Mechanical Characterization of Bituminous Materials

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Lecture No 20
Chemical composition of bitumen Part-04

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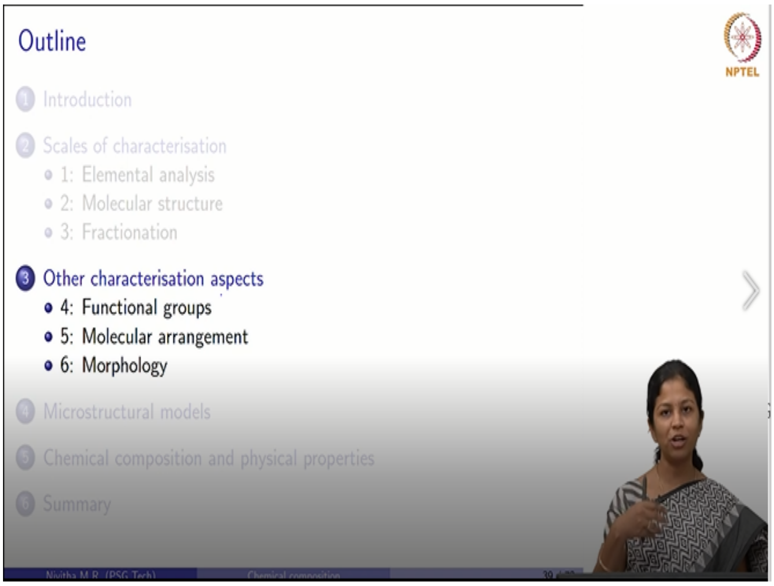

Next, we will move on to certain other characterization aspects which are available for bitumen. So, now, we said that separation of bitumen into fractions is convenient, it gives us a lot of information, but again we also said that when we sum up, we are not able to get the response of whole bitumen because we are not capturing the interactions. So, we need some techniques, which will give us information related to the chemical composition, when bitumen is considered as a whole instead of separating into fractions.

There are three techniques which are used in this regard. Again, there are many techniques, but I have focused in this lecture on three techniques which are commonly used for bitumen. The first one is functional group analysis, the second one is molecular arrangement and the third one is morphology.

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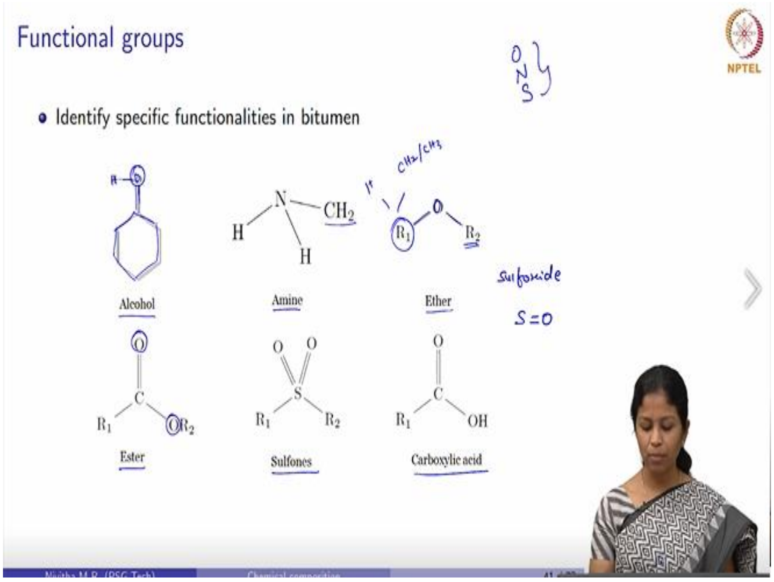

Let us now look into the functional groups which are present in bitumen. So, what are these functional groups? We said right the oxygen, nitrogen, sulphur are all hetero atoms which are present in bitumen and these hetero atoms are highly polar in nature. So, we need to study these hetero atoms in specific and see if they will influence the physical properties in a influential manner. So, what are these hetero atoms and what compounds they form in bitumen; that is what this functional group analysis focuses on.

