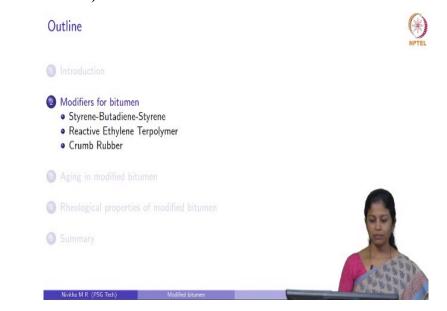
Mechanical Characterization of Bituminous Materials Dr. M. R. Nivitha Assistant Professor Department of Civil Engineering PSG College of Technology, Coimbatore

Lecture No - 34 Modifiers for Bitumen - Part 02

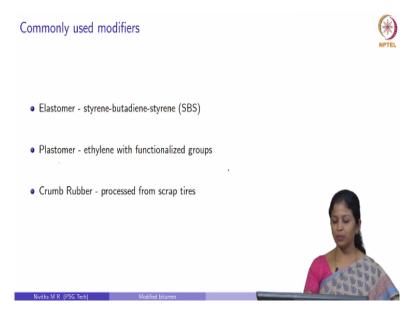
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Now, let us look into some of the commonly used modifiers for bitumen. So I have listed three type of modifiers here; one is styrene butadiene styrene which comes under the elastomer category and other one which is a reactive ethylene terpolymer which comes under the plastomer category again, I will tell you why it is called as a reactive ethylene terpolymer. And the third one is crumb rubber.

Now let us look into the interactions which each of these class of modifiers developed with bitumen. The first class of modifier, which is used for bitumen is styrene butadiene styrene.

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So this is again, I have shown you the same thing which is styrene butadiene styrene; plastomer which is an ethylene with functionalized group and crumb rubber is rubber processed from scrap tires. So we are going to take into consideration these three modifiers for bitumen.

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So these modifiers can develop different types of interactions with bitumen. So before getting into each of these modifiers in detail let us look into what are the types of commonly developed interactions between modifier and bitumen. So there are three types of interaction which are commonly reported.

The first one is a physical interaction. The second one a chemical interaction and the third one is an inert case. Let us see what each of them are. The first one here is a physical interaction. So this physical interaction means the interaction between the modifier and bitumen is only physical. So, what do we mean by physical? There is no change in chemical composition, or there are no formation of new compounds in this case.

So that is when we call it as a physical interaction. So then how do the interactions develop? So this interaction is mainly due to the swelling of polymer. So we add polymer to bitumen; the polymer absorbs the lighter fractions which are present in bitumen and then it swells in volume

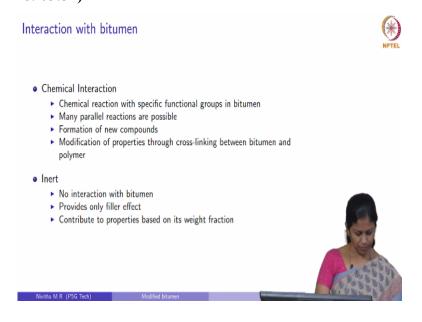
right? So we know what are the lighter fractions that are present in bitumen. We have classified the fractions of bitumen based on the Corbett procedure.

So we have saturates, we have naphthene aromatics, we have polar aromatics and we also have asphaltenes right? So these are the four fractions from the Corbett procedure. So the saturates and naphthene aromatics fraction are called as the lighter fractions. So what happens is the concentration of these lighter fractions is very high in bitumen and its concentration in the modifier is zero right?

It does not have any of these lighter fractions; It is only styrene butadiene and styrene. So when we add this modifier to bitumen this lighter fractions try to maintain equilibrium. So they try to move in from bitumen matrix into the modifier matrix. So this modifier also absorbs these lighter fractions and then it increases in volume, right? So this is the physical interaction phenomena that happens in certain classes of modified bitumen.

So like I said, there are no formation of new compounds here and the modification of property is cross linking in polymer. So, I will show you an image of how cross linking happens when we look into SBS and crumb rubber modified bitumen. So this is the physical interaction that happens in some classes.

