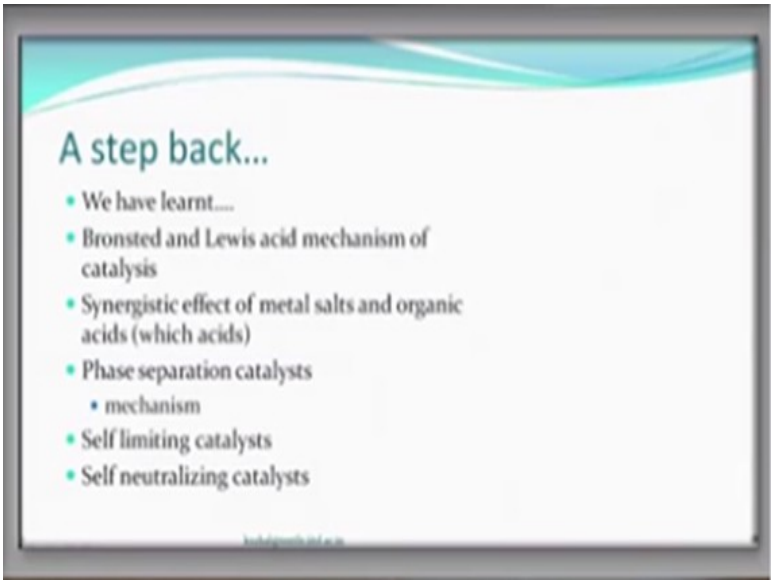
Textile Finishing
Prof. Kushal Sen
Department of Textile Technology
Indian Institute of Technology-Delhi

Lecture-06
Other crosslinking agents

Welcome back to this course on textile finishing. Let us first understand and revive what did we do till now.

(Refer Slide Time: 00:29)



So, what we have learnt with that the N-methyl compounds can be crosslinked with cellulose that is the hydroxyl group of cellulose via an acid catalyzed mechanism. So we can either have a bronsted acids where the proton is available for reaction or we can have a pure lewis acid mechanism where metal salts the metal will actually act as a lewis acid and it will catalyzed.

The other thing which we also learned is that there is synergistic effect if metal salts are available along with a carboxylic acid basically an acid which is hydroxy acid alright. For example acetic acid will not work but citric acid, glycolic acid are good examples of the hydroxyl acid which should be the either alpha or beta hydroxy. We also discussed about another class of catalyst call

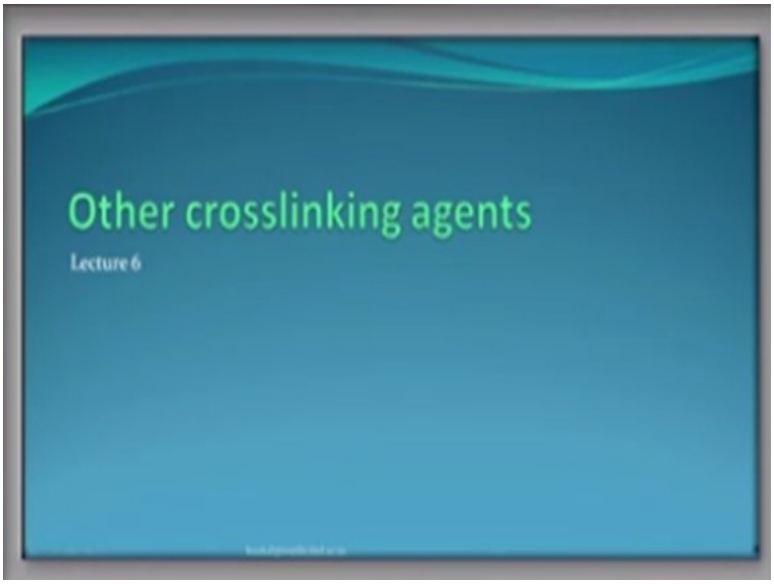
the phase separation catalyst in which we have various ways in which the precipitation can occur one of the phase can be separated.

And in these types of catalyst as the concentration of the solution increases one of them which is less acidic and which has low solubility product precipitates. And once it is precipitates the pH decreases further rapidly and so as the phase separate the pH becomes more acidic and so catalyst can then become more effective. The other class of catalyst that we discussed was self limiting catalyst, that is they would evaporate as the curing takes place.

And you may not have to wash the fabric because nothing maybe left that is just the catalyst part of it, if the monomer or the crosslinking agent does not react fully. Then you will have to obviously wash, some of one of the examples for example is hydroxy methane sulfonic acid right. The other type of catalyst that we discussed in this class was self neutralizing catalyst one of the example was the basic aluminum chloride or aluminum chlorhydroxide.

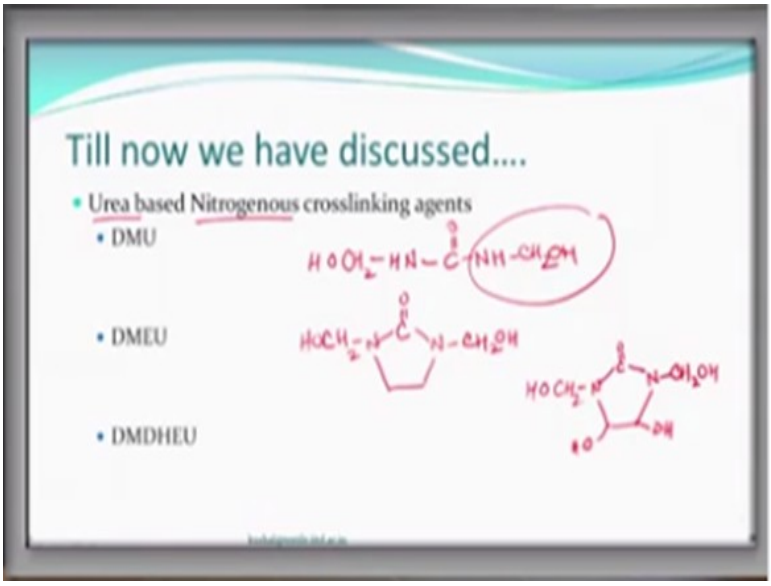
They are excellent buffers, so the metal salt obviously acts as the Lewis acid and does all the catalytic activity. But because of the hydroxy groups present in this whole structure it remains more or less buffered and does not damage the factors, so this is what we learned about the catalysis last time.

