Textured Yarn Technology
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Lecture - 33
Solvent texturing

So, we just pick up another method and a topic which relates to texturing but Solvent texturing. So, till now what we have been talking about was thermal means, we did mention in the case of cellulosic spun yarns that is possible to use solvents also, but solvents can be used for any fibre which responds to the solvents. So, it has been used for various purposes, but we will discuss how this can also be utilised for texturing.

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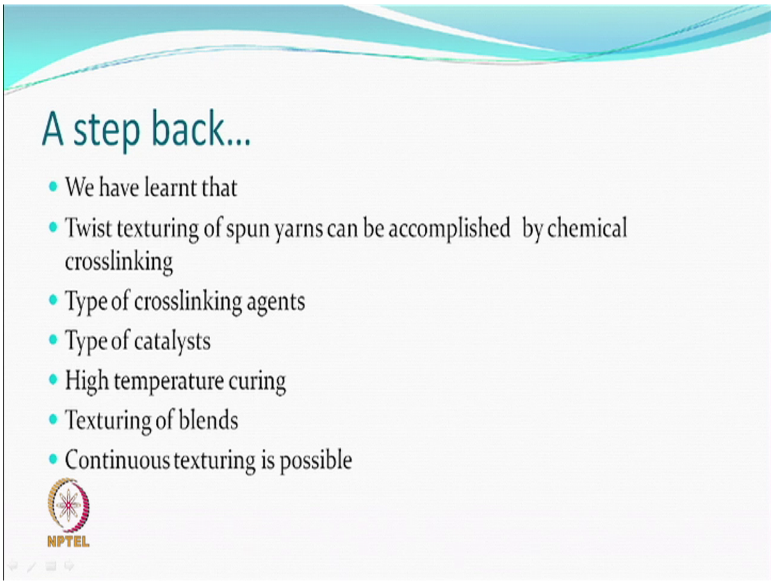

A step back…

- We have learnt that
- Twist texturing of spun yarns can be accomplished by chemical crosslinking
- Type of crosslinking agents
- Type of catalysts
- High temperature curing
- Texturing of blends
- Continuous texturing is possible

So, in the last lecture we learn that twist texturing of spun yarns can be accomplished by chemical cross linking which means you have a cross linking agent and then you do some chemical reactions under a certain temperature and time conditions which also means you have a specific type of cross linking agents which are bifunctional. And you need some catalysis so that the reaction can take place at a reasonable temperature, so, that the degradation of the fibre does not take place.

And the concept of high temperature curing; that means, which is close to the setting temperatures of synthetic fibres, one can go which also means that you go to higher temperature reduce the time. And if you use this type of a method of curing, then you can do texturing of blends as well and if time becomes shorter than continuous texturing in a false test machine is also possible. So, texturing by solvents is what we will work on. Theoretically this should be similar to what we do a thermo mechanical texturing.

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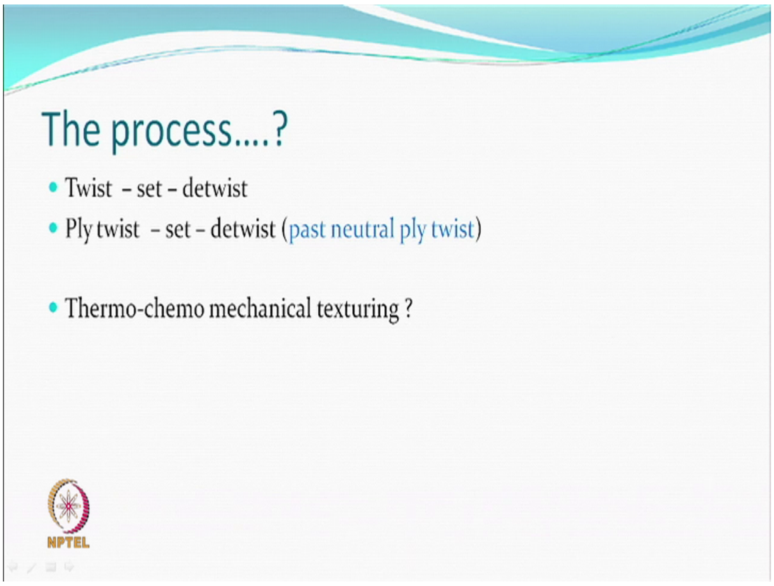

The process....?

- Twist - set - detwist
- Ply twist - set - detwist (past neutral ply twist)

- Thermo-chemo mechanical texturing ?

So, the process in general would be similar process, so you do twist set detwist this is the process people have used. Generally people has used in a batch process that you actually make a twisted yarn (Refer Time: 02:51). And then do the solvent process and then the twist after the process over, that can be done and this kind of a thing can be done only in multifilament yarn.

If you have a spun yarn and then you can use the process which is slightly modified process which is the ply twisting set and detwist as we mention last time, do if the two yarn which I have been ply twisted then you can go past the neutral ply twist and the end. But the setting will be different here and the setting can be through the solvent process.

So, this also can be considered as thermo chemo mechanical texturing, because using a solvent which is a chemical you may use the temperature higher than let us say room temperature to rapidize the process and mechanical because we are twisting detwisting, so all that is there. So, this is also in the same category of texturing processes.

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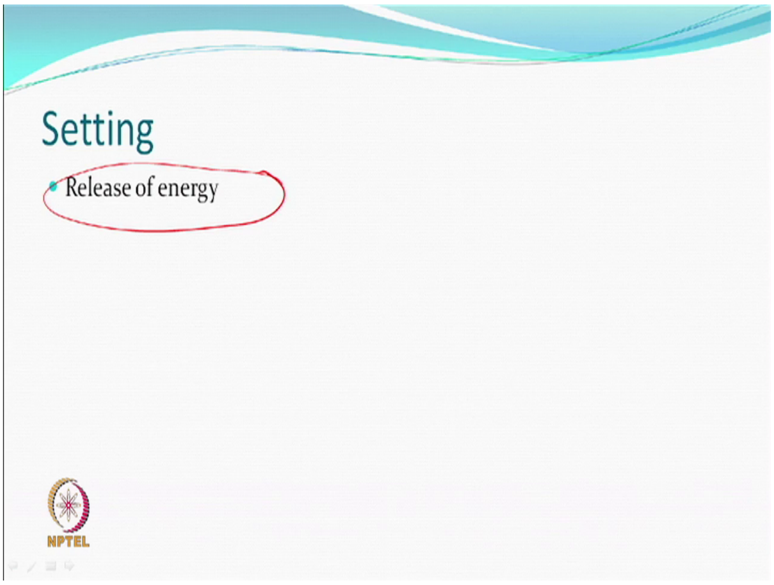

Setting

- Release of energy

So, setting which is the key component is by release of energy that is why we can say that this is just like thermo mechanical texturing which believes in release of energy. As against what we discussed in the previous lecture was that we use cross linking agent which is not setting by release of energy, does it going back to the same thing.