So, these hetero atoms are attached to carbon atoms in different manner and depending upon how and where they are attached, they form different functionalities. Let us first take alcohol; we know how alcohol is defined right? We have a benzene ring which is present here and to this benzene ring, we have an OH functionality right? So this is an alcohol an OH attached to a benzene ring right?

So, we have oxygen present here right? Similarly, we have something called as Amine. So, we have nitrogen and we have three hydrogen atoms which are attached to nitrogen and either of them can be replaced by an ethyl or methyl group. So, depending upon how many hydrogen atoms are replaced by ethyl or methyl group, they are called as primary, secondary or tertiary amine.

Similarly, we have ether; we have two functionalities, this can be either hydrogen or it can be CH_2/CH_3 any functionality right? So, we have 1 hydrogen or any functionality which is present here, bonded to oxygen to another functionality right? So this is ether. Similarly, we have ester, where a carbon is double bonded to an oxygen molecule and single bonded to another oxygen molecule. So this is called as ester.

So we had ether, where there is oxygen bonded to two functionalities and we have ester, where carbon forms double bond to oxygen and single bond to oxygen. We also have sulfones, where the sulphur is double bonded to two oxygen molecules, we also have sulfoxide, where sulphur is bonded to just double bonded to one oxygen alone. Sulfones are when sulphur has double bonds to two oxygen molecule.

Similarly, we have carboxylic acid, we know that it is C double bond O and then OH. So these are some of the common functionalities there again lot of functionalities.

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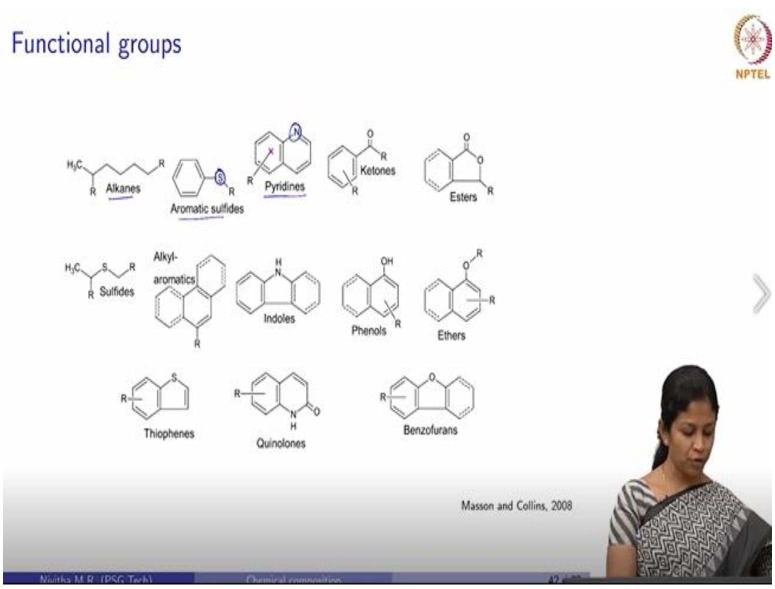

If they are attached to the aromatic structures again, they will have different names. So we know what alkanes are, we have aromatic sulphides, when sulphur is attached to an aromatic compound. Similarly, pyridines when nitrogen is present ketones and we have esters; a lot of other functionalities which are present in bitumen. So, these functionalities are very useful when we look into aging.

So, aging is something which is happening because of the oxidation of bitumen and there is oxygen related functionalities formed as a consequence of aging. So more about this functionalities in bitumen and formed on aging, we will discuss when we discuss about aging. So, these are some of the functionalities, again hypothetically which can be present in bitumen, and we have many other functionalities also which are not listed here.

But then we can identify a specific functionality, which is present in bitumen without separating into fractions.

