Principles of Polymer Synthesis
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Lecture - 43
Synthesis of Industrial Polymers (Contd.)

Welcome back. In the last class we have talked about polyurethane synthesis which was of course, a continuation of the previous class before that, and then we talked in detail about the preparation of liquid epoxy resins. So, today we will start from that point.

So, let me draw then the general structure of epoxy resins. So, general structure of epoxy resins is something like this.

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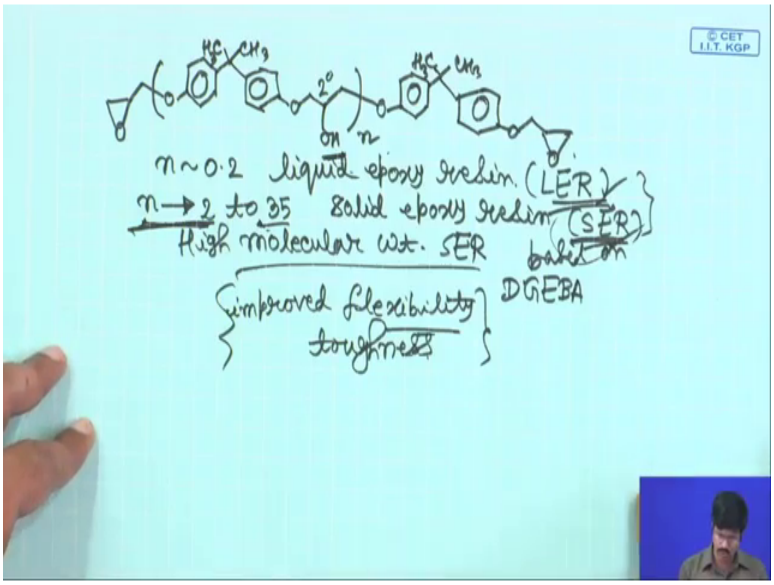

So, you have the bisphenol a that is present here CH 3 CH 3 here and then you have the unit here and then secondary alcohol. So, this is the general structure. And we told that if your aim is close to point two you will get what you call as the liquid epoxy resins highly viscous liquid epoxy resin, LER. And we have also discussed that a way of getting liquid epoxy resin is to have a high proportion of epichlorohydrin low proportion of bisphenol a typically 10 to 1.

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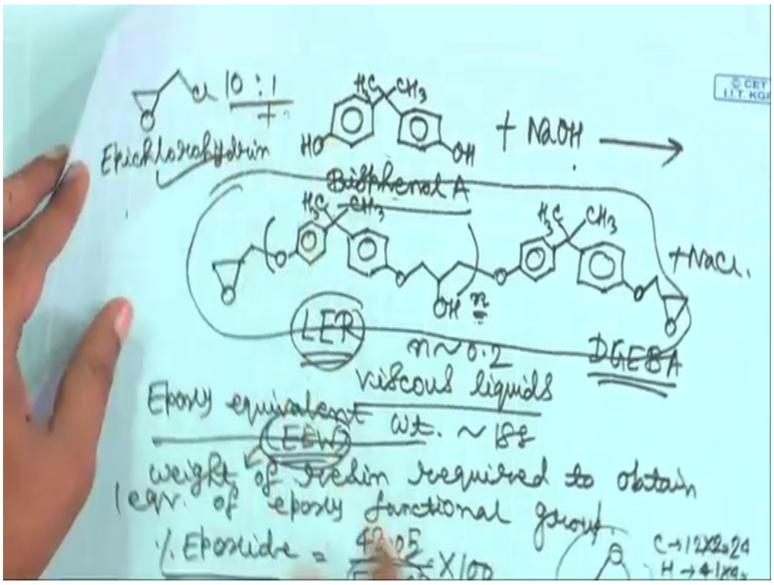

