Mechanical Characterization of Bituminous Materials

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

Lecture No 21
Chemical composition of bitumen Part-05

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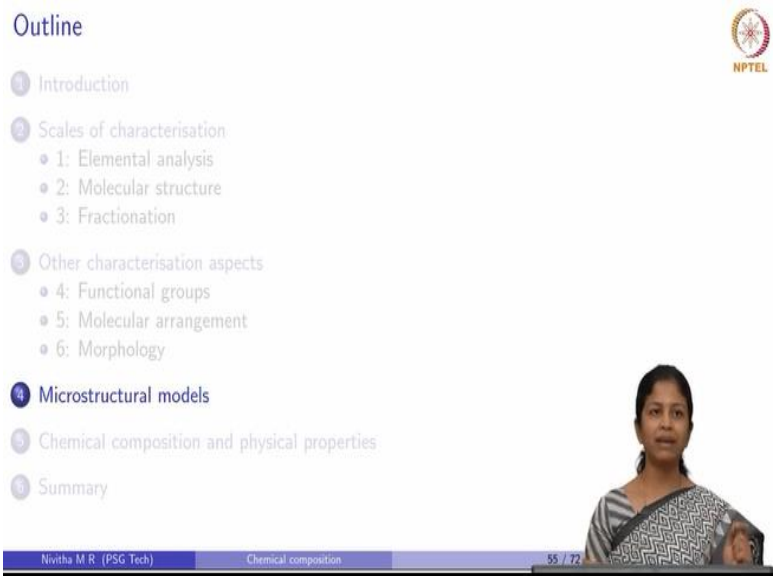

In this lecture we will continue about the micro structural models for bitumen. In the previous two lectures we had discussed about the different scales of characterization and what are the other characterization aspects that have been used on bitumen. So in this lecture we will focus on the micro structural models and what is the relation between the chemical composition and physical properties of bitumen.

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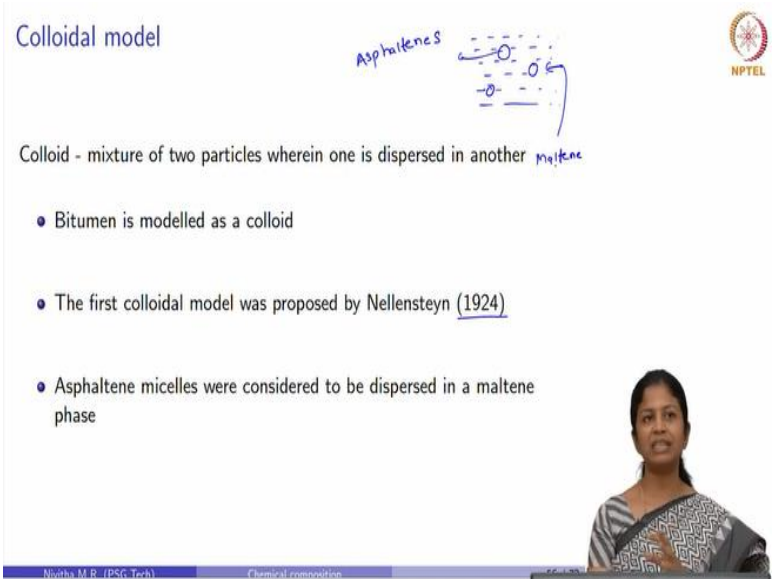

So when we look at the micro structural model, bitumen was modelled as a colloid, as early as 1924. In 1924 Nellensteyn proposed a first colloidal model. So what do I mean by a colloid? we have two materials one is dispersed in another. So we have one component which is dispersed and another one which forms a matrix. So we can represent it something like this right?

So we have some particles which are dispersed in something else. So this was the initial colloidal model which was proposed in 1924 by Nellensteyn. So here this particle which is dispersed was called as asphaltenes; one which forms the matrix is called as maltene. So there are two components; the dispersed phase is called as asphaltenes and the matrix which is the medium in which these asphaltenes are dispersed is called as maltene.

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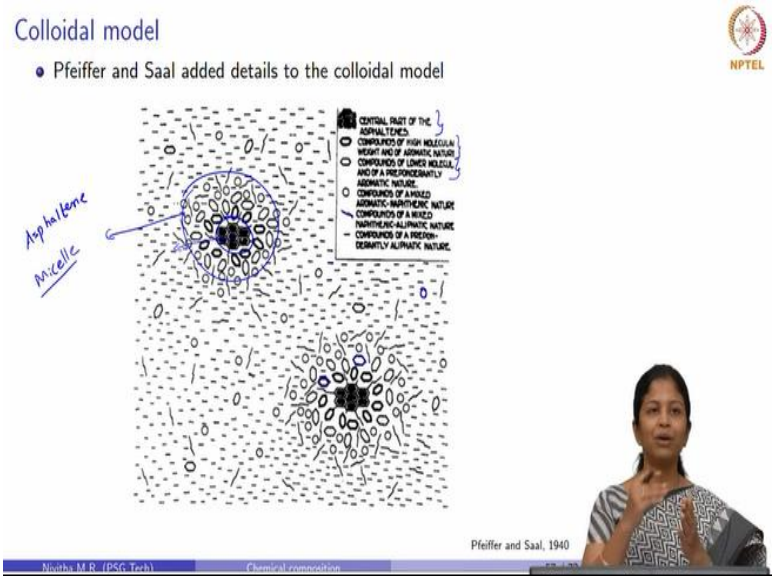

Later, Pfeiffer and Saal worked extensively on this colloidal model and they proposed a hypothetical structure considering different fractions of bitumen. So here they have different fractions; let us look at one by one; the filled black one right what we see here this forms the central part of asphaltenes right? So this is the asphaltenes agglomerated together which forms the central core.

