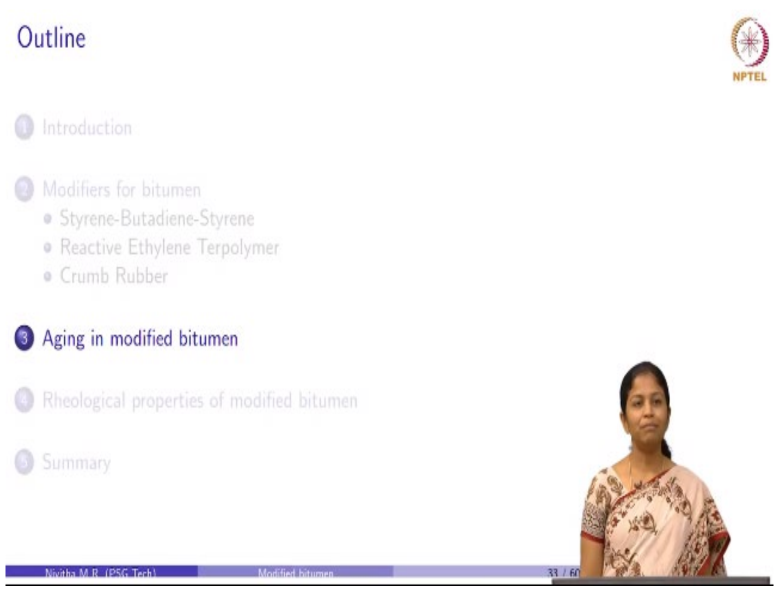
Mechanical Characterization of Bituminous Materials
Dr. M. R. Nivitha
Assistant Professor
Department of Civil Engineering
PSG College of Technology, Coimbatore

Lecture No - 35
Modifiers for Bitumen – Part 03

(Refer Slide Time: 00:13)



Welcome back to this lecture on modified bitumen. So in the previous class we have been discussing about different types of modifiers that have been used for bitumen modification and how few of the modifiers interact with bitumen. So we have seen that styrene butadiene styrene undergoes a physical interaction whereas plastomers mostly of reactive ethylene terpolymer group undergoes both physical and chemical interaction.

And we have also seen that crumb rubber undergoes physical interaction and it also has some inert materials in it and we also saw that under specific conditions it can also undergo chemical interactions. So in this lecture today, we are going to see about aging in modified bitumen and also the rheological properties of modified bitumen. So before we start aging I want to touch upon two topics: the first one is what happens when the unmodified bitumen ages?

So we have seen this in detail in the previous lectures, so the aging in unmodified bitumen is a result of the oxidation process and various other factors but we have predominantly attributed it to the oxidation process, so because of the absorption of oxygen there is formation of oxides mostly carbonyl and sulfur oxide. So these oxides are more polar in nature and so they try to form agglomeration and they increase the viscosity of system.

So this is the background on aging which happens in base bitumen in the presence of oxygen. The next thing which I want to touch upon is the production of modified bitumen, so in the last class we just saw it in brief when we were discussing about certain factors of modified bitumen and we are not discussing that in detail in this lecture because that is mostly industry related; for different type of modified bitumen they tweak the production process and they do lot of other things to make them compatible and also meet the specific grading requirements.

So we are not discussing about that in detail but I just want to tell you how the production process goes on. The production process happens when the modifier is added to bitumen at high temperatures; the blending temperature is again here a variable, depending upon the type of modifier and the base bitumen, the blending temperatures can vary from 150 to 185 degree Celsius.

So at these temperatures the modifier is added to bitumen and they are sheared at very high shear rates. The shear rate here varies from 3000 to 6000 rpm, so this is to make a homogenous blend and distribute the modifier uniformly in the base bitumen. So this is done for about 20 to 30 minutes again depending on the type of modifier. So after this initial high shear period there is a low shear period.

So this low shear period is specifically required for modifiers which contain elastomers. So we have seen that these elastomers absorb the lighter fractions which are present in bitumen and swell in volume, so this is mostly due to the diffusion process. Diffusion of lighter fractions which are present in bitumen into the modifiers, so we need to provide sufficient amount of time for this diffusion process to occur.