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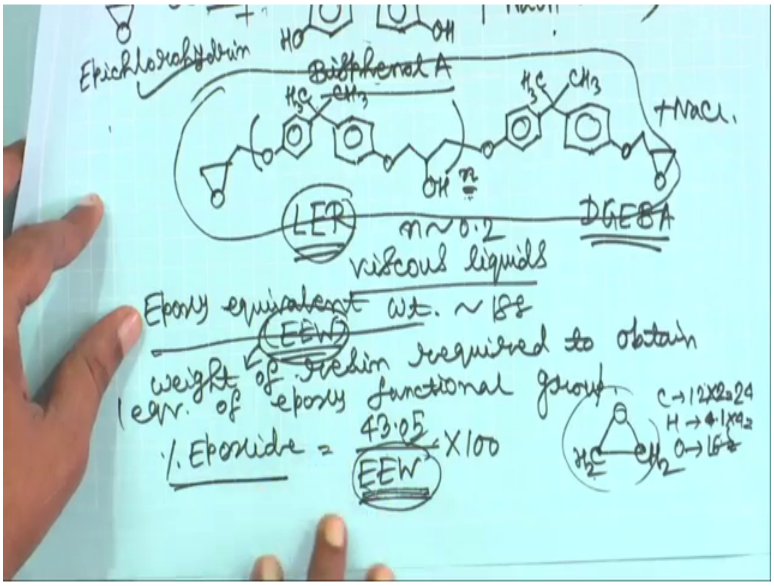

Then more than 85 percent of the reaction mixture the product that will be your glycidyl ether of bisphenol a that will contain that glycidyl ether of bisphenol a which is this structure.

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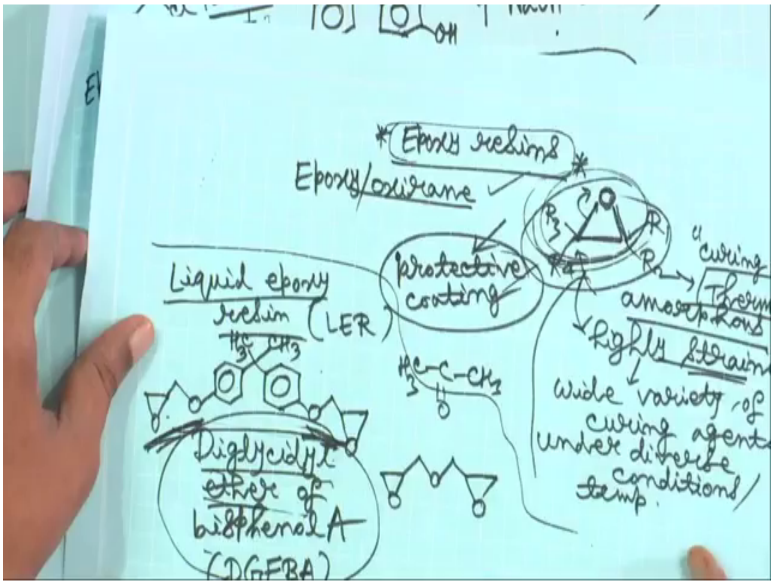

That means more than 85 percent of the material that is produced that will have your N value 0 and rest of that will be either N equals to 1 or N equals to 2, 5 to 15 percent of that. So, average of N is close to 0.2 and it will get what you call as the liquid epoxy resin.

Now, what is at the other end of the spectrum? If your N is 2 to 35, so if you have a high degree of from moderate to high degree of polymerization N is 35 or 2 or in between 10-15 whatever then what you get is solid epoxy resin SER. And of course, the epoxy equivalent wait for solid epoxy resin will be higher than liquid epoxy resin because liquid epoxy resin it is it is a smaller molecule and that smaller molecule has two equivalent of epoxy units and solid epoxy resin depending on the value of N, N very very high then it is a bigger molecule it still has two epoxy units.

So, basically the proportion of epoxy is less. So, the epoxy equivalent weight is higher you can also calculate according to the molecular weight because if you take the weight which is equal to the molecular weight we will get two equivalent of epoxy units.

So, that divided by 2 will give you your epoxy equivalent weight and that is also important because you want to ultimately cure this material you can react with the cross linker in order to make a thermoset material. So, you want to how much of epoxy linkage is there so that you will use that much amount of cross linker all right.

Now, so of course, if you are looking at high molecular weight solid epoxy resins of course, they could be not of very high molecular weight also because the N may be N equal to 2 is also not very high or if it is N equals to 30 35 then it is high molecular weight. Now, these materials of course, these are all based on based on diglycidyl ether of bisphenol A which is this N equals 0 then you have this diglycidyl ether bisphenol A. So, these solid epoxy resins that characterized by the presence of the secondary hydroxyl group this secondary hydroxyl group in the repeat unit and theoretically two terminal epoxy units are present.