(Refer Slide Time: 03:59)



Now we shall spend some time on crosslinking agent which are other than the N-methylol crosslinking agent. After all what you require was there should be at least 2 functional groups attached, so that a crosslink can be formed when we mean this crosslink we have many covalent crosslinks can be formed. So, they will remain more permanent and the same mechanism of this recovery can be established.

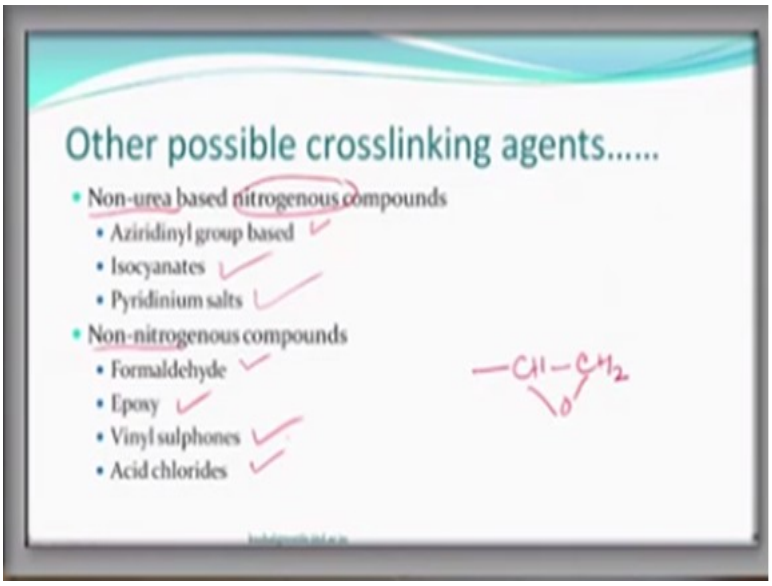
(Refer Slide Time: 04:33)



So, in the earlier lessons that we would discuss, so we had nitrogenous urea based crosslinking agents DMU if you remember this is the structure right, remember this structure. DMEU was a cyclic urea which had the structure like this. So, it is a cyclic urea with the an methylol structure and in the DMDHEU we have 2 more hydroxyl groups attached in this original cyclic structure essentially all of them are N-methylol compounds.

So, these were 3 important otherwise we could have many more number of N-methylol compound based on melamine and derivatives of some of these cyclic compounds including DMEU or derivatives of DMPU. So, there can be many such number of crosslinkage in but what we remember this is the group which we are interested in which actually reacts at a suitable temperature and if kept for a certain suitable time.

(Refer Slide Time: 07:33)



Today we will look into another possibility where the N-methylol group is not be functional. So, other possible crosslinking agents, so one is a non-urea based nitrogenous, so they may have nitrogen as one of the key elements. But they would not be urea based for example Aziridinyl group based compounds, isocyanates, pyridinium salts they have nitrogen ok they have nitrogen but they are not urea.

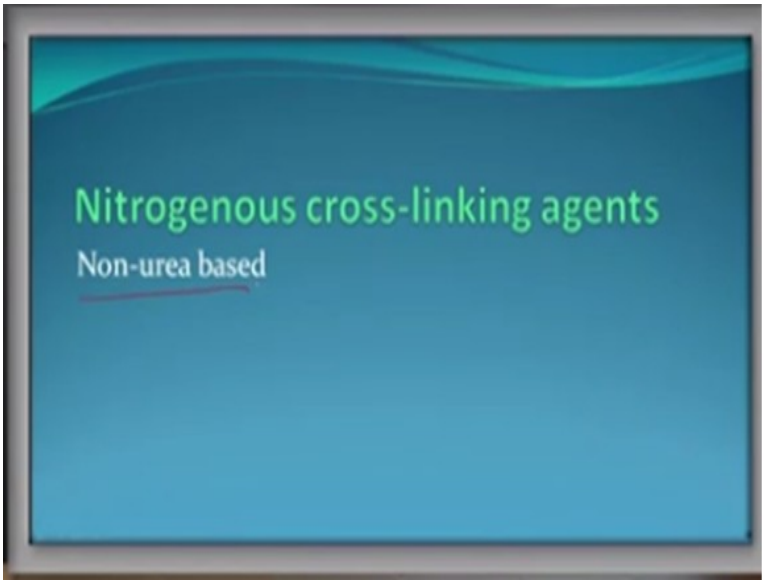
We can also look into other group of chemicals which can be used as crosslinking agent which are non nitrogenous ok. If we just look simple compound like a formaldehyde itself which also does not have any nitrogen and theoretically the N-methylol compounds were found by formaldehyde itself. And therefore it is possible to react simply with formaldehyde also whether you do it or not it is a separate story it can be done.