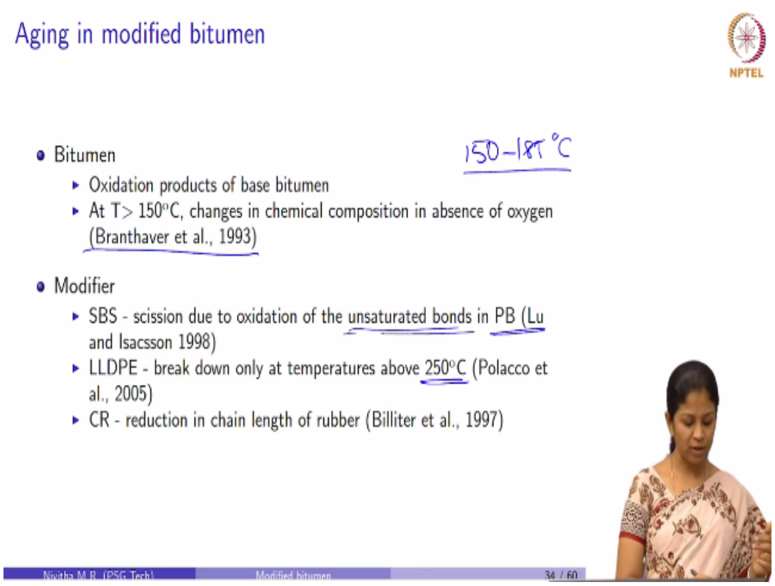
So that is why most of the elastomer-based modifiers like SBS and crumb rubber, we need to provide a digestion time, this is called as a digestion time or time to develop interactions. So after this high shear blending which occurs for 20 to 30 minutes at 3,000 to 6,000 rpm these binders are then subjected to low shear, again we have temperature high temperatures but not as high as 150 to 185 maybe roughly around 100 to 120 degree Celsius.

So at these temperatures this modified bitumen blend is now subjected to low shear, so the shear rate here can be between 500 to 1000 rpm. So this mix is subjected to this shear rate for about 6 to 8 hours and in this time period it is expected that the interactions will develop. However in the case of certain modifiers like plastomers we do not have any diffusion process happening right?

So there is diffusion process because of the diffusion of lighter fractions into polyethylene but this poly ethylene absorbs only very small fraction of lighter fractions and we do not have to provide long time for this digestion process to occur. So we have seen that in the case of reactive ethylene terpolymer the interaction is mostly because of chemical bonding, so once we add the modifier to bitumen, they start forming chemical bonds and the interaction process is over at that stage, so we do not have to provide these long duration of digestion period in the case of reactive ethylene terpolymer.

So maybe a half an hour or one hour time period is provided at low shear conditions for the blend to homogenize. So we need to remember these two things when we start looking into the aging that happens in a modified bitumen.

(Refer Slide Time: 05:19)



So we are going to now look at the aging in modified bitumen under two heads, one is what happens to bitumen as in when you age it? The second one is what happens to modifier? So when you look at the aging in bitumen, we know that there are oxidation products which are formed in bitumen, the carbonyl and sulfoxide compounds and we know that temperature is a catalyst to this oxidation process.

So at high temperatures the rate of formation of these oxidation product is higher. But there is something else which also happens to bitumen at high temperatures which we had not seen during the aging chapter, so that is the changes in chemical composition of bitumen at high temperatures where temperatures are greater than 150 degree Celsius

So in the study by Branthaver et al., they have shown that at temperatures greater than 150 degree celsius even in the absence of oxygen there are some changes which happen to the chemical composition of bitumen. So this we need to remember because when we are producing modified bitumen, we are heating bitumen to temperatures in the order of 150 to 185 degree Celsius, so we need to take into account the changes that happen in the base bitumen in these temperature ranges.

The second one is what happens to modifier at high temperatures? So there are some literature available in this regard and I have just put it under three heads, one is for SBS the second one is for linear low-density polyethylene and the third one is for crumb rubber. So in SBS what people have reported is, at high temperatures there is scission. What do you mean by scission here? Which is breakage of the molecule into smaller units.

So this happens because of oxidation in the polybutadiene fraction which is present in SBS so we know that SBS is composed of polystyrene and polybutadiene, so this polybutadiene component oxidizes at the unsaturated bonds which are present in this material and as a result of this oxidation it breaks around into smaller units, again we need to take into the account of the high shear rates that we are using.