Now, these kind of materials this solid epoxy resins they are widely used in the coating industry and if you compare them with liquid epoxy resin they; obviously, have a long longer backbone than the liquid epoxy resin they will have even longer backbone depends on value of N in value is high means even longer backbone. So, if you look at this material you have different cross link points you can either cross link to epoxy linkage you can open up the epoxy linkage and then you can cross link or you can cross link through this hydroxyl unit which is in the repeat unit

Now, if you compare between solid epoxy resin and liquid epoxy resin the epoxy linkage is the distance between the epoxy linkages is higher for solid epoxy resin than for liquid epoxy resin because this molecule is longer this N has value from 2 to 35. So, if you cross link then the distance between the cross links on an average is higher for solid epoxy resin than liquid epoxy resin.

So, if the distance between the cross links is higher then what you will get is improved flexibility, and we will also get improved toughness of the material the material will be less stiff of course, because the distance between the cross links has increased, but then the material will be also tougher because the points at which they are cross linked is the further apart and so the material can absorb more energy before it breaks. So, that becomes tougher.

So, that way you will have a difference of property between the liquid epoxy resin and solid epoxy resin and these kind of flexibility and toughness this is something that is much sought after for the particular uses usages that we talked about. So, that is why the solid epoxy resins are you know used quite widely in the coating industry. Also you could cure the resins through the hydroxyl units if you want. So, then you will create different network structures, different performances. So, you have the flexibility. So, if you understand the structure you know how to play around with a structure and you know how to modulate the properties.

Now, there are two processes through which I mean in general there are two processes which can be used to prepare your solid epoxy resins.

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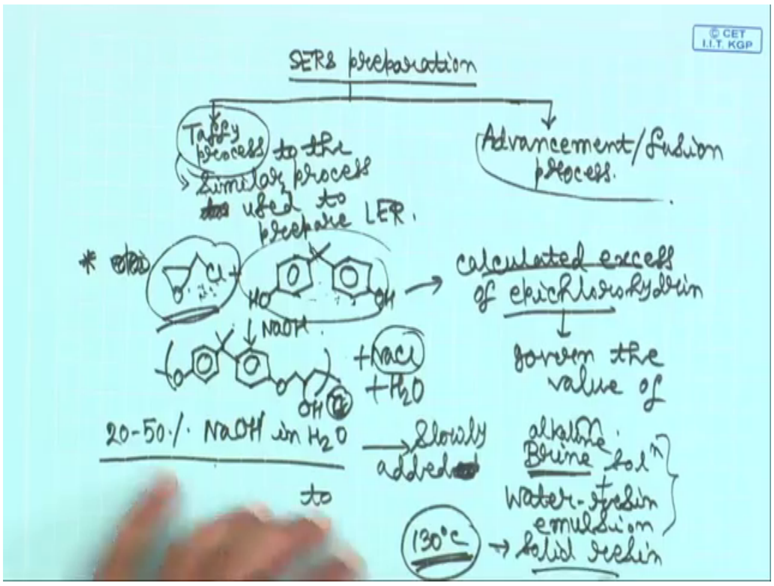

So, solid epoxy resin preparation. One of the processes is your taffy process taffy process and the other one is advancement or fusion process.

So, the taffy process that you are using it is a very similar process to the one used for prepare preparation of liquid epoxy resins. So, similar process, now this is a this is similar this is similar to the process used to prepare liquid epoxy resin. So, what you do here you directly obtain your solid epoxy resin by reacting your epichlorohydrin which is this with bisphenol A in presence of sodium hydroxide you know if you take 10 to 1 ratio then you get liquid epoxy resin. So, you take a lower ratio and depending on how low the ratio is you can modulate the value of N.

So, of course, the N value can become very high if this ratio becomes lower and lower I mean 10 to 1 being the reference point. So, if this ratio becomes lower than 10 to 1 depending on how lower it is becoming N value will increase accordingly. So, ultimately then this is a way to prepare high molecular weight epoxy resins or in other way in other words solid epoxy resin. So, you will get a product which is having a repeat unit like this the methyl groups I am not writing down, but the methyl groups are there. So, these two bonds have methyl groups and. So, this is your repeat unit we have talked about this before all right and in the process your sodium chloride is formed and water is formed.

So, taffy process is simply the process it is it is very similar to the process to prepare your liquid epoxy resin only difference is that for liquid epoxy resin you take 10 to 1 close to 10 to 1 ratio of epoxy of your epichlorohydrin to bisphenol A. And you are then reacting with sodium hydroxide.

