Mechanical Characterization of Bituminous Materials

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Lecture No - 33
Modifiers for Bitumen – Part 01

Today, we are going to talk about modifiers for bitumen. So what are these modifiers? Modifiers are materials which are added to enhance some specific property of bitumen. So we have this base bitumen of different grades which is used in country. So we want to enhance some specific property of this material; improve its performance in certain aspects; then for that purpose we add modifiers.

So this addition of modifiers to bitumen can be looked into in two ways. One is we identify an area where a specific improvement in property is required. For example we have locations where the temperatures are very high, say 60 degrees to 65 degrees, the pavement temperature raises from up to 60 to 65 degrees. So in those locations we want to minimize the rutting in pavement; then we add a certain class of modifier to minimize rutting.

So what we need to do here is, add a modifier which will improve the stiffness of this bitumen at high temperatures. So similarly we have different aspects of bitumen we will look about it, so for each of those aspects we have different modifiers which can be added; so this is one perspective. The other perspective is there are certain modifiers which when disposed to the environment cause harmful effects on the environment. So these modifiers can be added to bitumen; and it can be seen if these modifiers enhance certain properties of the bitumen.

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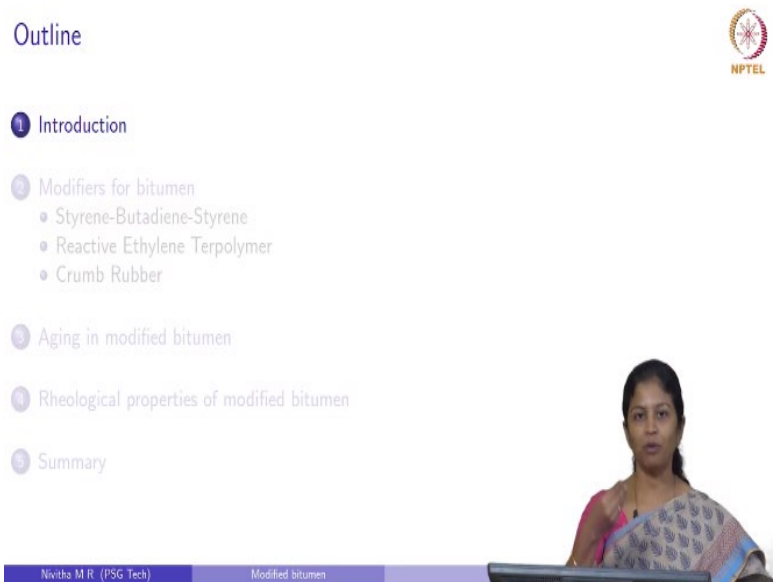

First, we will introduce the modifiers which are available for bitumen and what are those properties of these modifiers; And then we look into what are some of the commonly used modifiers for bitumen; How they interact with bitumen; And then we will look into how aging happens in a modified bitumen; So in previous lectures we have seen how aging occurs in bitumen.

So the aging in modified bitumen is slightly different from how it occurs in base bitumen; so here we are going to specifically focus on the aging in different types of modified bitumen. And then finally we are going to look into the rheological properties of modified bitumen. So how the addition of modifiers alter certain properties of modified bitumen? So, that we are going to look into and then finally summarize.

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Why do we need modifiers for bitumen? So you can see a picture here; so the pavement in our country in most cases is something like this what we see in this image on top here right? At least if not most of the pavements many of the pavements face this condition at the end of monsoon season. So most of the pavements have some sort of distress much before their design life. So we know that in IRC37 the stipulated design life for a pavement is 15 years.

So we design a pavement for 15 years with a notion that they do not undergo rutting or cracking for the entire duration of 15 years. But the reality is that we see most of our pavements undergo at least either of these two distresses in the first few years say in the first five years after they are constructed right? So there are many reasons for these distresses what we see in pavement.

So one reason that can be said is the properties of the bitumen which is used to prepare the mix. So there are various other reasons like the properties of the mix, the properties the how they are mixed together? Lot of factors. So what we are going to focus here is how the properties of the bitumen influence the distresses in pavement. So ultimately what we want to do is convert pavements which are in the condition shown above to something like what is shown here right?