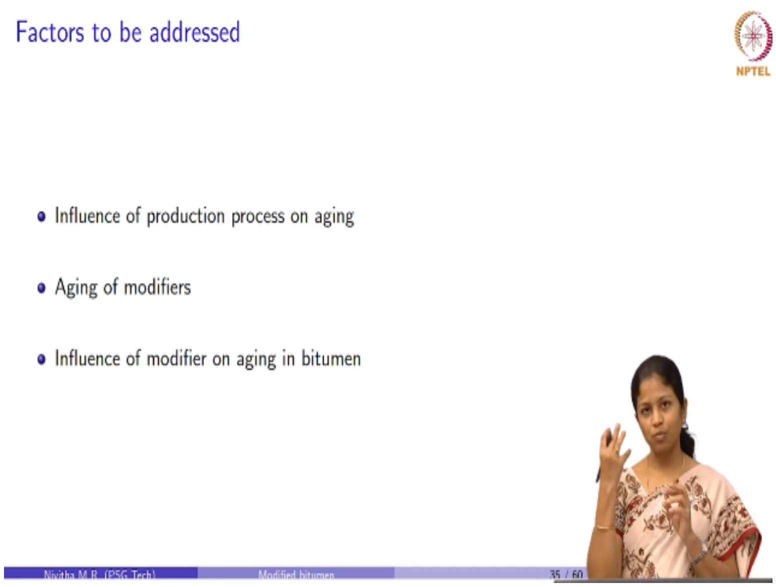
So if we have very high shear rates, we need to ensure that we are not breaking the polymer molecule into smaller units at high shear rates. What happens if this polymer is broken down into smaller units? what we have seen in the interaction of SBS is that we have a cross-linked network, a highly entangled network and that causes an increase in stiffness of this material.

Now if this polymer units are broken down into very small units, then we do not have that kind of an entanglement which will improve the properties of base bitumen. So during production process and during aging we need to ensure that there is no scission or which is also called as degradation of the polymer. So that is one thing in the case of SBS; in the case of linear low-density polyethylene people have shown that it breaks down only at temperatures above 250 degree Celsius.

Again it varies for different type of polyethylene, this study is specifically focused on linear low-density polyethylene. So upto 250 degree Celsius they did not see any scission in the case of LLDPE. The third one is crumb rubber, so in the previous lecture we have seen that at high temperatures there is depolymerization and devulcanization in the case of crumb rubber. So what does this devulcanization do?

The sulfur units are broken down the sulfur is removed from crumb rubber, so we have a smaller units, the second one is depolymerization which is similar to SBS, breakdown of this styrene-butadiene rubber component into smaller units. So all of them can happen during the aging process in the case of modified bitumen.

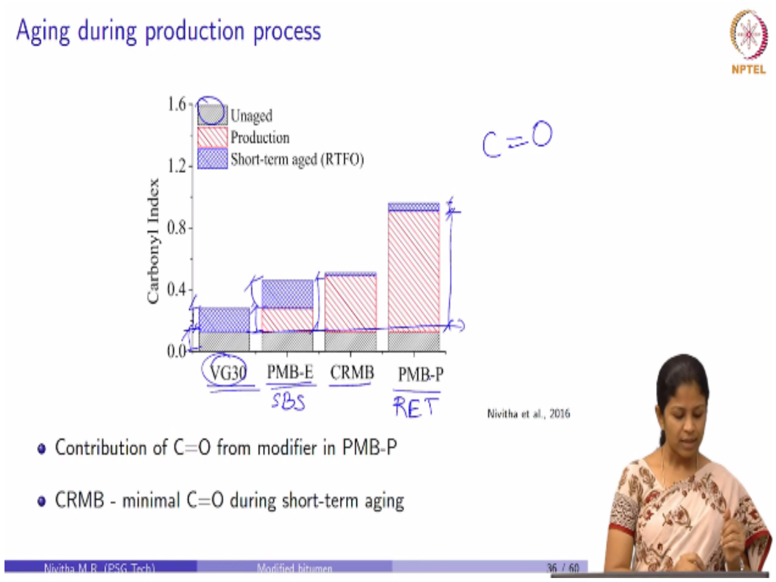
(Refer Slide Time: 09:14)



So this we are going to now look under three heads: one is the influence of production process on aging. So is there any aging that happens, because we have seen that bitumen is subjected to high temperatures about 150 degree Celsius, we can also expect an oxidation process to happen there in the case of the base bitumen itself, in the case of modifier we see that there is breakdown of all these units and there is also some amount of aging which happens in the modifier itself.