Epoxy compounds which are basically compounds based on this group, so epoxy compounds, vinyl sulphones, you probably remember the reactive dyes based on vinylsulphone groups. So vinylsulphone can also be reactive groups, acid chlorides can also used which do not have any nitrogen in them.

(Refer Slide Time: 09:32)

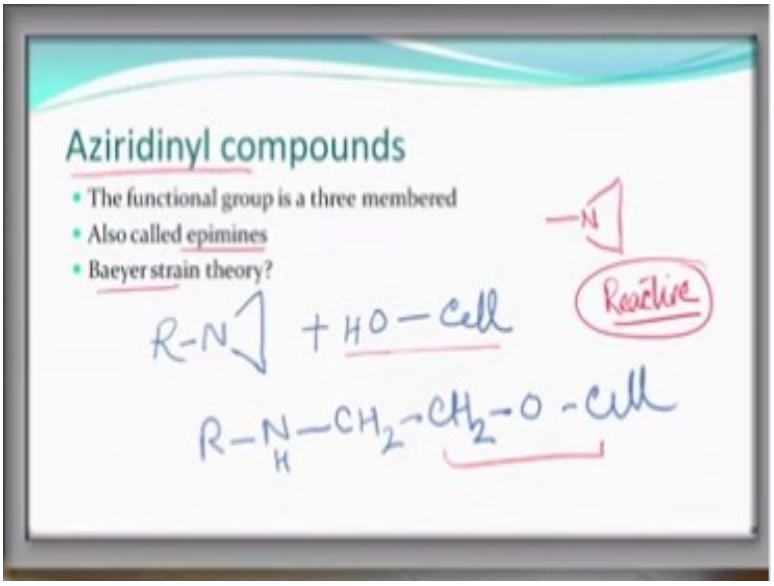
In addition 2 more classes of compounds actually have been quite commercially successful and being recommended for crosslinking purposes. One of them is based on glyoxal the others are carboxylic acids, so today we shall discuss little bit about these crosslinking agents and how they can be reacted with cotton.

(Refer Slide Time: 10:10)



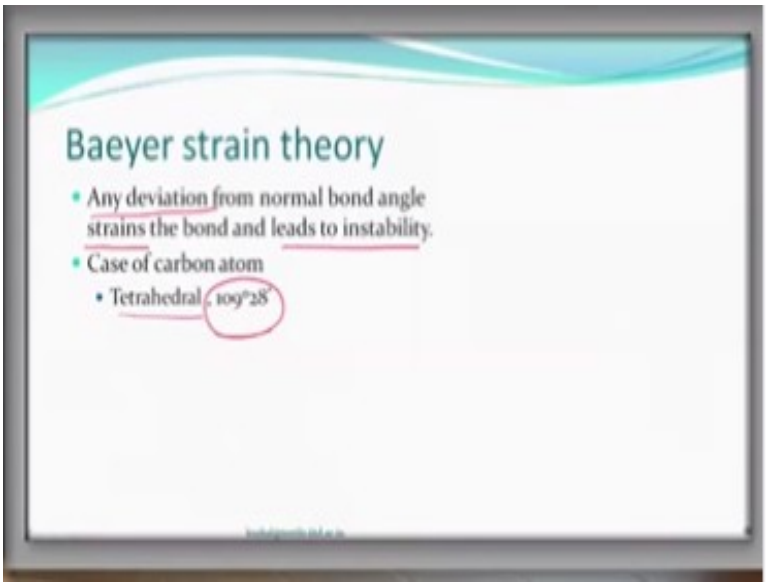
So, let us first talk about nitrogenous but non-urea based crosslinking agents.

(Refer Slide Time: 10:19)



Interesting compound which we know as Aziridinyl compounds or sometimes also known as epimines ok. So, epimine basically or Aziridinyl this is the group that we are looking at a cyclic group which is N-CH_2-CH_2 cyclic compound. Now cyclic compounds are reactive and theoretically you can form a link of this type that you have this compound any compound and then cellulose hydroxyl group is available and in acidic medium a reaction of this type of a link crosslink is possible, you know why these compounds are more reactive. So, you may have we taught sometimes about this Baeyer strain theory, what is this theory.

(Refer Slide Time: 11:52)



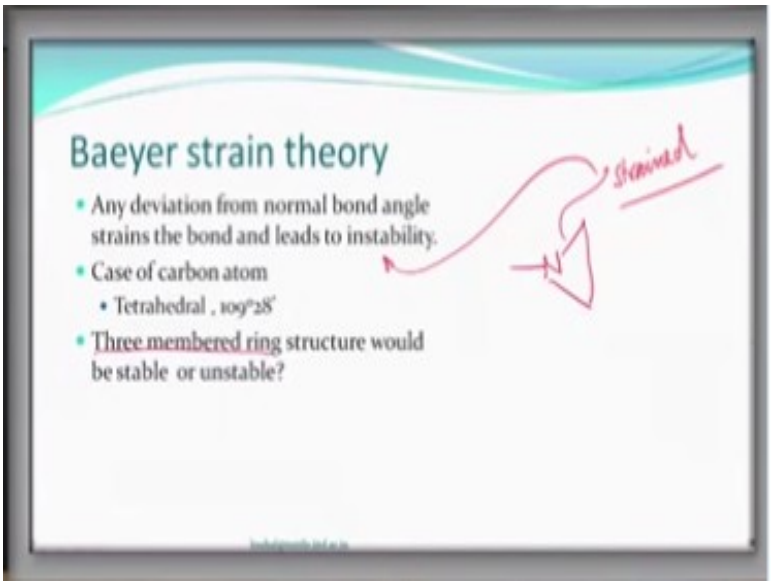
It says that any deviation from normal bond angles what is the normal bond angle, so any element like a carbon. For example forms 4 bonds if you remember you can make covalent

bonds in a tetrahedral kind of a structure and the bond angle is 109 degrees 28 minutes alright, this is the angle. That normally carbon would like to form bond like methane for example all the -CH groups will be having this angle, so that is the bond angle.

