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

Lecture-05 Catalysis and catalysts

Welcome back, the course on textile finishing. We have covered some distance on the crease recovery finishing. We are going to continue with that for some more time.

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Let us see what did we do, we have learnt number 1, where crosslinks formation is facilitated by a pad dry cure process why drying is important because it reduces the possibility of migration of chemicals to the surface. We have checked that the crease recovery angle would increase if the concentration of the crosslinking agent is increased in the bath as a result the actual crosslinking increases, the add on increases and if that happens then we will see that the crease recovery angle will also improved which is our main motive.

We have understood the Rebenfeld's hypothesis which talks about why viscose and cotton behaved differently when in dry and wet condition and when they are crosslinked. The formation of crosslinks according to the Rebenfeld's hypothesis in cotton is going to decrease the strength while in the case of viscose it will increase the strength and you know because the crystallinity of cotton is much higher compare to that of viscose.

And therefore the non-uniformity in the case of cotton only increases which does not help in retention of this strength and the strength decreases. So, most the cases in almost all cases the strength is going to go down because of the reasons the losses strength losses due to the acid presence due to the temperature of curing which is could be high and of course crosslinking based on which fibre we have talking about.

The stiffness generally would always increase because the intermolecular movement is going to be restricted which obviously helps in recovery of creases but it can make the fabric little stiffer. So, we accept that this can be measured by bending length also we have concluded that the abrasion resistance also would go down after crosslinking.

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Let us look at some of the calculations before we go further and I like to see how you respond to this. Let us say somebody has said that what would be the concentration of chemical in the bath liquor. So there is a bath liquor which contains the chemical, the chemical could be from our proposal let us say crosslinking agent. And for some optimization process it is being concluded that you want 2% add-on on the fabric.

So, now the question is obviously you know the difference between add-on and you also know the difference between the content, so we are talking about add-on alright. So, what we are looking at is 100 gram of fabric is being used then will become 102 grams, so for 2% add-on is required. So, what is asking is the concentration of the chemical required in the pad liquor ok we we know already what how much do we want on the fabric.

So, there are 2 processes which we are already said that that one could be an exhaust method ok and somebody must know to say well this is the question please try and answer this question how do you answer this question. Well let me ask you again when somebody says concentration what does it mean we have to define a unit. So, what is missing in this question is the unit you do not know what unit people are asking for is it percentage or is it in grams per litre.

So, that has to be defined, so this was a missing links so you cannot obviously answer this question. So, let us see we say well we are looking at the concentration in grams/litre ok, so can you answer this question now, what will be the concentration in grams/litre of a chemical in the bath liquor if 2% add-on is required on the fabric. Can you answer this question now Can you answer this question now No, well.

You cannot still answer the question because there is some data still missing one must say what is the ML ratio M L Ratio it is not been defined. So, if ML ratio has not been defined how can you calculate the concentration alright. So, let us say we define the ML ratio now as 1:100 you know what does it mean that means 1 gram of fabric if it is to be treated then you are looking at 100 ML of liquor alright, can we solve the question now.

Exhaust process means whatever is actually in the bath gets exhausted onto the fabric, so how much you should take in the bath what should be the concentration. Now we are talking about in grams/litre yeah we can still not answer this question why. Because you want to still know what is the exhaustion percentage based on the data previous history one would know because all these reactions in some way or the other are equilibrium processes.

There may not be 100% reaction there maybe only 90% reaction the rest maybe only in the bath 90% goes into the fabric 10% remain the bath, so this can alter your calculations right. So, let us assume here the exhaustion is 100% it is a very ideal situation where everything which is in the solution finally goes to the fabric then what would be the concentration of the chemical in the bath liquor, now you can calculate, now you have everything.

So, you want 2% that means 2/100 and the ML ratio is 1:100 but you want in liters and not in percentage. So, what we are looking at 1000 ML versus this is 100 and so this comes out to be 0.2grams/litre right, is this clear.

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Let us say we have another case where we say we want to do by padding the questions still remains the same and let us say the concentration required also here is also in grams/litre. Now can you calculate can you calculate what is missing what is missing, missing is wet expression. So, in the case of padding we need a parameter called wet expression you can squeeze the mangle more you will have let wet expression you can reduce the pressure more wet expression.

So, based on the wet expression the amount of liquor is going to be picked up. Now you quite sure what an expression is right. So, what will be the case, you want 2% add-on that means 100 gram of the fabric will take 100 gram of liquor. So, if you consider this as 100% expression this value then the concentration the pad bath is close to 20 gram/liter 20 gram/liter. In the previous

case it was 0.2 grams/litre, what I wanted to tell you was that the concentration of the chemicals in the padding systems is much higher compare to the exhaust system with this alright.

