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Lecture-02 Wrinkle Resistant Finishing

Welcome back to our second lecture on textile finishing, let us see what we had done in the last lecture.

(Refer Slide Time: 00:28)



We had learnt that there are several unit operations in textile chemical processing and starting with singeing, desizing, dyeing etc, finishing is one of the final unit operation. This operation adds tremendous value to the product you also learn normally what could be the objectives of finishing. One of the interesting objective here is that it does enhance the aesthetics also another important role and objective of finishing is to improve the functional performance of textiles.

So, to achieve this there are number of finishing treatments which can be categorized into mechanical or chemical. The mechanical finishing processes could generally we dependent on the machine itself, well the chemical finishing processes would be more dependent on the

chemical structure of the compound of course as we said that machines would always be required to do any finishing treatment.

But the emphasis in a chemical finishing process is the chemistry of the chemical compound that is being used in the mechanical it is only the machine, machine part which is the most important agent to affect the change in the functioning or aesthetics, let us go further.

(Refer Slide Time: 02:27)



So today we will concentrate little more on wrinkle resistant finishes and learn a few things about it, what do we learn.

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We will first understand the need, why it happens and why we should do it other is do we have some strategies to impart wrinkle resistant finishes and what are those strategies. And some relevant finishing agents also that can help this cause will also be discussed today.

(Refer Slide Time: 03:14)



So before we take up the topic let us look at some of the fabrics alright.

(Refer Slide Time: 03:22)



This is a fabric of cotton right this is a cotton fabric at the movement it looks good. But if I press it you can see the creases, you see the creases they are more clear now. We start with a fabric which look pretty plain, nice looking and now suddenly it has so many creases, this so many creases you can clearly see, see that. (Refer Slide Time: 03:54)



It was is more clear now yeah, so look at what happens to the cotton fabric. The moment you compress it in your fist bended crease it, the more you do it the more creases you can see. I am sure you may not like to wear this type of a material or a garment for that matter.

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We look at another fabric which is this fabric alright. This is the fabric which is woolen fabric and if we try to do the same thing and see what happens. This is a fabric which does not have crease I try to do similar thing and then look at this it has less creases of course I can still do more it may see. But compare this fabric with what we saw on this, you see the difference, did you see the difference.

This is the difference that we have talking about and that is why we may say we may like to have some kind of a treatment. Let us look at another fabric, this is polyester which is the polyethylene terephthalate and this if we try to do the same operation here. There are some creases you can see but look at this that means some fabrics because of the chemistry being different this is wool, this is polyester.

And let us see another fabric which is nylon fabric, it already have some creases because the way I handle it. But if we do further this you may still find that the situation does not change much

alright, look at this. So the cotton among these is creasing but the synthetic ones crease less but let us look at another natural fiber fabric which is a silk based fabric.

This fabric has not been degummed properly anyway it has micro creases you can see them. And if you do something like this, this also develops more creases than let us say a fabric which we first saw is the wool fabric. That means based on the chemistry or maybe the treatment that may you were like to give some of these fabrics would crease more or less and if they crease naturally more what are we going to do about it alright.

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This is what we may like to see, so what have we learnt that cotton creases the most. So, let us see why does this happen, is there any relation with bending as crease formation, why. (Refer Slide Time: 08:23)



Because we just took and crushed it, so there were more creases, so possibly there may be a relation. One of the interesting thing is whenever you bend anything in this case may be a fibre, so you will always get a compression zone and an extension zone. So, the outer side obviously is getting extended inner portion of the bend is getting compressed. And therefore there must be some strain and stresses getting developed in this region.

Because mechanically you are doing when we try to squeeze something like this obviously a bending is happening. And in this bending process some portion are getting on the outer side and therefore they are getting extended some which are inside this bending area are going to be compressed. Now this is the way we believe every time we do this crush type of a thing or any other such process.

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Let us see interestingly what do we have let us say this is the paper alright. This is the paper and this paper I have bent and therefore there is an extension and there is a compression zone alright. Now this paper is a thin from this side the thickness the paper is less, this is there like for example, in this case you had external portion which you can see and the internal portion also which you can see.

If I just leave this it becomes still the same plain paper, there are no it recovers, so bending is ok but after bending it recovers, so it is a different property altogether. That means we are interested in bending of course whenever we do something we sit down somewhere some crease can be formed, what will be important is does it come back, it is coming back no creases. But if suppose I make the bend very sharp.