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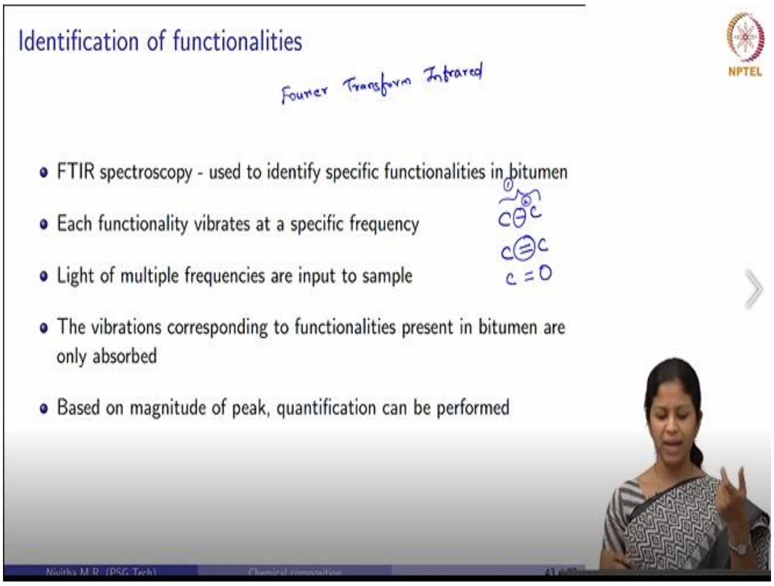

So, for that we use a technique called FTIR spectroscopy, which is nothing but Fourier transform infrared spectroscopy, this technique is very conveniently used to identify specific functionalities which are present in bitumen. So, how is this technique used? So, we said right we have number of elements which are present in bitumen bonded in different manner. So, say for example, we have carbon bonded to another carbon right? This will vibrate in a different manner compared to carbon double bonded to carbon.

So, each bond right has a natural frequency of vibration, we should have learned about this in chemistry right? So each has its own natural frequency of vibration, but this natural frequency of vibration is going to depend upon what are the two elements that are bonded and this is the first factor and what is the nature of bond that they are having; depending upon these two factors the frequency of vibration is going to differ.

So a carbon single bonded to carbon will vibrate at a different frequency compared to a carbon double bonded to carbon. Similarly, a carbon double bonded to carbon will vibrate at a different frequency compared to a carbon double bonded to oxygen. So, this is the basic principle which is used in FTIR spectroscopy to identify different functionalities. So, how this technique works? we have light of multiple frequencies, which are input to the sample.

Now, whatever is the natural vibration which is already present in the material, because of all these functionalities will be absorbed when the light is passed into the sample and whatever is not present in the material will come out undisturbed. So, this is the principle which is used in FTIR spectroscopy. So, based on the magnitude of the peak and the intensity of peak, we can quantify the elements which are the functionalities which are present in bitumen.

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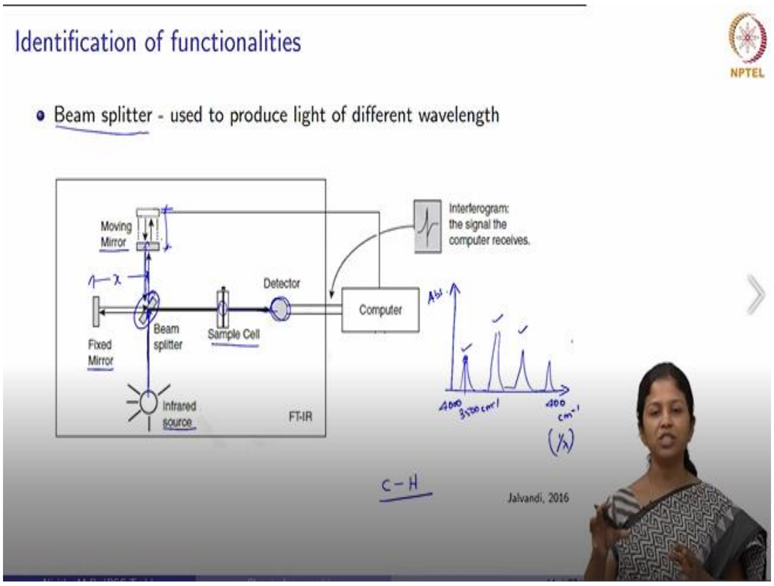

I will just explain in brief about this technique. This technique has a beam splitter, which is used to produce light of different wavelength. So, we see here, the first thing is we have an infra red source here. So, light is now input onto the beam splitter, right? This beam splitter splits this light into two different components. So, these two different components fall on a fixer mirror which is placed in here and then a moving mirror which is placed here.