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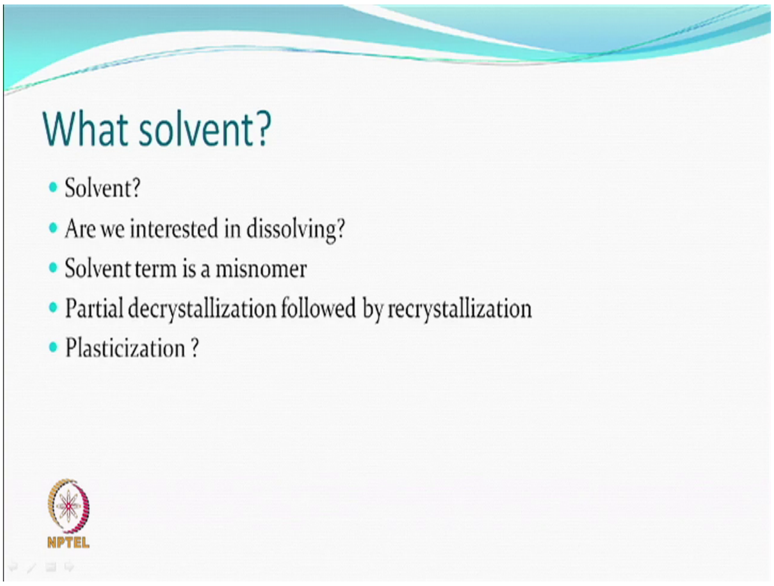

What solvent?

- Solvent?
- Are we interested in dissolving?
- Solvent term is a misnomer
- Partial decrystallization followed by recrystallization
- Plasticization ?

So, solvent: the word solvent always means it will dissolve something right, but we are not interested in dissolving the fibre it is something like we are not interested in melting the fibre in the thermo mechanical texturing. So, in some sense this term solvent is a misnomer. So, it is not dissolving the fibre actually this term has come because almost various organic compound a called solvents.

So, they are solvent for something or the other not necessary for the fibre which we want to texturize, but what will you do? Because in the earlier case we are interested in partial melting and recrystallization, here also we are interested in partial decrystallization followed by recrystallization because, if we do not do this decrystallization, the molecular change may not be able to do justice to the setting.

There is release of energy means what? Either they will disorient or they will crystallise? So, those process are common and so this will happen only when you do some decrystallization. So, these type of material is a solvent which we call are going to do decrystallization and we will be interested in recrystallization. Like you said heating and then cooling, so that also will be there.

Solvent uptake and solvent removal final product, will not have a solvent, but solvent will be required during the process. So, if these solvents are not the real solvent which dissolve then what are they? They could be considered as a plasticizers, effect as a plasticizing effect; that means, the distance between the change is being increased because of the presence of some such molecules.

So, whatever intermolecular forces were there they will be broken down because these solvent molecules will enter diffusing things, this is how anything dissolves. So, they are also going to break intermolecular forces, they will also allow relaxation and then stabilization of a new structure. So, all those three things which were being done in the thermal thermo mechanical texturing, they also will be valid here as well.

Only thing is there you are using kinetic energy to separate the molecules, here in some sense some kinetic energy maybe there because every molecule at a given temperature vibrates. So, all those vibrations become 0 only it absolute 0, otherwise there are vibrations of various kinds, but it is facilitated if a solvent molecule is available. So, it will again go between the molecules break the crystallites and obviously, partial because we do not want to lose the fiber itself.

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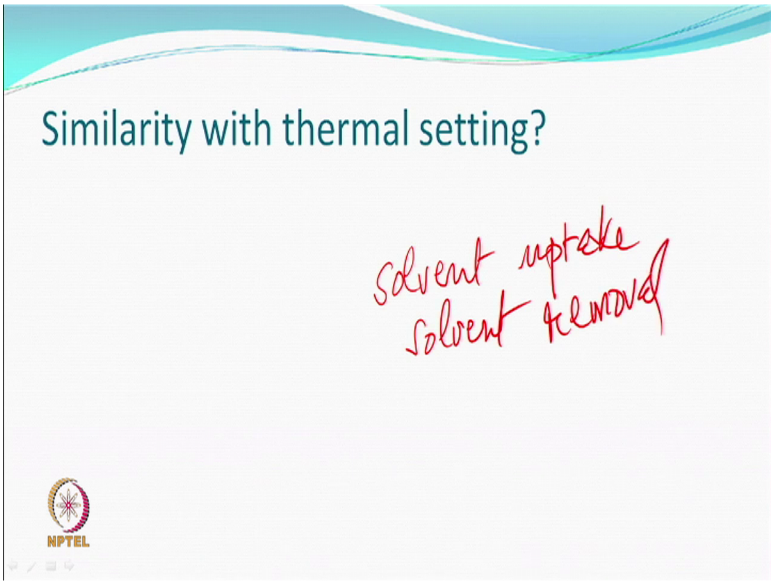

Similarity with thermal setting?

Solvent uptake
Solvent removal

So, this is the similarity that you have discussed with the thermal setting ok so partial melting, recrystallization, relaxation of molecules to the best energetically favourable configuration. So, you do heating, cooling here you have solvent uptake and solvent removal.

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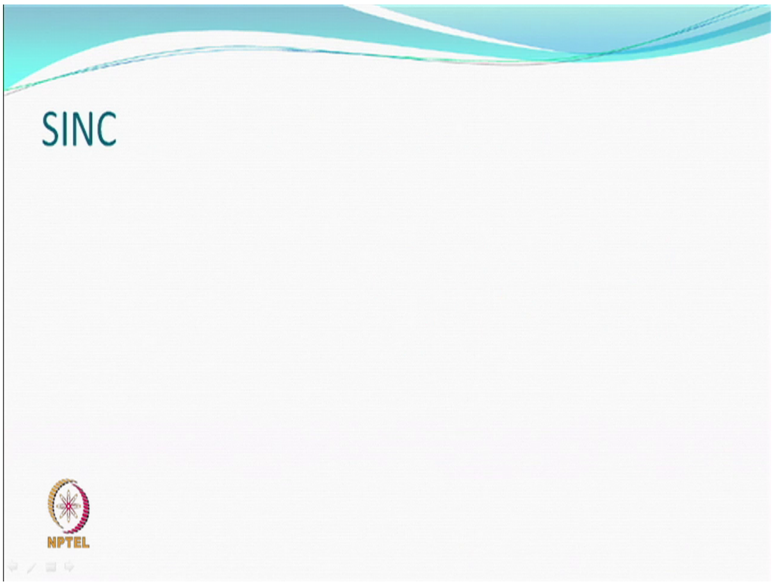

SINC

So, this type of a crystallization can be considered as a solvent induced crystallization. That crystallization was thermally induced crystallization, then you have a stress induced crystallization like you do drawing, then the crystallization take place, now this is solvent induce crystallization. Crystallization is a thermodynamic process will take place, but you are facilitating the same relaxation of molecules by adding solvent to this polymer system.