So we are going to focus on influence of production process on aging and then we are going to see what is the aging that happens in the modifier itself; whether there is any significant aging that happens in the modifier during our short term and long term aging process. And the third one is the influence of modifier on aging in bitumen, so in the modified bitumen we have some external substance which is the modifier present in the base bitumen. So we need to see how this modifier influences the aging which happens in the base bitumen itself.

(Refer Slide Time: 10:18)



So the first one is aging during production process. So this is a study we had carried out on three different type of modified binders, this is an unmodified binder which is marked as VG 30 and this is an elastomer modified binder which is SBS modified binder and this is called as PMB-E which is an elastomer modified bitumen. The next one is CRMB which is crumb rubber modified bitumen.

And the last one is PMB-P which is a plastomer modified bitumen in specific reactive ethylene terpolymer, so we are going to compare the aging that happens during production process for all these type of bitumen. We need to note that we are able to do this because the base bitumen VG 30 which is represented here is the material which is used to prepare all these three modified bitumen.

Now suppose I have some amount of say for example about 0.18 say for instance carbonyl compounds in my VG30, now this carbonyl compound has to be taken as benchmark and only with this benchmark we can compare how much is the increase in the modified bitumen during production process. Now if I have a modified bitumen which is given by a supplier we do not know what was the base bitumen that was used for that particular preparation.

So then we cannot benchmark the base bitumen and compare how much is the increase during the production process for modified bitumen, so if we want to make this comparison we also need to evaluate the carbonyl index in the base bitumen and in the modified bitumen, then only we can get such information. So we know that the carbonyl and sulfoxide are the compounds which are formed during aging.

So we have taken carbonyl index to represent here. So let us now look at this figure, there are three colors which are given here the black color is for an unaged material okay, which represents the carbonyl compounds which is present in the base bitumen. So we call that as unaged, then we have the production process, so we represent that using a red color here, then we have the aging which happens during the conventional short-term aging procedures.

So we have seen what short term aging is and how it changes the properties of base bitumen and what is it used to represent. So this blue color represents the increase in stiffness of material or increase in formation of carbonyl compounds during short term aging. Now if we compare across all the modified bitumen since we use the same base bitumen, the black color here is going to be the same.

The baseline is going to be the same for all the three types of modified bitumen, so from this base bitumen we have evaluated what is the carbonyl index after the production of modified bitumen. So we can see that there is a small increase in the carbonyl index during production process for PMB elastomer, we can see this is the increase during production process, we can see what is the increase during production process in the case of crumb rubber.

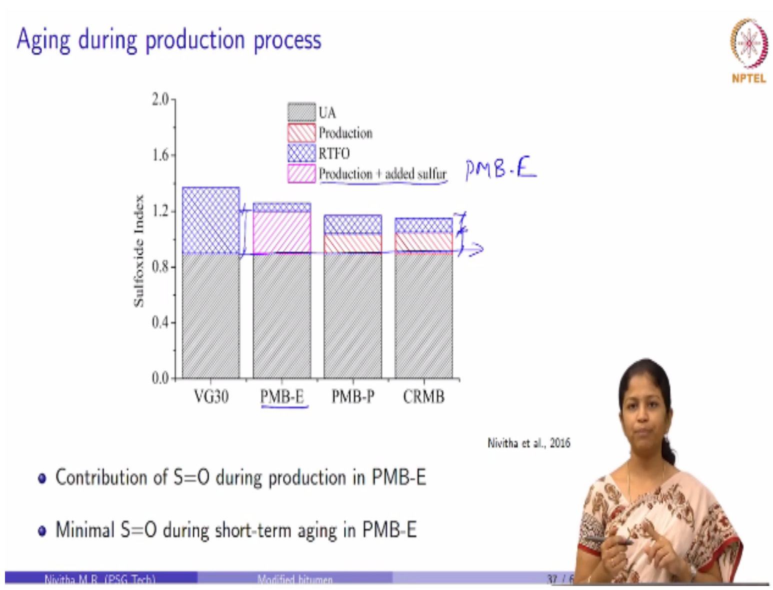
And we can also see what is the increase during production process in the case of plastomer modified bitumen. Now can we conclude that there is an increase say for example from 0.18 to say 1 the variation from 0.18 to 1. Can we attribute this increase to completely the oxidation during production process? No, because we need to take into the account the contribution of this carbonyl compounds from the modifier.