Improve its properties so that they do not face these distresses in their design life. So to look into that we need to see what are the distresses that are commonly occurring in a pavement?

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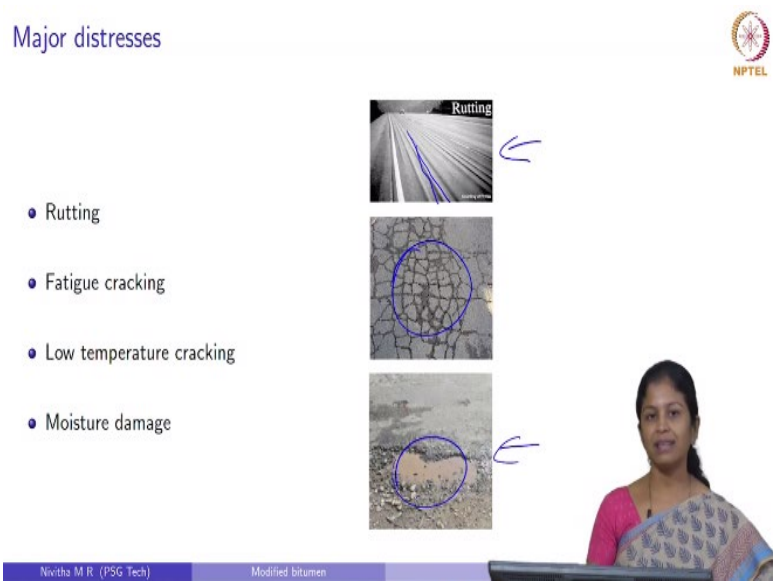

So these are some of the four commonly occurring distresses in a pavement; there are many others also. But for this lecture we will contain it to these four distresses. So the first and foremost among them is rutting. So what do we mean by rutting? Rutting is the longitudinal depression that is seen along the wheel path of a vehicle; you can see the image here right? which shows the rutted pavement.

That you can see; depressions here along the wheel path of the vehicle because the binder, the mix is not stiff enough to take up the wheel load. So we have rutting which is nothing but deformation along the wheel path which is due to the insufficient stiffness of the mix to take the wheel load. So there are various factors which contribute to this insufficient stiffness and one factor is insufficient stiffness of the binder right? So this is rutting.

The second distress is fatigue cracking, so we see a network of cracks here right? so this is called as fatigue cracking. So fatigue cracking occurs because mix is very stiff that the continuous repetition of vehicles causes cracking on the pavement. So this is fatigue cracking and this occurs at low temperatures because we know the effect of temperature on the property of bitumen.

So at high temperatures bitumen is very soft and that is why we see rutting here; at low temperatures the bitumen is very stiff so that it causes cracking. So we also have another distress which is low temperature cracking. So when the temperature falls sub-zero, the stiffness of the

binder increases drastically and even without passage of a wheel load we have cracks formed on the pavement; so this is called as low temperature cracking.

So fatigue cracking and low temperature cracking occur at low temperatures but fatigue cracking is more because of the passage of wheel loads whereas low temperature cracking can occur even without a vehicle traveling on a road. So more details about this you would have learnt in the session about the performance grade for binders. The next one is the moisture damage which is very commonly prevalent here. So what is this moisture damage?

Water is considered as an enemy to bitumen. So when water comes into contact with the aggregate particles coated with bitumen, water tries to remove the bitumen coating from the aggregate. So because of that the bonding between the aggregates is lost and so we have removal of aggregates from the pavement. So you can see this image here, wherein the aggregate particles are removed from the pavement. So these are some of the four commonly occurring distresses in pavement.