There are 2 things one is called bond angle there is called bond length alright, so they are all fixed thermodynamically based on the possible structures. Every element would have it is bond angle if they are making more than 1 bonds at least more than 2 bonds. So, any deviation that happen from the normal bond angle for whatever reason would put strain on the bond, the bond would like to remain like this and you want to bend it, change the angle.

The movement you change the angle there is a strain which leads to instability of the bond, if there is no strain this is the most stable structure thermodynamically this is the position that the atom or atoms would like to have. But for various reasons like I make a cyclic structure because I need it and there must be methods which can make sure that I get a cyclic structure, in that case those bonds are strained.

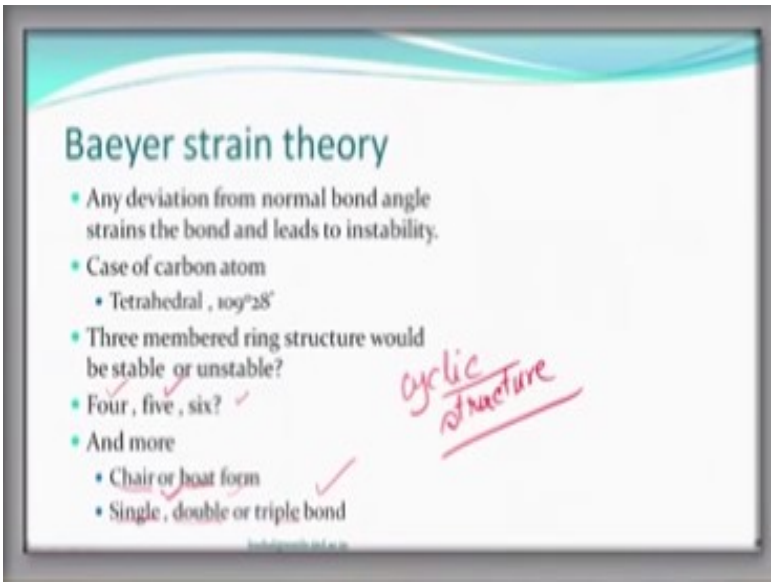
(Refer Slide Time: 13:50)



For example a 3 membered ring structure like the way we were talking about aziridinyl structure or epimine is a strained structures. So, these bonds are strained if you have any strain obviously this is the one which will result into some instability alright. So, 3 membered ring would be

stable or unstable it will be relatively less stable we should not say unstable it will be less stable or in the other way it will be more reactive.

(Refer Slide Time: 14:48)

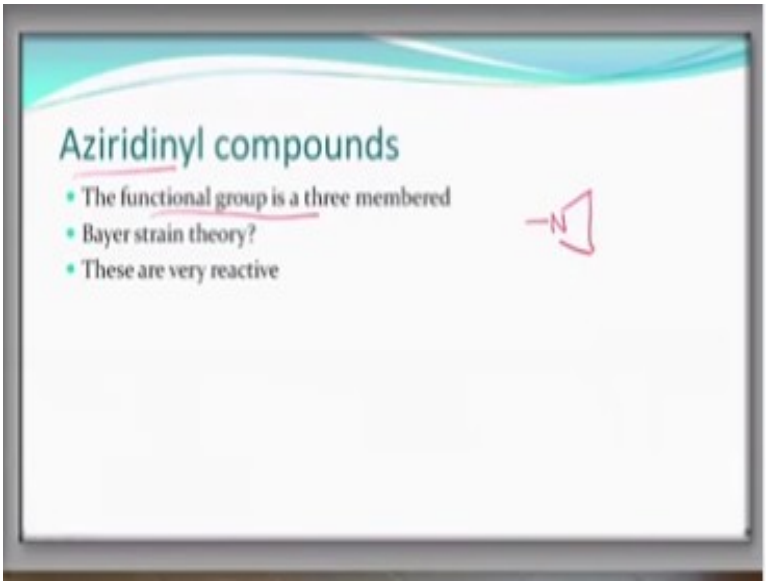


So, we talk about a 4 membered ring, 5 membered ring, 6 membered cyclic. If you have cyclic structures obviously if you can say the 3 membered will be more reactive then the 4 membered then the 5 membered then the 6 membered. Now a 6 membered ring also is strained but the strain could be less if the configuration and confirmation changes. For example a 6 membered rings can form depending upon the chemical either a chair form or a boat form to make them more stable.

If a 6 membered ring is plainer structure it will be in a way less stable if the same structure is able to form a chair or a boat form can take a assume will become more stable. Similarly you are also aware that the single bond carbon-carbon single bond versus a carbon double bond carbon-carbon triple bond. The triple bonds will be less stable than double and then double bond will be less stable than single bond.