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Now let us go further, so today we will talk about catalysis and catalysts. So, you remember we said that for crosslinking other than the crosslinking agent you require a catalyst ok. So, we will learn little more about it obviously we are talking about at the moment cellulosic systems fibers fabrics and we are looking at the n-methylol compounds alright we have not changed that crosslinking agent.

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So, if you remember for the N-methylol compounds these reactions are acid catalyzed, so you require some acid catalyst and it happens via a carbonium ion formation, so that is the way the reaction with cellulose that with the hydroxyl group of cellulose takes place which type of link is formed.

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We talked about the link, so link is ether is that clear this is what we are already done remember yeah.



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So, let us see what types of catalysts are suitable for affecting this type of a crosslink this type of a covalent bond.

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So, the various types of acids that can be used what becomes important for us is that which one are going to be helping us more, more means what that there is efficient crosslinking case of course that you would want. We would also want the losses due to the acid itself be less we may want that the losses due to curing temperature maybe less how can a catalyst help well catalyst may help you to reduce the curing temperature.

Catalyst may make sure that the fabric degradation is less if that happens then we can say that the optimization in terms of selection of catalyst may have been done. So, there are various possibilities as for as the catalyst are concern there could be free acids that means the acid is immediately available which means a proton. Latent acids which become acid at a certain time or maybe certain temperature there others are metal salts which are different which are something like Lewis acids.

Then people have also suggested use of mixture of salts and acids which can in some way help. Then we have a category of catalyst called the phase separation catalyst there during this process of let us say curing itself there is a separation of phase. That means a solid could be precipitated at some given point of time, so your phase get separated. Self limiting type that they actually almost get eliminated themselves at the end of the day. That means after the process after the reaction is over or chloro hydroxide there are many others also we will not discuss everything if you are interested you can always go down the literature and keep looking at various thing that people have tried over the years.

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So, let us talk about free acids, the free acids are the ones which very easily release the proton you remember in the mechanism of crosslinking there is a proton which is required which helps you to form the carbonium ion right. So, free acids are because they call free because they can very easily give you the proton alright some of the examples are from the mineral acid groups HCl, sulfuric acid, nitric acid these are the examples they can be used.

They will immediately in water give you start giving you the proton and the proton start participating. So, are you getting alarmed try thinking of using sulfuric acid with cotton at 150 degrees where the concentration obviously would be quite high there will be lot of degradation. The mineral acids in the pad dry cure situation are not very suitable because they will help in crosslinking but the fabric deterioration can also take place and so maybe we can think of something else.

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Organic acid they also are bronsted type acid give proton the only thing is they are known as weak acids weak acids. The mineral acids are strong acids right whether weak acids, so obviously their efficiency is going to be low but they will be little less harmful to the fabric ok. Acetic acid people may not use because it evaporates by the time the crosslinking itself takes place, so people may use other organic acids like citric acid, tartaric acid which would remain intact during the process of crosslinking.

That is at the curing temperatures we expect the losses to be less alright compared to the mineral that is why you can understand why people will try different things.

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Then there are other category which is also known as latent acids such as the acid is not immediately available like when you dissolve in water. The water does not really behave like a strong acid but at the time of curing it can happen. Some of the examples can be from the salts ammonium salts, so ammonium salt like ammonium sulphate or ammonium chloride they are water soluble but they do not behave like let us say HCl or sulfuric acid alright they remain.

Then the still weaker versions could be ammonium salt of citrate, citric acid, tartaric acid and that would mean that they will be available at a later stage not in the beginning. Therefore we will say well if any bad effect of the acid is there it will only happen during the curing stage and not while it is being dried, while it is being padded, while it is in store storage conditions alright. So, much before drying, during drying the degradation will less but when curing happens they will become active.

So, the time required or time available for degradation obviously is going to much less you agree, so they are going to be better in that sense.



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The mechanism what is the mechanism obviously the ammonia is one interesting gas which will come out during the process and the acid will be liberated and that acid is going to work like a bronsted acid and give you the crosslink. But we have try to avoid the initial portion when it does not behave like a strong or a weak acid in that sense.

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There are other examples which are not ammonium compounds but they are metal compounds metal salts. Some of the examples of the metal salts that we have been using for crosslinking are let us say magnesium chloride, zinc chloride, zinc nitrate these are some of the interesting compounds there are others also there can take aluminum salts also. The important thing is they act as Lewis acids that is why electron transfer are not really released a proton ok, that is one of the differences that we have.