So we have seen the composition of reactive ethylene terpolymer we saw that it composed of lot of C double bond O functionalities. We added the C double bond O functionalities in the form of acrylic esters and compatibilizers to improve the compatibility and storage stability, so this increase in carbonyl index in the case of PMB-P is because of the contribution of C double bond O from the modifier and the aging which happened during the production process.

So it is a net effect of both of these components and we can see that, what is the subsequent aging in all these materials. So we see in VG 30 there is some amount of increase during short term aging, we see a relatively larger increase in the case of elastomer modified bitumen, but in the case of crumb rubber modified bitumen, the subsequent increase during short term aging is very minimal.

And we can also see a very small increase in the case of plastomer modified bitumen. So crumb rubber modified bitumen is generally produced at high temperatures compared to the other two modifiers, so at such temperatures whatever is the oxidation that happens during short term aging, most of the oxidation is expected to happen during the production process itself. So during subsequent aging we see a very small increase in carbonyl index in the case of crumb rubber modified index.

(Refer Slide Time: 15:27)



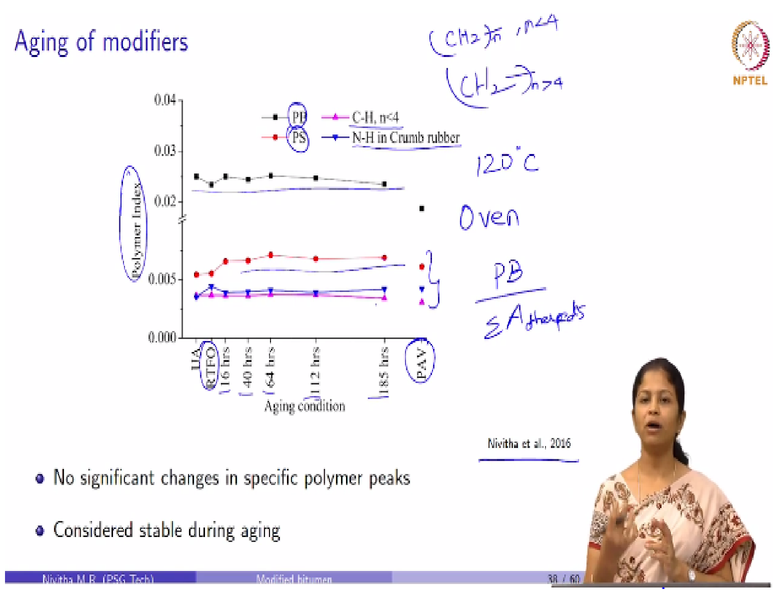
Similarly we can also see the sulfoxide index, so again here we have the same legend for the base bitumen, we can compare what is the sulfoxide index and from this base bitumen we can see what is the increase in sulfoxide compound during the production process and during short-term aging. But there is another case which is given here production plus added sulfur in the case of PMB-E.

So here for this specific modifier which was used here there was some additional sulfur which was added to improve the cross-linking in the case of SBS modified bitumen to improve the storage stability. So there are some cases for specific types of base bitumen and architecture of SBS we might need to add some additives like sulfur to improve the cross-linking. So that was the case in the case of PMB-E which was used here.

And that is why the increase in sulfoxide index in the case of PMB-E is again a net effect of the contribution of sulfur from the modifier and the contribution of sulfoxide which is happening during the aging process, but for the other two cases we can see there is a small increase in sulfoxide index during production process and we can also see what is the effect on subsequent aging right?

So there is some amount of aging which happens during production process, we need to take this into account, ideally a nitrogen blanket is preferred to minimize the effect of oxidation process. So in that cases we can see there is some reduction in the case of oxidation compounds which are formed during aging process.

(Refer Slide Time: 17:13)



Next we are going to look into the second topic which we were discussing which is aging modifiers. Now we have added modifier to bitumen, we have produced them, we are now subjecting them to subsequent aging. So we know that there are two conventional aging procedures one is short-term aging and the second one is long-term aging. So but both of them give us the ageing compounds only at a specific period of time.

Say short-term aging corresponds to the ageing which happens in the mix after it is being produced and it is laid right? long-term aging corresponds to the aging and the mixes which happens after 7 to 8 years of service in field. But we wanted to see what is the rate of aging and how rate of aging varies for the base bitumen and the three types of modified bitumen, so for that we had taken aging at different intermittent conditions.