We already talked about this process the mechanism of that that in the first step your sodium hydroxide or your hydroxide ion basically your base is acting as a catalyst in order to prepare your chlorohydrin and in the second step this chlorohydrin is dehydrohalogenated by the presence of stoichiometric amount of base and then you get your product. So, if you look at the process in slightly greater detail what you do is you take 20 to 50 percent of sodium hydroxide in water.

So 20 to 50 percent sodium hydroxide solution in water that is slowly added, slowly added to an agitated or a start will start mixture of epichlorohydrin and bisphenol A. So, this alkaline solution this sodium hydroxide solution you are adding slowly to an agitated mixture of or to a well start mixture of epichlorohydrin and bisphenol A and the reaction is highly exothermic.

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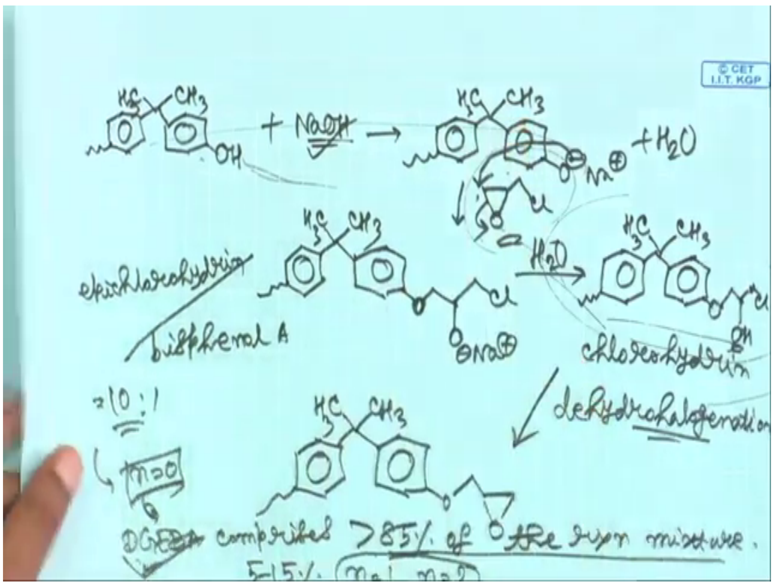

So, this coupling reaction proceeds during the initial stage is highly exothermic reaction and what happens is that. So, we talked about the coupling reaction it produces your chlorohydrin in the in the coupling reaction you will get a chlorohydrin. So, this is your coupling reaction. So, first it will be deprotonated and then that reacts with epichlorohydrin to produce a chlorohydrin. So, in the initial stages you will get this chlorohydrin as the reaction proceeds further and further this dehydrohalogenation will become predominant, all right. So, that is the overall process you are adding sodium hydroxide aqueous solution to a mixture of your epichlorohydrin and bisphenol A.

Now, for the taffy process what you do you just tweak the ratio of your epichlorohydrin to bisphenol a you bring it down below 10 to 1 in order to get the value of N that you want. Now, so what you do is you use a calculated you use a calculated calculated excess of epichlorohydrin and that will govern the value of N that will govern the value of N this value N, all right. And after the reaction is complete what happens is that this is a sodium chloride that is produced and the reaction mixture is also alkaline even a saturated solution of sodium chloride is your brine solution.

So, basically after the reaction is over you will get an alkaline alkaline brine solution and you will also get a water resin mixture your product has been formed your high molecular weight epoxy resin has been formed. So, this is water resin mixture basically this is on water resin emulsion what are resin emulsion. And what you do is that you separate out the phases and the resin that you have got you wash with water and then you heat it up to 130 degree Celsius typically around that temperature to remove your water and then you get your solid resin.

So, you will have a emulsion of water resin and alkaline solution you separate out the phases and then you wash the resin with water heat it up get your solid resin that is the procedure that is called taffy process. The other process is your advancement or fusion process.