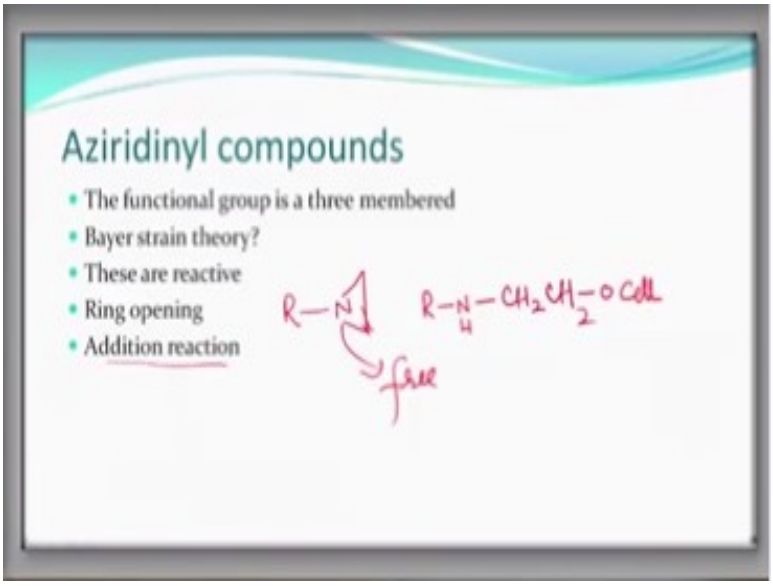
And what it therefore means is the reactivity of the double bonded structures the triple bonded structure is going to be high and that is what is the reason that these type of chemicals can become more reactive and what it also means is that maybe you can react at a lower temperature.

(Refer Slide Time: 16:53)



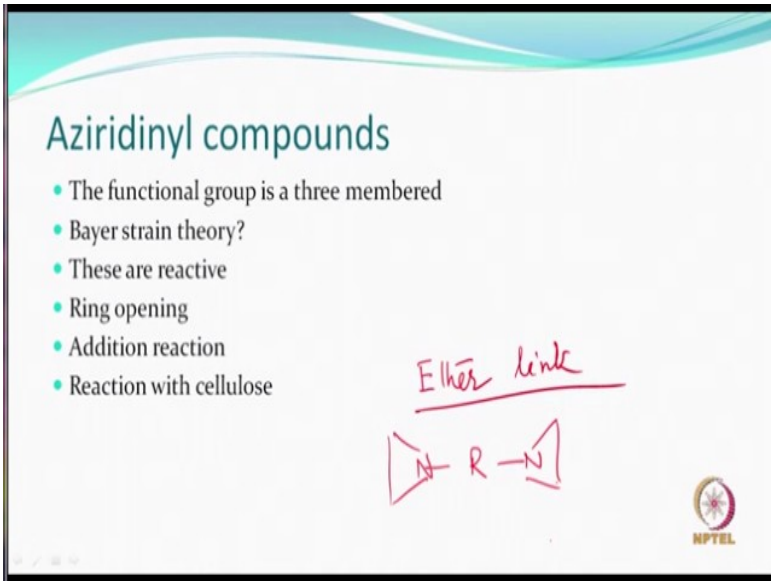
So, in this compound in these compound that we are talking there is a functional group as we talked about is a 3 membered structures, so is more reactive.

(Refer Slide Time: 17:10)



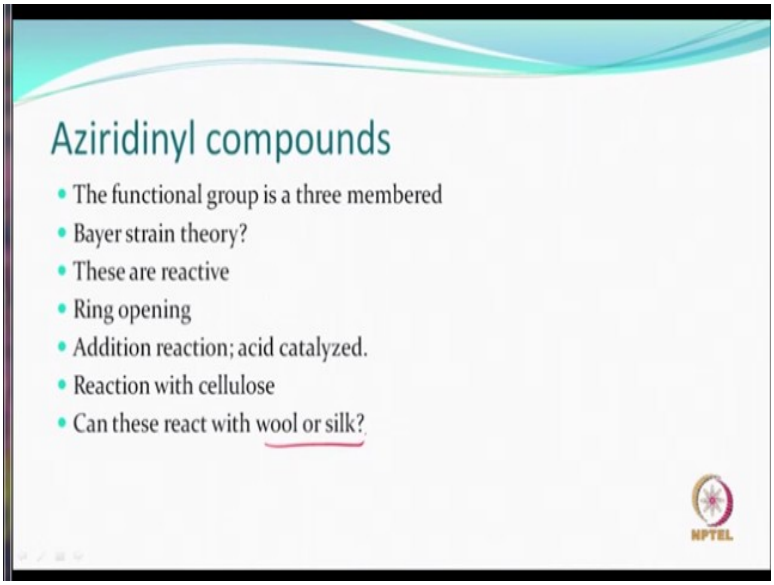
And therefore the reaction can take place by opening of the ring let us say we have a compound. So, in the first step you will have ring opening and after the ring opening finally you would get a structure, if we are reacting with cellulose something like this. So, ring opens from here this portion becomes free and then it can react with cellulose remember is there any loss of any element here no and therefore this reaction is in some sense we can call is an addition reaction ok.

(Refer Slide Time: 18:47)



