Principles of Polymer Synthesis
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Lecture - 42
Synthesis of Industrial Polymers (Contd.)

Welcome back; to this course on principles of polymer synthesis. We have been talking about the synthesis of poly urethanes in the last class and we will continue talking about that in today's class also. So, the topic remains the same synthesis of industrial polymers.

So, we will directly go back to what we were discussing in the previous class that was the spandex fibres. So, if you go to the structures now.

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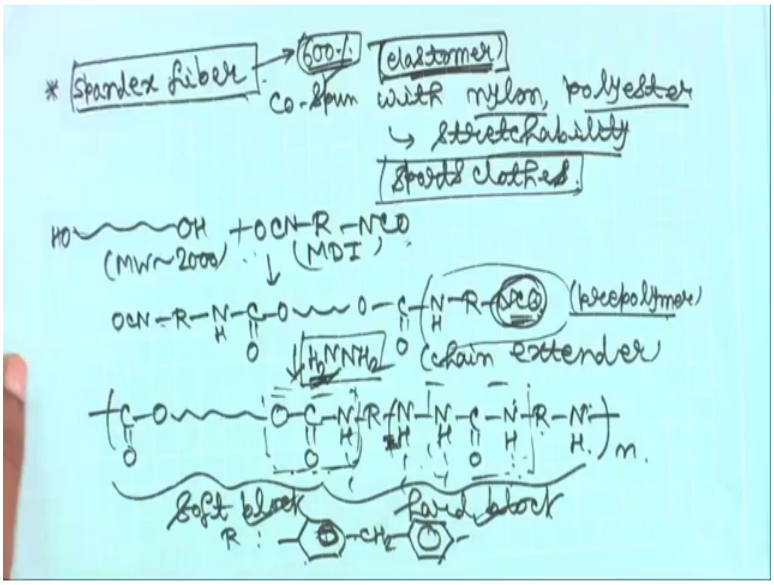

So, basically your dye all you could react with the diisocyanate and then you have your pre polymer, pre polymer and then you can react with your chain extender in this case you are reacting with a diamine.

So, in fact, this structure is not completely correct. Of course, you can figure out because previously I have already given you the principle of how to draw the structures. So, I am going to redraw the structure here.

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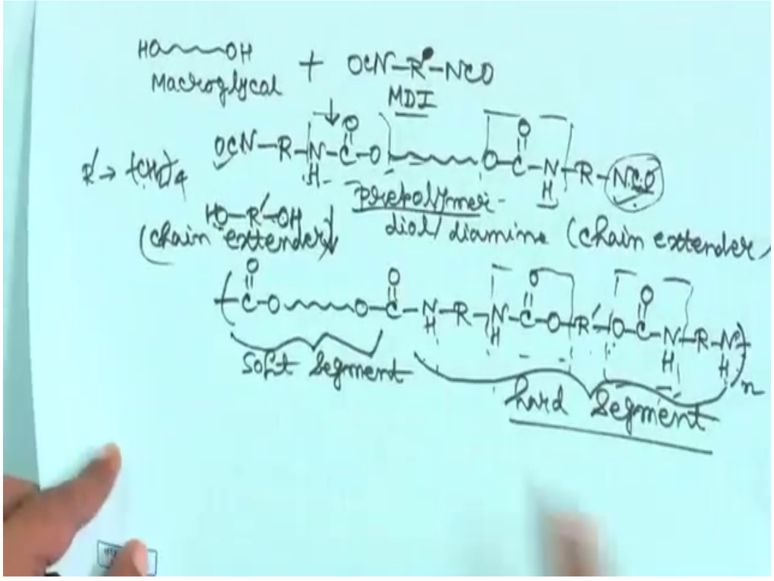

So, let me draw it up again.