And this one are surrounded by compounds of high molecular weight and aromatic nature. So we see this one here right I will show you here, so there is a hexagon which is having a dark outline. So these are compounds of high molecular weight and aromatic nature. So we have a central core of asphaltene surrounded by high molecular weight compound; then we have compounds of lower molecular weight and predominantly aromatic in nature.

So we have something here we show a hexagon here, with the lighter outline so these are lower molecular weight but aromatic in nature and we have these circles here which are compounds of mixed aromatic and naphthenic nature. So which means that they are aromatic and they also have cyclics. Then we have this line which is shown here compounds of mixed naphthenic and aliphatic.

So previously we had aromatic and naphthenic; now we have naphthenic and aliphatic nature and these straight lines are compounds of aliphatic in nature. So when we see the molecular weight and the size of these molecules keeps decreasing as we move from the centre of the core to outer space and they also said there is no significant boundary; you cannot say this is a particular thing which forms this is called as a micelle right?

So this is referred to as a micelle and this is there in the dispersed medium. So this one which is present here is called as an asphaltene micelle right? It is called as an asphaltene micelle and this is dispersed in a medium. So in this paper that Pfeiffer and Saal have proposed that there is no clear-cut boundary between this asphaltene micelle and the matrix in which bitumen is present.

So they say there are micelles which are present the central core formed by asphaltene and the molecular weight keeps decreasing as we move away from the central core but there is no clear-cut boundary when this micelle ends and when this matrix starts.

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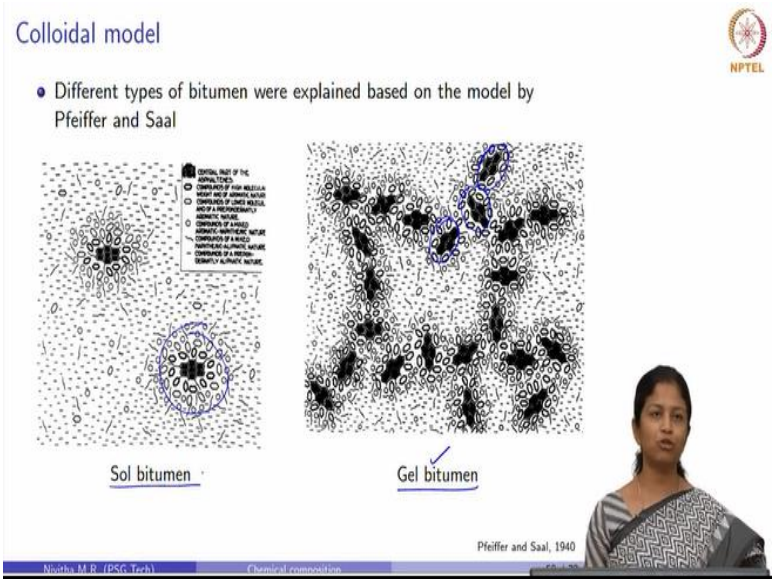

So this is the model by Pfeiffer and Saal and they use this model to explain a sol and gel bitumen. We will first start with a gel bitumen, we can see in this gel bitumen. We have all these micelles which are closely packed to each other right? So they have some strong attractive force between them and they are closely packed in this case but we have a sol bitumen wherein they are not as closely packed as in the case of a gel bitumen.

These micelles are spaced apart from each other. So bitumen any given bitumen can be of a sol type or of a gel type; so a gel bitumen generally has a higher viscosity value compared to a sol bitumen but we should remember here that, a given type of bitumen can exhibit both gel behaviour and sol behaviour depending upon the temperature. At low temperatures we can say that the microstructure of bitumen will exhibit something like that of gel bitumen.

Whereas, when we move to high temperatures this microstructure will exhibit something like as sol bitumen; so either given bitumen can have either of these two behaviour or two types of bitumen can have either of these two microstructure. So these were two types of models which were proposed by Pfeiffer and Saal and this is extensively used to explain the temperature dependent properties of bitumen.

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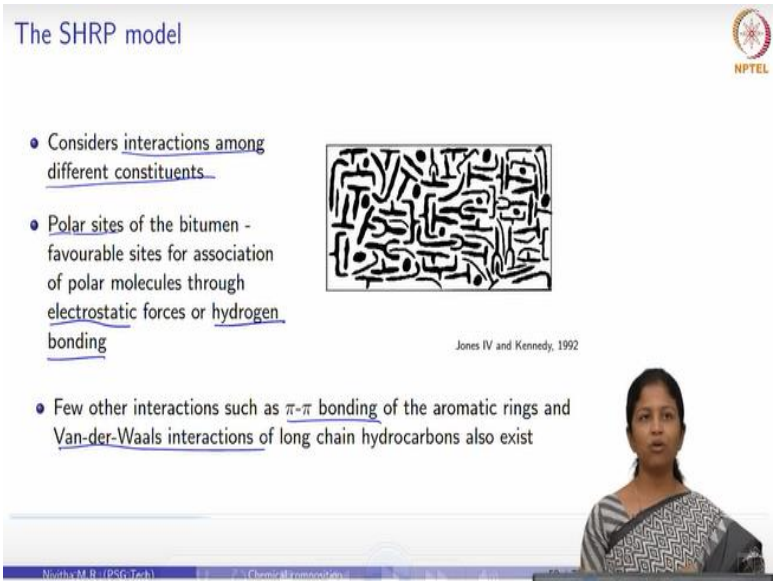

Then people proposed a model which is called as a SHRP model because in the previous model by Pfeiffer and Saal they did not focus on the interaction which exhibits at different points in a given molecule. So to capture these interactions the SHRP model was proposed. So this SHRP model considers interactions among different constituents. We said previously when we were talking about the fractionation technique we have different fractions.