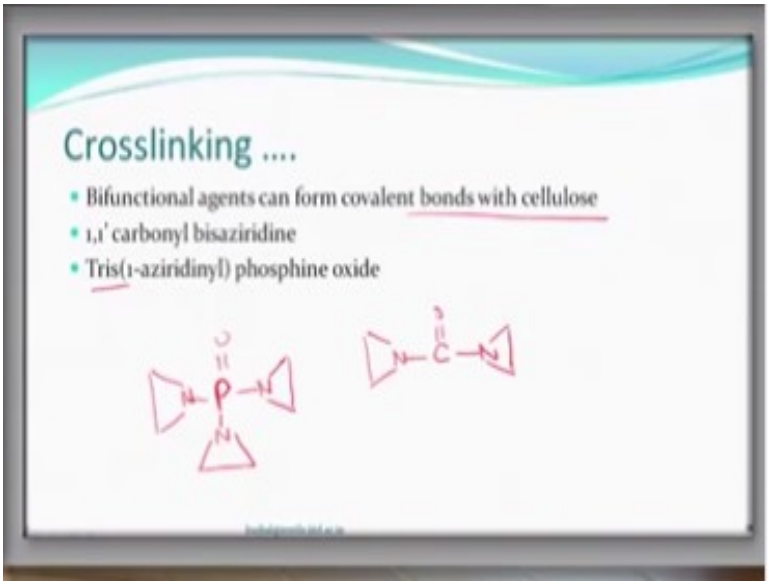
So, reaction with cellulose is what we saw that will make an ether link. So, you make an ether link so if you have to make crosslink then what will happen then you will have to have a structure which is of this type by functional agent. And this can react with cellulose and both ends for example both 2 hydroxyl groups of 2 different molecules then can form a crosslink. First by ring opening and then reaction, reaction would be generally in acidic medium.

(Refer Slide Time: 19:47)



Now this question is somebody asks can they react with wool and silk, yes they can react with wool and silk again by ring opening with the amines and therefore if someone is interested in developing crosslinks in routine fiber fabrics you should be able to use them quite easily.

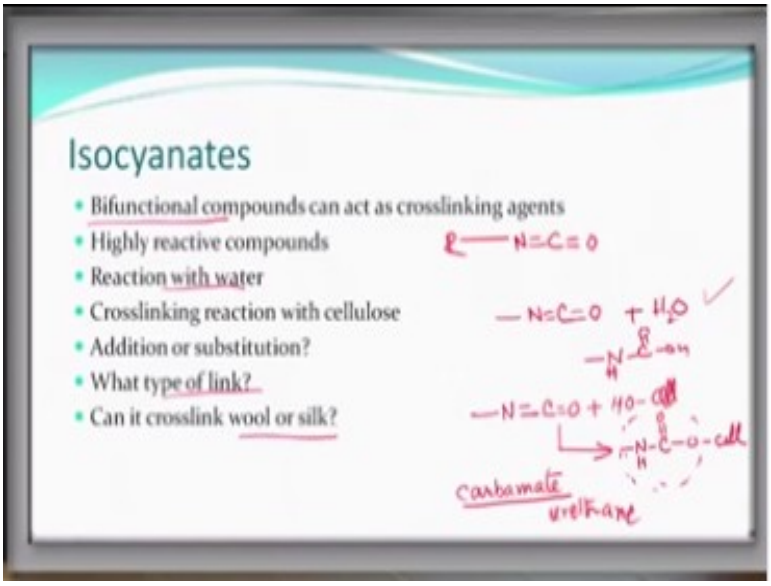
(Refer Slide Time: 20:17)



So if we look at compound like this, this cellulose one of the compounds could be carbonyl base aziridine. So, you have a carbonyl compound simple compound can react finally with cellulose by opening and you can make crosslinks. So, I hope you will be able to write the crosslinking reaction by opening these rings in 2 sides. The other compound also is there which is an interesting compound again which is based on phosphine oxide it is a tri membered 3 as aziridinyl groups because there is tris there.

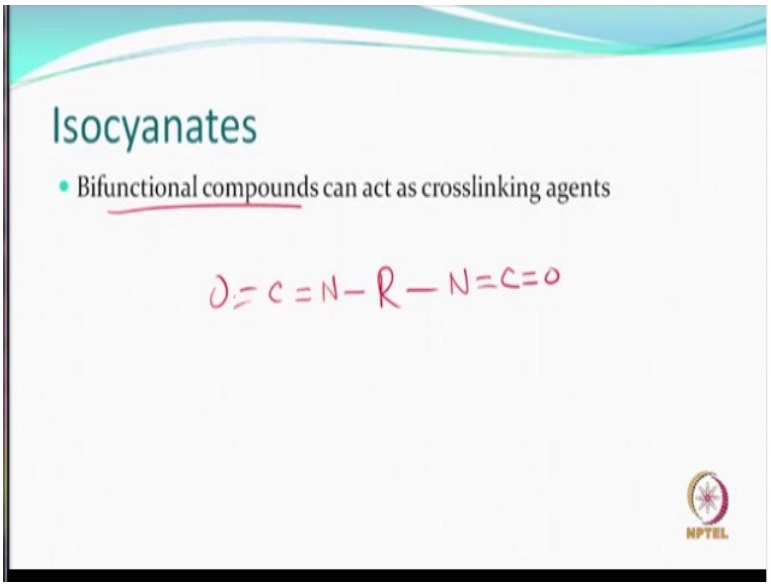
So, these type of compounds have been suggested to be used for crosslinking purposes, you can appreciate that a bifunctional agent definitely will give a crosslink and will be more flexible compound like this will give you possibly little more stiffer thing. But interestingly it also will introduce phosphorous into the structure which we will learn later can be good flame retardant.

(Refer Slide Time: 22:23)



The other compounds that we looking at are isocyanates if you have bifunctional isocyanates then you can obviously take them as a crosslinking agent, what is an isocyanate this is the kind of structure that you see in an isocyanate alright. Have you heard about this isocyanate these are very highly reactive systems and if you have any memory or if you have heard about the Bhopal gas tragedy where isocyanates were the ones which were being used there and they react very very quickly with water.