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The next one is a chemical interaction. So this chemical interaction is as the name suggests, it

has some kind of a chemical reaction. So there are some functionalities which are present in

bitumen and there are functionalities which are present in the modifier. So these two chemically

interact that is they joint together to form some new compound or they remove some material as

a result of their interaction

So something like that happens in case of a chemical interaction. There are also many parallel

reactions possible in a given modifier with bitumen. So there can be one component of the

modifier reacting in a certain way with one component of bitumen; the second component of

modifier can interact in some other way with another component of bitumen; because we know

that bitumen has a lot of fractions with varying properties and characteristics.

So this modifier can interact in different manner with each of the fractions that is present in

bitumen and there are formation of new compounds here and the modification of property is

because of chemical cross links that are formed between the modifier and bitumen. The last case

is an inert case that is when we add a modifier to bitumen nothing happens, there is no physical

interaction, there is no chemical interaction also.

So nothing happens here and the modifier just remains there something like a filler, right? We

said fillers improve the properties of base bitumen just by the properties by its weight fraction.

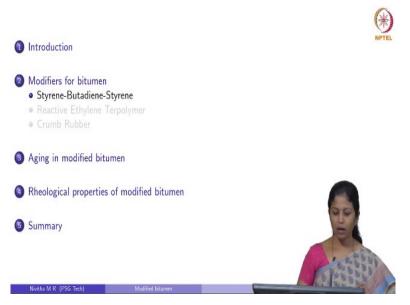
So these inert materials also do the same; they are just present there and they do not form any of

these chemical cross links or physical cross links in the base bitumen. So they provide only a

filler effect and it contributes to its properties based on weight fraction. So these are some

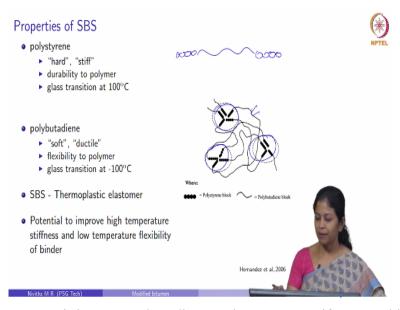
different types of interaction that different modifiers can develop with bitumen.

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Now look let us look into styrene-butadiene-styrene in specific.

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So as the name suggests it is styrene, butadiene and styrene. So if we see this is the structure of SBS, which is given here. So there is styrene blocks which is present in one end; there is a butadiene chain, again, there are some styrene blocks which are present here. So this modifier is designed in a very interesting manner. If you look into the properties of polystyrene, and polybutadiene, we will be able to understand that.

So, what is the characteristic of polystyrene? Polystyrene is very hard and very stiff right? It provides durability to the polymer, its glass transition temperature is 100 degrees Celsius, right?

So up to 100 degrees Celsius the material will be very stiff. So we understand what it means by a

glass transition temperature, right? So the material kind of retains it elastic properties up to 100

degree celsius right?

So it is very hard and stiff, it provides durability to the modified bitumen. The next component is

polybutadiene, so this polybutadiene is very soft and ductile right? So it provides flexibility to

the polymer and this glass transition temperature is -100 degree celsius, so above -100 degree

celsius, it kind of behaves as a ductile material. So we have two components of this modifier:

styrene which is very stiff with the glass transition up to 100 degree celsius; polybutadiene,

which is very soft with a glass transition of -100 degree celsius.

So when these two components are added to the modified bitumen, it has both improvement in

high temperature properties and low temperature properties; that is why in the initial slides when

we saw the effect of SBS on the distresses, we were able to say that this class of modifier

improved both its high temperature properties and low temperature properties right?

So this is the reason for the improvement in these two properties in the case of SBS. So this SBS

is commonly classified as a thermoplastic elastomer and it has potential to improve both high

temperature stiffness and low temperature flexibility right? So these polystyrene blocks what

happens is they arrange together to form some domain like this, so this is called as poly

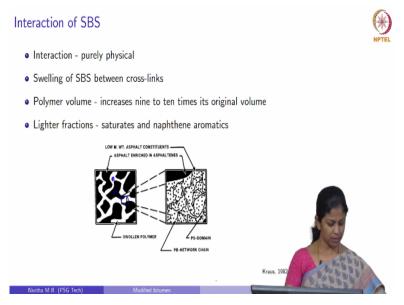
polystyrene domain.