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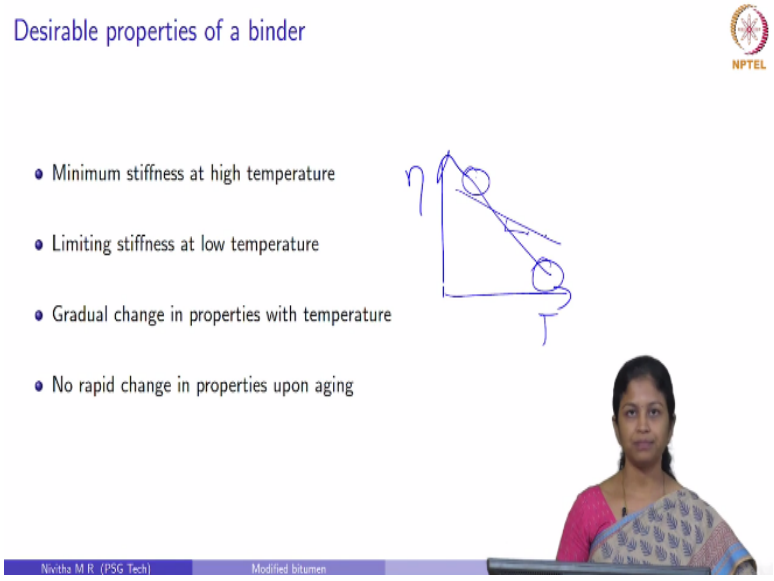

So how to minimize these distresses? To minimize these distresses, what are the desirable properties of a binder that we are looking into? The first and foremost is we need the binder to have a minimum stiffness at high temperatures, because we said at high temperature the binder is

not stiff enough to take the wheel load, so we need to improve the stiffness of this binder at high temperatures so that it will not rut under the wheel load.

So the first requirement is the binder should have some minimum stiffness at high temperatures. The second requirement is it should have some amount of limiting stiffness at low temperatures. Because at low temperatures we said cracking is the most predominant distress either be it fatigue cracking or low temperature cracking. So to minimize these distresses it should have a maximum amount of stiffness so that any stiffness above that it will undergo cracking.

So this is the second requirement. Third requirement is that the change in properties of the binder should be gradual, we need to have a gradual change in properties with temperature. So what do we mean here? so if I draw a plot of some measure of stiffness let us take viscosity with temperature, so the slope of this viscosity temperature graph should be minimal. So why do we say this? If this slope is large what happens is, the material is very stiff at low temperatures and the material is very soft at high temperatures, both of which we do not require.

So we want the properties to be very gradual with temperature as possible and the last requirement is there should not be any rapid change in properties with aging. So already we have seen in detail about aging and we know that aging increases the stiffness of the binder. And we have already said that we want an increase in stiffness. But we do not want it to increase so much that it will lead to fatigue cracking. So we need to keep a check on the change in properties with aging; so these are some of the desirable properties of a binder.

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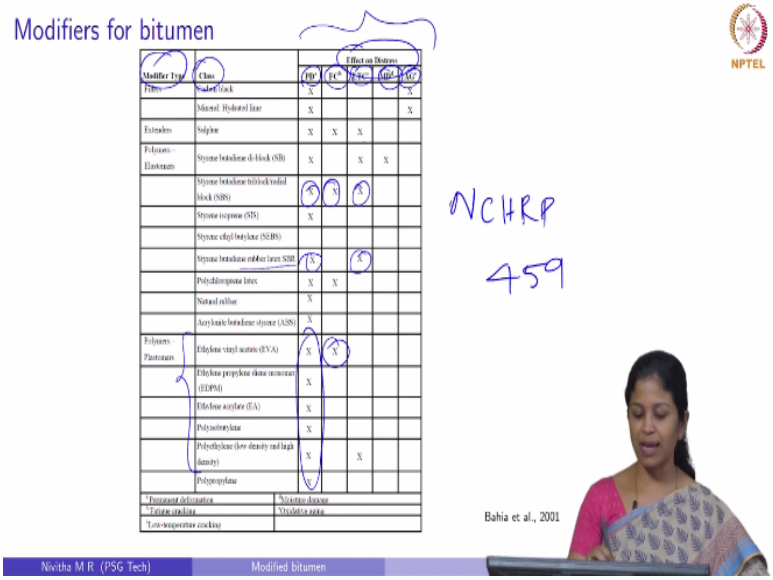

Now let us look into the commonly available modifiers for bitumen to address those requirements and few others also. So this is a very comprehensive table which is given in the NCHRP report, NCHRP459 by Bahia et al. So this table gives us a lot of information; the first column here, talks about the type of modifier, so what is the modifier that is used here? And the second one talks about the class of modifier.