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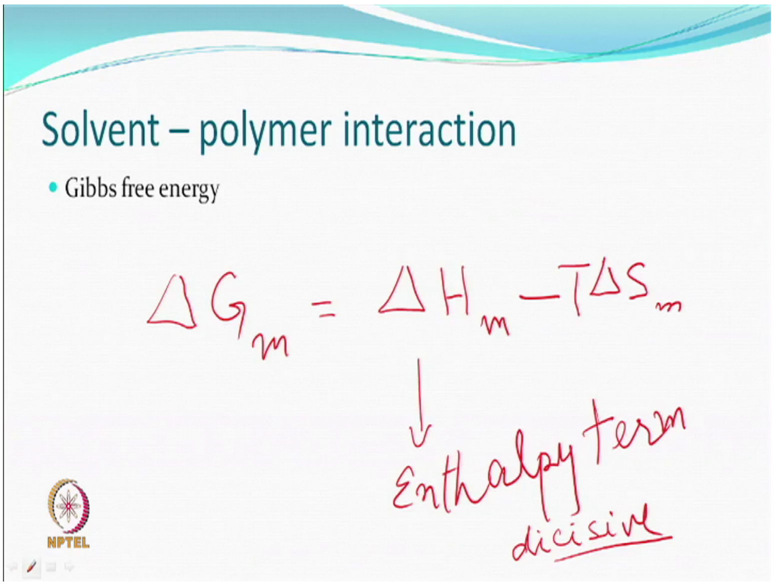

Solvent – polymer interaction

- Gibbs free energy

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

$$\Delta H_m \downarrow$$

Enthalpy term

dicisive

So, like we were talking about going to the lowest energy state, so when we mix two systems here like a delta G of mixing you have mixing two let us say two solvents are there you want to mix them. So, they will get their mix spontaneously or not spontaneously will also be dependent on this. So, when these kind of thing happens that energy that we are talking about can be also related to enthalpy of the system and it can be a determining factor as well because delta S is always going to be positive.

And therefore, the magnitude of this so called enthalpy will decide whether delta G is going to be negative or not. So, when you mix certain things you know that you mix sodium hydroxide in water there is heat which comes out, you put ammonium chloride in water it becomes cold. So, mixing itself because there is a energy involved something a molecule goes into the solution, so whether it likes to go into solution whether it not like to go into solution based on that the delta H of mixing is going to be determined.

So, in some sense whether your solvent which you are going to use is going to interact with the polymer or not like you take acetone and try to interact with polyester you may find there is hardly any interaction you can keep washing nothing, but if you take metacresol things can be different. Therefore, and that means, they are going to interact and that would depend on whether they like it or not.

Delta S increase everything likes in the world, so dissolution is going to be facilitated as well as delta S is concerned; that means, if someone can measure what is the heat of mixing, then maybe you can get an idea whether this solvent is going to really work, work better, work not so nicely right.

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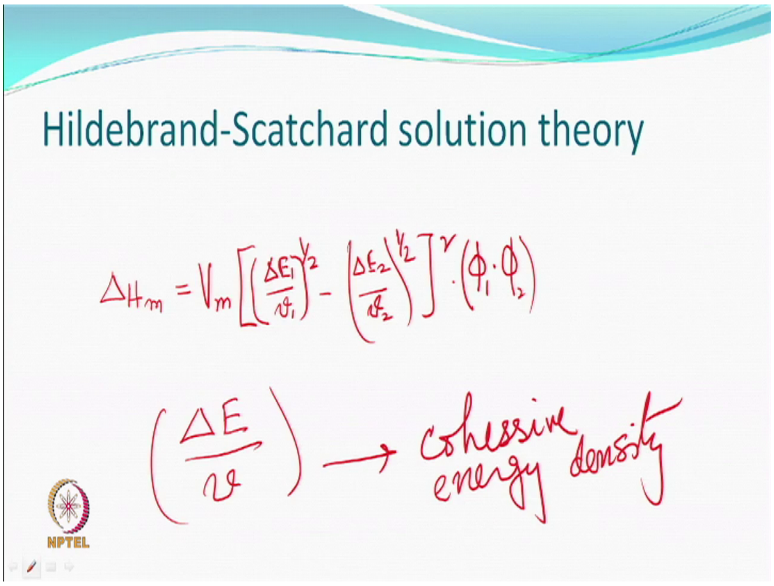

Hildebrand-Scatchard solution theory

$$\Delta H_m = V_m \left[\left(\frac{\Delta E_1}{v_1}\right)^{1/2} - \left(\frac{\Delta E_2}{v_2}\right)^{1/2} \right]^2 \cdot (\phi_1 \cdot \phi_2)$$

$$\left(\frac{\Delta E}{v}\right) \rightarrow \text{cohesive energy density}$$

So, there is this solution theory proposed by Hildebrand Scatchard with talks about that how can you calculate the heat of mixing? So, heat of mixing let say there are two solvent or a solute in a solvent, then it is related to this term which is the total volume of mixing also is related with a term called cohesive energy density. If is a more crystalline material, then it will be difficult the delta E to separate them is going to be more and the small v which is the molar volume of that material let us say a solvent it is going to moral volume it is called some moral volume.

So, it is related to the cohesive energy; that means, whether the molecules are in the crystalline form or they are amorphous already. So, if an amorphous system maybe you require less energy to separate them out and so there is one let us say solvent the other is solute. So, what is says that the cohesive energy density of these two things are related with square root of cohesive energy density and a difference of the square root of the cohesive energy density and if you square them up and multiplied by volume fraction.

So, how much is a solvent and how much solute, how much is a one solvent versus the other solvent? So, this is how these people proposed the theory based on which one can estimate the enthalpy of mixing.

Because in the previous case let us say enthalpy become 0, then is always negative. So, this term in some sense also is telling that if this cohesive energy density of the two are closed or are equal will be always difficult because there are two different molecules, so it cannot be same.

So, if it solvent then it is like energy of vaporization you know the activation energy, if is a solid thing then maybe activation in terms of the crystallite how the crystals will separate out right and so this is what they proposed.