So they form lot of domains like this and this polybutadiene chain which is seen here, it absorbs

the lighter fractions which is present in bitumen and it kinds of forms the flexible part to the

modified bitumen. Let us see how the interaction develops here in detail.

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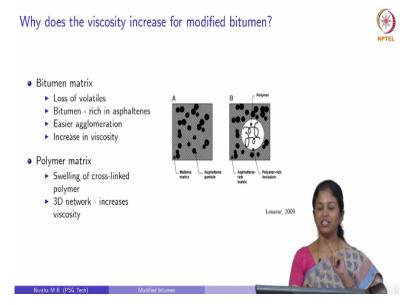


So this interaction here is purely physical, so we have already defined what a physical interaction is, the polymer absorbs the lighter fractions, which is present in bitumen and it swells in volume. So the swelling is something like the order of 9 to 10 times its original volume, so the modifier it absorbs the lighter fractions and it can swell from 9 to 10 times its original volume, this is the reason why we were able to see a phase inversion for the addition of 7 percent of SBS to base bitumen.

So we have seen that when we add 7 % the polymer dominates such that it forms the matrix, so this is because of this increase in volume on absorption of lighter fractions and these lighter fractions like I have already said they are saturates and naphthene aromatics, so this is a figure which is a hypothetical figure which was proposed in Kraus as early as 1982, so they have said that this is a modified bitumen and this is the polymer matrix which is seen in white color here and the black one here forms the bitumen and when you enlarge a portion of this modified bitumen we see something like this, which is shown here; so they have said that there are polystyrene domains which are seen as black dots here and the polybutadiene contributes to the white thing here which is seen as the base here.

So this is the polystyrene domain and this is the polybutadiene network chain right? So this is the morphology of SBS modified bitumen and many people were able to verify it using some microscopic based techniques right, so this is the interaction of SBS.

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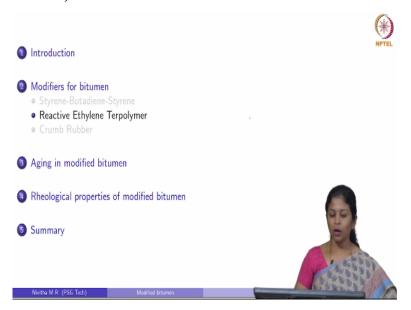
Now why does the viscosity increase for SBS modified bitumen? So we said right it improves its high temperature properties, so now when we add this modifier to bitumen, what happens to bitumen? What happens to modifier? So in the bitumen matrix there are some four things which happen. One is the loss of volatiles. So which means that these lighter fractions migrate from bitumen matrix into the polymer matrix, right? So there is a reduction in the volatile fraction which is present in bitumen, so we already have seen the colloidal model for bitumen.

People have already proposed that there are two at least two major fractions one is the asphaltene and the other one is maltene, so these asphaltene fractions are dispersed in the maltene base right? so this is a commonly used hypothesis to represent the microstructure of bitumen. So when there is a reduction in the maltene fraction so these asphaltenes have more tendency to agglomerate so when these maltene phases are removed they try to come closer to each other.

And then they try to agglomerate so when they agglomerate they try to increase the viscosity of the system, so this is the first reason which is proposed as one of the factors contributing to increase in viscosity in the case of SBS modified bitumen. The second one comes from the polymer; so this polymer absorbs bitumen we have already seen they form an intertwined network right?