What is the specific modifier that is used? And this column talks about what is the effect of this modifier on distress? So they have considered five distresses here. The first one is permanent damage which is nothing but rutting. The second one is fatigue cracking. Third one is low temperature cracking. Fourth one is moisture damage. And fifth one is aging. So what they have done is they have said what is the effect of each of these modifier on each of the distresses that are given here right?

So let us take an example: the first class which is given here are fillers, so what are fillers? Fillers are materials which are just added to this and they modify the properties of bitumen just by the volume fraction right? So how much of filler is added that much amount of influence it will have on the properties of base bitumen. So the first filler which is given here is carbon black. Carbon black is nothing but a black powder which is added to bitumen.

And this carbon black has a positive effect on the permanent damage. So if you add carbon black to bitumen and prepare a modified bitumen, the resulting modified bitumen will have a slight improvement in rutting properties. So what do they mean by that? it slightly increases the stiffness of the binder at high temperatures. Similarly it also has a positive effect on aging; so what do we mean by a positive effect on aging.

Without carbon black if we have x amount of increase in stiffness on aging with addition of carbon black it is going to be something let us say .8x or .9x something like that, less than; it is going to reduce the stiffness for the base bitumen right? So that is the information which is given here in this table which shows the effect of distress here. Similarly another additive is hydrated lime.

So this hydrated lime also has a positive effect on permanent deformation and aging of the base bitumen right? So this is one class of modifier. Similarly we have another class which are called extenders. sulfur is a very commonly used example of extenders. Extender is nothing but which is used to replace the weight fraction of material. Sulfur is a very commonly used extender here and we can see that sulfur has a positive effect on the permanent deformation, fatigue cracking, and low temperature cracking of the base bitumen.

The next commonly used class of modifier is elastomer. So this elastomer is very commonly used in field to modify the properties of base bitumen. So there are different varieties of elastomers which are used for this purpose, so they are styrene butadiene, styrene butadiene styrene, styrene isoprene, styrene ethylene butadiene styrene, styrene butadiene rubber, poly chloroprene latex, natural rubber and acrylonitrile butadiene styrene.

So these are some of the commonly used elastomers. So these elastomers have some elastic property and they try to improve the elastic recovery of the base bitumen. So let us see what is the effect of some of these elastomers on the distresses. Let us take SBS, so SBS is one of the commonly used elastomer; so in SBS we can see that SBS has a positive effect on permanent deformation, fatigue cracking and low temperature cracking.

So what do we understand by this? SBS improves the stiffness of bitumen at high temperatures and it also reduces the stiffness of bitumen at low temperatures. That is why we are able to see a positive effect on the permanent deformation caused at high temperatures and the cracking which is caused at low temperatures. But we have something like styrene butadiene rubber which is seen here.

It only improves the permanent deformation characteristics and low temperature characteristics and people did not see any positive effect on fatigue cracking. Similarly for other modifiers we can see what is the effect on distress that is given here. Another class of modifier is plastomers right? So again there are a wide variety of plastomers and you can see the list which is given here, it varies from ethylene vinyl acetate to ethylene poly propylene diene monomer to ethylene acrylate, polyisobutylene, poly ethylene.

Again in poly ethylene we have low-density polyethylene and high-density polyethylene and polypropylene. So you can see most of these plastomers have a positive effect only on the permanent deformation right? So what do they do here? They try to improve the stiffness of binder at high temperatures. But what happens at low temperatures? Except for ethylene vinyl acetate, we can see that none of the other modifiers improve the low-temperature stiffness of these binders.