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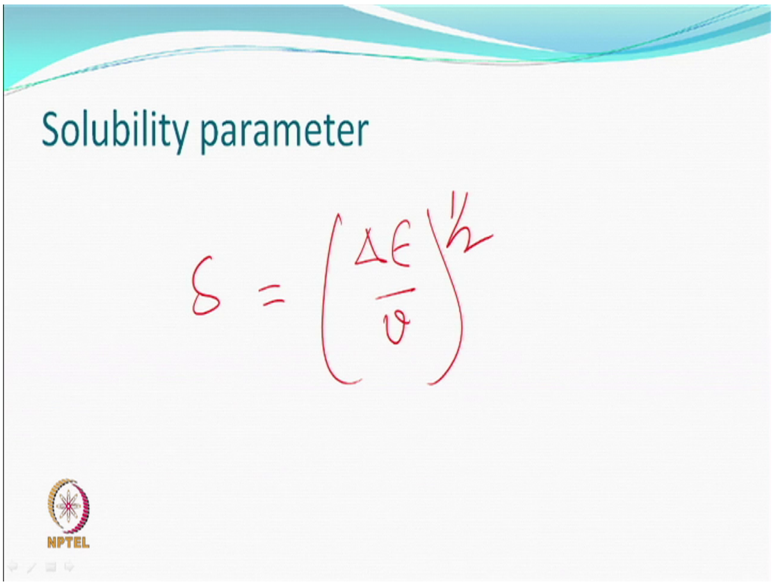

Solubility parameter

$$\delta = \left(\frac{\Delta E}{v}\right)^{1/2}$$

An incidentally they also then this particular term that the square of this is called the solubility parameter whether a polymer will dissolve in a solvent or not may not be governed only by a solubility parameter.

But it is a good indicator considering the previous equation if the solubility parameters through systems are similar quite near each other, then it may be possible that dissolution may by spontaneous right. Although we are not interested in dissolving with the mixing system, so we can always call some interaction.

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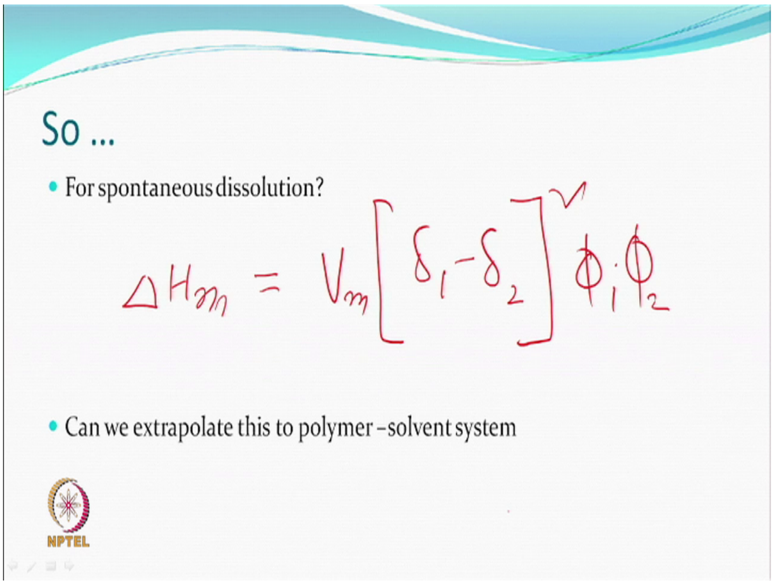

So ...

- For spontaneous dissolution?

$$\Delta H_m = V_m\left[\delta_1 - \delta_2\right]^2 \phi_1 \phi_2$$

- Can we extrapolate this to polymer -solvent system

So, for a spontaneous dissolution we may be requiring that delta 1 minus delta 2 is as close to 0 as possible right, if it is there then delta H m will be 0 and the interaction will take place better. Now, you extrapolate this hypothesis for polymer solvent solute versus solvent, solvent versus solvent is a very different situation, then polymer; polymer is a long molecule. And if you look at our polymer like textile, then you have a semi crystalline material.

So, diffusion in the amorphous region can take place easily relatively will take more time to get into that and so polymer this thing maybe not be directly applicable, but still if solubility parameters of solvents and solubility parameters of the polymers are available, then you can make a right some guess let us try this rather than try with this.

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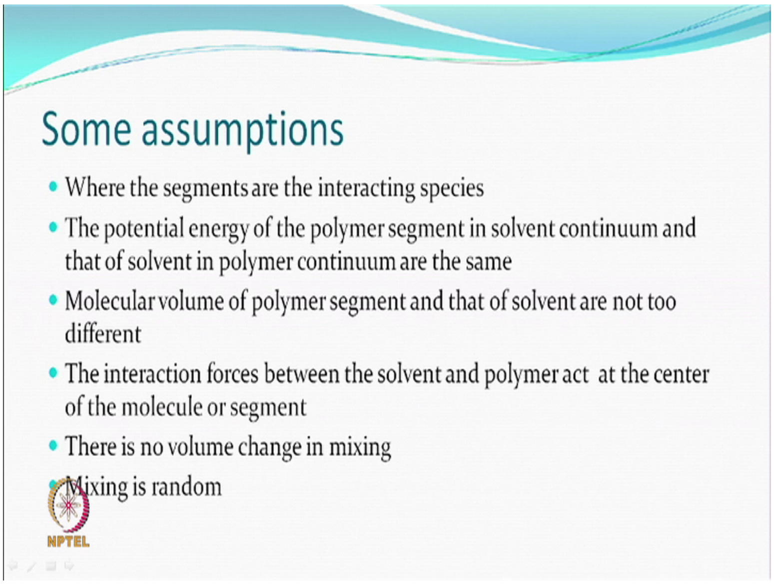

Some assumptions

- Where the segments are the interacting species
- The potential energy of the polymer segment in solvent continuum and that of solvent in polymer continuum are the same
- Molecular volume of polymer segment and that of solvent are not too different
- The interaction forces between the solvent and polymer act at the center of the molecule or segment
- There is no volume change in mixing
- Mixing is random

There are assumptions when you take polymer and a solvent and we use even this Hildebrand Scatchard equation that the assumptions, one of the assumption is that it is going to be quite difficult for somebody to say what is the centre of a molecule of a polymer.

So, a say well there maybe some segments which maybe moving like for example, we say segmental mobility, so it is not the whole polymer molecule is vibrating between sub segment which have free are vibrating. So, this is one assumption that if this kind of a thing happens whether you are not discussing the whole polymer then it will be more complex.

You also say that the potential energy this is interesting is; obviously, like potential energy of the polymer segment in this solvent continuum. So, there is a whole over solvent and there is this polymer potential energy the polymer segment and the reverse of it that the solvent in the polymer continuum, lot of polymer amorphous using a solvent is going there.