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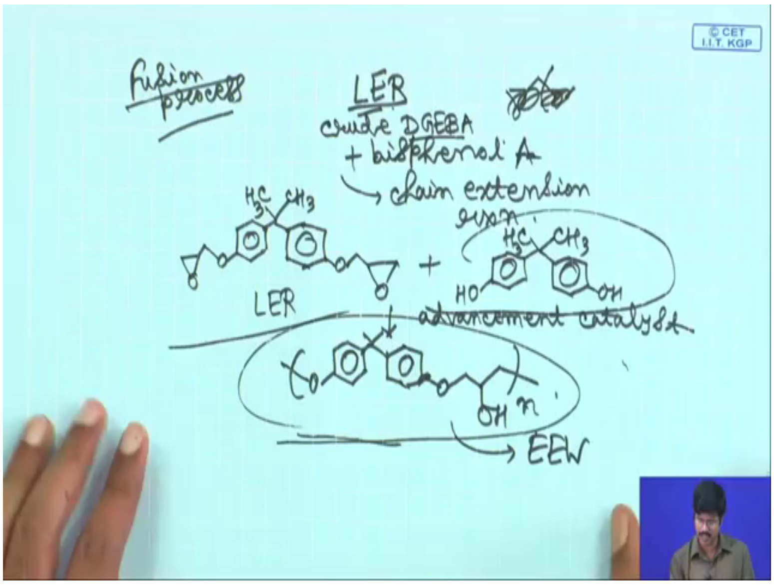

So, for the fusion or advancement fusion process what you do is you first LER your liquid epoxy resin ; that means, you take 10 to 1 ratio of this and you will get your liquid epoxy resin your N value. So, this is N your N value will be very low close to 0.1, 0.2. So, you have got your liquid epoxy resin. So, you start with this liquid epoxy resin or you can also say this is your crude diglycidyl ether of bisphenol A crude because this is not hundred percent diglycidyl of bisphenol A. So, this is your. So, basically you have this repeating unit here if you are looking at this repeating unit here and draw the general structure out. So, this is your general structure.

Now, this is your diglycidyl ether mostly you have diglycidyl ether LER liquid epoxy resin some part will be N equals to 1, N equals to 2 that is why you are saying this is a crude the diglycidyl ether of bisphenol A you take that and you react that with bisphenol a again because you know that when you are doing this epoxide when you are doing this preparation it depends on the ratio if this ratio is lower than N value is higher, but in this case what you are doing you already take a high ratio.

So, the N value is lower and then you add further amount of bisphenol A after. So, the process is the same it is a two stage process. Now, you add more bisphenol a. Now, what will, what it will do it will open up the epoxide linkages and it will it will extend the chain. So, that you will have these die these secondary hydroxyl unit inside it will extend the chain a your N value will become higher.

So, either you can take a high ratio of this to this to get your LER liquid epoxy resin and then you can add the bisphenol A which is your advancement process of fusion process or what you can do you let the start itself you take a lower ratio directly you get your solid epoxy resin which is a taffy process. So, for fusion process then you take your crude diglycidyl ether of bisphenol A and you react with bisphenol A.

So, this is your chain extension reaction, see in extension reaction and then you get your product. So, basically what you can do? You can depict it like this. So, this is your starting material. So, this is your crude diglycidyl ether of bisphenol A I mean I am just drawing as bisphenol diglycidyl ether of bisphenol A only I am not drawing some repeating unit here , but this is not 100 percent of these the starting material or the liquid epoxy resin all right. So, I am just putting LER even though this is what I have drawn is your hundred percent diglycidyl ether of bisphenol A.

So, that now, reacts with your BPA or bisphenol A and you are using what you call as advanced, an advancement catalyst and you get your product, all right. Now, this process if you are looking at this process the isolation of the product is quite simple because there is no need to remove a large amount of sodium chloride you remember that if you are using taffy process you have sodium chloride produced that you have to remove it separates so on and so forth. Those things you do not need to do and the degree of polymerization will be dictated by the ratio of your liquid epoxy resin to bisphenol A and if you have an excess of this liquid epoxy resin what will happen is that your polymer will have terminal epoxy units, all right.

So, if you are looking at this process a little more closely how much of relative amount of bisphenol A we have to use with the epoxy resin or the liquid epoxy resin to react with. How much of bisphenol A we have to use? In order to get a predetermined epoxy equivalent weight of the solid epoxy resin. So, this is your product right and we want a particular epoxy equivalent weight for this product. So, how do we calculate how much of bisphenol A we have to use to react with this liquid epoxy resin?

