are also quite tough they have high strengths and they have high thermal stability also and now. So, what we have told? The melting point increases when the ratio of the amide 2 CH 2 units increases we have seen here not only that the extent of hydrogen bonding interaction also increases and the crystallinity also increases.

Now, let us talk about a situation where either you have an even number of CH 2 units between the amide groups or you have odd and that will also change the properties.

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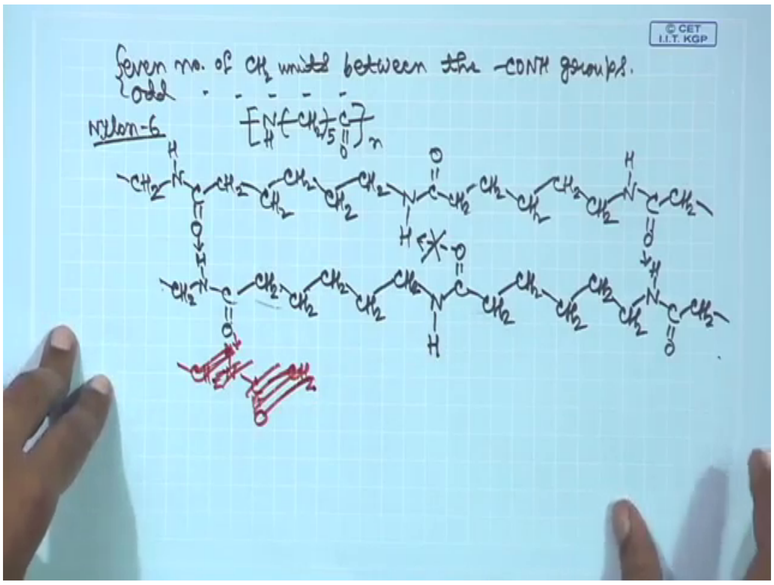

Let us say you start with nylon 6. Let us write down the repeating unit formula of nylon 6. The repeating unit formula is something like this CH 2 whole 5 CO and then whole in n number of units.

Now, let us draw an extended chain configuration of nylon 6. Let us draw this and we will see CH 2 NH CO NH CO and then you have between carbonyl and NH you have 5 CH 2 units. So, 1, 1 2 3 4 5 and then you have another NH unit and then again you have CO and then you have 5 CH 2 units again. So, it will be CH 2 CH 2, CH 2, CH 2, CH 2, 5 CH 2 units and then again you have NH CO CH 2. So, this is one chain.

Let us draw another chain here just below it. I want to investigate how the hydrogen bonding interaction is happening between the two adjacent chains. So, let us draw another chain which is parallel to this chain ok. Now, this chain has to be shifted a little bit on this side because it is the NH unit which will have hydrogen bonding interaction. So, I am just drawing like you have a I am just putting an arrow here. So, even hydrogen bonding interaction and then you have CO, CH 2, CH 2, CH 2, CH 2, CH 2 and then you have another NH here and then you have a CO CH 2 1 2 3 4 5 and then you have an NH CO CH 2. Now, you see here you have an hydrogen bonding interaction between the adjacent amide groups here you have an hydrogen bonding interaction, but somewhere in the middle the NH of one layer and the carbonyl of the other layer they are at a larger distance.

Because of the arrangement of the atoms if you are putting two the two of the chains parallel then somewhere in the middle this carbonyl is not at a right distance with respect to this NH in order to have an hydrogen bonding interaction. So, I am just putting normally I put the arrow from oxygen to hydrogen because the electron density is basically shifting from oxygen to hydrogen in order to make the hydrogen bonding interactions that way you can look at it.

So, I am just putting dot here because this interaction does not happen. So, if you put two chains parallel then all the possible hydrogen bonding interactions when I am saying all the possible hydrogen bonding interactions I am just counting the number of amide units and I am hoping all the amide units could engaging hydrogen bonding interactions. So, if they were to engage in hydrogen bonding interactions that will give you the total number of possible hydrogen bonding interactions.

But if you have two chains which are parallel then somewhere in the middle this hydrogen bonding interaction does not materialize; that means, all the potential hydrogen bonding interactions cannot be materialized when two chains are in parallel. In the case where you have odd number of CH 2 units between the amide groups. So, in order to make sure that between two adjacent chains all the hydrogen bonding interactions are satisfied what you have to what you have to basically do is that this particular chain you have to put in an anti parallel orientation with respect to the top chain.