So, whether it is inside solvent is inside the polymer; polymer is inside the solvent, this potential is approximately same. Otherwise what will happen is the solvent would not go inside because like let us say the potential energy increases, then why the solvent will go in? So, this is an assumption, that the molecular volume of the polymer segment and that of the solvent are not two different, so that segment which is moving, so that will be quite difficult to ensure this.

That the interaction forces between the two after all interaction means if suppose it was a Van der Waal force is been formed it is a polar polar bonds are being formed and they are the one which have to broken, so there is an interaction; so, one molecule going and replacing the other part of the thing.

So, the forces which exist between the solvent molecule and the polymer segment part, it is assumed that these forces will be acting at some centre of the molecule there is a molecule or a segment which is the centre that the mass. And there is a mass of the centre of that molecule of solvent they act at the centre to centre otherwise some of things may be difficult.

And this is interesting that there is no volume change in a mixing is like when you add sugar to water the sugar good amount of sugar is that dissolve, but you do not really sees change in the total volume. So, this is also part of an assumption which may be true may not be true.

So, if this is what their and the mixing is random like so you are doing agitation or whatever you doing said it is not that only one part is dissolving first then that next part goes. So, anywhere wherever solvent can go resolution and interaction will start there is kind of assumptions. So, within that and the parameter that we have some conclusions could be drawn.

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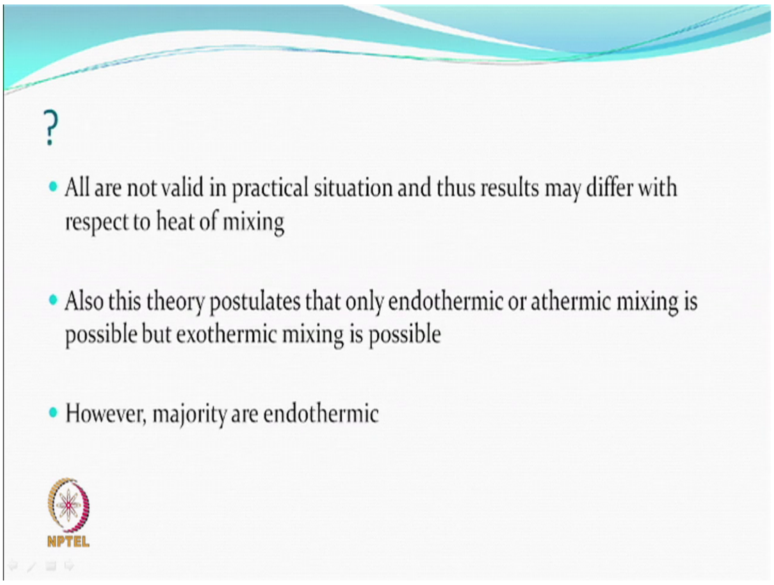

?

- All are not valid in practical situation and thus results may differ with respect to heat of mixing
- Also this theory postulates that only endothermic or athermic mixing is possible but exothermic mixing is possible
- However, majority are endothermic

So, this is true that all these are not going to be valid in a practical situation and therefore, the results which we obtained by the equation may differ from the actual measurement that you may do. Also this particular theory postulates that either the reactions of the dissolution and mixing process is either endothermic or is a thermic, if it is 0 then a thermic, if it is some positive then endothermic process.

But there is a possibility that you can have an exothermic mixing also, with this equation does not talk about which would mean it takes square, so this value is always 0 or a positive, but if negative thing is there it cannot; obviously, explain this part of it. But it also is the fact that majority of polymer solvent interactions are actually endothermic. So, to some extent you may be able to gets results which are all right. So, we just discuss some of the experiments people did.

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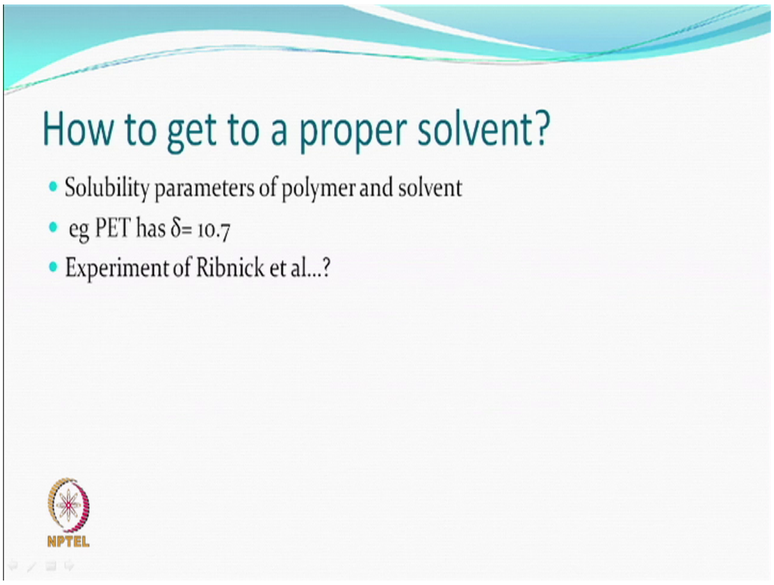

How to get to a proper solvent?

- Solubility parameters of polymer and solvent
- eg PET has δ= 10.7
- Experiment of Ribnick et al...?

So, one interesting results which people talked about was that polyester has a solubility parameter about 10.7. So, Ribnick and co-workers at an extensive work on trying to find out which solvent is going to work and which solvent or going to based on solubility parameter itself.

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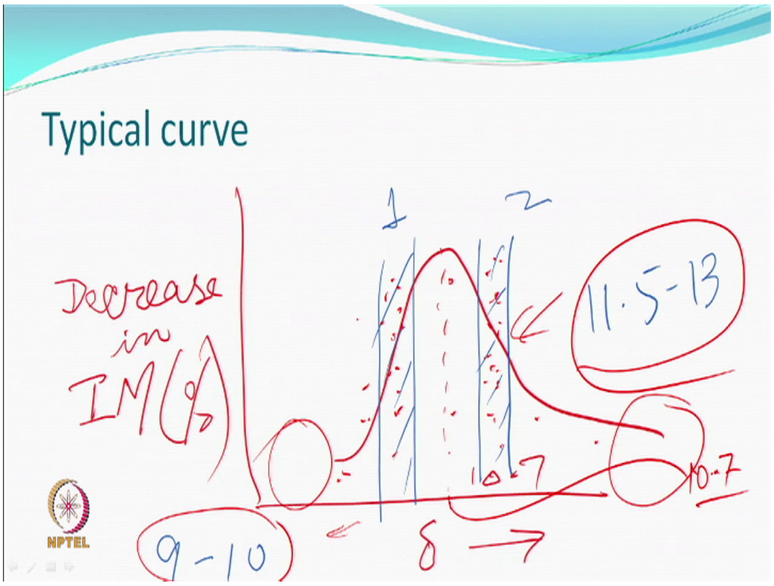

Typical curve

Polyester was very interesting case to begin with and what they found was that if you have lot of solvents they took lot of solvents somewhere having solubility parameter here, but a large number of here also, somewhere here, somewhere here, but there was a thing and some may have been here as well right some solvent.