And if I do this now it does not recover that, that crease has been formed you see that crease now, the crease is formed now, you do it further another crease is formed. And if you do like this well this is it, now it is not recovering, so why does it crease and why does it recover.

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So let us see a molecule like a cellulose which is in the cotton also in the paper do you see that the cotton also creases recovery is bad, the paper also creases recovery is bad. So we say well the both are made of cellulose but that is one part only, cellulose you see this molecule this is the repeat unit of the cellulose which is called the cellobiose, cellobiose unit. So what it has a, it has got a primary hydroxyl group and secondary hydroxyl groups.

So, we probably know already that the primary hydroxyl group reactivity will be higher than the secondary hydroxyl group reactivity that is one part.

(Refer Slide Time: 13:06)



But then what else, what else is that the molecules in the cellulosic fibres other than the structure that we have seen also make secondary bonds, what are the secondary bonds. The secondary bonds are hydrogen bonds, a large number of hydrogen bonds can be formed because you got so many hydroxyl groups. And these bonds are weak bonds alright they are weak bonds, so what happen when they have weak bonds.

During this process of crease formation these bonds may break also, why these hydrogen bonds are weak bonds. Because the energy required to break them is less, let say between the hydrogen bonds can be formed between the hydrogen of ion oxygen and oxygen and oxygen like in water hydroxyl group and oxygen like in water itself and so some of these things. Although the energy level will vary even hydrogen bond energy level vary depending upon sometime there called a strong hydrogen bonds to weak hydrogen bonds.

But generally they are secondary and relatively weak but in the cotton cellulosic fibres the intensity of these bonds is very high, the so many hydroxyl groups and there is so much of a possibility of making so many such bonds. And that is the reason why cellulose by itself is quite strong the cotton fibre is pretty strong. Although they are weak one but if they are intensely available to do this to share the load and so the strengths etc are pretty high.

However in the case of bending things can happen differently we do have crystalline structures in the cellulosic fibres the cellulosic fibres let us say cotton for example has higher crystalline structure compare to this course which is less crystalline structure they are cellulosic fibres. So, do you see here is the possibility of formation of hydrogen bonds everywhere, so between the thing which we have intermolecular hydrogen bonding and sometime intramolecular hydrogen bonding also is possible see that.

So many possibilities of making hydrogen bond, the moment they are near each other the molecule some of this bonding can happen. So as such the fibres are good we do not have too much of issue with the tensile property particularly dry tenacity if you talk about but we must remember these are secondary bonds and they are weak bonds.

(Refer Slide Time: 16:18)



You see this structure which is got some bonds which are these called cystine disulfide bonds. Now these bonds are covalently linked the carbon to sulfur, sulfur to sulfur and sulfur to carbon they are covalently linked. So, they are covalent bonds where do we see them we will see them in wool. Wool is a protein fibre as we said last time also that the molecules are also called polypeptides.

So, peptide that mean the any kind of a protein is formed by various amino acids which are essentially alpha amino acids, so you get a polypeptide link. But interestingly a wool has other

bonds also it has hydrogen bond possibility as we mention it has got the possibility of electrovalent bond at different pH levels it has obviously a possibility of hydrophobic bonds. On top of it, it also molecule has helical structure all of that make this material after creasing this material can recover.

(Refer Slide Time: 18:46)



They make this material crease resistant.

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But silk it has the possibility of all hydrogen bond formation, electrovalent bond formation, it has the possibility of hydrophobic bond formation but has no possibility of having covalent bond. So you the chemical structure is different, the behavior is also different, different fibres, so what is the interesting thing which is coming out.

(Refer Slide Time: 19:37)



One is we are more interested in recovery from any wrinkles that have been formed, so there is a term which is used which is called resiliency. Resiliency as 2 components one is resistance to deformation other is recovery from the deformation. Now a textile fabric can resist of course but the forces like this are too harsh and too strong for it to resist.

(Refer Slide Time: 20:15)



But it can recover, if it recovers then we will find that the crease visibility becomes less. Because it recovered from the crease, crease can be found because mechanical forces could be strong. But recovery is the one which we are going to be more concerned about.

(Refer Slide Time: 20:45)



So, what was different in wool, silk and cotton intermolecular crosslinking so the fibre which is naturally covalently crosslinked is wool right. If such type of a covalent crosslinking is not available then what happens, then we will not be able to recover not as nicely remember.