So, what happens if you put that in an anti parallel orientation? If you put that in an anti parallel orientation so what I will do is that let us forget that the top chain exists because this chain and this chain are the same because they are parallel chains. So, let us now forget that a top chain exists. I will draw another of this chain in an anti parallel fashion here and then see if all the hydrogen bonding interactions can be satisfied and that is something that I am going to draw with a with a red pin just to differentiate the two. So, CH 2 and then you have NH. So, I have flipped this chain here. So, you see this was CO.

So, basically this was CH 2 CO NH. So, I have flipped this unit. So, if I flip this then it will come like this.

So, basically you have to invert the entire molecular chain in order to get to your anti parallel orientation ok. So, you have NH. So, you have an hydrogen bonding interaction that is possible here, now NH CO ok. So, CH 2 sorry actually I have drawn it wrong, but it is not a problem what I will do is I will take a fresh paper and I will draw it again just to avoid the confusion [noise. Anti parallel orientation I the structure was not correct.

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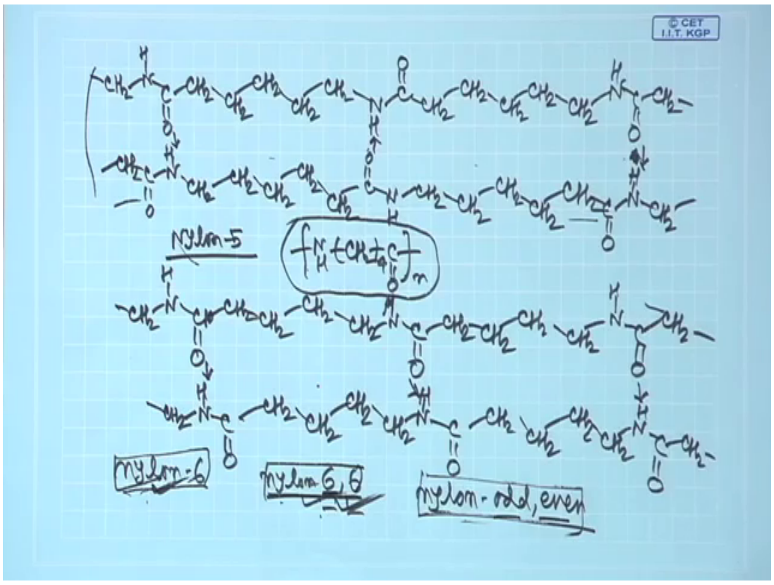

So, let us draw one chain again. So, it is CH 2, NH, CO, CH 2, CH 2, CH 2, CH 2, five CH 2 units are there and then you have an again one amide unit and again you have five CH 2 units and again you have one amide unit.

Now, let us invert this chain like this and then you have a anti parallel or anti parallel orientation. So, if you invert this it will be CH 2 CO NH. So, you have an hydrogen bond interaction that that is realized here and then because you have inverted. So, you are coming from this side, so CH 2, five CH 2 units 1 2 3 4 5 and then you have a carbonyl unit again carbonyl hydrogen bond is possible and then you have an NH. So, you are going now towards this direction here. So, you have five CH 2 units 1 2 3 4 5 and then again you have a carbonyl which is here and then again you have an NH unit which is here sorry the arrow should be like this and CH 2.

So, you see unlike the situation in the in the previous stage where the two chains were in parallel orientation all the hydrogen bonding interactions could not be realized. If you take the bottom chain and if you flip it over, so it will have an anti parallel arrangement with respect to the top chain and which becomes something like this bottom chain then all the hydrogen bonding interactions could be realized.

So, you need to go into this anti parallel orientation in order to realize all the possible hydrogen bonding interactions between adjacent chains when you have odd number of CH 2 units between your subsequent amide groups. However, if you have say nylon 5 let us say we talk a talk about a situation where you are dealing with nylon 5.

This was nylon 6 of course, so nylon 5 it is basically your NH CH 2 whole 4 CO whole n, this is nylon 5. So, you have 4. So, you have even number of CH 2 units between the amide units. So, what happens? So, you have say let us draw one layer like this NH and then you have 4, so NH CO. So, I am coming like this NH CO CH 2 CH 2 CH 2 CH 2 4 CH 2 units and then an amide unit is there NH this is the structure. So, just drawing the chain. So, NH and then again you have a CO and you have 4 CH 2 unit after just you have to draw one chain and then the next chain you can draw parallel to it.