The interaction among these fractions is very, very important. So this SHRP model tried to focus on these interactions, they say the polar sites of bitumen are favourable sites for association of polar molecules through electrostatic forces or hydrogen bonding. So previously when we were talking about hetero atoms we said they are points through which the strong attractive forces will occur between different molecules.

So these attractive forces are because of electrostatic forces or hydrogen bonding right? So this is the basis on which SHRP model was built and they also said it can have few other interactions such as pi-pi bonding of the aromatic rings. These aromatic rings undergo some kind of a pi bonding and there is also Van der Waal interaction of long-chain hydrocarbons.

So these are few other interactions that were proposed as a result of this SHRP model but then this SHRP model was not further expanded to add more details to these interactions.

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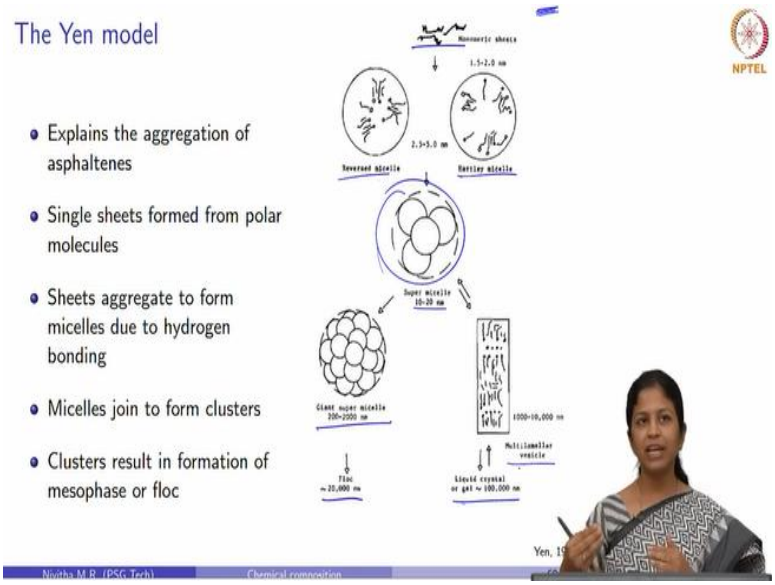

There is another model by Yen, where they have proposed a structure for these asphaltenes. They have said that these asphaltene core forms the micelle or these asphaltenes form the core of this micelle and they try to say what is this micelle composed of. So they say these asphaltenes have some kind of an arranged structure, so they form a monomeric sheets right? So they form some kind of a sheet like structure something like this some orderliness in the amorphous fraction.

And these monomeric sheets join together to form different types of micelles you can see what is the size of these monomeric sheets from 1.5 to 2 nanometre and they join together to form micelles which are to 2.5 to 5 nanometre. Now these micelles join together to form a super micelle which is of 10 to 20 nanometre. So we have different micelles joined together to form a super micelle which forms a giant super micelle or it can also form a multi lamellar vesicle.

So they can either be arranged in form of a sheet or they can take the form of a micelle which is in the form of a globule. So then they joined together to form a floc or in other case they can join to form a liquid crystal or a gel. So that is what they also say; it can be either present in a gel state or it can be present as a floc in a sol state also. So this is the hypothesis which they have proposed in relation to the asphaltene molecule and they also did some microscopic studies to identify the sizes of this each of these micelles.

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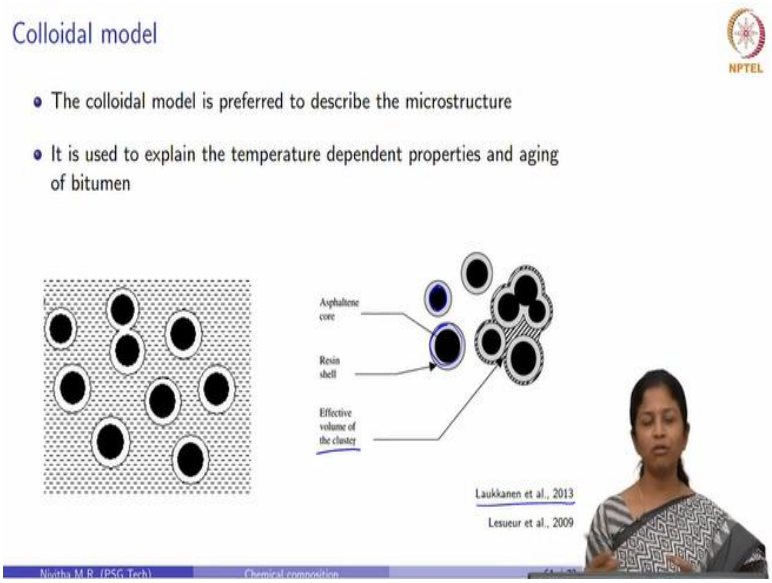

So these are some of the colloidal models which are available today but still the colloidal model which was proposed by Nellensteyn and further expanded by Pfeiffer and Saal is currently used. So this colloidal model is preferred to describe the microstructure even today and in the year 2013 Laukkanen et al. used this colloidal model to explain the temperature dependent properties and aging of bitumen.