So if you want to use these modifiers we can prefer these modifiers only for locations where high temperature stiffness needs to be improved but we need to keep in mind that it does not alter any of the low-temperature properties of the base bitumen right? So this is another class of modifiers.

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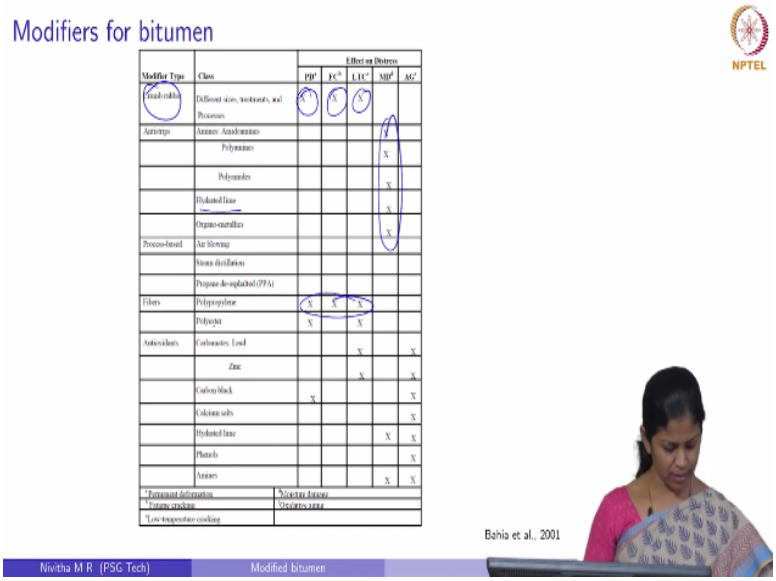

Let us move on to a few other classes of modifiers again crumb rubber right? crumb rubber comes from the scrap tires. So we have these car tires right? car truck tires which are disposed; so the disposal of these tires caused a severe hazard to the environment. So people started thinking about different alternatives to dispose this material and using it to modify bitumen was one of the alternatives.

So what they do here is they shred those tires into particles varying from 600 to 900 microns and they are added to bitumen to prepare modified bitumen. So they found that the addition of crumb rubber had a positive effect on permanent deformation, fatigue cracking and low temperature cracking. So again like the elastomers it also was seen to improve the high-temperature stiffness and also reduced the low-temperature stiffness.

So because of the positive effect, the crumb rubber modified bitumen became one of the popular means to dispose of the waste tires. Then we see another class of modifiers which are antistrips, so we see stripping right? Stripping is nothing but the removal of the film of bitumen coating the aggregates. So antistrip is nothing but the modifiers which are added to minimize or reduce this stripping action of the water.

So we can see again a wide variety of antistrips: amidoamines, polyamines, polyamides, hydrated lime, organo-metallics. So these are some different variety of antistrips and we see that

all of them have a positive effect on moisture damage. Because that is what they were intended to; reduce the effect of moisture damage on the pavement. Then we have something like processed based.

So when you looked into the types of processes we saw what is air blowing? What is steam distillation? And what is propane de-asphalted bitumen? So they are also classified as a type of modification to bitumen. In many countries the bitumen which is directly obtained from refinery processing is called as a straight run bitumen. Any modification, even be it air blowing or propane de-asphalting is considered as a modification.

So in some cases, this is also considered as a type of a modified bitumen; but there was no positive effect on the types of processes on the distresses. This was not quantified at this point of time. And then we also have some fibers which are added to bitumen. So we have polypropylene fibers, polyester fibers. So we can see this polypropylene fiber again has a positive effect on all the three distresses. The permanent deformation, fatigue cracking and low temperature cracking.

Similarly we can see polyester again has a positive effect on permanent deformation and low temperature cracking right? The last one is antioxidants, so antioxidants are materials which are added to bitumen to reduce the effect of aging, because we know that aging occurs due to the oxidation process. So antioxidants are added to reduce the effect of aging on base bitumen right? So this is a comprehensive summary of different types of modifiers available for bitumen and the effect on the distresses.