So, I am now going to draw two parallel chains again. So, two parallel chains I am going to draw. So, one hydrogen one interaction is possible here CO and four CH 2 units 1 2 3 4 and then you have an NH hydrogen bond interaction possible here and then you have a CO, CH 2, CH 2, CH 2, CH 2 and then again you have an NH hydrogen bond interaction possible. So, you see if you have even number of carbon atoms between the amide units if you place the two chains in an in a parallel fashion you will have all the hydrogen bonding interactions satisfied unlike the case where instead of four CH 2 units you have five CH 2 units then in order to affect all the hydrogen bonding interactions you have to flip the chain one of the chains and put it in an anti parallel fashion.

So, that is the reason why if you have odd number of CH 2 units between your amide groups what you will see is that it will have a the system will have a lower melting point and percent crystallinity if you compare the system with a with a nylon which has even number of units. So, if you if you look at this situation here say if you are looking at nylon nylon 6 and if you are looking at nylon 6 6. So, basically nylon 6 6 we have a higher melting point and higher crystallinity than nylon 6 because you have even number of carbon atoms between the subsequent CO NH groups, but here you have odd number of carbon atoms. Even if you have odd number of carbon atoms a number here is even you understand that.

Say for example, you have even number of carbon atoms and the number here is odd. So, if you compare between then nylon 6 and nylon 6 6 nylon 6 6 will have higher percent crystallinity and it will have higher melting point. So, you have to keep in mind this even odd thing and the same situation will also. So, this nylon even even, so if you now consider a situation where it is nylon odd even, so this is nylon even even number right if you have nylon odd even this will also have a lower crystallinity and lower melting point then this. So, that is the point at which I wanted to arrive as far as this is concerned.

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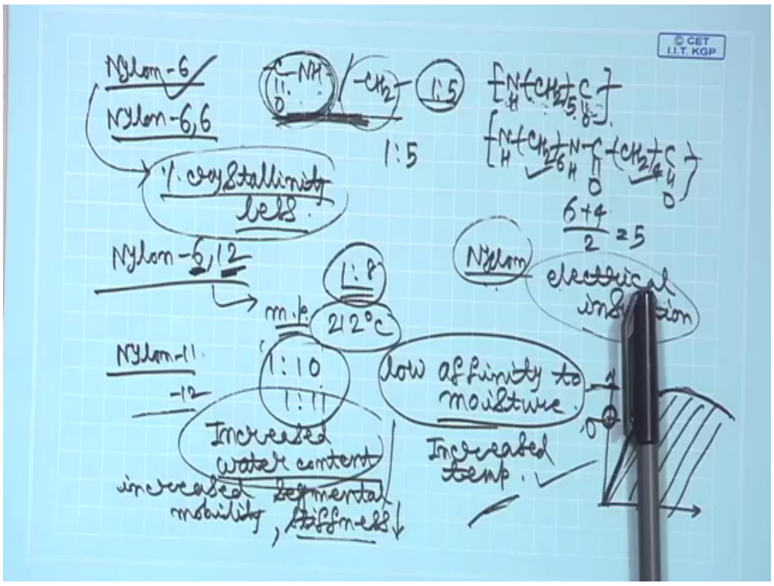

If you, so that is what I was telling if you compare nylon 6 the ratio of CO NH unit with respect to the number of CH 2 units if you compare that with say nylon 6 6. So, for nylon 6 what is the formula it is NH CH 2 whole 5 CO like this ok. So, how many carbon atoms are there between the amide units? 5 carbon atoms always. So, this ratio is 1 is to 5. For nylon 6 6 this ratio is also 1 is to 5, we told that because nylon 6 6 is NH CH 2 whole 6 NH then CO CH 2 whole 4 CO.

So, basically 6 units here and 4 units here, so it is 6 plus 4 divided by 2 on an average 5. So, for nylon 6 6 also the ratio is 1 is to 5. But because you have odd number of CH 2 units between the NH and CO groups in nylon 6 that will that will retard crystallization

crystallization. So, percent crystalline unity will be less for nylon 6 when you compare with nylon 6 6 percent crystalline is less. So, these thing also have to keep in mind how many carbon atoms are there in between other than this ratio.