So what was done in this particular study is the base bitumen and the three modified bitumen were aged at 120 degree Celsius in a conventional oven, so it was subjected to aging and at intermittent periods samples were drawn out. So what are these intermittent periods that was used here? one is after 16 hours of aging, after 40 hours of aging 64, 112 and 185 hours. So at each of these intervals, samples were drawn out from the oven and the carbonyl and sulfoxide index was evaluated.

And the conventional procedures RTFO and PAV we were also carried out on this sample, so we can see that in most of the cases the 185 hours aging represented closely the indices which are obtained during the PAV aging. So that is the first exercise that was done here, the second exercise is to identify the modifier and quantify the aging which happens in the modifier. Now we have mixed modifier and bitumen.

We cannot age modifier separately because that will not tell us what happens during the aging process, so in the modified bitumen we have to identify the modifier separately and quantify the aging that happens in the modifier, so for that we had identified specific functionalities in the case of modifier. So we know that FTIR spectroscopy can be used to identify specific functionalities in different materials, we have seen this in the lecture on chemical composition.

So this FTIR spectroscopy was used to identify specific functionalities which are present in modifier, but not present in bitumen. So then you can quantify them in the spectra at different aging conditions and see how it increases with aging. So we have chosen four functionalities here, one is polybutadiene and the other one is polystyrene. These two components can be clearly identified in bitumen because in this region there is no peaks which are obtained in bitumen.

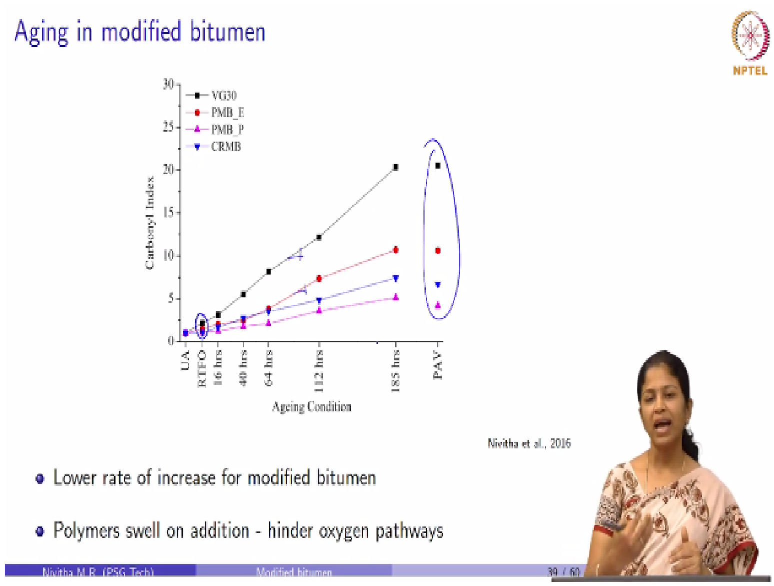
And then we have also taken NH, the amine peaks in crumb rubber, these amine peaks are seen as very sharp peaks and they can clearly be identified, so we have taken these amine peaks as a representation of crumb rubber and we have also taken CH4 peaks. So in bitumen there are more peaks corresponding to CH2 where n is greater than 4, but in the case of this plastomer we were also able to see lot of peaks corresponding to CH2, where n is less than 4.

So this peak was used to represent the plastomer, so these were the four peaks which were considered in the case of modified bitumen. And these peaks were monitored at different aging conditions, so let us now see how the polymer index varies as a function of aging. So this polymer index here which is shown here is nothing but this specific, say for example if we calculated for polybutadiene, it is nothing but the polybutadiene area divided by the summation of area of other peaks which are present in bitumen. I am not getting into the details related to this, if you want the details you can refer to this paper right?

So we have calculated this polymer index and from this polymer index we can see that there is no change in this polymer index at different ageing conditions in the case of polybutadiene, we can see that there are some initial fluctuations initially, but you can also see the y-axis what is the sensitivity. So we can say that there is not much of a change in this polymer index for polybutadiene across different aging conditions.

Similarly we can see in the case of polystyrene there is a small increase but then not substantial variation from 40 hours to 185 hours of aging. Similarly we can see in the case of CH and NH 4 also. So from this what we can conclude is that during the conventional aging, short-term and long-term aging, there is not much of a change or there is not much of an aging that happens in the modifier, so the modifier just remains there and it does not contribute to any of the aging that happens in the base bitumen.