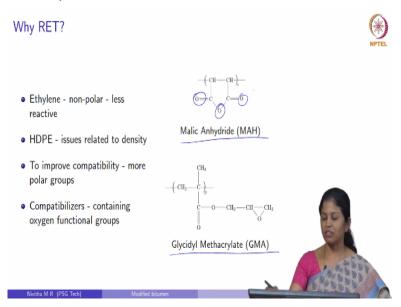
We have polystyrene domains these polybutylene chains are present there, so they absorb they form intertwined domains so this cross linking which is again physical in nature, there is no chemical cross linking here thy are only physically interlinked. so this, physical cross linking increases the viscosity of the system so this increase in viscosity comes from two aspects, one is the change in properties of the bitumen matrix and the second one is because of the change in the physical state of the modifier, which is added to bitumen.

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Now we are going to see another class of modifiers which are called as reactive ethylene terpolymer, so now I will go through it.

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Ethylene is one of the commonly used plastomers right? When we have elastomers we have

referred as SBS when we come into the plastomers, ethylene is one of the commonly used

plastomers, but ethylene, as such cannot be used for bitumen modification right? The reason is

ethylene is non-polar; when we defined the desired properties of a modifier, we listed that there

should be some polarity in the modifier so this ethylene is non-polar.

And so it will not react with bitumen in any of these manner, so we need to make these two

materials interact with each other right, so to make them interact we have some compatibilizers

which are added; so what are these compatibilizers? these are materials which are added to

improve the compatibility of the modifier with bitumen right? So there are some two types of

commonly used compatibilizers one is a Maleic anhydride and the second one is Glycidyl

methacrylate.

So how does this improve the polarity? we have already seen hetero atoms and when they are

present in a specific form, they try to increase the polarity right? So we have oxygen which is

present here and you can see there are few other oxygen molecules forming double bond with

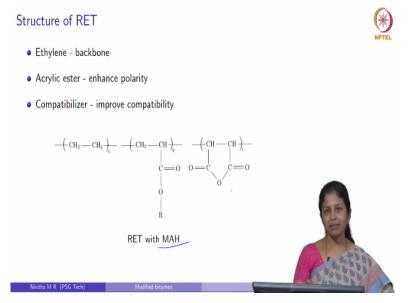
carbon, so this is the maleic anhydride structure so because of this they add polarity to the

modifier

So these two components or either of these components are attached to this ethylene chain and it

forms a reactive ethylene terpolymer, so let us look into how the structure of RET is defined.

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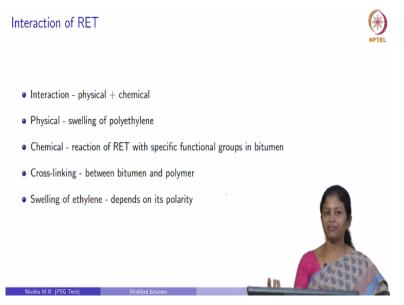


So we have three components. One is an ethylene component which forms backbone. So we are trying to only modify ethylene, so ethylene still remains as a backbone for this type of modifier, so we have an ethylene backbone, then we have an acrylic ester it can be butyl acrylate or any other acrylic ester, it is to improve again the polarity of the modifier and then we also have a compatibilizer to improve the compatibility.

This compatibilizer will try to form some compounds when which is added to bitumen right? So this is ethylene chain, this is the acrylic ester, and then this is the compatibilizer. So these are three components which are present in a reactive ethylene terpolymer, it is not necessary that ethylene can be modified or it has to be modified only in this specific manner; there can be different ways in which we can modify a normal plastomer.

The ultimate aim is to add polarity and improve its compatibility with bitumen, so similarly this is a structure of maleic anhydride. Previously I had shown you glycidyl methacrylate similarly here we have maleic anhydride. So again here ethylene chain, the acrylic ester and then we also have the compatibilizer which is present here, there are some literatures which have hypothesized how the chemical interaction between the compatibilizer and bitumen can occur.

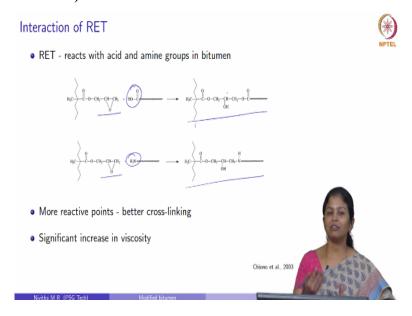
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So this interaction here is more mostly physical and chemical here. So why do we call it as a physical here? We have ethylene again it is a polymer it has a tendency to absorb some amount of lighter fractions which is present in bitumen, so that is the physical interaction which happens in the case of a plastomer.