(Refer Slide Time: 21:27)



This paper is recovering from bending but does not recover from sharp bending because something must have change, why it was recovering, why is it recovering. It is recovering because when we bend some stresses are imparted strain energy because expansion and compression happen is being stored. If the strain energy is being stored then obviously by opening it releases the strain energy, rebend again there is strain energy stored in this whole process.

Here the molecules are getting to change their position with they do not like and so when you release the stress they come back. But when you do this they are not able to recover because at that point it such kind of a sharp creasing something has happened, what is that something some of the intermolecular bonds have broken. The primary bond which is a covalent bond of the main molecule that does not change, that does not break by this process, what is broken is intermolecular bonding that was in these case was hydrogen bond which is weak and so you can break it alright.

But wool has covalent bonds intermolecular covalent bonds therefore this becomes an interesting part if covalent bonds are available then the strain energy get stored the bonds gets stressed but they do not break. And so if then the force are released they would like to recover by releasing that energy which has been stored during bending process, that is the way we look at it.

So, that is are wool, if naturally this crosslinks are not available then we have to create them. So, we have got a principle now if we can create crosslinks intermolecular crosslinks then we would have an opportunity to see that the recovery is becoming better of course resistance also will be increased. But we have more interested in recovery so what do we need, we need a crosslinking agent now.

So, the chemistry of a compound also equally important there should be crosslinking agents which can react with the molecules of the fibre whichever the molecule which we are interested in to create covalent bonds.

(Refer Slide Time: 24:45)



That is somebody would like to know, so we now have what we call as a crosslinking agent. This crosslinking agent we think will be able to crosslink some of the molecules and so when you bend such a molecule after it has been crosslinked it will be able to recover. So, by looking at this what kind of a agent would you want, would you want a monofunctional agent. Monofunctional agent that means there is got one functional group which can react, is it good may not be because if this is the molecule it reacts at one place the other is tangling.

If this is happens then we may not be able to get what we are interested in because if we went this can slip, what we need therefore is not less than a bifunctional agent. So, we would not be able to do our job with the monofunctional agent, we would require minimum of a bifunctional agent. So that this is got 2 functional groups which can react with a neighboring molecules of the fibre and create a crosslink, what about polyfunctional will they not form crosslink of course they will also form crosslinking.

The only thing which will normally happens is that if use a polyfunctional agent the network structure 3 dimensional network structure can be formed. As for a resistance to bending is concerned definitely it will be more resistant and hopefully if everything is alright it recover also from the deformation but it may change some of the property which you may not like. **(Refer Slide Time: 27:13)**



For example see this fabric it is so soft, if this becomes stiff like this paper.

(Refer Slide Time: 27:21)



You may not able to wear so Polyfunctional agents crosslinking agents can create a 3 dimensional network which can make the fabric stiffer. So, unless and until you requires stiffness it may not be a good idea, so generally people will like to have bifunctional agents which maybe the crosslinking but polyfunctional can also crosslink.

(Refer Slide Time: 27:53)



So **so** far what we have done you understood crease resistance finishing would be required and can be obtained by some crosslinking portions. So initially what we shall do is we look at the cellulose base systems based fabrics, how do we do the crosslinking there, they are widely used also. And so it will be nice that we learn something about them before any other fibre.

(Refer Slide Time: 28:25)



But before we go further we must know how do we evaluate crease recovery this type of a situation whatever is happened is good or bad but how do we this is which one is worse than the other treated material or after treatment how much it has improved. That we would like to understand only then we can say whether performance has improved. So also again you

remember we are talking about recovery and not resistance, resistance as we said it can resist but if the external forces are strong it has to bend.

(Refer Slide Time: 29:19)



So we do have a measure we call it crease recovery angle measurement, so you put a crease and after putting a crease you see how much recovery takes place and that measurement or the parameter which we measures call the crease recovery angle. Sometimes it is also known as CRA which is crease recovery angle or WRA which is wrinkle recovery angle. This is expressed as a sum of angles of recovery in warp and weft direction for a woven fabric.

So we have weft direction woven fabric and warp direction so you measures separately the recovery and add them. And so if you say recovery in the warp direction is this much in the weft direction this much, the total CRA would be a sum of these. If there are other fabrics well if it is a knitted fabric you will talk about courses and wales. If it is non-woven you can talk about machine direction and cross to the machine direction and that is how you can measure and report the values.