This fixed mirror is at a specified distance X from this beam splitter, whereas, this moving mirror keeps varying with time spatially. So, we have this moving mirror can vary from this position, this moving mirror can vary from this position to this particular position. So, depending upon its position at that point of time, the amount of time taken for this light to fall on this mirror then reflect back is going to vary.

So, when the time varies the wavelength is going to vary. So, there will be variation in frequency. So, we have a fixed mirror were always the time is constant, so, the frequency will be constant, whereas, this moving mirror will keep varying specially with time. So, depending upon the time this will produce light of different wavelength, these two are again combined back at the beam splitter.

So, what happens now is with respect to time, we are going to have light of different wavelength. So, that is how light of multiple frequencies are produced. Now, this falls on a sample cell. So, when this light falls on a sample cell, we have our material which is placed inside this sample cell. So we have different functionalities in our material and we said that each functionality is vibrating at a specific frequency.

So, whatever is this frequency of vibration is absorbed by this sample which is present here and then it will vibrate at a higher amplitude and whatever is not present in the material will come out and it will be detected using a detector. So finally, what we will get out of this technique is this we can have as a wavelength or wave number and this will be the amplitude right? So, we will get some peaks like this right?

So, this will be based on frequency. If we define it in wave number which is inverse of wavelength, for bitumen, we can define it from 4000 to 400 cm^{-1} right? This is wave number which is nothing but inverse of wavelength. So, we will have a range from 400 to 4000 cm^{-1}. This is the different range of wavelength which we have input to sample and depending upon the components which are present in bitumen.

So, all these peaks say that at this particular position there is something which is present in bitumen, let us say this happens at 3500 cm^{-1} right? From literature, we will be able to identify what is the functionality that vibrates at 3500 cm^{-1}. Now we have different materials, right? How do we arrive at this information? Let us take this C single bonded to H; this C single bonded to H will vibrate in a very small range of frequency, irrespective of in what material this is present.

Whether that is present in our skin or in bitumen or any of these materials we see around, this CH is going to vibrate only in a very short span. The span will vary maximum of 10 centimetre inverse, so it will vary only in that range. And that is used to identify what is the specific functionality present here and what is the environment in which it is present. So, then I see a peak at 3500, I refer the literature, I will be able to see what is the peak that is occurring at 3500.

So, I will be able to say whether that particular functionality is presented in bitumen or not. Similarly, we do for the other peaks. So, using this referencing we will be able to identify what are the functionalities that are present in bitumen.

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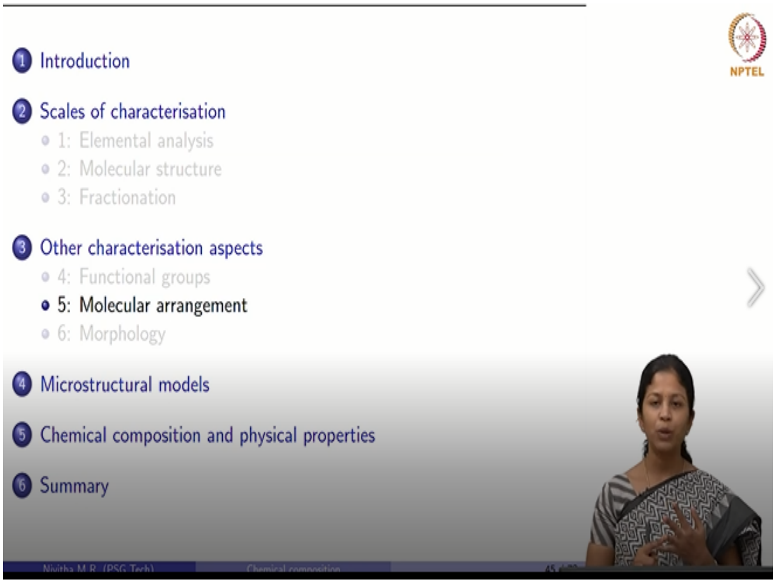

So, that is with regarding the identification of functional groups in bitumen. Next we will move on to the other technique, which is molecular arrangement.