And what they observed was that majority the solvents which were considered as nice solvents, they appeared in some bands which are if you just draw a curve like this normally you would expect wherever this matches, it should be the maximum interaction. But they found that their interactions which happened nicely are actually those solvents line two bands. And the typical case there was, so this is the value 10.7, the typical case was acetone; acetone is very close to 10.7, but acetone does not affect polyester.

So, in some sense there was some speculation as to what has happened? So theory is completely failed, but they found that know that on both sides there is some range let us say between 9 to 10 and between 11 to 11.5 to 13 this band, these solvent so very active. And so after a bit of a study they could understand that polyester has two segments; one is aliphatic segment which is because the glycol, other is the aromatic segment because of phthalic acid.

So, these segments vibrate and interact in different ways and so polyester by itself on an average may have some value, but these segments have different way to interact because they are different as a chemistries part. Because when somebody says that only the segment of a molecule is going to work, so which segment is actually interacting. So, it has got two different segments which are interesting segment.

So, they found that solvents which are lying on this left side are more interacting with the aromatic segment, solvent on this side interact with the aliphatic segment. So, there is complexity in trying to explain it is very easy when you have simple molecules of solute and a solvent or two solvents mixing can be very easily explained and why may will get good results. When you take talk about polymer it may not really happen in that way, but at least it still is near.

So, the solvent which are very far off are not good obviously, but exactly in the centre also they are not one or two solvents we are not really working because they were either happy with the aliphatic part of the polyester nor the aromatic part of the polyester therefore, it is segmental stuff. And what they had measured about solubility and decrease in the initial modulus of the material fibre is there, so if solvent is dying plasticizing it is entering. So, the module is it will be compliable material, so you measure the modulus.

So, you do a stress strain curve and then take the modulus at every point at different solvents; obviously, treated of certain fix time and then you plot this curve. So, it is a complex experiment and at the end you draw a some conclusion, but is a very interesting observation which was considered by these workers.

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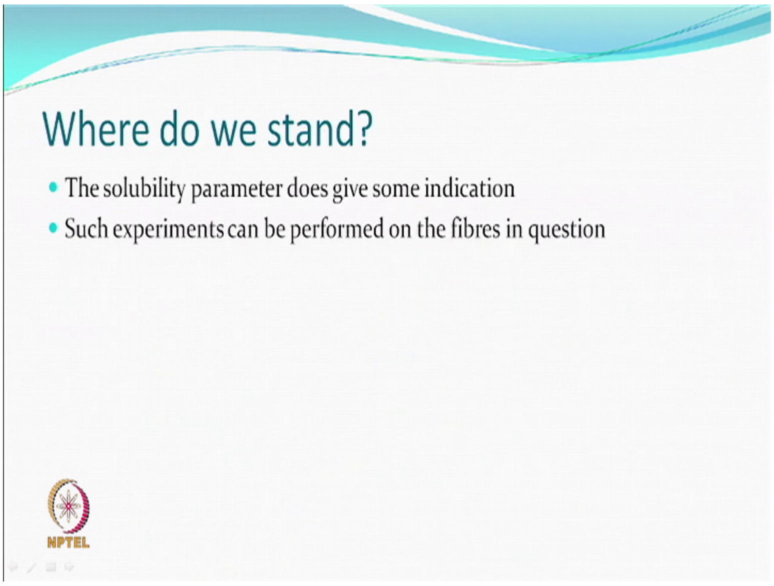

Where do we stand?

- The solubility parameter does give some indication
- Such experiments can be performed on the fibres in question

So, what you stand is that the solubility parameter does give some indication that the solvent is going to be more interactive or not. And such performance such experiments can be performed on various fibre that somebody is interested in and then think of going for texturizing.

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Shrinkage studies

- Thermal
- Solvent

One more study was done which was not measuring the solubility parameter, but directly measuring the effect of solvent. So, there are two things which happen with solvent is it can either help in crystallization. So, you measured how much crystallization is taking place it is a long process. So, you do some treatment then go and measure the crystalline development crystalline development, then say well this is acting more or reverse of it.

So, our material which is called the textile it shrinks when you heat and it also shrinks when you put in a solvent. So, if you take a fibre, but a length and then put it in some solvent which interact which you certainly find the fibre shrinks right. So, if and that it is dependent on the interaction that happened. So, some shrink; shrink studies and shrinkage of the fibre filament which takes place in a certain solvent could also be a quick indicator, whether it is going to work or not work.

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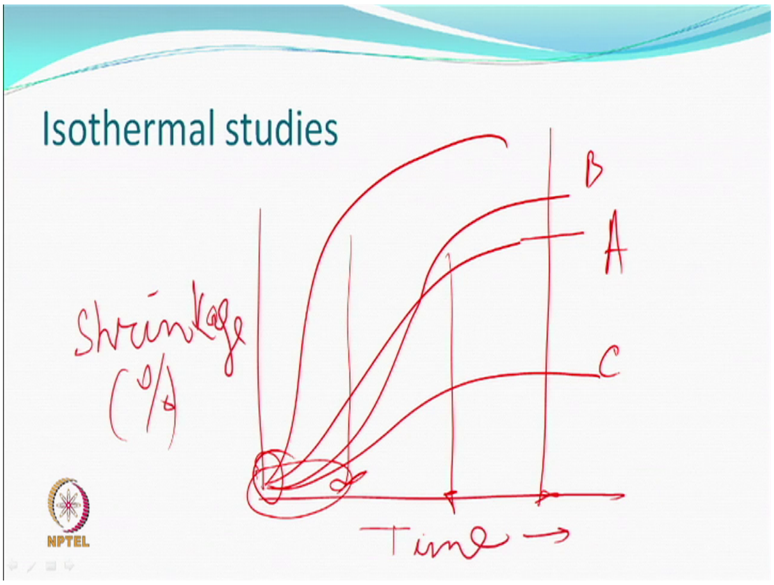

Isothermal studies

Some studies which will call the isothermal study that you have a fixed temperature at which you are observing the shrinkage of fibre with time, nothing is instantaneous, so it is not that just you put there inside the thing in suddenly everything will shrink it will take time. And why would it take time? Because initially solvent must diffuse inside only then changes in molecular orientation will take place.

So, invariably some curves which you draw with respect to time maybe like this and after sometime you may find there is an equilibrium shrinkage which has been obtained at a given temperature ok, if you change the temperature the curve will be different. So, it is a isothermal study that is why we said can be a thermo chemo mechanical texturing because the same solvent you work at a higher temperature if you can then maybe systems can work faster. So, the rate of shrinkage can change within the same solvent as you change the temperature or you have a solvent A and you have a solvent B which may work like this may work like this.