So, if you look at for example, nylon 6 12, nylon 6 12 what is the average a amide to methylene group ratio. So, here you have so, what is the average ratio it is basically. So, there are 6 number of carbon atoms between NH 2 groups and there are 10 number of carbon atoms between the carbonyl groups. So, 10 plus 6 16 divided by 2, so it will be 1 is to 8 like that.

Now, if you look at nylon 6 12 it was a reasonably high melting point its around 112 degree Celsius and strength is also reasonable. So, this nylon 6 12 is an excellent compromise between nylon 6 6 and higher nylon even higher nylons say nylon 12, nylon 11 because when you go there the crystal unity is even less because there are lot of CH 2 units.

So, we will go there now little bit more say if you are looking at nylon 11 nylon eleven what is the ratio of CO NH 2 CH 2 units 1 is to 10. If you are looking at nylon 12 the ratio is 1 is to 11. So, these are more like your polyethylene like materials and typically these materials have long aliphatic chains as you see with respect to the number of amide units. So, they will also impart low affinity to moisture. So, affinity to moisture will be less this is also important things to consider because when you have this ratio when this ratio is higher when this ratio is higher; that means, the say this is 1 is to 5 here. So, every 5 CH 2 units you have once have CO NH unit on an average and here every 10 CH 2 units you have once CO NH unit.

Now, this is a polar group. So, if you have a proportion of this polar group less as you have seen in nylon 11 on nylon 12 with respect to say nylon 6 6 then what will happen is that your affinity towards moisture also will become lower. So, the more is the amount of the CO NH unit the more is the affinity towards taking up water or higher proportion of amide groups leads to higher water absorption that is what I wanted to say.

So, there will be then increased water content if you expose it to moisture and then what is the use of this particular point that I wanted to mention here, what is why we are concerned about moisture content of the material. That is because if you are you have these nylons you can use in electrical insulation, electrical insulation. So, the resistivity of this nylon is very important and what happens is that you do not want water absorption in this particular system the nylons that you are using for electrical insulation you want them to absorb very low amount of water.

So; obviously, then you can you should not use nylon 6 6 you better use nylon eleven or nylon 12 because the ratio of CO NH 2 CH 2 units is much less; that means, your l alkyl segment the proportion is much higher. So, it is much more non polar the system and. So, the system will absorb much less water under equilibrium condition. So, those things are important. So, you would rather use nylon eleven for electrical insulation than nylon 6 6 ok.

Now, also another thing I should tell you what is the effect of say for example, taking up water. So, when the material takes up lot of water, when say for example, is a higher proportion of amide groups and if it is exposed to moisture. So, where it takes up a lot of water then what will happen is that, so increased water content in the material increased water content in the material this will have the same effect as increased temperature.

So, what will happen is that same effect as increased temperature which means if you have increased water content you will have increased segmental mobility and not only that your stiffness of the material will also drops stiffness or the Young's modulus of the material will also drop. It is the same effect that you see for increased temperature. And your tensile strength will also drop, but the toughness of the material or the impact strength of the material will increase as I told before that the toughness is not the same as your strength of the material. So, if you are plotting your stress on the y axis and strain on the x axis, so let us say it goes like this initially a linear portion.

So, the slope of this curve is basically giving you Young's modulus or the stiffness. So, the material may have very high stiffness, but it can break here then the material is not very tough or impact resistant, but the material can have very high strength also because this is what determines the strength of the material this point. So, it can go like this. So, high stiffness and high strain, but you can brake here. But instead if it does not break if it goes like this deforms here, so I told before that the area under the curve tells you how much of energy it can absorb before it breaks.

So, if the material is like this then the material is tough also. So, what happens is that if it takes a lot of water then a Young's modulus will drop. So, that slope will become lower and the tensile strength also will drop so; that means, the maximum point that it reaches along with respect to the y axis will also be lowered, but it can actually take much more area under the curve it can be deformed much more because the segmental mobility of the chains also increases. So, those things you have to keep in mind.