So they say that there is an asphaltene core which is present in bitumen; this is further surrounded by the resins fraction and they also use this to calculate the effective volume of the cluster. So these are some of the attempts which are made in this regard expanding on the colloidal model; it is used to explain the temperature dependent and aging properties of bitumen. So we will discuss more in detail about these factors when we talk on aging of bitumen.

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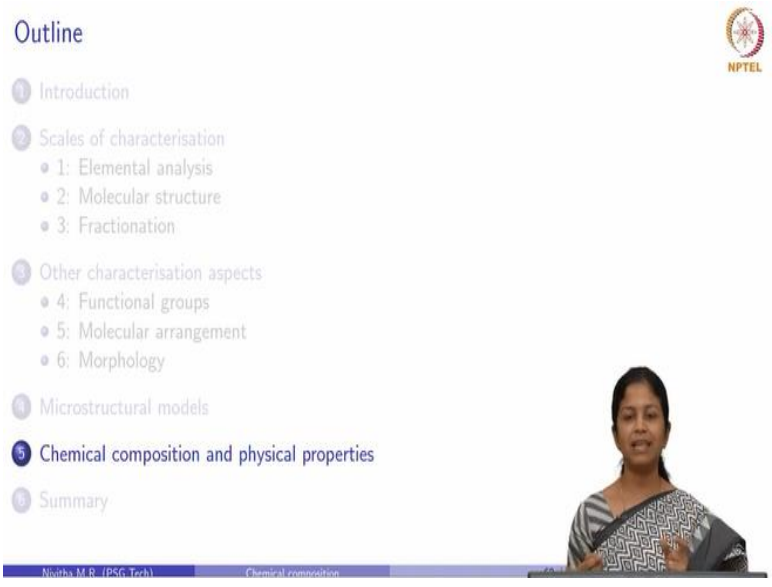

Next we move on to the relation between chemical composition and rheological properties of bitumen. So ultimately we understand that the chemical composition is what is influencing how a material behaves. So we need to understand how the chemical composition influences each of the rheological properties of bitumen. So why do we need to understand this, so we have some particular property of bitumen say for example moisture damage.

We need to reduce the moisture damage in bitumen; so then we need to make this bitumen have more affinity towards the aggregates and when moisture interferes this system it should not rip away this bitumen from the aggregates very easily. So for that purpose we need to ensure a strong bonding between bitumen and the aggregates. So for this purpose people have said that specific functionalities in bitumen can improve the interaction between the aggregates and bitumen and reduce stripping.

So one such functionality is amines; the presence of amines can improve the bonding between aggregates and bitumen and reduce stripping. So if we have a bitumen with more amount of amines which is present in it then we can say that it will reduce the stripping properties. So if we have some links between the chemical composition and rheological properties then we will be able to say or tweak the chemical composition of bitumen to obtain the rheological properties that we desire.

Or in general we can say that we will be able to design bitumen with specific requirements; but still this is not a very simple task; it has lot of steps involved in it and it is very complicated; we will understand what leads to its complexity.

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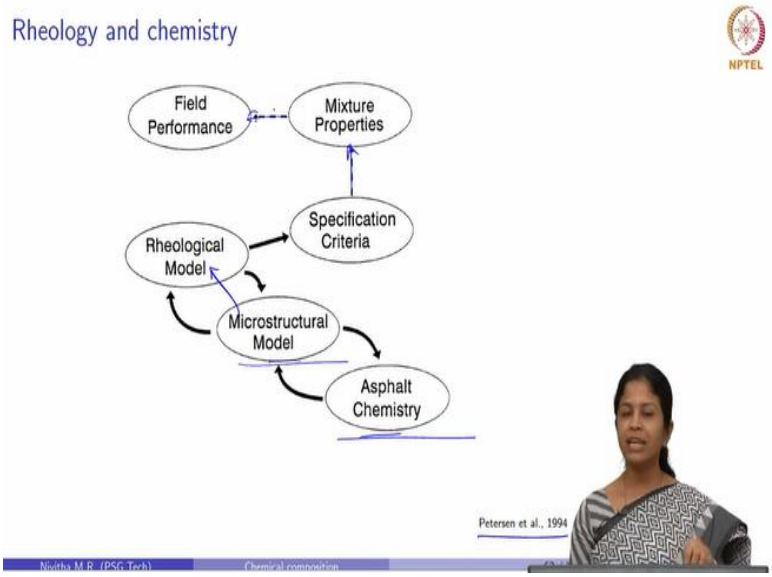

So this is an image given by Petersen et al. where they have tried to relate the asphalt chemistry to its field performance. So we understand that asphalt chemistry focuses on the chemical composition of bitumen. So for many other polymers we can say that this is the structure of this particular polymer; this is the manner in which each of these molecules in this material is arranged and so it will lead to this kind of a performance.

So when we want to predict the performance they derive models from its microstructure. They say that, if this microstructure is behaving in this manner it will lead to this kind of rheological response. So such correlations are possible for simple polymers but for bitumen it is very difficult to arrive at such correlations because we know the variability that is induced in the material because of the crude source, processing methodology.