The second one is chemical, this chemical interaction is because of formation of chemical cross links between the polar components which is present in the modifier and certain fractions which are present in bitumen right? Again the degree of swelling of ethylene depends upon the polarity.

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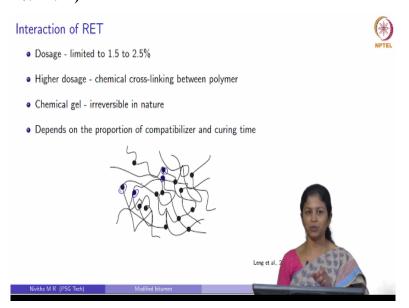


Now let us look into some of the hypothetical reactions which were proposed for the reactive ethylene terpolymer with bitumen. So we can see here this is a glycidyl methacrylate. So this is a study by Chiono et al., they have said that when this reactive ethylene terpolymer is added to bitumen it has a higher tendency to react with the carboxylic acid groups which is present in bitumen to form a chemical cross link something like this which is given here.

Similarly this can also react with the amine groups we know NH2 is amine, so it can also react with amine groups which is present in bitumen to form something like this. So the modifier and bitumen are now chemically cross linked. They are no more two different entities, there is some chemical cross link between them, so this chemical cross link can happen at a number of sites so we have number of molecules in bitumen with COOH functionality.

Similarly we have a number of molecules in bitumen with amine functionality, so this modifier can interact with a number of carboxylic acids and a number of amine groups and form a number of chemical cross-links, so we have a tendency to consider this as a positive effect right? More amount of cross linking, so we have a better increase in stiffness of this property, but it does not happen that way, there is a limit to which this cross linking can be beneficial.

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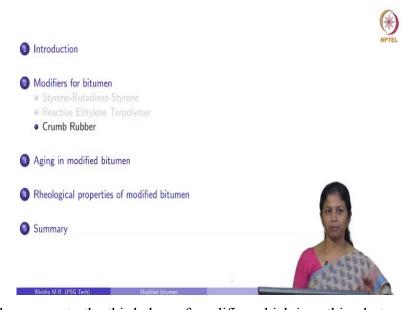


People have shown that in the case of reactive ethylene terpolymer, the dosage has to be limited to 1.5 to 2.5 %; what happens when the dosage is higher? it kind of forms a number of cross

links with bitumen because again we said there are different components in bitumen and we also have different points for cross linking from the modifier, so because of this they have a number of cross linking points as shown here.

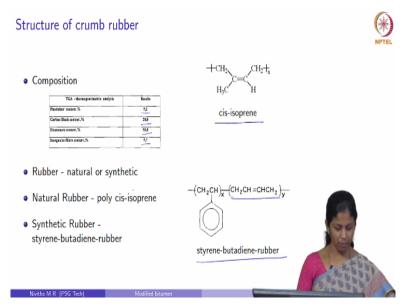
And then it forms a kind of a chemical gel, a very stiff material whose viscosity increases substantially, so because of this formation of a chemical gel, it becomes kind of an adhesive kind of a material, it is no more a modified bitumen, so in the case of reactive ethylene terpolymers the dosage is advised to be limited to 1.5 to 2.5 %. Again, it depends upon the type of base bitumen, the type of modifier used, a number of variables, which will determine the dosage.

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Next we will move on to the third class of modifier which is nothing but crumb rubber.