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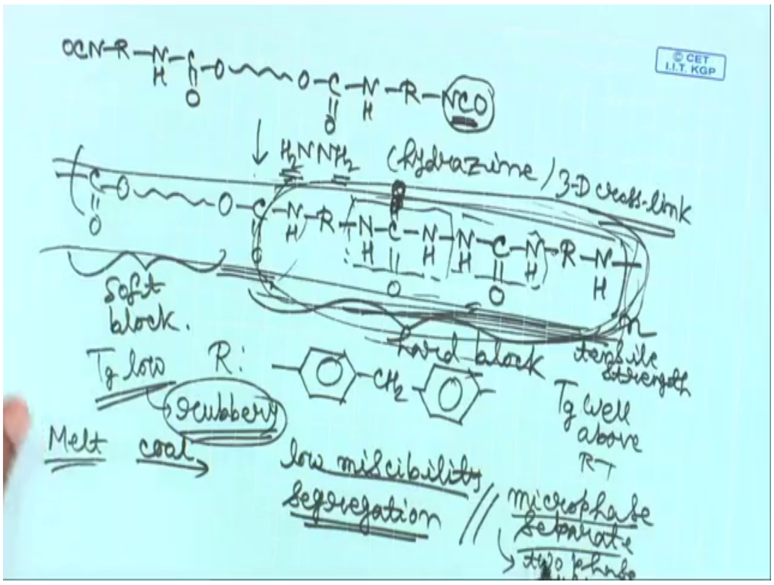

So, you have now, produced your N C O N H C O O. So, this is your pre polymer.

Now, this pre polymer you are reacting with it with hydrazine with hydrazine which is your chain extender. So, basically what you have to do is the following you have your polymer chain. So, you start from this side and you have N H R. Now, this N C O will react with amine all right because that that N C O here was missing. So, that was the mistake. So, you have to when you are doing this you have to do it very carefully and you have to look at all the atoms that you are reacting. So, this N C O will react with NH 2. So, that will be your N H C O. So, in fact let me draw the carbonyl on this side because I am drawing all the carbon is for the bottom it does not matter. So, N H C O and then you have this amine. So, this will be N H, N H and then again you have you have to react on this side that I mean with an isocyanate. So, then again it will be N H all right and then you are drawing up the rest of the molecule R N H N. So, this structure is correct.

Actually here what is isocyanate the reaction of isocyanate with amine that particular part was not drawn here. So, this structure is your correct structure. So, basically what you will have here, then is your urea linkage and you will have the urea linkage here and you have the isocyanate you have the urethane linkage here. So, this is your hard block and this is your soft block all right, and your R is this in this case this is methylene diphenyl diisocyanate that you are reacting.

Now, the polymers that you have prepared by this process the polymers that you prepared by this process say you either you talk about a polymer which is based on a chain extender using a diol or you can use a chain extender which is a diamine in this case a specific dye anime we are using. So, what you will have is in both the cases you will have a soft segment which is your flexible segment which is generated from your macro glycol unit and you have a hard segment which has a possibility of lot of hydrogen bonding interactions all right, between your urethane linkages if you are reacting with a diol or your amide linkages if you are reacting with a diamine.

So, this is your hard block and this is your soft block. So, for the hard block the T g is well above room temperature for the soft block the T g will be low. So, this soft block will be rubbery in nature and this hard block you know, so this will provide the material with the strength. So, we will discuss it in more detail.

Now, so what you do let us say you have a melt of this material and you cool this down. So, what happens? This hard block and soft block they do not mix very well. So, they have a low miscibility. So, they have low miscibility low miscibility of hard and soft blocks that leads to segregation. So, when you cool down the melt what happens the hard blocks and soft blocks they do not mix and they segregate. So, basically they will what you call as micro phase separate. So, basically you will get a two phase system. So, you have a two phase system.

Now, the domains that are formed by this hard block what will happen is that those domains will be crystalline because they are neatly held by these strong hydrogen bonding interactions. So, you will have a crystalline domains and those domains will basically provide 3D cross link centres for the whole material cross linking is because of the hydrogen bonding interactions all right.