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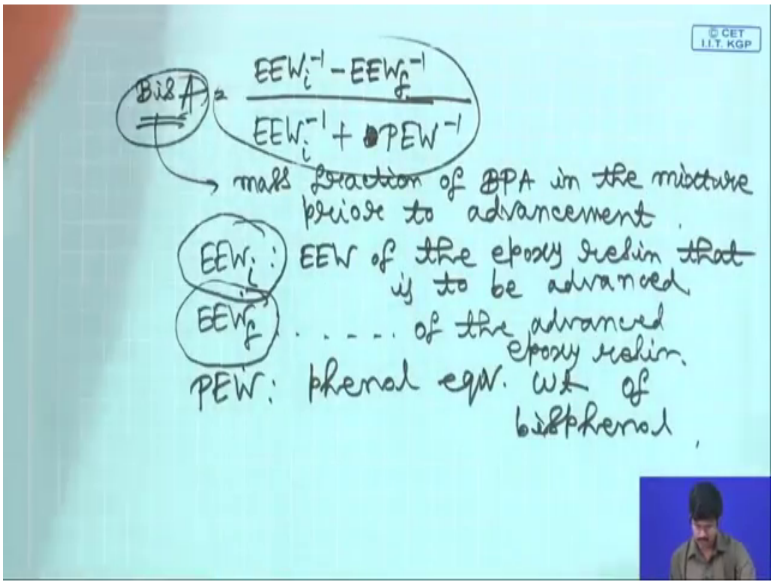

So, there is a simple way to calculate the formula is something like this I will explain let me draw this up first. This is the formula where this bis A this actually tells you this is the mass fraction of bisphenol A in the mixture prior to advancement. So, before the reaction occurs this much amount you have to take before, before the reaction of liquid epoxy resin occurs with the bisphenol A. So, this tells you how much of bisphenol A you have to take for the reaction, all right.

Now, EEW basically tells you the epoxy equivalent weight. So, this is the epoxy equivalent weight of i, i means initial. So, this is basically the epoxy equivalent weight of the epoxy resin that is to be advanced. Means that is the epoxy equivalent weight of your starting liquid epoxy resin that is a EEW i, i means the initial and EEW f is the epoxy equivalent weight of the final or the product or the advanced epoxy resin. See the process is called advancement process. So, the product that you will get a solid epoxy resin that is called advanced epoxy resin. So, you have advanced from this stage to these states that is the reason why you call it as advanced.

So, this is the targeted epoxy equivalent weight of the solid epoxy resin this is the epoxy equivalent weight of the starting liquid epoxy resin, and PEW is basically the phenol equivalent weight of bisphenol, all right. So, from this formula you can find out how much of bisphenol A you have to use in order to target a specific value of epoxy equivalent weight. In other words this tells you how much of bisphenol A you have to use in the reaction with liquid epoxy resin in order to obtain a specific value of N for the fusion or advancement process.

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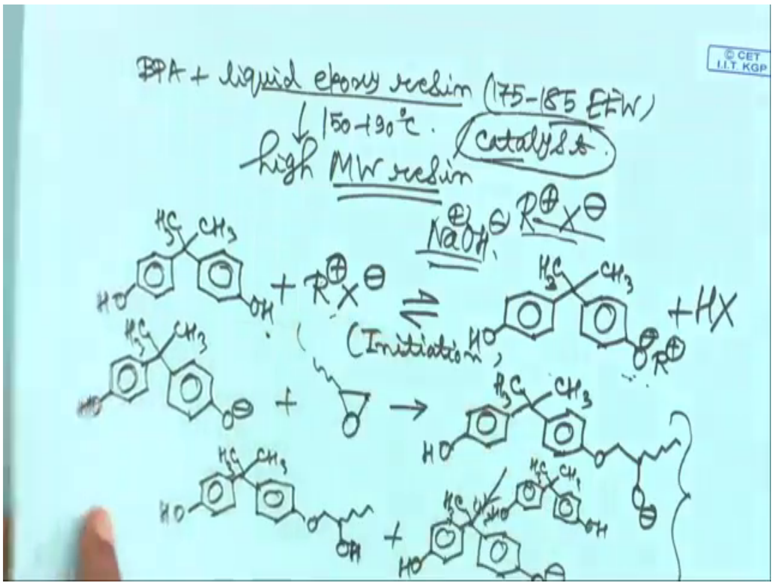

So, basically what you do here in this process in your advancement of fusion process you take your bisphenol A and the liquid epoxy resin you take the mixture and this liquid epoxy resin will have typically an epoxy equivalent weight between 175 to 185 all right. And then you heat it up to between 150 to 190 degree Celsius and in the presence of a catalyst which if it is often called an advancement catalyst and then you get your high molecular weight resin.