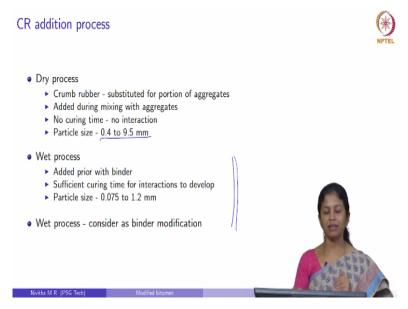
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So again, I have just added natural rubber also to show you, what this natural rubber is composed of, it is called as cis-isoprene, we have isoprene in a cis-isomer format, so this is natural rubber and we have crumb rubber which the main component of which is styrene-butadiene rubber, so this table here shows what are the components of a crumb rubber? So we have some amount of plasticizer which is about 5 %, Carbon black about 28 % and elastomers about 58 % and then inorganic fillers about 5.7 %, again, we need to remember that the previous cases where materials which were designed specifically to modify bitumen, but crumb rubber is not like that, it is a, material which is disposed of and we are trying to make the best use of this material to improve the properties of base bitumen.

So in addition to what we desire, we might have certain other components also in the case of crumb rubber modified bitumen. So this elastomer which is present here about 58 % is nothing but styrene-butadiene rubber. The previous case what we had seen is styrene-butadiene styrene, this styrene-butadiene this rubber component, right? So this is styrene-butadiene rubber. And so this is the composition of crumb rubber.

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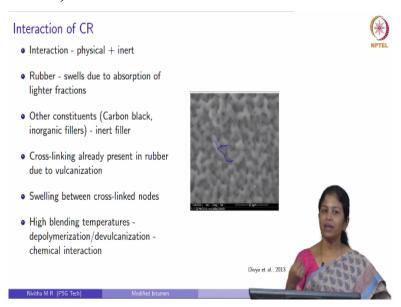
So this crumb rubber addition to bitumen can be done in two ways: one is a dry process and a second one is a wet process. So, what do we mean by a dry process here? So this crumb rubber is shredded into bigger particles, you can see the particle size here is about 0.4 to 9.5 millimeters. So it is shredded into bigger particle and it is added to replace some portion of aggregates right?

So, this is one of the application of crumb rubber, and it is added during mixing with aggregates. So when we add aggregates into the batching plant we also add crumb rubber, we mix it and then we add hot bitumen to it, right? So this is the dry process, so there are no interactions that are developed here. Because we said that we need the lighter fractions to move into modifier and then the physical interaction will happen.

Here also there is some elastomer right? it is in the form of styrene-butadiene rubber. So it can also form some kind of a physical interaction with bitumen but in the dry process we are not giving them sufficient time for the interactions to develop, right? So this is a dry process and a wet process is wherein the modifier is added prior to bitumen before batching. So in laboratory or in field we can add the modifier to bitumen, prepare a modified bitumen and this modified bitumen can now be used to prepare modified bitumenous mixes, right?

So these two are different. So the second one wet process is what we call it as a binder modification and what we are going to discuss about crumb rubber modified bitumen is based on this wet process.

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So this interaction of crumb rubber is again physical, inert and in some cases people also say chemical interaction, but that has not been verified to the required detail, right? So like I previously mentioned there is a styrene-butadiene rubber component which is presented in crumb rubber, so this styrene-butadiene rubber will absorb some of the lighter fractions which are present in bitumen and it will try to swell in volume.

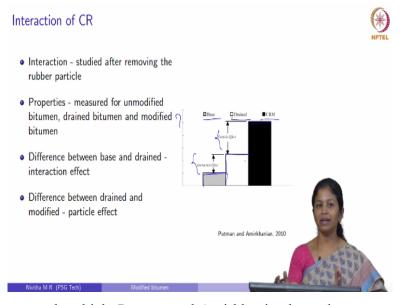
So this is an ESEM image of crumb rubber modified bitumen which was captured by Divya et al., you can see the intertwined network here which is intertwined network here, which is present in crumb rubber modified bitumen? So it again swells and tries to form a three dimensional network, mostly a physical type of interaction and we also have other constituents which are present here, it can be carbon black, inorganic fillers, a lot of other constituents

These constituents remain as inert fillers. They do not participate in the interaction process. And cross linking here, we already have a cross linking which is present in crumb rubber. We know that vulcanization is a process which is carried out for tires, right? So because of this

vulcanisation, there is already some amount of sulphur which is present in this crumb rubber forming chemical bonds.