And those domains or that domains formed by the hard segments those will be responsible for the for the tensile strength of the material and for the stiffness of the material, all right. So, if you look at the situation a little bit more closely. So, what will happen? When you cool the system down, so you have these kind of domains that will appear. I am just drawing it in a very simplified way.

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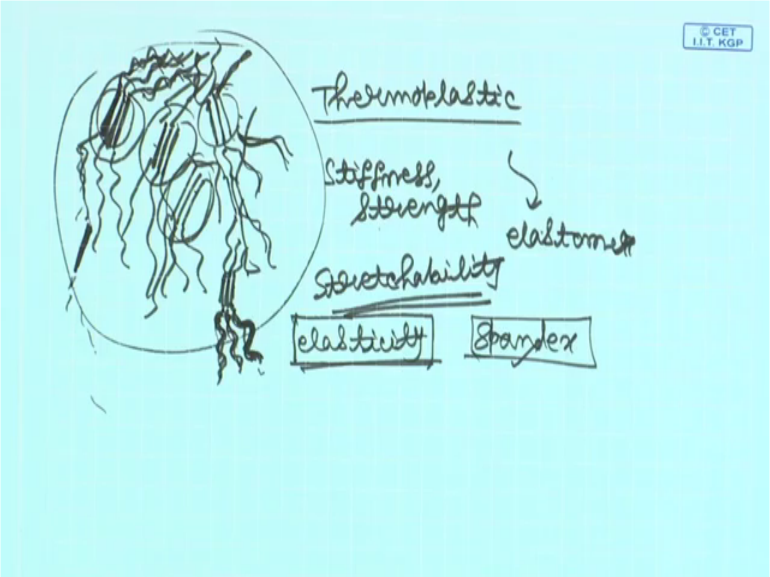

Now, these domains are basically your this part your poly urethane this segment. So, let me let me say each rod that I am drawing is basically this particular block and the other say this rod is from one polymer chain this rod is from another polymer chain this rod is from another polymer chain, and so and these flexible units that you are having from each polymer chain those are basically your macro glycol that polyester part.

So, you see that for each rod here I am drawing on both sides this kind of flexible chains and then of course, at the end of this flexible chain you can have maybe another rod. And then again you have this kind of stuff because you basically have a hard domain and a soft domain and then this polymer molecule you know you have a hard domain and then a soft domain a soft domain on this side again another hard domain another soft domain like this.

The point is that the hard domains will come together through hydrogen bonding interactions. So, they basically provide 3D cross link centres for the whole system and these cross links are basically present in the material which will have what you call as a soft matrix which is made of this flexible chains which are basically your polyester part all right so obviously, then you have this kind of cross links and these cross links will basically give you the stiffness of the material and this will also give you the tensile strength of the material.

But when you heat this material up the interaction between the different chains, the hard blocks in the domain that interaction will disappear because the interaction is basically your hydrogen bonding interaction which is reversible. So, if you heat it up the material becomes processable.

That is why it is a thermoplastic material because if you heat it up it will start to flow and if you cool it down. Then again these crystalline domains will appear these are your crystalline domains those crystalline domains will appear and they will provide this kind of cross linking interactions and they will give you the stiffness and the strength of the material.

What about the term elastomer? If you are looking at these flexible chains actually this drawing becomes more complicated after because in each domain for each rod you will have all these flexible chains on both sides after the flexible chain you will have another hard segment so on and so forth. So, this material if you look at this material in a in a more in a closer detail you have these soft segments that are protruding out of these hard blocks.

Now, the soft segments they are coiled sometimes like this or they are you know wavy like this. So, what you can do when you are extending this material until these soft domains are extended to their full length you could continue to extend. So, they will break. So, what will be the breaking point at which all these flexible chains they become straight. So, basically you can say that these flexible chains contain hidden lengths. So, they can be extended.