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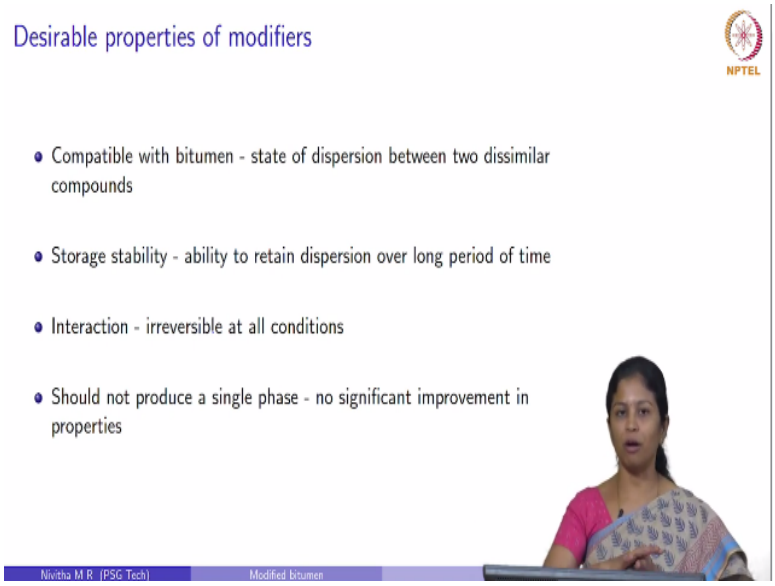

Now let us see what are the desirable properties of modifier? So this modifier should be compatible with bitumen, this is the first and foremost requirement of a modifier. So what do we mean by compatibility here? We have two different materials and we are mixing these two materials and making them to behave as a single material. So the first material we have here is bitumen, the second material we have here is a modifier.

Now there are different ways in which both of them can blend together. The first case is a completely miscible case or I will start with immiscibility first, so the first case is totally immiscible. So what do we mean by immiscible here? They two do not mix with each other, they will always separate out at any given condition. A common example of immiscibility is adding oil and water.

So when we add oil to water what happens is that maybe during application of some mechanical action they might seem to be together but once we keep the container down they will always separate out. So they are considered as immiscible fluids right? So the other case is they can be immiscible but they can have some kind of compatibility between them, so when we add one material to other they will remain as two phases but they will act together and result in some improvement in properties.

So this is called as immiscible but compatible material. The third cases a totally miscible case wherein the first material will completely dissolve in the second material and they both will now behave as one material. We will not see the two phases that we were seeing earlier in this case. Now what is the requirement for a modified bitumen in this case? Alright, we have a totally immiscible case, we have immiscible but compatible case and we also have a totally miscible case.

So what we desire here is immiscible case but a compatible with compatibility; so this is the required case for modified bitumen. So only when we have compatibility then the material will be storage stable. So what do we mean by storage stability? We prepare this modified bitumen under laboratory conditions; after preparation of this modified bitumen we store it right? So once we store it once when all the mechanical action is removed and then it is stored normally under room conditions, they should not phase separate out.

So only if they are compatible they can be storage stable. So compatibility and storage stability is the most commonly required characteristic of a modified bitumen. And this is the most complicated thing to achieve in preparation of a modified bitumen. We have n number of polymers available and we can add any of these polymers to bitumen right? but they have to be compatible.

That is the first factor which limits most of the addition of polymers to bitumen right? Second one is storage stability as we have defined, so it is the ability to retain the dispersion of modifier in bitumen over a long period of time. And the third one is the interactions that develop between the modifier and bitumen: it should be irreversible at all conditions, say we heat bitumen to 180 degrees they should not phase separated out.

We apply some amount of load on the modified bitumen then they should not phase separate out. So under any given condition the mixing or the blending between the modifier and bitumen should not phase separate out. So that is called as the interactions which are irreversible at all these conditions and the last one is it should not produce a single phase. So we were talking about miscible case right?