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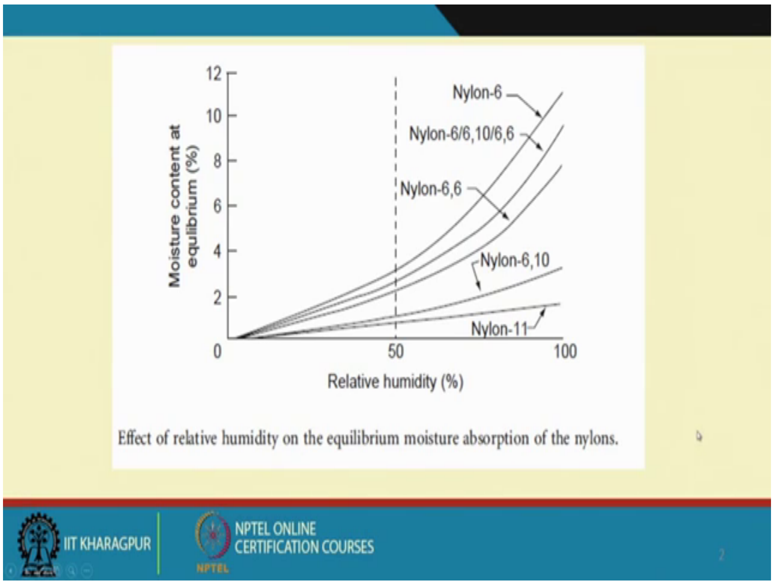

So, if you now look at the power point slide in the computer. So, here are some data here. So, if you plot the moisture content at equilibrium on the y axis and the relative humidity on the x axis. So, how much; so this is the effect ability humidity on the equilibrium moisture absorption of the nylon.

So, you see if you compare between nylon 6 6 which is somewhere here and nylon eleven which is somewhere here the equilibrium moisture content which is given by the y axis is much lower for nylon 11 than nylon 6 6 that is because the proportion of amide units is much lower in this particular situation.

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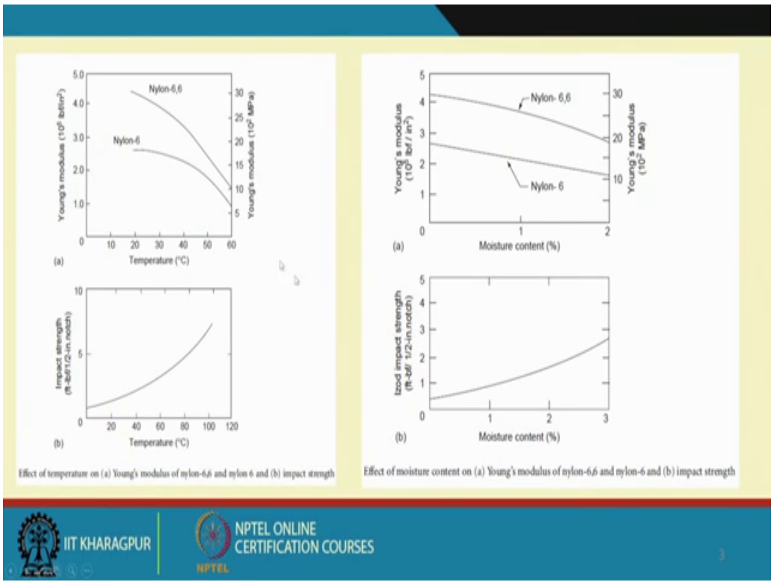

Now, if you also compare, so on the y on the on the left side is the effect of temperature on Young's modulus. So, if you see here. So, Young's modulus as we increase the temperature the nylon 6 6 and nylon 6 both for both the Young's modulus will decrease. In fact, I mean the for as low as 20 percent increase in the moisture content.

So, if you compare this with this you see Young's modulus decreases with temperature and if you also increase the moisture content parallelly let us say you are comparing these two results. You see if you increase the moisture content then also your Young's modulus drops this is something I told before that increase in moisture content will have the same effect as increase in temperature.

So, if you increase the temperature is your strength drops or Young's modulus also the Young's modulus drops and you see it starts off from a higher Young's modulus I told you that nylon 6 6 will have higher stiffness because it has more hydrogen bonding interactions because of the higher proportion of CO NH units. No, actually both have the same proportion of CO NH units, but you have odd number of CH 2 units between the amide groups here that is why the hydrogen bonding interactions is somewhat impeded with respect to this. That is why the Young's modulus starts from higher value.

And you will see that the drops here the same effect is observed when moisture content also increases. However, you see the bottom graphs these are for nylon 6 6 as you increase the temperature or as you increase the moisture content your impact strength or the toughness goes up.

So, what we will do is we will stop here and we will continue to discuss about the properties of these materials, their uses and all. So, we continue to talk about polyamides in the next class.

Until then thank you and good bye.