So, from there your stretchability will come because you are material is stretchable your material is not only stretchable, but your material is also having quite high stiffness. Stiffness because of these kind of appearance of these kind of crystalline domains of hydrogen bonding interactions between the hard polyurethane segments and the material is also thermoplastic because these interactions will disappear these domains will disappear when you heat it.

And the material is also elastomeric because what happens is that they are stretchable because you have all these soft flexible chains which can be extended to their complete length until they are extended to their complete length you can keep stretching. And when you remove your applied force applied outside force they can come back because I mean they do not start to flow when you keep applying force because ultimately what happens is that these soft blocks they are covalently bonded to the hard blocks.

So, they just do not go away. So, the flowability of the material is restricted because a soft block is connected to the hard block and when you release your applied stress what will happen is that it can come back to its original situation. So, it will have this kind of stretchability and of course, the material will have elasticity because it can come back whatever chains you have if you stretch them completely and then if you release them.

Now, these chains are not going anywhere they are connected to these hard blocks. So, then they can again come back to their you know curly this kind of situation when you when you remove the applied force. So, what will happen is that the material will also have elasticity.

It will be non-linear of course, because your stress versus strain is not linear after, but it will still be elastic that is why it is called thermoplastic elastomeric material and as I am already told before that the spandex has used in your fabric in your clothes especially for sportswear, you will course go spin this particular fiber with your nylons or with your polyesters. So, this also will go into the fabric that will give the stretchable property to the material that can withstand a lot more we are entire, all right.

So, I think that is more or less that all that I wanted to talk about poly urethanes. But one of the other uses also is as you know forms because those materials typically what can happen is that you know the carbon dioxide can evolve when you break these urethane linkages. And if you suitably process the material this carbon dioxide can you know create a lot of volume inside the material and then you can have what you call as a foamy material. And this kind of thermoplastic forms they can be used in you know automobiles the interior of the automobile they can be used in the dashboards of the automobile or they can be used to make up the seats also. So, those are some of the uses that you should keep in mind.

So this finishes our discussion on thermo plastic poly urethanes in particular and poly urethanes in general. So, we talked about the synthesis of poly urethanes specifically, we talked about the thermoplastic elastomeric nature of the poly urethanes, how you can create hard blocks and soft blocks, how the hard blocks can come together when you cool down the melt and you create the crystalline zones or the hard domains that gives you the 3D cross linking points of the whole matrix and that provides the stiffness to the material.

And how those interactions will break when you heat the material up and then you get your thermoplastic material. And when you try to stretch the material they can be stretched to 6 times or even 7 times like that. So, 600 percent strain for example, the spandex fibers to 6 times their length they can be they can be extended and that is because they have all these flexible chains that can be extended to their complete length I mean they also contain the heated length as I am telling you.

And they are also attached to your hard blocks so they do not just go away. So, if you remove the applied force they can come back. So, that elasticity also is ingrained into the material elastic property is also ingrained in the material. And last, but not the least this thermoplastic property if you look at the thermoplastic property and if you somehow create some covalent cross links in the material then that will destroy the thermoplastic properties. Why I am talking about covalent cross links is because if you remember in the last class we talked about the biuret and allophanate cross links like your isocyanate can react with your urea linkage or it can react with your polyurethane linkage both are present in the system because in this case you are using say for a spandex you are using a diamine specifically hydrogen as the chain extender. So, what can happen is that these kind of cross links can form and once this cross links are formed they are covalent.

So, what do you think that they should then destroy the thermoplastic nature because covalent bonds , but the point here is that these crossings are reversible I already talked about it before. So, when you heat the material up these cross links will break. So, the material becomes flowy again.

So, even though such cross links like a allophanate biuret such cross links can form in the material they will break when you heat the material up of course, you have to heat the material in order to get the flowy nature or the processability out of it the very definition of thermoplastic. So, the thermoplastic property is not destroyed. The bottom line is that this property is not destroyed despite the presence of these kind of cross links all right.