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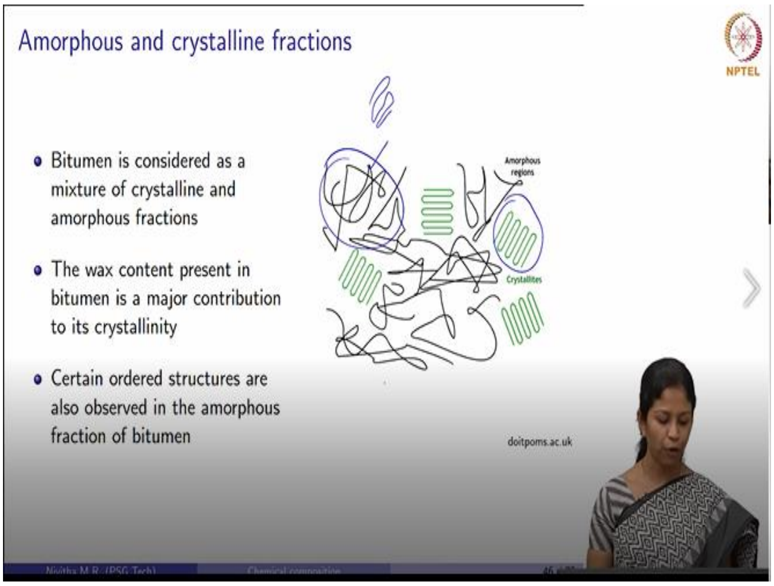

Molecular arrangement is how these molecules are arranged together right? We say right we have an amorphous material, we have a crystalline material; what do we understand by crystalline material? A crystalline material is one wherein, it has an organized structure or it has an arranged structure that is what we called as a crystalline structure. It is of an ordered form.

Whereas amorphous materials are present in random, they do not have any orderly arrangement, but again in some cases, they might have some kind of orderliness, but still they are amorphous in nature. Here you can see in this image, which shows the crystalline and amorphous regions, you can see that this is the crystalline fraction, you can see how they are arranged in an orderly manner.

And you can see how this amorphous fraction is present in a random manner, sometimes this amorphous fraction can be present something like this, where we can call it as orderliness but then the orderliness is defined differently for crystalline and amorphous fractions right? In bitumen, the wax content which is present in bitumen, contributes to the crystalline fraction. Most of the linear long chain compounds right, these alkanes and paraffins constitute the crystalline fraction of bitumen.

Whereas the aromatic fraction are mostly present in amorphous form and then like I said, there are certain ordered structures, which can be observed in amorphous fraction also.

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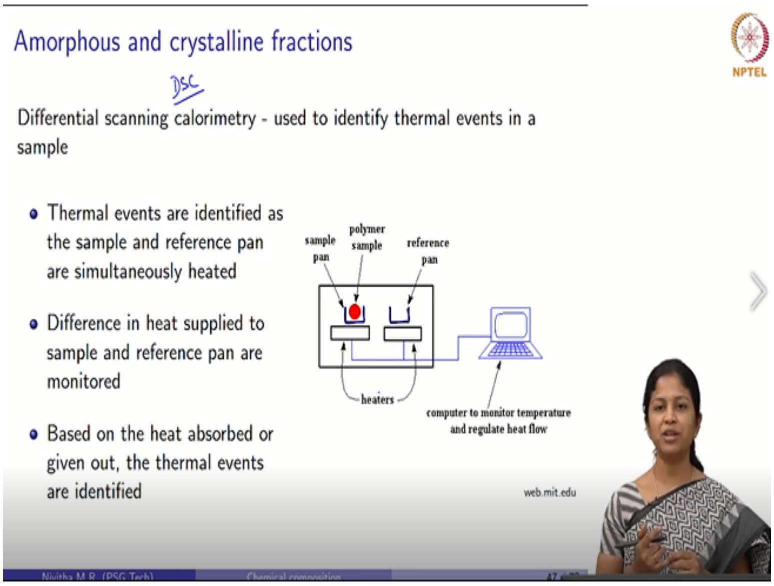

So, how is this amorphous and crystalline fraction are identified in bitumen? For many polymers people use this definition to identify the thermal events which are happening in bitumen, which are happening in polymers. So, in the case of bitumen also, we tend to use this technique to identify what are the thermal events which are happening in the material. So, for that purpose, we use a differential scanning calorimetry.