(Refer Slide Time: 22:40)



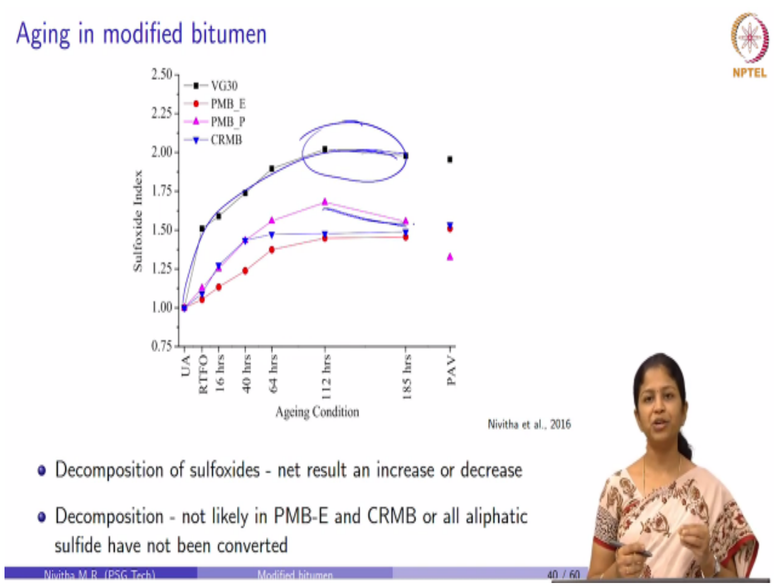
The next one is we are going to see what is the aging that happens in the modified bitumen itself. So for this we had taken the modified bitumen as a whole, quantified these compounds, carbonyl and sulfoxide index, at different aging conditions as we had seen before. So we can see what is the rate of aging. If we do an RTFO, we will get only this point and only this point. We will not be able to see what is the rate of aging here.

So at different conditions we can see from this image how the carbonyl index varies, so the rate of increase in carbonyl index, the slope here is very high in the case of the unmodified bitumen. And the slope is relatively lower in the case of elastomer modified bitumen and then crumb rubber modified bitumen and finally the plastomer modified bitumen, so this is again from this we cannot conclude that elastomer ages more compared to crumb rubber compared to plastomer.

No, we cannot jump into those conclusions just based on this study, this is valid for the type of base bitumen, for the modifier, for the specific conditions considered in this study. So if you vary the conditions or if you prepare with this some other type of base bitumen or some other modifier, these conditions can vary right? So it cannot be used for any ranking purpose; I am just showing it to you here as an example.

So then we can see that there is relatively lower formation of carbonyl compounds and lower formation of sulfoxide compounds right?

(Refer Slide Time: 24:16)



This figure here shows the sulfoxide index, so again we can see there is a higher formation of sulfur oxide index in the case of VG30 and relatively lower formation of sulfoxide compounds in the case of elastomer, plastomer and crumb rubber modified bitumen. So the formation of carbonyl and sulfoxide compound is relatively lower in the case of modified bitumen compared to the unmodified bitumen.

And we can see that the sulfoxide here, tends to saturate here. So we know from the aging lecture we have seen that there is formation and decomposition of sulfoxides which happen simultaneously after a certain period of aging. So the net effect in this period is a sum of the formation of sulfoxides and the decomposition of sulfoxides, so the net effect is what we see here, so that is the second thing which we have to focus in the case of sulfoxide index.

And we can also see there is not much decomposition in the case of elastomer and a crumb rubber modified bitumen whereas in the plastomer modified bitumen, the decomposition is more predominant compared to the formation of sulfoxides that is why we are able to see a reduction in the sulfoxide index. So why does this reduction in formation of carbonyl and sulfoxide index happen in the case of modified bitumen?

So a hypothesis which is relevant to this is, we know that there is a formation of a 3D cross-linked network, these elastomers absorb some amount of lighter fractions and they swell in volume, so because of this increase in volume they hinder the availability of oxygen to the bitumen molecules. So in the aging lecture we have seen that the rate of aging and the magnitude of formation of these carbonyl and sulfoxide compounds depends upon the availability of oxygen to bitumen molecules.

We have also seen that for bitumen molecules where the air void content is very less, the formation of oxidation and sulfur oxide compounds are very less. So because of this availability of oxygen molecules are relatively low in the case of modified bitumen, we see less formation of these compounds in the case of polymer modified bitumen