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So, what would be the mechanism of these things because there is no proton now, so what happens, well something like this we can expect. So, this is our crosslinking functional group N-

methylol instead of proton we have let us say a metal ion this metal ion gets associated under the conditions that we have almost in a similar manner. And then the metal hydroxide separates and then again you get back the carbonium ion in the presence of heat and of course our cellulose hydroxyl group.

Similar reaction can now take place a proton comes out and what you get is a link which we considered remember as a acid ether link is created. So, instead of water it is the hydroxide of the metal that is get separated here the mechanism still remain the same as the carbonium ion mechanism. So, it works and people found that this type of a thing is able to retain strength much more is quite efficient and works Now it is the question is which type of metal ion that may you use, which type of metal salts there may like you use. Then what happens to this MOH, this is interesting again.

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Now the MOH can react with the proton that has been generated during this process and again you can get a metal ion and water which can evaporate and so and so forth. That means metal ion is back, so it is not that we have consumed metal ion. So, the MOH which was generated here gets converted to metal ion again of course there was a possibility that this proton can directly react with this as well can react.

So, it is got 2 ways the efficiency is increased either the proton reacts with the hydroxyl group and again goes back to the same mechanism or it can react with the metal hydroxide and create a metal ion, efficiency of these is very good strength losses are less. So, these are mechanism you understand.

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The interesting thing of course is well you can use aluminum base compound, magnesium base compounds what the difference between them is oxidation number. Like magnesium for example is got 2 aluminum for example is got 3 number oxidation number there for reactivity. So, it is being seen that the activity of the metal salt is high if the oxidation number is high. So, aluminum is very very highly active compound.

But it is actually too active and people may or may not like to use it directly, aluminum chloride is very reactive very active and so the efficiency may more but you can still see some possible degradation because it is pretty fast. People have generally state with magnesium compounds, zinc could have worked the same way only thing is zinc these days comes in toward the heavy metals and so environmentally people may prefer magnesium which is a lighter metal compare to let us say zinc, aluminum could have been preferred very easily. But it is very highly active, so directly chlorides of aluminum are not suggested for use.

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Another interesting suggestions which people have tried and used is mixtures of metal salts that we just been talking about and hydroxyl acids are we say hydroxy acids metal salts are good catalyst working as Lewis acids right. And we have seen their mechanism which is interesting mechanism which makes them more efficient and based on the oxidation number of the metal the reactivity will be high, the activity will be high, the activation will be better.

So, efficiency of those compounds the metal salts is good but interestingly if you use a mixtures of metal salts + carboxylic acids. Then there is some synergistic effect but these carboxylic acids are α - or β -hydroxy substituted carboxylic acids ok. These carboxylic acids are α - or β -substituted hydroxy acids alright, so they are not ordinary carboxylic acids, there is something interesting, how do they act.

They act by decreasing the ionization constant of the metal salt, now you remember in the metal salts the metal ion is the important one, so by doing this it happens, so becomes easy. (Refer Slide Time: 28:59)



That way they increase the efficiency of catalysis ok and thereby reduce the temperature of curing, now you will obviously like it. Let us say if the temperature of curing reduces from to 120 degree centigrade from 150 degree centigrade. So, that is a saving an energy that is one part but more importantly damage thermal damage to the textile also going to be very less here. So, by decreasing ionization constant they increase the efficiency of catalysis and help thereby reduce the temperature of curing.

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So, in sense we can say that they give us synergistic effect ok, so they help each other that is what the synergistic effect. So, one can use various compositions like 40:60 or 50:50 or 60:40 and one can get lot of work has been done on this. But that only says that if you use metal salts

and carboxylic acids you will be able to increase efficiency reduce temperature. So, some of the examples of these are let us say glycolic acid which is a simple acid ok.

So, it is a hydroxy acid other is a citric acid if you remember citric acid this is tricarboxylic acid compound and there is a hydroxyl group here, so it becomes a hydroxy acid ok, So, these are hydroxy acids which are either the hydroxyl group is either in alpha position, alpha position is this or in a beta position. And such type of acids if they are, so this is not only the example or is such carboxylic acids which will have the hydroxy substitution at alpha or beta position can be used as a mixture.

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Will acetic acid work, if we just pour it will acetic acid work, acetic acid would not work, why it would did not work because it is not a hydroxy acid ok. So, this hydroxy acids where the hydroxy group is near the carbonyl group of the carboxyl group then they can help in making complexes that way they will make a complex and they ionization. Therefore will become easy from the whatever salt that you may have metal salts which could be sulfates or chlorides of metals. So, that is how the mixtures of metal salts and carboxylic acids can help right ok.