So this absorption and swelling will happen in the nodes between these sulfur molecules, right? So there is already a chemical cross linking which is present in crumb rubber and the high blend at high blending temperatures what happens is there is depolymerization, this crumb rubber tends to break down because the Sulphur unit will be devulcanized it is broken down from the modifier unit and there is devulcanization which happens at high temperatures. So when this devulcanization happens people say that there are possibilities of development of chemical interaction, but mostly it is reported as a physical interaction and inert material.

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Now there is one study which, Putman and Amirkhanian have done to quantify the effect of this interaction and filler effect on the improvement in properties of this crumb rubber modified bitumen. So here is an image here which shows let us take the y-axis as some measure, it is a viscosity parameter. What they have done here is they have taken crumb rubber particles, they have added it to bitumen, prepared crumb rubber modified bitumen and then using some method they have filtered out these crumb rubber particles. So we have a base bitumen, we have a bitumen in which crumb rubber is mixed and then filtered out a third case is a crumb rubber modified bitumen as in. So you can see here a base bitumen, the second case is crumb rubber

particles are added to bitumen, a crumb rubber modified bitumen is prepared, but then after some

amount of time these crumb rubber particles are removed from bitumen.

So that is called as drained case and the third one is an actual crumb rubber modified bitumen

itself. So they had measured the viscosity of bitumen in these three states. So we have some

viscosity for the base bitumen, which is seen here, right? So then we have something; an

improvement in viscosity in the case of the drained case.

So in the drained case, we need to make sure that there is no crumb rubber particles, which is

present here. So whatever is improvement in viscosity in that case is because of the presence of

crumb rubber in bitumen and how it had interacted with bitumen. So what would have happened

here, it would have actually tried to absorb some amount of lighter fractions. So it removed the

lighter fractions, which is present in bitumen and that could have resulted in increase in viscosity

in the case of a drained case.

And the third one is a crumb rubber modified bitumen as in. So the difference between the base

bitumen and the drained the bitumen is because of the interaction effect and between the drained

case and the crumb rubber modified bitumen is because of the particle effect, because the

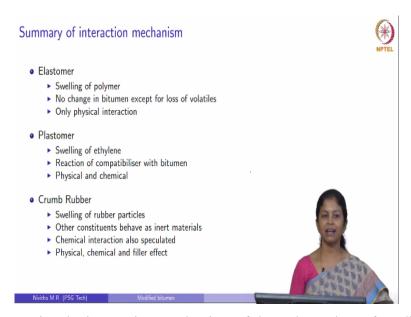
remaining increase in viscosity is because of the presence of crumb rubber in crumb rubber

modified bitumen.

So by this way, people had tried to see what is the effect of the modifier and the filler part which

is present in crumb rubber modified bitumen.

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Let us now summarize the interaction mechanism of these three class of modifiers with bitumen. So in the case of elastomer, it is very clear, the interaction is mostly physical in nature. So we have the modifier which absorbs the lighter fractions, which is present in bitumen and then it swells in volume. So there is no change in bitumen except for some loss of volatiles. So it is purely a physical interaction here.

In the case of plastomer, in specific here a reactive ethylene terpolymer, we have two kind of interactions one is a physical interaction and the other one is a chemical interaction. This physical interaction is because of the absorption of lighter fractions present in bitumen by the ethylene backbone. The chemical interaction is because of the reactions of certain functionalities which are present in bitumen with some polar groups, which are present in the modifier.

So we have both a physical interaction and a chemical interaction, which is present here. In the case of crumb rubber modified bitumen, we have a physical interaction and an inert case which is reported and some kind of chemical interaction which can be developed. So this physical interaction is because of again the absorption of lighter fractions by the styrene butadiene rubber component, which is present in crumb rubber.

The inorganic fillers and the carbon black which is present in crumb rubber can act as fillers and at high temperatures when there is devulcanization and depolymerization, a chemical interaction

can also develop. So in this class will stop with the summary of interaction mechanism; in the next class will continue with regarding to the ageing in modified bitumen and rheological properties of modified bitumen.

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