Now, the general form of this advancement catalyst is something like this, an example will be again sodium hydroxide N a plus O H minus ok. So, this is the general form like this. So, the mechanism is something like this. So, you have your bisphenol A that is present here. Now, this bisphenol A it reacts with your advancement catalyst and it is deprotonated. So, basically in a reversible fashion, so basically you will have a product which is like this O minus R plus and HX is produced all right. Now, this is a initiation step.

So, in the next step what happens, this phenolate ion that you have produced that will react with your epoxide. Now, I am just drawing a long chain here or some chain here because it is a liquid epoxy resin at the end of which you have an epoxy linkage even if it is diglycidyl ether of bisphenol A it has the epoxy linkage. So, this will attack on the less hindered side here more accessible here. So, it will produce this unit.

Now, this in the next step it can actually take one proton from bisphenol A. So, this is your bisphenol A. So, it can take a proton from bisphenol A and it can give you the product which is your extended chain. So, this will be this molecule all right. And what is produced? So, bisphenol A has lost a proton and that proton has come here. So, this is your product. So, the bisphenol A now, becomes a phenolate ion. So, you started with a phenolate ion and you get back the phenol ate ion. So, this is basically your propagation step.

So, in the initiation step step your catalyst will deprotonate to your bisphenol A. So, you create this phenolate ion and then there are two steps in the propagation in the first step that will react with the epoxide in the less hindered position it will attack and create this ion which will then take up a proton from another molecular bisphenol phenol A to produce your product. In the process it creates a bisphenol A phenolate ion.

So, this bisphenol a phenolate ion can again react with another epoxide and it can produce this molecule or if it has some epoxide linkage at the end of it so this can react with that epoxide linkage and it can extend the chain. So, that is why it is a propagation step and that is how you create your polymer by advancement process. So, you start with bisphenol A and your liquid epoxy resin and this is how you proceed.

So, finally, what I am going to tell you about a little bit about the cross linking process of these epoxy resins, cross linking of this epoxy resins.

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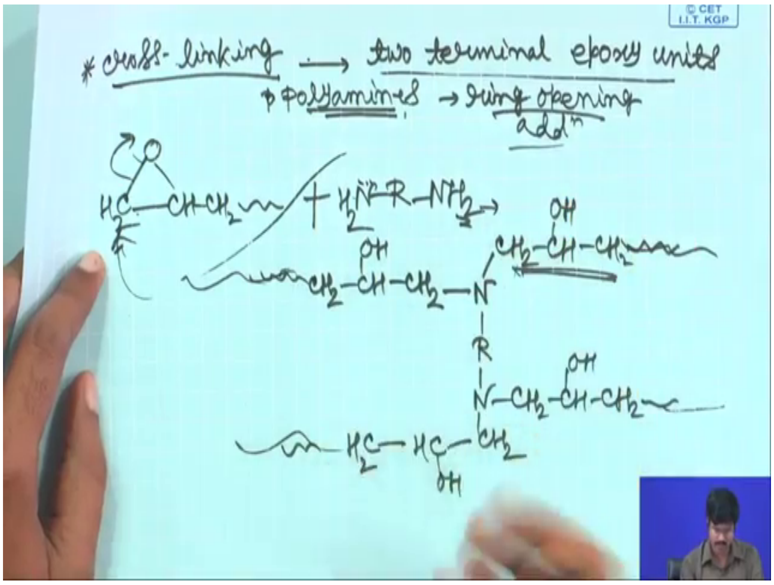

So, you can either use the two terminal epoxy units, you can use the two terminal epoxy units. But if the molecule is very very long then of course, your epoxy equivalent weight is very high; that means, in order to get one equivalent of epoxy unit you have to have more amount of the polymer. So that means, your epoxy proportion is lower. So, in that case your cross linking distance will be much much higher if you do not want to do that then instead of using epoxy units as the cross linking points you could use the secondary hydroxyl units that are present in the repeating unit of the molecule to also cross linked. So, those two we will show here.

So, the most common cross linking agents are you know poly amines all right. So, basically this is your ring opening addition of amine to the epoxide. So, it goes like this. So, you have an epoxide linkage at the end of your polymer chain that can react with let us say you are using a diamine. So, that can react with the diamine and then ultimately the product that you will get is something like this because the diamine can attack here and open up this hydroxyl unit and depending on how many you know nitrogens you have you can attack that many times.

So, basically all these protons ultimately will be replaced by these these chains. So, what I am saying is you will have a product which is something like that CH O H because it has opened it up and then you have CH 2 and then you have a nitrogen ok.