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Then we have another type of a catalyst which we call as a phase separation catalyst. The typical characteristics are like this if you plot the concentration of the catalyst the log concentration of the catalyst and measure pH. One sees this type of a curve that means at some critical concentration the pH suddenly changes why does it happen. Because there is at this particular thing there is a phase separation and why will the concentration change well when you are drying a fabric after padding the water evaporates.

So, concentration of the chemical is going to change is that right if that happens one of the salt may precipitate one part of the salt may precipitate and suddenly the pH again starts to decrease that means it becomes more acidic. So, why would anybody be interested in this that then same thing during drying it is very high pH kind of acetic pH when it behaves let us say like a weak acid as the drying takes place it start behaving as a strong acid or pH reduces.

And so one can avoid degradations alright, some of the examples of these types of catalysts belong to magnesium dihydrogen phosphate, aluminum dihydrogen phosphate, they can act in, in this manner phase separation.

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Phase separation catalysts: mechanism A solution of magnesium dihydrogen phosphate at equilibrium would contain H , H2P04 , HP04 Among the anions, H₂PO₄ predominates; the solution behaves like a weak acid [Mg(H2P04),]] / [HT] X

Let us say what is the mechanism, so if you have a normally a solution let us say of magnesium dihydrogen phosphate at equilibrium it may contain magnesium ion of course it can contain some proton, it can contain H_2PO_4 ion. It can also contain HPO_4 ion also, so these are the types of ions anions which and cataions which will be present in the solution at a certain concentration obviously because we have taken dihydrogen phosphate this predominates.

And so it behaves a like a weak acid at this time and so the availability of proton as we talk about is proportional to the concentration of a proton therefore is proportional to. Because it is like a weak acid, so it is square root of this let me just see if I can make it more clear because a weak acid therefore it behaves like a weak acid. Let us say what happens when we start drying that is the concentrations water goes out the concentration of the whole system catalyst system in starts increasing.

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So, as the drying takes place at a typical concentration less soluble salt that is magnesium hydrogen phosphate precipitates alright. And then the equilibrium shifts, so it is a second rate constant let us say which is the this type of an equilibrium is again established. So, more of this H_2OPO_4 will now get converted to HPO_4 and so that more hydrogen ions will now gets start generating, this is second equilibrium constant.

Because the salt started precipitating therefore this will start again giving more and more of protons. And if we consider that the solubility product of this compound is S and if we take this equation 1 and then equation 2 and then substitute this we will get.

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And considering that under general circumstances the concentration of magnesium ion this is going to be half of the concentration of dihydrogen phosphate ion. Then this can become square, root at the previous case it was proportional to square root the hydrogen ion concentration was proportional to square root. And now it is proportional to square that is how suddenly it becomes more acidic that is the way a phase separation catalyst works.

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So, what is the mechanism finally, so there is in a way we have precipitation of a phase. In this case this was hydrogen phosphate, magnesium hydrogen phosphate less solubility precipitates first. Then the dihydrogen phosphate starts releasing more proton suddenly because something has precipitated at a particular concentration. And so phase separates acidity increases and so they are also very efficient compounds which reduce degradation.

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Self limiting catalysts • Hydroxymethane sulphonic acid • HO-CH ₂ -SO ₃ H • Very efficient catalyst • Works at low concentrations	$50_2 + H_2 = +1.50_3$ HCH0 + $H_2 = 50_3 = H_0 - CH_2 = 50_3 H_1$
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Another interesting group of compounds are called self limiting catalysts. Now self limiting catalyst how do they work, one of the ways one of the examples is hydroxymethane sulphonic acid hydroxymethane sulphonic acid which is prepared from sulfurous acid which can be prepared from sulfur dioxide and water it is an equilibrium reaction which can give you sulfurous acid.

This sulfurous acid if it reacts with formaldehyde can give another equilibrium reaction and make hydroxymethane sulphonic acid. So, this hydroxymethane sulphonic acid works like an acid catalyst something like sulfurous acid which can also give a proton but it is suppose to be a very efficient catalyst very efficient catalyst works at low concentrations.

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And is self limiting self limiting what it means is that because it was an equilibrium condition reaction. So, this can as we have said would break into formaldehyde back + sulfurous acid which will react and after the work is done this can go back to SO_2 + water they all evaporate nothing is left on the fabric. So, this catalyst evaporates along with water also but at a curing temperature, so during drying you can have the drying conditions at curing it will catalyze.