And it also exhibits a viscoelastic behaviour, so we have to quantify what is the effect of different parameters like time, temperature and all the other variables on this behaviour and finally we have to relate it to the field performance; again field performance; each and every location is subjected to different environmental conditions. The effect of temperature, rainfall and the availability of oxygen, the properties of mixture are a number of variables which will affect the behaviour of binder.

So even if we have two binders and we want to compare its performance depending upon the location where the binder is used, its performance is going to be different. So correlation between chemical composition, its rheological properties is the first step; then rheological properties to field performance is the second step. We also have a small step here which is the mixture properties.

So establishing this big link is very complicated as far as bitumen is concerned. So people say that we have asphalt chemistry, so based on that chemistry we try to propose a micro structural model right? Model to describe the microstructure of bitumen; based on the micro structural model we have to propose a rheological model and from the rheological model we will be able to arrive at specification criteria.

Because ultimately the binder is going to be used in field and whatever is the specification requirement we will be able to tweak it depending upon the variability in asphalt chemistry and the microstructure. So this rheological model will result in specification criteria and using the specification criteria we will be able to specify mixture properties and from mixture properties the field performance right?

So we have a big link here and we have a number of steps here. So ultimately the interest is to correlate the asphalt chemistry to field performance. So lot of attempts are being carried out in this regard but we need to understand the variability associated in each of this step in the process.

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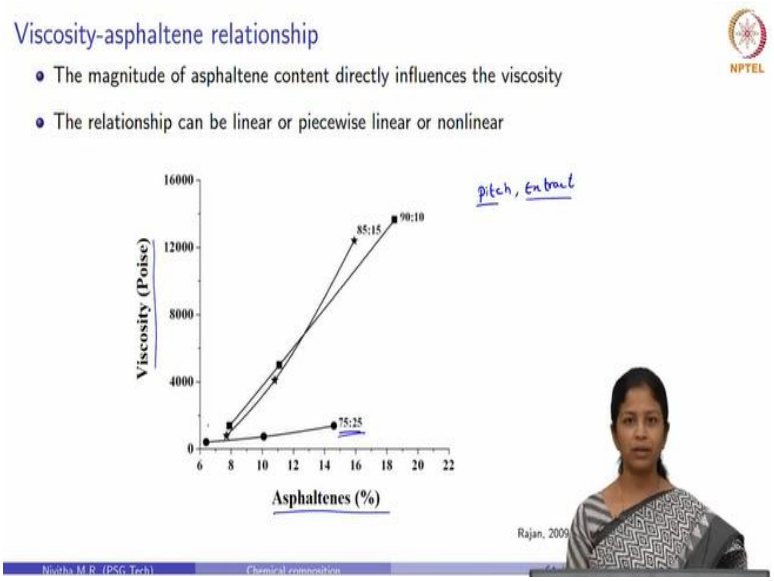

Let us now see what are the attempts in this regard; the foremost attempt is to correlate viscosity to asphaltene because we said the asphaltene fraction is of high molecular weight and when they aggregate or agglomerate together they tend to increase the viscosity of the system. So people propose that the amount of asphaltene content which is present in bitumen can directly influence viscosity.

Then later a number of studies tried to verify this fact, so we can see in this regard we have asphaltene content on the x axis and we have viscosity on the y axis. So we can see that depending upon the type of bitumen again this is three different type of bitumen with different proportions of pitch and extract. So from the lecture on the refinery processing by this time you will know what a pitch is; what an extract is.

So this pitch and extract were combined in different proportions, so in one case 75 % of pitch and 25 % of extract. In another case 90 % of pitch and 10 % of extract and in the third case 85 % of pitch and 15 % of extract. So they were combined in different proportions to get bitumen of different grades. So we can see in each of them the increase in asphaltenes reflected in an increase in viscosity of the system.

However the slopes were different depending upon the proportion of pitch and extract but still we can see that there is almost a linear relation between increase in asphaltene content and increase in viscosity. Sometimes people have observed that this linearity can be piecewise linear which means that it can have one particular slope up to a specific concentration of asphaltene And a different slope for another range of concentration of asphaltene but this viscosity and asphaltene relation was strongly established.

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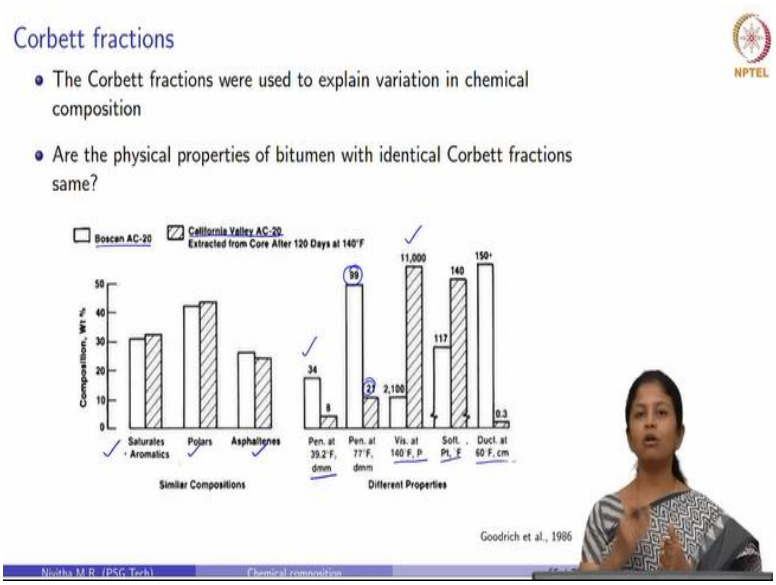

Then people started looking at the Corbett fractions and they tried to see if this variation in Corbett fraction or if the magnitude of this Corbett fraction can be related to the physical properties of bitumen. So they have taken two different type of bitumen; one is a Boscan AC-20 and the other one is a California Valley AC-20. So two different type of bitumen and we can see the composition; these saturate plus aromatics combined together the polar aromatics and asphaltenes. They are almost identical in these two types of bitumen.