So I told you that it is not desired; immiscible with compatible case is what we require. So why we do not want a completely miscible case? then what happens is the modifier will completely dissolve in bitumen and the effect of this modifier on bitumen will be very minimal right? We will not see any positive effect on this modified bitumen which is on a quantifiable basis right? So we need it to behave in two phases but have compatibility between these two phases so that they will not phase separate out.

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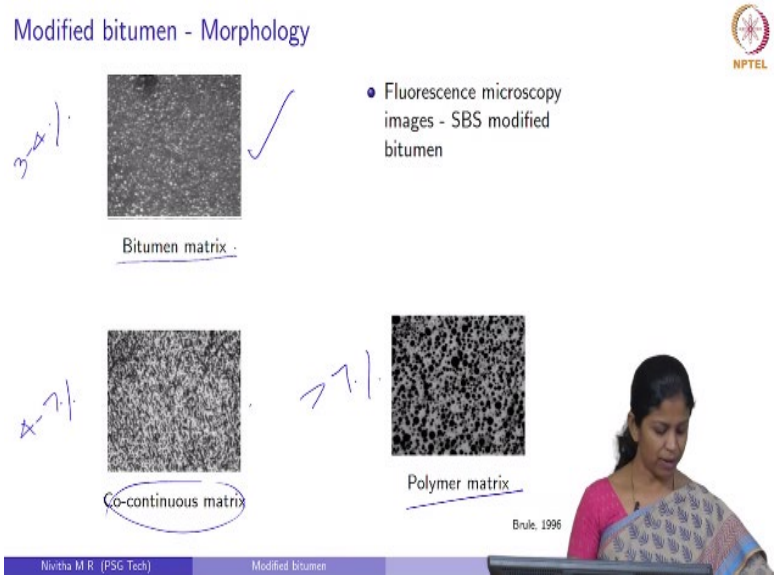

Now let us see the morphology which shows the distribution of the modifier and bitumen. So this is a study by Brule where they have shown the distribution of SBS in bitumen at different concentrations. Let us take the first case where we have a bitumen matrix, so this roughly happens when the concentration of SBS is between 3 to 4 % right? So when we add SBS in concentrations of 3 to 4 % and when we mix it under standard blending conditions, we have a case where the modifier is uniformly distributed in the bitumen matrix right?

So we have two phases here: one is the matrix which is bitumen and the second one is the modifier which is distributed uniformly in the bitumen matrix, so this is the first case. The second case is, we have a co-continuous matrix, we have a bitumen matrix and the modifier matrix which coexist. Like the previous case we do not have one base and something dispersed in the second. So here we have both of them existing in a co-continuous matrix.

So this roughly happens when the concentration of the modifier is between 4 to 7 %. Again these are rough numbers; it can vary depending upon the type of base bitumen, type of modifier, lot of variables right? The third one is a polymer matrix, this is called as phase inversion; so this happens when the modifier forms the base and bitumen is now distributed in the modifier matrix. So this roughly happens at concentrations greater than 7 %.

When we look into the interaction of SBS with bitumen we will see why addition of 7 % of SBS causes something like a phase inversion. You should remember that we are only adding 7 % of SBS to bitumen but we can see that is significant enough to cause a phase inversion here right? So these are different cases of morphology which can exist for a modified bitumen.

And what we prefer here is something like this, the modifier uniformly distributed in a bitumen matrix. We do not want this because this is not stable; they both exist in a co-continuous manner and they do not form a stable material, so we do not want this phase. This phase is also not desirable because now it is the polymer which forms the base and the properties of the polymer is going to dominate here, so it kinds of behaves like an adhesive.

So we do not want this also, so what we desire here is a modifier distributed in bitumen matrix and accordingly we have to determine the dosage of modifier.