So, some can go like this, so very less time here, so it is like a sigmoidal curve. So, this shows if this is longer means the rate the induction time is more, so first diffusion takes place and then it will say. So, when you say I want to put it for a certain time where the setting should take place this type of an equilibrium must be achieved. So, you can say well this can go to of this time or this can go up to this time this can be you can complete accomplish your processes earlier, so it is like the same kind of thing.

So, same solvent or different solvent at different temperatures can give you these things and so you will have an idea it is a quicker solvent, so I get work on this. It takes C for example, takes lot of time and also shrinkage is not very high which also means that the intermolecular changes in orientation or crystallization may not be so fast or may not be so much without solubility parameter.

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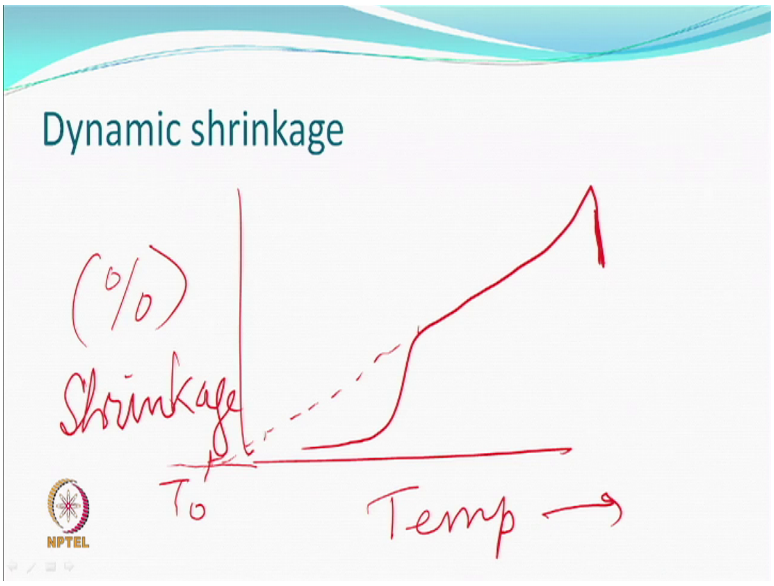

Dynamic shrinkage

Then other shrinkage test was done where it is not isothermal, but you are increasing the temperature. So, you have a fibre which is hanging in a solvent, but a certain weight your measuring shrinkage. So, start from a lower temperature, so you find that well the shrinkage is not very high to begin with at a certain temperature suddenly shrinkage starts, after certain temperature the curve become slow which means for that temperature equilibrium shrinkage approximately coming.

So, here this temperature is rising like you have a DSC you see a rate of heating you can set of the rate of heating, similarly you can have a cell where the fibre is hanging and the temperature of the solvent in the cell is increasing let us say at a constant rate right. So, time is also part of this whole game right, so rate of increase of temperature is there. So, you get a curve like this till at a temperature it becomes all most it just breaks because totally getting into the resolution part of it, so you can get this curve. From this curve they could relate one interesting thing, that is if you extrapolate this part of the curve and go to some point which we call it T 0 temperature for 0 shrinkage.

So, is not absolute 0 is some temperature where in this solvent there will be no shrinkage to find that out right, so if you go there no shrinkage, so; obviously, you will not work there. But what they correlated that this temperature which is T 0 could be co relative the glass transition temperature of the polymer solvent system. Like you say the when you have a nylon in a dry state t g 60 65 you put in water the t g becomes below room temperature ; that means, the glass transition temperature is dependent on the interaction that take place on the case of polyester in water t g does not change.

So, in some sense this is also indicating that polymer solvent are going to interact right. So, if this T 0 becomes higher or T 0 is lower, if T 0 is minus think the new you quit sure at room temperature also you can do texturing. If the T 0 is coming to let us say 40 degree, so definitely you cannot do anything below 40 degree you have to go above 40 degree to do certain things.

Therefore, we say it is a combination of time and temperature and a solvent polymer together this particular curve is a very useful curve coming think of it know they very useful curve you just put a pole filament in a solvent where you can change the thing draw this curve. And then you suddenly get another parameter which is quite indicative whether it is going to be interacting higher less and where and what temperature you should use to get effective let us say texturing which means decrystallization recrystallization of it.

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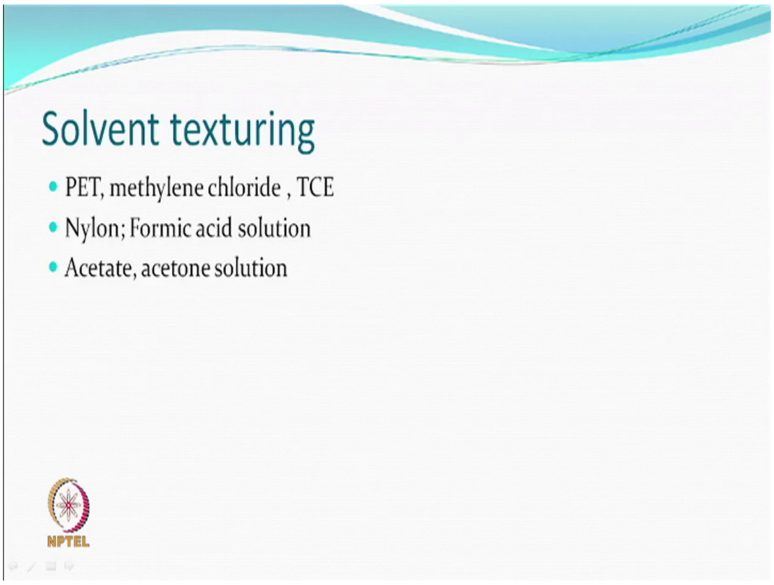

Solvent texturing

- PET, methylene chloride , TCE
- Nylon; Formic acid solution
- Acetate, acetone solution

So, some people did solvent texturing how as I said take the filament do the twisting take the (Refer Time: 32:53) put it in a solvent for a certain period of time, remove the solvent either by drawing or by a non solvent and then untwist and you get beautiful effects. But obviously, the time required here is not 0.1 second, 0.2 second time required could be in minutes or seconds, but this time as we know can be changed if we increase the temperature.

For example, polyester with two solvents; one is called methylene chloride this solvent as a boiling point which is low right. So, you cannot go at a temperature is higher than the boiling point. So, you will be working at a lower temperature, rate of setting would be lower interacting it is not that it is interacting interactive, but at low. So, all experiments will have to be done at low TCE which it trichloroethylene its boring point is high, it also interacts.