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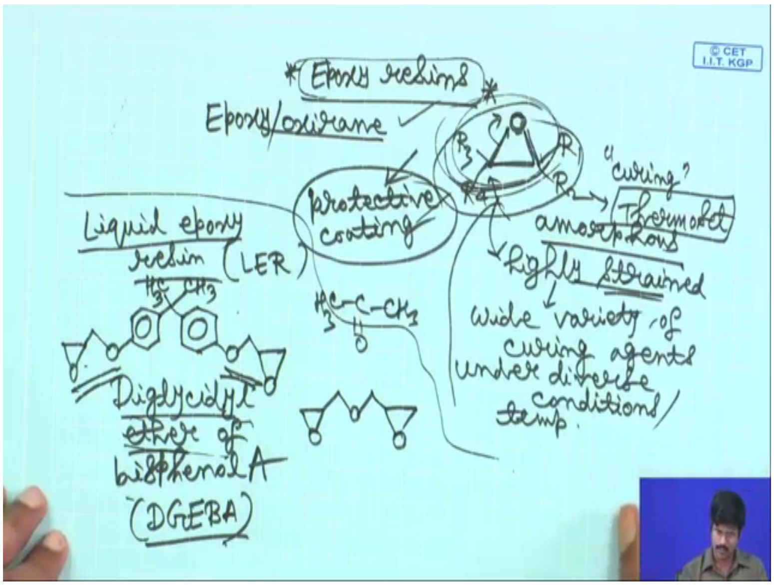

So, that finishes our discussion on urethanes what we will start about start talking about next is epoxy resins.

So, epoxy resins they are typically characterized by the presence of more than 1 3 membered rings and those rings are typically you know the epoxy rings or you can call them them as epoxide rings or oxirane. So, typically those are you know epoxide rings like this 3 membered ring with an oxirane this is your epoxide and just putting different groups there.

So, epoxy resins are typically characterized as I told by the presence of more than one such linkage and this epoxy linkages can be opened up and you know if you have a nucleophile that attacks a or it can open up here like that. So, you can cross link chemically a material which has these kind of linkages you open up and then cross link and that is called your curing, and ultimately what you can get or thermoset materials materials which have permanent cross links which cannot be further processed by heating. And typically these are amorphous thermo set materials and they will have excellent mechanical strength and toughness good adhesive properties so on and so forth good corrosion resistance.

Now, that is why typically you will use these as in protective, protective coating applications, protective coating applications and you know this is a 3 membered ring and an oxygen is present. So, this is a highly strained highly strained system highly strained. So, that is why they can react with a wide variety of curing agents, under diverse conditions under diverse conditions or diverse temperature different temperatures. So, that is what imparts versatility to this epoxide linkages because ultimately are going to get thermo sets by opening up these epoxides and preparing cross linking cross linking different chains and these are highly strained as I have already told and wide variety of reactants wide variety of cross linkers or curing agents you can use.

When you discuss the synthesis of epoxy resins you start with what you call as liquid epoxy resin or LER which is based on this molecule. This is diglycidyl ether of bisphenol a die. So, the abbreviation is diglycidyl ether of bisphenol A, DGEBA. So, your liquid epoxy resins are typically based on DGEBA. We will explain why.

Now, a little bit more about the name. So, if you have an alcohol on both side this is your bisphenol A we already talked about bisphenol A. So, basically you start with phenol which is a phenol ring and then O H you react your phenol with acetone if you react your phenol with acetone then a condensation reaction occurs and you get your bisphenol A O H on both sides. Now, diglycidyl ether linkage is basically this. So, this is diglycidyl ether ok. So, you see that the unit is there on this side on this side that is why this diglycidyl ether of bisphenol A, all right.