And what is the test, the test is you cut out some sample in a certain dimensions had 2 inch by 1 inch dimensions for example. And then bend them fold them put certain amount of weight for a certain time, for example 2 kilogram for a minute and then remove the weight and measure the

angle which has been recovered after removal of the weight and obviously for a certain period let say here 1 minute so you load and remove the load.

(Refer Slide Time: 31:26)



So how it is done, so you have a load you bend it like this, so this is the bent so will be sharp bend because you have putting the load if say 2 kg it is a heavy load. So there will be a sharp crease formed and then if you remove the load we expect this to keep rising. But important will be that if it is starts rising after sometime you may find that the gravity is working against this rise and so you will get a value which difference so how do we do the test.

So what people have designed is that you have a dial which obviously talks about angles. You have some clamp, in this clamp this fabric folded fabric after removal load is put in the clamp one end goes inside the clamp the other end hangs freely this is the center. And so it will start recovering in this direction the fabric edge will recover in this direction in order if it recovers more than the gravity will start acting.

To avoid that you start rotating the dial in the opposite direction and therefore this clamp also. So that the hanging portion always remains vertical, so there may be an edge you keep matching the edge as it is rotating, so that the gravity effect can be taken care of. And so after 1 minute you say how much recovery has taken place and that will be your crease recovery angle in one direction than the other direction and then you add them up will be total crease recovery angle.

(Refer Slide Time: 33:42)



An equipment may approximately look like this where you can see this is a clamp area and this is the freely hanging edge the hanging portion of the fabric. And say you measured that this remains vertical it remain vertical, so that is how we measured the crease recovery angle. So, whenever you do a treatment you would like to know whether we have improved the crease recovery performance or they have not.

(Refer Slide Time: 34:24)



So, let us look at what we have learn till down, we have learnt why creases are formed how can we overcome this deficiency and how can we calculate crease recovery of a fabric treated or untreated. Let us see how can we make the cellulose based fabrics wrinkle resistant.

(Refer Slide Time: 34:58)



Wrinkle resistant finishing has to be done we were talking about fibre in the chemistry, so the textile is available in the fabric form, is available in the yarn form, is available in the fibre form. So, which product is what you think we should be applying these chemicals and getting through the crosslinking process is a fibre or the yarn or the fabric which one. So, as far as chemistry concern you can do it on all of them but people would like to work on fabrics.

They are almost the products that we see fibres that yarn are the one which have help them to go ultimately. The reactions will happen in the fibre within the fibre the chemicals will be able to diffuse inside the fibre whether you take yarn or a fabrics. So, ultimately the fibre has to be modified but the treatment may be done on a fabric which is a better idea.

(Refer Slide Time: 36:20)



Let us look at the crosslinking agents, so we did say that we would probably like to have generally a bifunctional agent. So it is clear that we need to create crosslinks between the molecules you know generally intermolecular crosslinks, why because that is how these crosslinks are covalent because they are covalent. Therefore they will stretch by during bending but will not break and if they do not break then we will be seeing that the recovery can take place.

So, covalent bonding will be required which has strong bond they do not break and so we would be doing this.



(Refer Slide Time: 37:08)

Now let us look at crosslinking agents.

(Refer Slide Time: 37:21)



The crosslinking agents can be they as we said they are they should be bifunctional but they may be broadly classified as someone which are nitrogen based crosslinking agents and they are non nitrogen based crosslinking agents. That is how we can divide of course you can have sub classifications of all these as well.

(Refer Slide Time: 37:53)



So initially what we do we will be talking about some of the nitrogenous crosslinking agents and we will be working with cellulosic material right.

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So we shall first learn about urea based you know what is a urea they will look at the urea based crosslinking agents. Their advantages and their limitations and initially we will focus on cellulose and so any reaction that we are talking about is we are talking of these agents with cellulosic fabrics right which are could be cotton or viscose or polynosics or high wet modulus fibres etc, what is common in them their chemistry.

And therefore all the crystallinity maybe different in different orientation maybe different, in different fibres but the chemistry is common. And which is this chemistry which as we said before has got many primary hydroxyl groups which will be relatively are more reactive. And therefore will participate in crosslink formation, you may appreciate that we may not be interested in using all the hydroxyl groups for crosslinking purposes.