This is called as the DSC, differential scanning calorimetry to identify the thermal events happening in the material. So, if we want to study functionalities, we are using FTIR spectroscopy. If you want to study the thermal events happening in the material, we are using some other technique which is DSC. So how this technique works, we have a sample pan right? So, we have two pans here, a sample pan and a reference pan.

In the sample pan, we place our sample and in the reference pan it is just left empty. So, both of them are attached to heaters and then we specify constant rate of increase in temperature right? So we want the temperature, say for example; to increase from 0 to 100 degrees Celsius at the rate of 1 degree Celsius per minute, let us say it for an instance.

Now, this sample pan is supplied with some amount of heat energy to maintain that rate of temperature increase. This sample pan is also subjected to some amount of heat energy, but the amount of heat energy supply to the reference pan and the sample pan can vary. Now we have our sample which is placed here, as temperature increases there are thermal events happening in the material.

So it can absorb some amount of heat energy and go to another state or it can let out some amount of heat energy and go to another state. So, when it is releasing some amount of heat energy, we need to supply only lower amount of heat to maintain that rate of increase in temperature. So in that case the amount of heat energy supplied to the sample pan will be reduced compared to that of the reference pan.

So, this information is used to identify the thermal events which are happening in this material.

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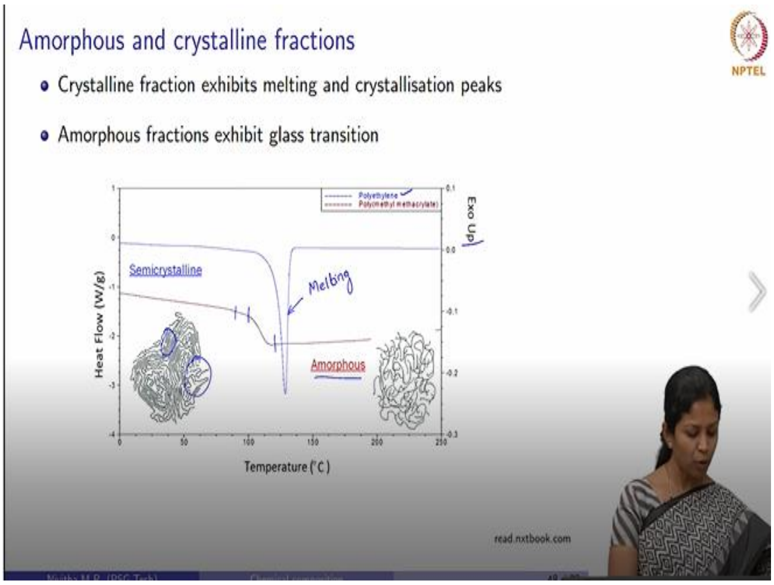

So, we have a sample plot here, which is again defined for polymers. We have two plots one for a crystalline, semi crystalline material in fact and another for an amorphous material. The semi crystalline material which is used here is polyethylene; we can see that it has some amount of crystalline fraction which are arranged in an orderly manner. It also has some amount of amorphous fraction. This is called as a semi crystalline material.

So, what is the thermal event that we are seeing here? At a temperature of about 125 degrees Celsius or 130 degrees Celsius, we see a very sharp peak here. This peak corresponds to the melting that happens in polyethylene. So, this is a melting peak that we see for this particular material polyethylene. So, we see here that there is Exo Up when this heat is given out it is called an exothermic reaction and this is Exo up and endothermic is down.

So, we see a sharp peak in the case of a semi crystalline material, whereas, in the case of an amorphous material, we see that there are no thermal events up to 90 degrees Celsius and as temperature increases, we see that there is a gradual drop right? So, the transition in a crystalline material is very sharp, whereas the transition in an amorphous material is gradual. This transition is called as a glass transition temperature.

So, this glass transition temperature is not very sharp. So, we defined this onset and the end of transition and people use different methods to arrive at the specific glass transition temperature from this information. So, we now see how the thermal events are described for a semi crystalline material and an amorphous material.