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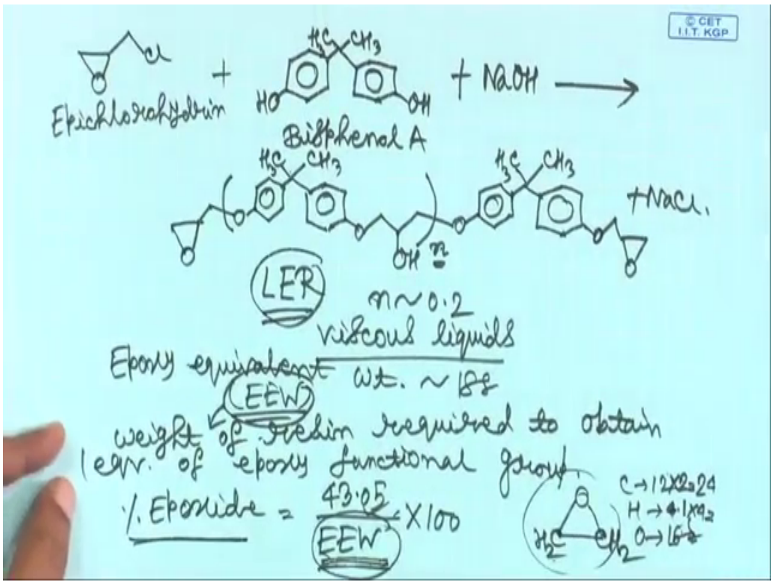

$n \sim 0.2$

viscous liquids

Epoxy equivalent wt. ~ 188

(EEW)

weight of resin required to obtain 1 eqv. of epoxy functional group.

$\%\ \text{Epoxide} = \frac{43.05}{\text{EEW}} \times 100$

So, the synthesis of liquid epoxy resin is done by the following scheme. So, you react what you call as epichlorohydrin you react your epichlorohydrin with bisphenol A you react epichlorohydrin with bisphenol A this is bisphenol A in presence of sodium hydroxide and then the product that you will that you will get has the formula like this.

So, this is your bisphenol a unit here, in the secondary alcohol inside and that ends with the glicide glycidyl ether. So, basically if you look at this particular molecule this is the general formula of the of the product this is oxygen this is a general formula of the product. So, you can see that if this n is 0 then basically what you have got is your diglycidyl ether of bisphenol A on this side glycidyl ether this side glycidyl ether and then have bisphenol A. So, if this is not there then you have a bisphenol A and on both sides like glycidyl ether.

So, basically this is DGEBA, but if you have, so it all depends on the ratio between the two if you have an excess of this typical it is 10 is to 1 then what will happen this n value will be very close to 0. Mostly you will have DGEBA or diglycidyl ether of bisphenol a, but when this proportion of this starts to become lower less than 10 to one. So, this is 10 to 1, if it is less than 10 to 1 then this n value also will start to rise as you can see that one more unit of bisphenol A has come inside here. So, of course, if the ratio changes then this n, so this is the general formula. So, this n also the value of this n also will change. So, we will discuss this in little more detail now.

So, this will be your, this is the general reaction for epoxy resins. Now, this will be a liquid epoxy resin when the degree of polymerization which is your n, it is very low, n is very close to 0.2 that is why we told that a liquid epoxy resin is based on your diglycidyl ether of bisphenol A this value is very very low. So, this is typically mostly diglycidyl ether of bisphenol A.

Now, as I as you can see already and you can suspect the typical commercial liquid resins on liquid epoxy resins their viscous liquids their viscous liquids the n value is very small and their what you call as epoxy equivalent weight the epoxy equivalent weight is around 188. What is this epoxy equivalent weight? what is this term that I have introduced here? Epoxy equivalent weight the definition is something like this, this is the weight of resin required to obtain one equivalent of epoxy functional group all right.

So, let us say. So, if you see for example, diglycidyl it in ether diglycidyl ether. So, one molecule has two epoxy units if you look at this molecule let us say n value is very high still this one molecule has two epoxy units. But if you compare with this of course, this molecular weight is lower than this molecular weight, so which will have which of these two molecules will have higher epoxy equivalent weight this molecule will have higher epoxy equivalent weight because this is the weight of resin required to obtain one equivalent of epoxy functional group.