So from the Corbett fractions perspective they both can be considered as identical bitumen but when we look at the physical properties we can see how they vary. We will start with penetration, so we should mind that the units are given a degree Fahrenheit. So when we look at penetration at 39.2 degree Fahrenheit. We see that the Boscan AC-20 has a higher penetration value compared to California Valley AC-20.

So this one is a softer material compared to the other one at 39.2 degree Fahrenheit. Next when we move on to penetration at 77 degree Fahrenheit again we can see that this material has more penetration value indicating that it is a softer material compared to the other case.

Now when we see viscosity, we also see this viscosity at 140 degree Fahrenheit again we can see that this California Valley AC-20 has higher viscosity which means that it is a stiffer material again at 140 degree Fahrenheit compared to Boscan AC-20.

Similarly is the softening point and ductility at 60 degree Fahrenheit. So we can see that the asphaltene fraction the Corbett fractions are same in both the materials but we see that their physical properties are completely different. So as we defined earlier it is not the magnitude of the Corbett fractions alone but how they interact with each other is also going to influence the physical properties in a significant manner.

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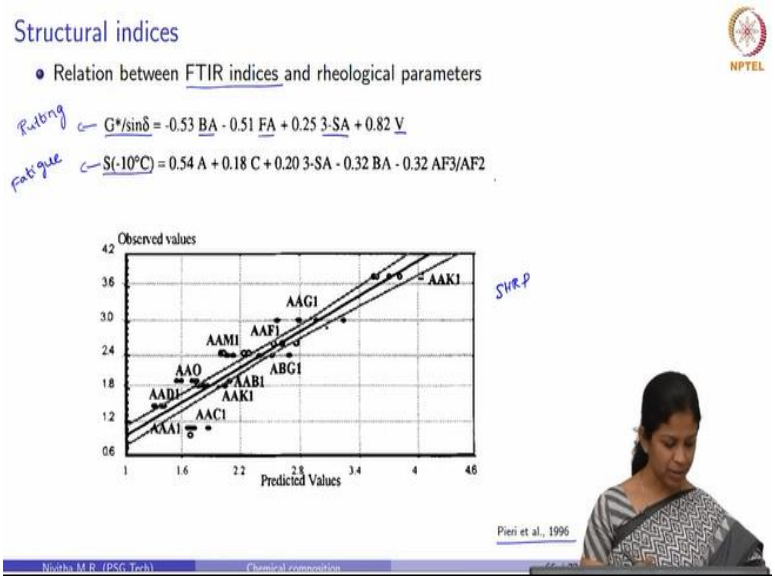

Next we will move on to another attempt where they tried to correlate the performance grade properties of bitumen to its elemental composition and the functionalities that are present in bitumen. So this was a study which was conducted by Pieri et al. So there they had taken bitumen from different sources, so we can see AAD1, AAO, and AAM1. So these are bitumen from different sources classified under these names by SHRP right?

So we have different types of bitumen; they try to establish a correlation between certain indices calculated from FTIR spectroscopy right? So what are these indices? you have some amount of this functionality present, you normalize it and that we call it as FTIR index and that is correlated to the rheological properties of bitumen. We will use some parameters which we have learnt in performance grading for this purpose.

They have taken G*/sinδ we know that this G*/sinδ is used to represent the rutting properties of bitumen. Similarly stiffness at -10 degrees is used to represent the fatigue properties of

bitumen right? So they have used these two parameters to represent the rheological parameters and a number of parameters are seen on the right hand side right?

So these all relate to the elemental composition and the functionalities. So what this BA? it is the branching index. So it says how much of the aliphatics which are present in bitumen are in branched form. Similarly this FA is the factor of aliphaticity which says how much of the composition in bitumen are present in aliphatic form; similarly three substituted aromatics that is the aromatic structure but number of substitutions that are present.

This V says the vanadium content that is present in bitumen. So they were able to obtain a correlation between the G*/sinδ and a regression equation arrived using these four parameters. You can see using this regression equation they predicted the G*/sinδ; they measured this G*/sinδ using a rheometer and they were able to get a positive correlation.

Similarly they also explained the stiffness at -10 degree Celsius using another regression equation with a different set of parameters. So such correlation between the rheological parameters and the chemical composition was possible but most of them are regression equations in nature. They are not fundamental equations explaining the microstructure of bitumen.