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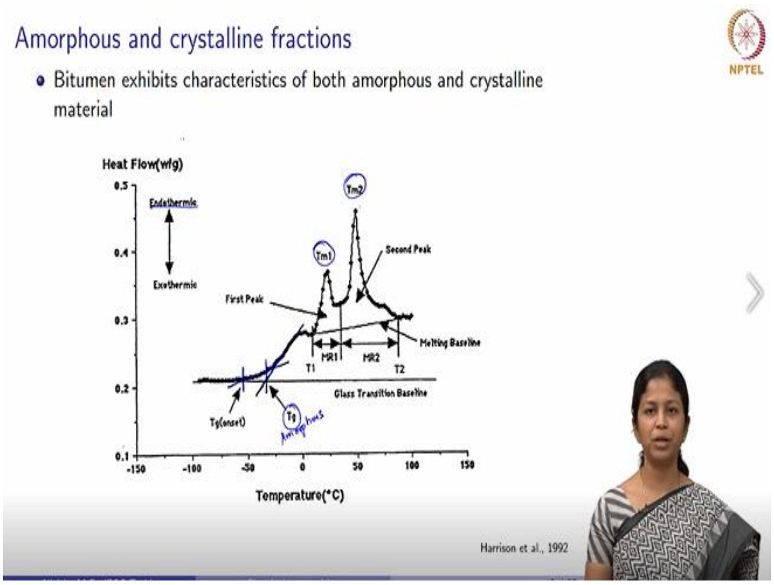

Now, let us look at the DSC plot of bitumen. Bitumen exhibits characteristics of both amorphous and crystalline fractions. It has both amorphous fraction, we said it is because of the aromatic content in bitumen and it is also because of the crystalline fraction mostly due to the alkane fraction which is present in bitumen. So, here we see, initially we see that there is a glass transition temperature here.

We see there is a TG onset and this particular point is defined as TG because it is taken as the slope of this region, slope of this region and the intersecting point is taken as the TG here. So, this is how the glass transition is defined and this corresponds to the amorphous fraction that is present in bitumen. And we have two melting peaks, it is defined as TM_1 and TM_2. Here we see that endothermic is given up.

So, that is why these melting peaks are shown above the horizontal line. In the previous case, we saw that Exo is up, so the peak was down. So, we need to be careful when we interpret a DSC plot depending upon whether exo is up or endo is up, we might get a peak above the horizontal line or below the horizontal line. The second information is, we are seeing two peaks here; we have two melting peaks which are seen here.

The first melting peak is TM_1 and the second one is TM_2. So, why do we have two melting peaks? We are already defined that bitumen constitutes of a number of components. So we said they are different in size, composition, properties, all of these parameters. So depending upon what is the size and nature of these crystalline fractions that is present in bitumen they can show thermal events at different temperatures.

Because of this factor, we are able to see multiple peaks in the case of bitumen which is not observed in the case of a few simple polymers, right? So, this is one information which is very useful in the case of bitumen.

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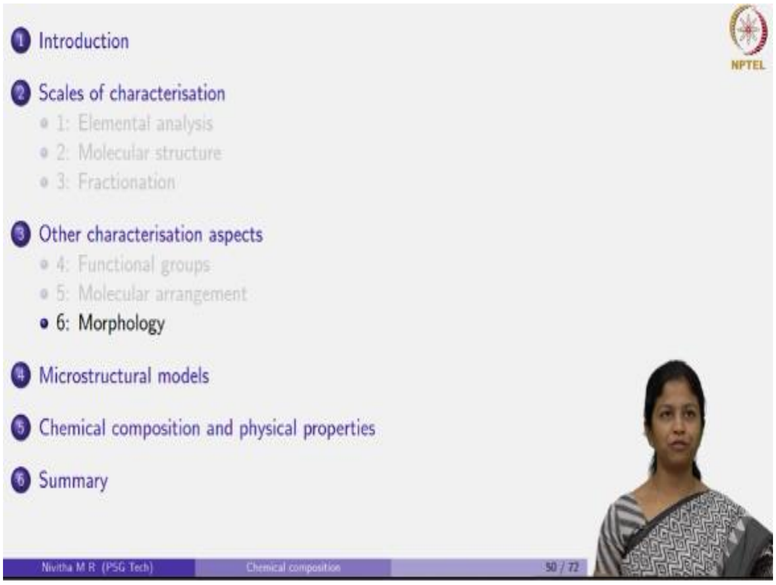

And the next one is morphology related information. Next, we look into the third characterization aspects of bitumen, which are the morphology based techniques. So, what does morphology mean? Morphology gives us information about the surface how this surface is composed?