So, it has two protons. So, basically after it has attacked here it can attack to another epoxide linkage. So, that can be opened up again it will be like this and then you have R again it has NH 2 to hydrogen. So, instead of 2 hydrogens you will have reaction with 2 different chains I mean if you have 2 hydrogens it reacts with two different chains to replace the hydrogens and you will have a product which is like this. So, this is how you have cross linked. So, this is one chain, this is one chain, this is one chain, this is one chain. So, you have cross linking. So, this is one of the ways to cross link.

So, the final thing I would like to say is that. So, here, you have you know, so the process is this nitrogen attacks here this opens up and then you have this unit all right. And then you what you will have? You will have an H 2 plus here and you have O minus here. So, one of the protons can go here.

So, it will be O H like these an e will have NH and that that lone pair can attack another epoxy unit, there can attack another epoxy unit and then you have NH plus and it will be O minus and that hydrogen will go like this. So, depending on how many hydrogens you have that many number of units can come. So, you have 2 hydrogen, so the nitrogen. So, you have 2 units 2 units, so basically 4 chains have been cross linked.

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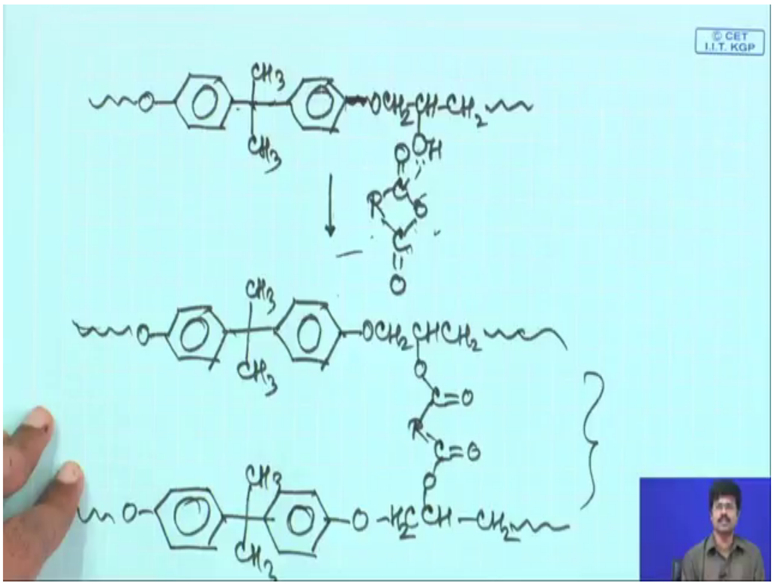

Now, as I told you can also cross link through the repeating unit hydroxyl unit the secondary hydroxyl that is present in the repeating unit. So, I am just drawing the bisphenol A in a different way again you have a tetra substituted carbon atom here. So, let us say this is the chain and CH 2 CH in the repeat unit you have secondary hydroxyl group we already showed this before and then you have the long chain. So, the typical curing agent that we use to cross link to the secondary hydroxyl units is an anhydride and typically it is a it is something like this cyclic anhydride you use.

So, I will just draw it like this all right R is some unit it could be also say for example, phthalic anhydride. So, in that case it will be an aromatic ring benzene ring so on and so forth. So, what will happen? This oxygen it can attack here and it can open up like this and also another oxygen from another chain or that oxygen from the secondary hydroxyl from another chain that can attack here and open up like this.

So, ultimately what you will have is a product which will be looking like this CH 3 CH 3 sorry this is not a wavy bond. So, O CH 2, CH, CH 2 and then oxygen carbonyl this opens up and then R CO O and then you have another CH CH 2 here and then you have CH 2 O. So, this is how you can link up two polymer chains cross linking.

So, I have shown you two processes through which you can cross link the epoxy resins either through the terminal epoxy linkages or through the secondary hydroxyl units present inside. And depending on the kind of performance that you want you can modulate this thing you can also create solid epoxy resins with a high value of N or with a medium value of N and so on and so forth. And the presence of epoxy gives you a lot of versatility in order to use different kinds of curing against different temperatures and all. We did not go into those many specific details, but I thought that is just talking about the general principles should do and should create a solid base for you in case you want to explore this thing further.

So, what we will do is we will stop today here and in the next class we will talk about the synthesis of poly carbonates, and then we will go into the structure property relationship of poly carbonate.

Till then, thank you and good bye.