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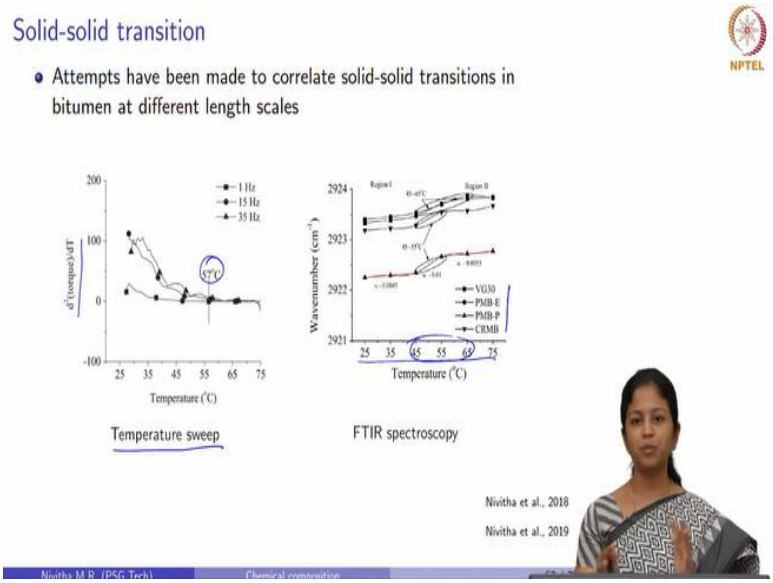

Next we will move on to another attempt which tried to capture the solid - solid transition in bitumen. So what is this transition in bitumen? we know that bitumen exhibits a wide range of behaviour right? So it starts from the elastic solid at one end to a viscoelastic fluid or a

Newtonian fluid at another end. So there is a wide range of behaviour exhibited by bitumen; in the working temperature range it exhibits a viscoelastic response.

Again we know that the viscoelastic response can be sub-classified it can be called as a viscoelastic solid like or a viscoelastic fluid like. So you know all these basics and what each of them mean, so then there was a study which was conducted to find out when the transition between the viscoelastic solid like and a viscoelastic fluid like occurs in bitumen. So this was measured at two different length scales; one is using rheological test, a temperature sweep test.

So again you know what is temperature sweep test? The torque was measured from this temperature sweep test and a torque derivative was calculated with temperature. So this torque derivative was observed and at 57 degree Celsius some transition in the material was indicated by this parameter. Similarly the FTIR spectroscopy was done at different temperatures both of them in the same temperature range from 25 to 75 degree Celsius.

It was done for different set of binders again here we can see in the temperature range between 45 to 65 degree Celsius depending upon the type of bitumen we were able to see some transition in the material. So these are an unmodified, elastomer modified, plastomer modified and crumb rubber modified bitumen. I will not get into the details as they get more research-oriented.

So I will just stop with this attempt where they have used techniques at two different length scales to quantify a particular aspect of this material and we are able to get some identical correspondence between these two different scales of measurement.

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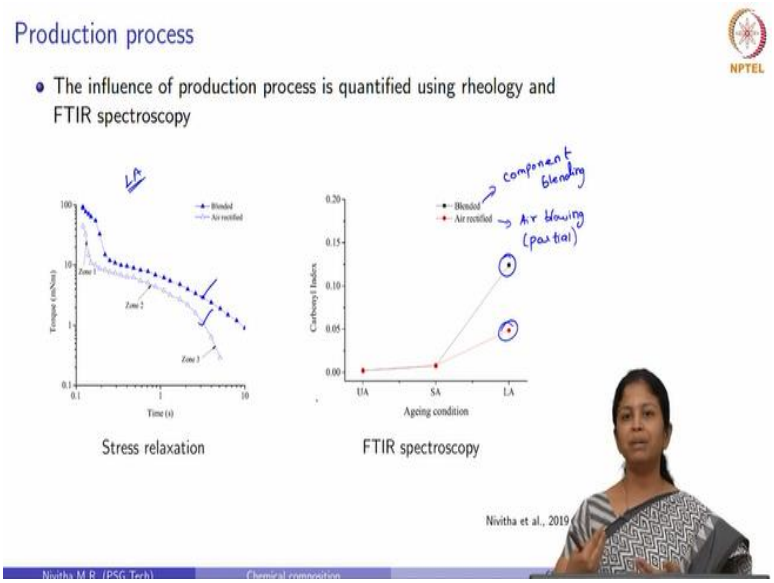

Next we will move on to another study where in the influence of production process was quantified. So we know that we have bitumen from two different processes in India; one is blended or which is called as component blending; the other one is air rectified or air blowing. It is partial air blowing alright? So these are two different techniques which are commonly used in India.

So bitumen of a particular grade was obtained from each of these two different processes. When we look at the stress relaxation behaviour of these two types of material, we can see that the stress relaxation behaviour is completely different for a blended material compared to an air rectified material. Though they fall under the same grade they behave differently; this is what I mentioned when I initially started this lecture on chemical composition of bitumen.

To understand why two bitumen of the same grade behave in different manner we need information on the chemical composition. So for that FTIR spectroscopy was performed and the carbonyl index was calculated in unaged, short term aged and long term aged condition. Again this stress relaxation corresponds to long term aged condition. So in the long term aged condition it was seen that the blended bitumen has more carbonyl index compared to the air rectified bitumen.

So what this carbonyl index is what it means; we will discuss when we talk about aging; but there is some parameter which can quantify aging. So it was seen that how this material ages is completely different and there is a correlation between carbonyl index and stiffness of the material; higher the carbonyl index it is generally said to increase the stiffness of the material for most cases.

So this blended material has more amount of carbonyl index and that was the reason for the increased stiffness in the stress relaxation test that was observed. So again here we can reason out why two bitumen behave in different manner by studying the chemical composition.

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So these are some of the attempts which were carried out to correlate chemical composition and rheology; again it is not a very simple task we need to understand the lot of variability that is associated in this process.