That could require too much of a chemical and may change the character completely, the chemistry itself will be so different like we said about the triacetate. There all hydroxyl groups have been replaced by an acetate group and therefore the chemistry has change and so the physical property is also change it is a very different fibre. So we are not going to be interested we want to bring in some crosslinks intermolecular crosslinks and so some of the hydroxyl groups will be used for this purpose.

(Refer Slide Time: 40:12)



So one of the urea based crosslinking agent is called the DMU, DMU means dimethylol urea, it has got a group which we reactive group which is called M-methylol group. And it is formed by condensation reactions of formaldehyde and urea, so urea and formaldehyde condensates finally give us a compound called the DMU. This group is called the N-methylol group, so reactive what is urea, urea is simple compound like this.

But when we react with formaldehyde then what we get, we get another compound which can be now called the DMU or a urea derivative. So we have now N-methylol groups on both sides, so it is a bifunctional agent 2 functional groups on one side and the other side. So if they react they will be able to form a crosslink, how let us see.

(Refer Slide Time: 42:50)



So cellulose as we said is got many hydroxyl groups and to simplify this we can denote cellulose as cell-OH it does not mean we are talking about only one hydroxyl group or those cellulose has 1 hydroxyl group, no, cellulose has many hydroxyl groups. It just to make the life little simpler in expression so at the end of the thing you will have this DMU which is this compound where it reacts with cellulose under right conditions of crosslinking.

Then we expect something like this to happen that 1 hydroxyl groups of cellulose molecule may react like this, the other molecule can react on the other side and so 2 cellulose molecules or the 2 hydroxyl groups of 2 different molecules can react in this manner and form these bonds which are covalent bonds, the basically CH₂-O-C what is this, what type bonds are these, these are ether linkages, so ether linkages are formed.

So a DMU which is dimethylol urea can react with cellulose to make a crosslink of this type and once this crosslink has been formed our principle position which was there always that the molecules are there. So we have made some crosslinks and hopefully they will be able to help in recovery from the strains that maybe because of our bending increasing. So in some sense we have solve the problem.

(Refer Slide Time: 45:59)



Every time you do a process and that is what the engineering is all about, so you obviously have got a benefit in terms of what you wanted like the crease recovery will be better. But there can be some limitations one of the limitation which people complained about was called a fishy odour. I mean this it looks like as if dead fish if you have pass through them some kind of a smell you may have noticed that is the kind of an odour which basically is nothing but the smell of formaldehyde.

So from where the formaldehyde is come the formaldehyde was used to make DMU well it is already reacted, yes, it has reacted. So as long as it is reacted the formaldehyde is not free, the fishy odour comes only when the formaldehyde becomes free. So free formaldehyde will give you a fishy odour, so how does from where does the free formaldehyde come. So every reaction, chemical reaction is an equilibrium reaction 1 when you react maybe 99% reacts 1% may not react.

So that unreacted portions but that maybe become a part of the fabric in case you have not taken it of but fortunately you may if you wash the fabric the free formaldehyde may get removed. But another equilibrium part of it is that every reaction which has happened also although very strong can also go through reverse reaction hydrolysis you wash the fabric which has been treated by DMU, so there is reverse reaction is also possible. After all what is bonding, bonding is a contract, some better contract called the covalent bond and the weaker contracts could be hydrogen bond but there is a contract. So equilibrium reaction happen it may hydrolyze maybe very less but it can hydrolyze and when it hydrolyses a free formaldehyde can be generated in the washed fabric in the stored fabrics in the fabric which have been kept in a moist condition for a long period.

So when you open it you see smell, so people did not like it that is one part and so one worries about it. Also this compound being a simple linear chain was found also to self polymerize instead of just crosslinking with cellulose it could react with itself and polymerize. And if something that happens that means the film kind of a thing maybe formed and if that happens people observed stiffness.

After reaction the fabric stiffer compare to when they were not treated and so these became some of the limitations and people wanted to do something about it.

(Refer Slide Time: 49:56)



Another problem with a DMU now we talking about DMU was a chorine retention problem. Sometimes people do their laundering and washing in solutions which may contain chlorine compounds like bleaching powder, hypochlorous compounds, sodium hypochlorite. And if that thing happens then we have a problem called chlorine retention problem what is a chlorine retention problem as that if some compounds like this are available.