(Refer Slide Time: 23:26)



So, bifunctional compounds can react with a crosslinking agents, the reaction with water could be can give you a carboxylic group. This reaction with water is it an addition reaction or a substitution reaction, this reaction also is an addition reaction. What type of a link does it form

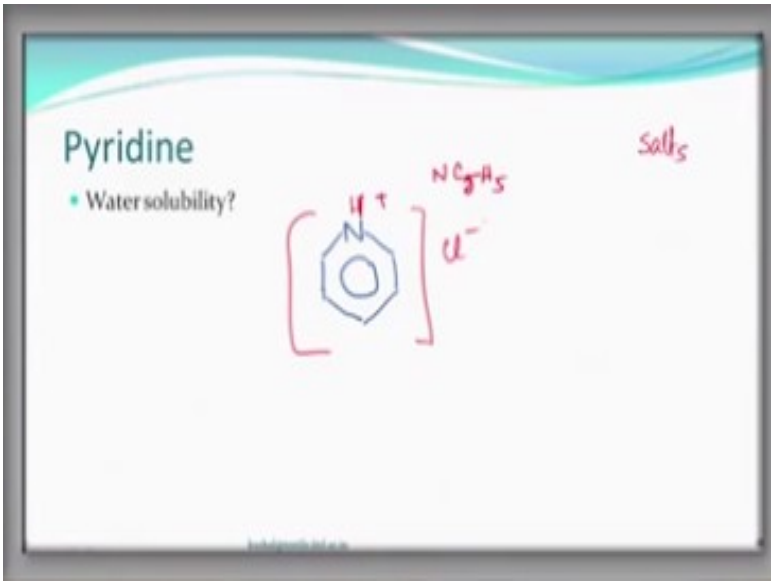
with let us say instead of this if you had cellulose this will able to form a link. So, this link which is which contains N-CO double bond and O is also known as carbamate or also urethane, you heard quite a lot about polyurethane.

So, you would require some compounds which can react like this, so it reacts very much with water itself. The one thing you can be quite sure is you will not be able to do any crosslinking reaction in water medium right. And the reaction is instantaneous it is room temperature and could be very exothermic and therefore you may have to do this reaction with cellulose or any other such material that you want to do in through a solvent medium where the reaction will not take place with the monomer till the time.

The other compound like this cellulose hydroxyl groups or an alcohol or an amine is brought. So, they can also actually link amines that means primary amines or any remain which are available let us say in wool and silk fibers. So, you can see it is possible to do crosslinking within the intermolecular spaces of wool and silk as well. So, the thing that we have to remember is there it can be only bifunctional agents which can react with compounds like this alright.

So, you can just have simple compound so various types which can be generated synthesized are could be anything and you will be able to do a crosslinking. Can you write the crosslinking reaction with cellulose if you have a compound like this I am sure you can do it, do it yourself.

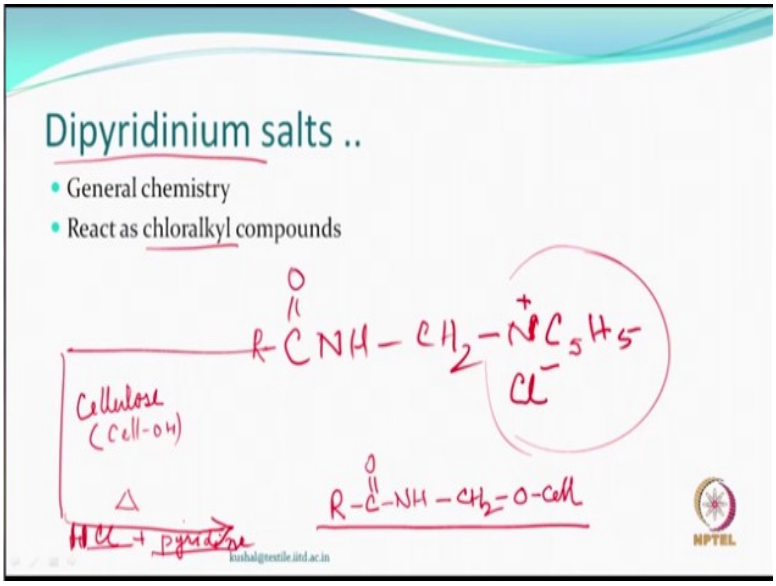
(Refer Slide Time: 27:55)



Another nitrogen based compound is pyridine not very popular these days but it is a very interesting compound as such which is got a nitrogen in the 6 membered ring. So, sometimes it can be written also as NC_5-H_5 alright. But this is not so much soluble in water benzene is also not soluble toluene also is not water soluble, so this also compound is not water soluble. But if you make salts then it becomes water soluble.

For example the H if it is aerate here it becomes takes a positive charge the nitrogen and then you have let us say chloride ion. So, you can have salts of pyridine which can be used for crosslinking purposes the pyridine salts are interesting compounds let us see what kind of interest that can generate.

(Refer Slide Time: 29:30)