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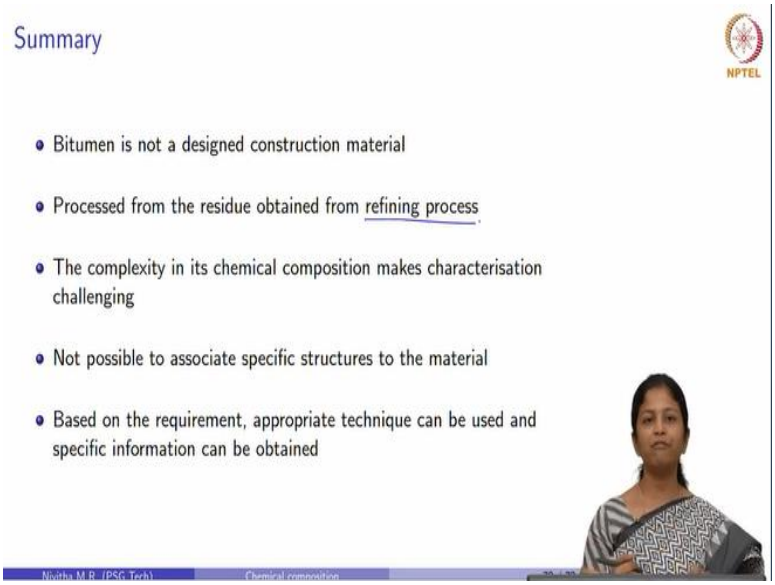

Now we will summarize what we have learnt in this topic on chemical composition of bitumen; so like I mentioned earlier bitumen is not a designed material we have not designed bitumen specifically for paving purposes. It is the end product which is obtained from the refinery processing. We have taken this material and we have tweaked it for paving purposes.

So there is complexity in its chemical composition because of the crude source and the processing methodology.

So this complexity makes the characterization challenging and we also saw that it is not possible to associate specific structures to this material. We said we can identify the elements which are present in material but it is not possible to identify and define the molecules which are present in this material. So that is why we are using some fractionation techniques; again depending upon the requirement we have to use appropriate techniques.

So initially we saw characterization at an elemental scale, then at a molecular scale, then finally at a fractionation level. So depending upon what is the application that is required for bitumen, we have to use different techniques.

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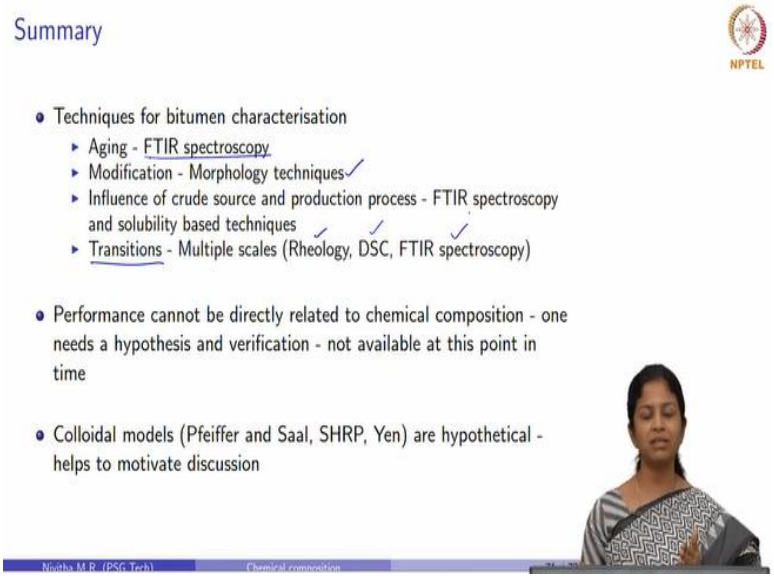

So these are few of the techniques which are used for bitumen; for aging we saw that we have to identify functionalities in bitumen so we will be using FTIR spectroscopy. For modified bitumen we saw morphology related techniques were very successful. So for modification purposes we are going to use morphology related techniques, for information on crude source and production process we can use FTIR spectroscopy to quantify the changes at the micro structural level.

And we can also use solubility based techniques which are nothing but the fractionation procedures and to identify transitions which happen in this material it has to be evaluated at different scales, the rheological property to show transition occurs and the micro structure

related techniques to show why this transition occurs so we have a combination of rheology, DSC which is nothing but differential scanning calorimetry and FTIR spectroscopy.

So ultimately we want to relate performance to the chemical composition of bitumen. So for this purpose we need some hypothesis, what do I mean by hypothesis here? we need to say that bitumen behaves in this particular manner and we need to choose an appropriate technique to verify that hypothesis. So initially people spoke that this elemental composition and the functionalities have some relation to the rheological properties of bitumen.

So if we see the study by Pieri et al. which we discussed they have functionalities on one end and they thought that it is going to influence their rheological properties. So they chose a parameter $G^*/\sin\delta$ to capture their rheological parameters. They chose few functionalities and hetero atoms; then they try to make a correlation. So this correlation between chemical composition and rheological performance has to be made with some hypothesis and choosing appropriate technique to verify the hypothesis.

Finally colloidal models though we know it is limitations are still preferred to represent the microstructure of bitumen. So it helps to motivate discussion as they form a hypothesis and we can verify what this hypothesis says for bitumen. So with this we will wind up our discussion on the chemical composition of bitumen. I thank you for your time here.