Because the sulfurous acid being produced then the formaldehyde the $SO_2 H_2O$ all of them will evaporate nothing will be left and theoretically they say you do not want to wash. Because in all cases at least even if there is a 100% crosslinking whatever catalyst that you have used you may not like to continue with a catalyst and people therefore have to wash to remove the catalyst or unreacted monomers, unreacted crosslinking agent, so therefore it is called self limiting.

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The problem of course the gases are evolving sulfur dioxide you may not love it, water you do not mind , formaldehyde that is coming out which has to be handled. So, you will have to have some type of a arrangements, so that these gases are purged before they go out that is can be an issue. But otherwise they threy work pretty nicely strength losses are less and you do not need to wash actually because there is no catalyst left also.

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Another compound in this category is chloro hydroxide base systems which are various salts that can be use an aluminum is one of them. So, aluminum chloro hydroxide sometimes also known as basic aluminum chloride do you remember aluminum chloride by itself is highly acidic. If you look at this compound is highly acidic and as we said we would like to use a metal salt magnesium chloride rather than aluminum chloride ok.

So, to reduce this reaction in fact when somebody says that there is a theory which says while aluminum chloride does not dissolve in water but almost reacts with water becomes aluminum hydroxide and HCl can come out and so and so forth. The unlike just dissociation the aluminum lying one side of them chloride lying on the other side. But if you want to reduce this activity one of the ways is to produce hydroxides of this.

But if you look at aluminum hydroxide it is not a very useful compound it just precipitates, so in between this what we have compounds which can be in some sense they have chlorine ion as well will available and hydroxyl group also available. And so one of the ways in which various series of hydroxides can be produced with different pH ranges once you have a certain ratio of chlorine and hydroxyl group.

Then you will get a different kind of pH for example if suppose you have a thing which says $(Aluminum)_2$ (Hydroxy group)₅ (Cl)₁ it is kind of an association alright. So, more of hydroxyl less of chlorine, so difference from it is not hydroxide it is not obviously chlorine has been reduce quite a lot. So, compounds of this kind where this could be (Aluminum)_n (Hydroxide)_m (Chlorine)_{3n-m}, these type of compounds are called chloro hydroxides.

And based on this ratio they can be mildly acidic therefore sometime they are called basic element otherwise they could be highly acidic aluminum chloride but it is a basic aluminum chloride. So, you have replaced good amount of chlorine and substituted with hydroxyl group. (Refer Slide Time: 51:41)



They have excellent buffering capacity and therefore pH is controlled the metal salt will be available when required in a limited capacity could do the catalysis. And because they are mildly acidic quite and so some people may say need not wash but that does not mean that there is no aluminum left on the fabric, chlorine may go, hydroxide maybe there, so just a suggestion but people may like to work otherwise also.

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How much catalyst one should use, so you can understand what is our interest, interest is crosslinking and therefore the ratio or the amount required would based on the efficiency of the catalyst of course. And the reason that is being used instead of defining at that the define on the way to the fabric and solution we say how much resin we have used and based on that you would

define how much catalyst we require approximately 8 to 12% on the weight of resin sometimes crosslinking agent also known as resins right, why.

Because our aim is to only crosslink and therefore they must be in some way equivalent to what is required for crosslinking reaction.

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In a typical bath finish bath you may have many agents including the crosslinking agent, the catalyst, you may have a wetting agent you know why we have the wetting agent. And sometimes some people can add softener why is the softener whatever we will learn it later but at least the word says that it is going to make fabric little softer. And why we are interested because we just understood that by crosslinking the stiffness of the fabric increases ok. And so you add softener to compensate that or maybe make it more soft also and that is how it goes.

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So, what have we learnt we have learnt that we have Bronsted and Lewis acids and they have mechanisms of catalysis which is similar but different organic acids and metal salts can be used synergistically to increase the efficiency of catalysis maybe when reduce the temperature of curing which acids hydroxyl or hydroxy substituted carboxylic acids. Phase separation catalysts we talked about mechanisms we have learnt how they work by separation of phase self limiting catalyst which evaporate at the end of the reaction. And pH controlling catalyst which are the and one of the examples is like basic aluminum chloride.

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You may go to your lab check out whether these kinds of catalysts are liquids or solids whether they are hygroscopic check what is the solubility in water. And maybe you like to check the pH of a 1% solution of acid what is the pH level of different catalyst that we just discussed.

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So, we stop here and take a next topic in the next lecture which will also be related to crosslinking agents but of different types of crosslinking agent, thank you.