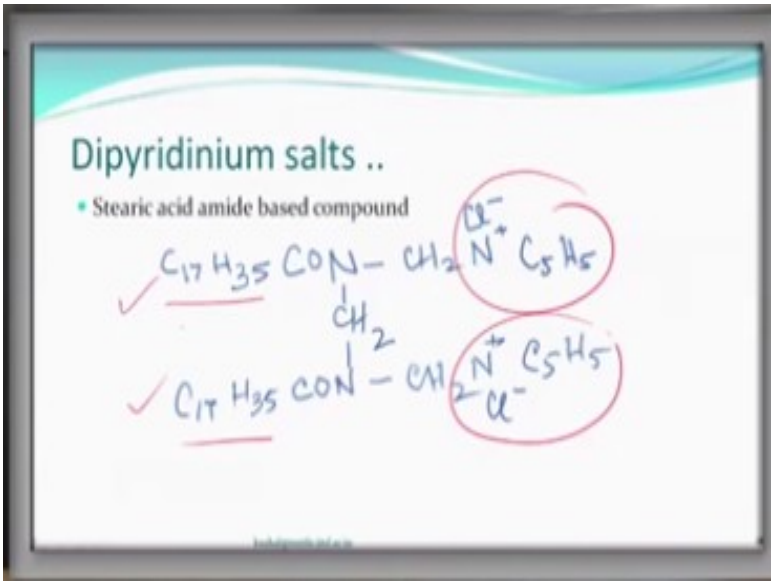


So, first of all one must remember that if you have a dipyridinium salt then they can work as crosslinks. They react as chloralkyl compounds ok for example this is an interesting compounds this is the pyridinium salt $C_5H_5N^+N^-$ it has reacted with any other compound for example an RCONH an amide kind of a compound which is reacted in this manner through a thing.

So, the reactive group is here now if you put let us say cellulose which we will representing as cell-OH and you heat. During this process what will be there is an HCl will come out and + pyridine will come out. So, HCl and pyridine will come out when we heat and so what we will get is some structure of this type. So, reaction can happen and you will get a link with cellulose.

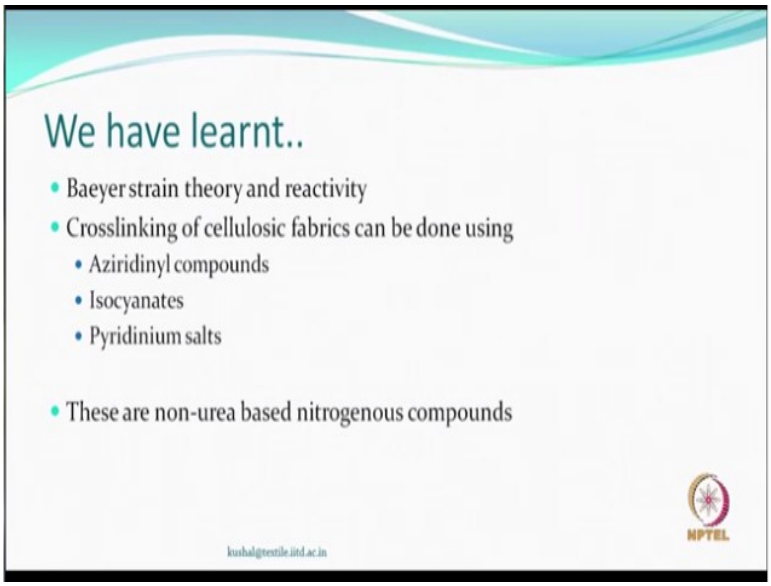
They react as if they are chloralkyl compounds like there is a chlorine which is going to get replaced and pyridine gets separated which obviously one has to take care that it is not very easily mixed with the drain water on things and you should be carefully taken away. Because HCl is going to be evolved, so mild basic conditions are going to be good, so that the HCl becomes during the reaction as a sodium salt or some such things, so that it is neutralized.

(Refer Slide Time: 32:21)



So, one of the interesting compounds is a compound which is got the large alkyl group and an amide also, an amide which is also linked with another CH_2 group and then you have 2 such groups present here which by the same mechanism as we have discussed before can react and form a crosslink right. But interestingly if you have groups like this also attached people could have interested in this kind of compound then you get water repellency which will talk about later ok.

(Refer Slide Time: 33:08)

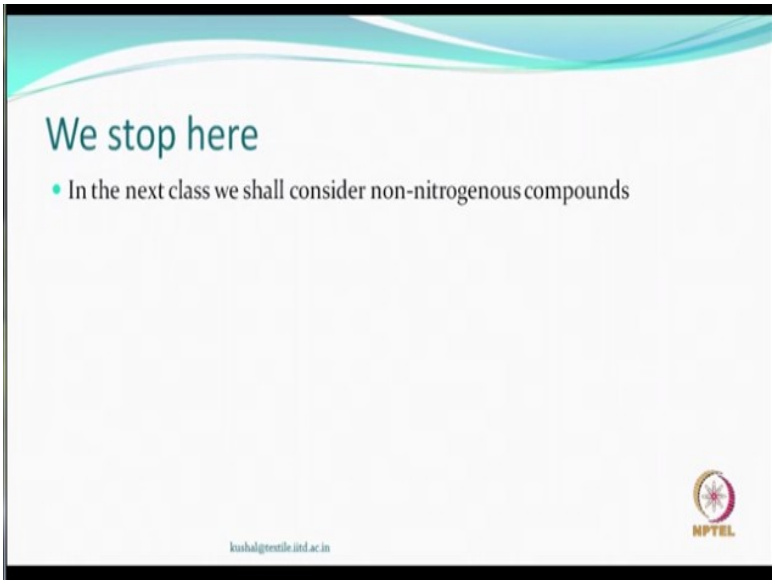


So, what we will learn today, we have learnt there is a very interesting relationship between the reactivity and the cyclic nature of a group which is explained by the Baeyer strain theory. So, if you have a 3 membered ring it is going to be more reactive compare to a 4 membered ring

compared to a 5 membered ring and then the 6 membered ring, so reactivity can change because there is a strain on the bonds.

Then we have also learn today that the crosslinking of cellulosic fabric can be done by using non urea based nitrogenous compounds like aziridinyl compounds, isocyanates and pyridinium salts ok remember all these are non-urea based nitrogenous compounds alright.

(Refer Slide Time: 34:20)



So, we stop here and in the next class we shall consider non-nitrogenous compound that also can be used for crosslinking purposes ok, thank you.