So, if you take say the molecular weight is x. So, if you then take x gram of this molecule then you will get two equivalent. So, one equivalent of this molecule is basically your x gram of molecule is basically your molecular weight is x let us say in that case it is x gram will give you 2 equivalent. So, how many grams will give you one equivalent? That will be x divided by 2.

So, that will be your epoxy equivalent weight. But if you look at here this is also we say y divided by 2, if y is your molecular weight, but the molecularity is lower. So, the epoxy equivalent weight here is lower. So, this is the definition. Then weight of the resin required to obtain one equivalent of epoxy functional group. So, since the molecular weight is lower in order to obtain one equivalent you will require lower amount of this. So, basically it is like how much is the proportion of the epoxy units present in the molecule.

In a nutshell this is the concept that is being provided by epoxy equivalent weight. If this epoxy equivalent weight is high that means, the proportion of the available epoxy units is lower in the molecule because with respect to the molecular weight if you have a very high molecular weight, then also one equivalent of the molecule is providing two equivalent of epoxy units and if you have a small molecular weight then also it is providing two epoxy units. So, of course, if you have a small molecular at the proportion of the epoxy units is higher. So, that is what is given by this epoxy equivalent weight.

So, then the percentage of epoxide percentage of epoxide present in the material is basically 43.05 divided by epoxy equivalent weight into 100. So, of course, if your epoxy equivalent weight is higher then your percentage of epoxide is lower. So, if your n value is higher than your epoxy equivalent weight becomes lower and what is 43.02. So, if you just take the epoxide here. So, carbon is 12 hydrogen is 2 plus 2, 4 oxygen is 16. So, so this is 12 into 2, 24, is close to 44 actually it is not that because the there will be some decimal points 20 plus will be 12 point something hydrogen is basically 1 into 4, so this is 1 point something and oxygen will be 15 point something like that. So, this is basically your 43.02 close to that will be your molecular weight of this particular unit.

So, that divided by epoxy equivalent which is your percentage epoxide. Why you require to know this? Because when you are curing your epoxide resin you need to know how much of curing agent you have to use that is why you need to know what is the proportion of epoxy present in that particular molecule. And that is what is given by your epoxy equivalent weight.

So, of course, if it is asked to you what is the epoxy equivalent weight of diglycidyl ether bisphenol A you should be able to find out because you know the molecular weight and you know how many epoxy units are there. So, you can find out and the same way you can also say what is the phenol equivalent weight of bisphenol A principle is the same. So, you can find out by that principle.

So, what we will now, do is we will try to take a closer look at this particular reaction. So, so the first step in this particular reaction is the base catalyzed coupling of this bisphenol A with epichlorohydrin. So, what happens here is the following.

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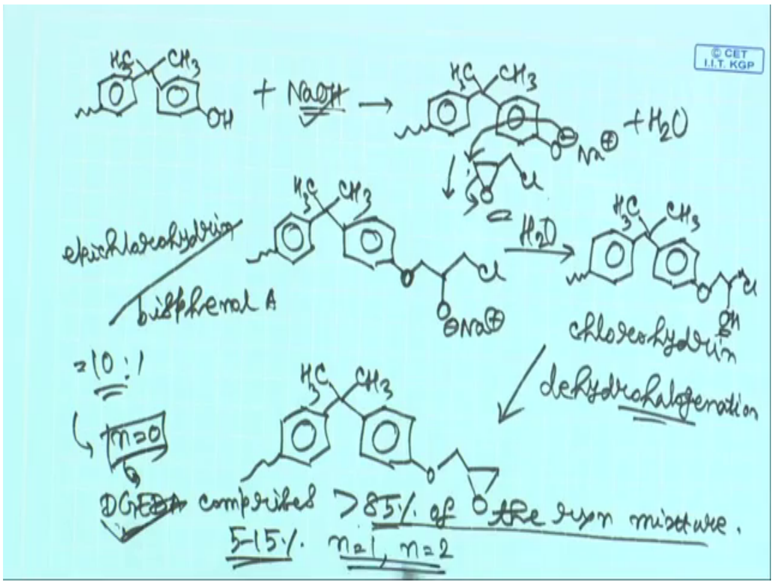