So, you can actually say we will do this you know setting may be at 80 degrees, so if you do at 80 degrees times can reduce. So, you can come from minutes to seconds, so that is what is there. So, people have worked with methyl chloride on polyester, people have worked with tetrachloro ethylene ethane; tetrachloro ethane all right. Nylon formic acid you know resolves nylons right, but you do not use formic acid, but you use solutions of formic acid in water.

So, if you reduce the concentration did not resolve, the same solvent if you reduce the concentration to act like a plasticizer and so you will optimise what is what concentration? So, acetate with acetone or also methylene chloride in a different concentration have been used acetate for example, we said it cannot be texturize with thermo mechanical means because the tensile strength goes down rapidly when the temperature and crystallization occur.

So, in such cases you have a solvent assisted texturing you can go to higher temperature whatever the they say the solvent can go or just below that and the temperature will be much lower for doing this compared to if there were no solvent. So, such material like we say acrylic fibre cannot be made spun, so you do solution spanning.

So, if you say acetate fibre cannot be thermally thermo mechanically textured, but you can do solvent assisted thermo mechanical, thermo chemo mechanical then can be done without degradation time is sorry. So, people obviously, have worked on the blend also in a solvent itself.

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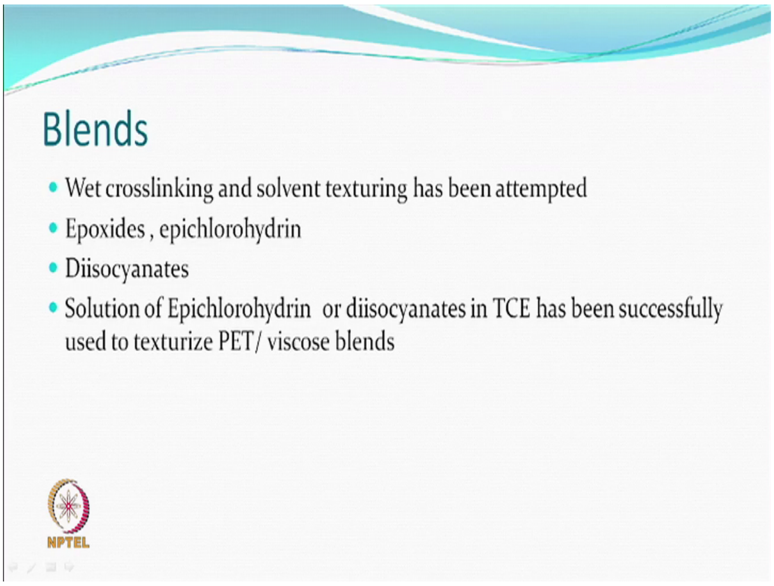

Blends

- Wet crosslinking and solvent texturing has been attempted
- Epoxides , epichlorohydrin
- Diisocyanates
- Solution of Epichlorohydrin or diisocyanates in TCE has been successfully used to texturize PET/ viscose blends

What is there is a blend, so how do we work round? One solvent for one part of the fibre and the other solvent for the other part of the fibre may be different like polyester viscose they different kind of solvents and there is a blend. How do you work? One work that was done that if you use a solvent where a cross linking agent can be dissolved and conditions are created in such a manner that cross link takes place in the wet state called the wet cross linking not a dry cross linking like in the last lecture we discuss.

So, in a wet state some of the agents can make covalent cross link. So, let say epoxide one of the example is the epichlorohydrin it can make cross link in a wet state. And what solvent? Diisocyanate also we said can diisocyanate does not like water alright, but it can be dissolved in organic solvent.

So, if there is a organic solvent which interact let us say on one part of the blend, let say polyester. Epichlorohydrin in that solvent if done correctly will do a cross linking, so you can have a simultaneously cross linking going on and the synthetic part of the fiber acting as because the solvent polymer interaction and in one go you may be able to texturize. So, texturing of polyesters go blends have been attempted like this as well.

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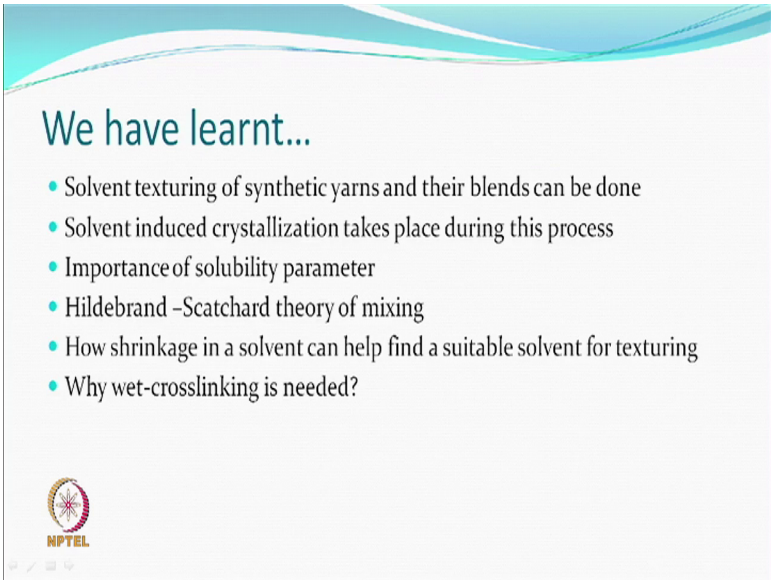

We have learnt...

- Solvent texturing of synthetic yarns and their blends can be done
- Solvent induced crystallization takes place during this process
- Importance of solubility parameter
- Hildebrand -Scatchard theory of mixing
- How shrinkage in a solvent can help find a suitable solvent for texturing
- Why wet-crosslinking is needed?

So, we stop here, so solvent texturing of synthetic yarns and there blends can be done. Solvent induced crystallization takes place; here we can just mention somebody ask a question does the crystallisation take place during solvent up take or solvent removal? Whether the crystallisation will take place during solvent up take or solvent removal? Is not necessary; is exactly whether they crystallization take place during heating or during cooling? Main thing is when the solvent is there molecule can move around right. So, they will go to a new configuration when it is possible to go, if you completely remove then they cannot obviously.

But yes again you will get a curve like you have the rate of crystallization curve in a solvent also which will mean during solvent uptake decrystallization will take place and recrystallization can also take place. And of course, finally, when you remove the solvent then it is freezing in position like you are solidifying or stabilizing structures, now motions will not take place so much because solvent have been removed from the molecules.

So, solubility parameter which we go went through can also give some idea and the Hildebrand Scatchard theory of mixing talks about the enthalpy measurement and shrinkage in the solvent can help to find a suitable solvent for texturing. And we also understood why wet cross linking may be needed right. If you are already wet cross linking also could be done in a solvent there we are.

Thank you.