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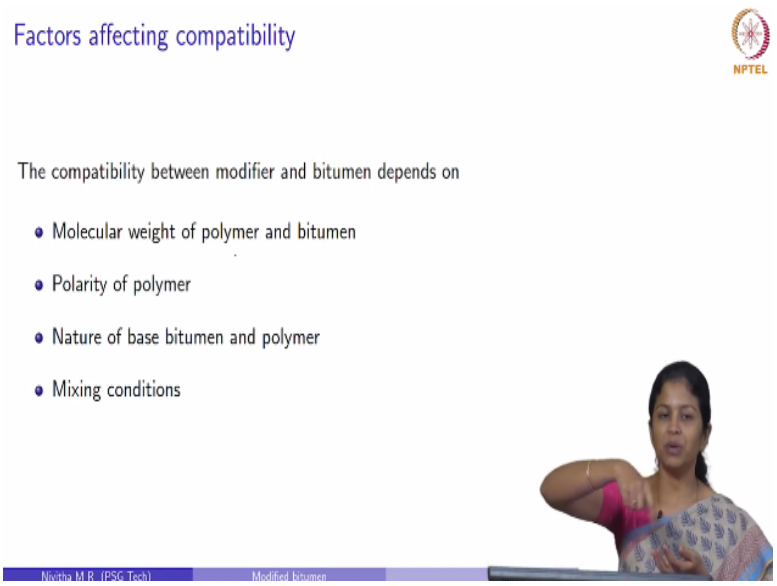

Now let us look into what are the factors that affect compatibility between modifier and bitumen and leads to each of these phases. There are some four important factors again, there are many factors but I have listed only four important factors or four factors which are commonly referred. So the first factor is molecular weight of polymer and bitumen, so if we add two materials of highly differing molecular weight right?

So then they tend to phase separate; again it depends upon the specific gravity of these materials. So to give an example here many people add high density polyethylene to bitumen to modify bitumen right? So this high density polyethylene the specific gravity is about 1.35 to 1.4, whereas the specific gravity of bitumen is roughly around 1.06. So the specific gravities of these two materials are totally different and then they easily tend to phase separate.

So phase separation is commonly reported in case of high density polyethylene modified bitumen, so we have to keep a check on the molecular weight of the polymer. We need to see what is the molecular weight of the base bitumen; we have already discussed in the slides on chemical composition discussing about what are the types of molecular weight and how to measure that for bitumen.

So we need to check the molecular weight for bitumen, the molecular weight for the modifier and see to that they do not vary so much that they lead to a phase separation. The next one is

polarity of the polymer, so some polymers are highly non-polar. So what do I mean by non-polar? they do not form any kind of interaction with base bitumen right? so only if we have some kind of interaction, it can be any sort of interaction.

But some sort of interaction should develop between the base bitumen and modifier. So only then they will try to be compatible and retain the compatibility over a long period of time. So we need to add modifiers which have some amount of polarity, so that is the second requirement. Third requirement is nature of base bitumen and polymer, so this nature of base bitumen is a very tricky factor.

So you would have discussed about the refinery processing, types of crude source, types of processing methodologies available India and its implications on the properties of the base bitumen. So we do not have a large control on the properties of base bitumen but we need to take into account that a same modifier can work to improve the properties in a significant manner for one kind of base bitumen but it may not work for another kind of base bitumen.

So what do I mean by one kind and other kind? So there might be one bitumen which is which is coming from one particular crude source or which has undergone one type of processing method so that can be suitable for certain kind of modifiers whereas bitumen from some crude source and from some type of processing methodology may not be suitable for some other kind of modifiers, so we need to take into this fact also into account.

And the last parameter is mixing conditions, so when we prepare modified bitumen we have bitumen; we add modifier to it; so we mix them at high shear rates and then for some type of modifiers, we give them some amount of time for the interactions to develop right? So this is the production process in brief.

So this mixing condition: the shear rate in which the modifier is blended with bitumen, the type of blade that is used, the temperature at which blending is carried out and the amount of time for which blending is carried out. All of them have a significant effect on the properties of modified bitumen, if not for all modifiers, at least for some kind of modifiers. So again we need to take

into effect of these mixing conditions right? so these are some of the factors which affect the compatibility and the properties of the modified bitumen.

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