So, I am just drawing this part is some general part and then you have the bisphenol A hydroxyl unit on this side, all right. So, this reacts with sodium hydroxide. So, this is this acts as a catalyst and then you will have O minus Na plus and then water that is produced. Now, these reacts with your epichlorohydrin. So, of course, this will attack on this side which is hindered which is less hindered side and this will open this up. So, ultimately what you will get is the following all right.

And if this is protonated, this will be protonated my water. So, what you will get is basically, so secondary hydroxyl unit this is how the secondary hydroxyl unit will be generated this is called your chlorohydrin. So, the this is a basically base catalyzed coupling of bisphenol A, bisphenol A with your epichlorohydrin to give you a chlorohydrin and then the second step is basically a dehydrohalogenation dehydrohalogenation of this intermediate which is a stoichiometric amount of base. So, the first step the base is acting as a catalyst, it is a catalytic amount because this is regenerated you can see O minus it takes up a proton and then O H minus will be generated you start with O H minus you get back to O H minus, so, that will be your catalytic amount.

And the last step it will be stoichiometric amount because it can abstract this proton here and this O minus this O minus can attack on this site and the chlorine will be going out. So, ultimately you will have a dehydrohalogenation stoichio with stoichiometric amount of base for the last step and this will be your product. So, you have CH 3 CH 3 and then you have. So, this is your product.

Now, something that you should keep in mind and something that I also told you that what you are going to do is usually you are going to use 10 is to 1 of epichlorohydrin to bisphenol A. High ratio of epichlorohydrin to bisphenol A has to be used in order to minimize the in order to minimize the value of, in other words in order to maximize the yield of diglycidyl ether of bisphenol A all right. And in fact, here if you are using, so epichlorohydrin, so your epi chloro hydrin to bisphenol A, this ratio if you are taking 10 is to one then what you will have is that you will have maximum amount it will be n equals to 0 the product will be your diglycidyl ether of bisphenol it is a equals to 0. And this monomer will comprise, so this monomer.

So, the DGEBA diglycidyl ether of bisphenol A it will comprise more than 85 percent of the reaction mixture the product will be more than 85 percent will be DGEBA reaction mixture.

And typically, so this is your liquid epoxy resin preparation. So, more than 8y 5 percent of the reaction mixture will be your diglycidyl ether of bisphenol A which is this molecule. So, your n value is very very small I already told n is quite close to 0.2 very small value. And 5 to 15 percent, so rest of it will be higher all ecommerce mostly it will be n equals to 1 or n equals to 2 compounds. So, on an average then the value of n will be very very low and that will be your liquid epoxy resin.

So, to summarize what we have talked about epoxy resins until now, that this epoxide linkage is a highly strained system. And so this makes it versatile to be reacted with different curing agents under different sets of conditions different temperatures. And so it is based on diglycidyl ether of bisphenol A and this is your diglycidyl.

So, this is your diglycidyl ether linkage and you react with your epichlorohydrin with bisphenol A presence of sodium hydroxide to generate your final structure of epoxy resin and depending on this ratio if this ratio is very very high typically 10 to 1, then this n value is very very small and what you will get is a highly viscous liquid and that will be a liquid epoxy resin. And typically your n value is close to 0, n equals to close to 0.2, 0.3 like that getting your liquid epoxy resins and we also talked about the concept of epoxy equivalent weight.

So, what we will do in the next class is we will continue discussing about the preparation of epoxy resins. More so, we will start talking about the solid epoxy resins and then we will also talk about how to cross link these different epoxy resins.

So, until then, thank you and see you in the next class.