Then they may replace this hydrogen which is called the labile hydrogen by this chlorine, that means hydrogen on the nitrogen can be replaced by chlorine atom because you have had some possibility of any such compounds called the hypochlorite and so hence so forth. So are we bother about it, yeah. We have bothered not because the chlorine it is have been attached if it is attached chlorine normally it is ok but if it also can get hydrolyzed in heat and moisture.

Then the chlorine comes out and it can become HCl, HCl can be a problem I am not sure we were recall that the cellulose by itself because so many ether bonds. And ether bonds are also susceptible to acids, so acid hydrolysis break down happens. And so you can see yellowing degradation of the fabric also, so this is your chlorine retention.

(Refer Slide Time: 51:55)



So retention and release, so this is a compound which is got a labile hydrogen on nitrogen some kind of a hypochlorite compound may come in contact. It can form an NCl type of a replacement and once that happens and you provide heat and you provide moisture. Then this compound can go back to this but in the form can make another hypochlorite due cause and which can produce HCl.

So if this is happen then obviously it is not so good, so these are some of the limitation that we talked about. So as a engineer you should always appreciate that you can do one good thing which is very nice but it can be associated with something else. So you have to find a solution for that also, you cannot just say well this is done nothing more can be done. Therefore we keep researching and therefore there is all when anxiety in researchers to what can be done further.

(Refer Slide Time: 53:11)



One of thing which people did a next compound which came into commercial existence is called the DMEU, what is the difference. Now you see this is a compound which is like urea it is like the carbonyl group is here, so this is the carbonyl group this is like an urea group which is the Nmethylol. So it is got methylol group which can react but it is a cyclic compound, so there is this area is the ethylene additional ethylene has been added and so it becomes a cyclic compound.

So it is a cyclic urea, so this compound which is called dimethylol ethylene urea so DMEU. So ethylene group as we have said has been introduce to make a cyclic compound, you can always calculate the molecular weight of DMU and molecular weight DMEU obviously which one is higher obviously DMEU is going to be higher. But what you interestingly see is the nitrogen, this nitrogen has no labile hydrogen alright does an interesting part here just because you made a cyclic, no labile hydrogen or nitrogen.

(Refer Slide Time: 55:00)



So how does it reacts, let us see first the reaction, so one of the advantage could be the chlorine retention no chlorine retention if no retention no release so good idea. Let us see how the crosslink will look like, so we have the cyclic compound DMEU it can again make an ether link with cellulose and create a crosslink. So it is cyclic no hydrogen here and that means no chlorine can be retained and though no release + once become cyclic the self polymerizing tendency reduces quite a lot.

And so people found that it does not self polymerize it, it only crosslinks we are interested in formation of crosslink we not interested in formation of a polymer or self polymerized material we are not interested and so the DMEU gives you this advantage.

(Refer Slide Time: 56:54)



And a limitation so we have always look at what is difficulty. One of the thing which people would say after crosslinking what have we done you have reduce the number of hydroxyl groups available on the cellulose. Because those hydroxyl groups have been use to make the crosslink, see you make increase the hydrophobicity it is not that the all the hydroxyl groups are gone very few hydroxyl groups have gone.

Will try to do some calculation at some time to see how many such crosslinks would be required to give some reasonable amount of crease recovery. But some hydrophobicity is introduced which is which cannot be denied.

(Refer Slide Time: 57:49)



So let us see what have we learnt, we have learnt why do creases form into fabrics you ok something do with a fibre but we measure in fabrics, what is resiliency, that is it is resistant to deformation and recovery from the deformation. And how does this resistance to creasing be increased that is done by crosslinking and so we have also learned about crosslinking agents, which type of crosslink agent will require.

We will also have seen that DMU could be an effective crosslinking agent, it has some problem related to fishy odour and chlorine retention. And also self polymerization but if we make it a cyclic urea compound like DMEU then some of these challenges could be handled right.

(Refer Slide Time: 58:57)



So you can do it yourself, test it yourself, obtain different types of fabrics, check which one creases more. If you can correlate with it is chemistry very good. Also see if fabric structure has any role to play in recovery or creasing itself and knitted structure versus the woven structure versus different kinds of views, you may like to see it yourself and maybe come out with some explanation has to why one of them is recovering more than the other or creasing more than the other.

(Refer Slide Time: 59:35)



So, here we stop and we will meet in the next class thank you.