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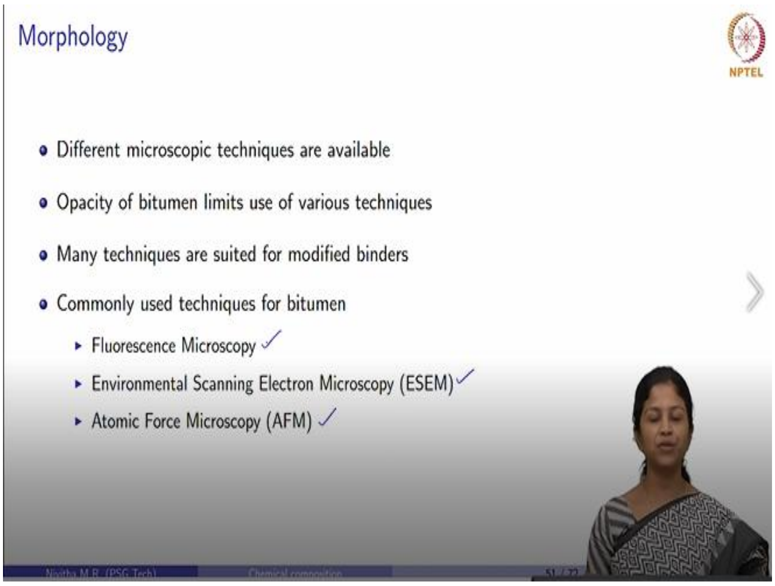

So, the use of microscopic techniques has not been very successful in the case of bitumen, there are n number of microscopic techniques available for bitumen but the limitation here is bitumen is opaque right? Its completely black, it is opaque, it does not allow light to pass through it. So because of this many of the microscopic techniques cannot be used for bitumen. So there are few techniques which are successfully used for bitumen.

And I am going to focus on three such techniques which are fluorescence microscopy, environmental scanning electron microscopy and atomic force microscopy. So, the normal optical microscopy may not be successful in the case of unmodified bitumen. Even this fluorescent microscopy is very successful in the case of modified bitumen, again modified bitumen which consists of fluorescent particles.

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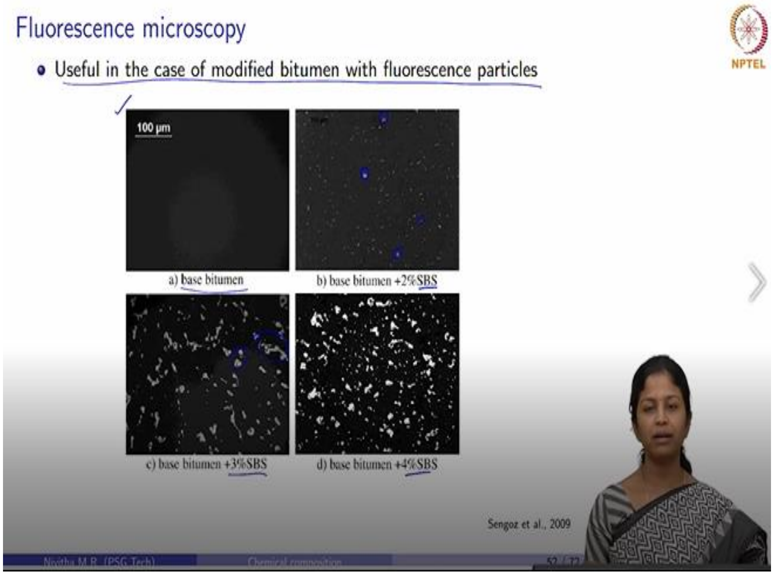

Let us now see what each of these technique are. The first one is fluorescence microscopy, so we need to note that it is useful in the case of modified bitumen with fluorescence particles. Fluorescence particles means particles which can emit light. So here, there is an image of a base bitumen, which is an unmodified bitumen and this one modified with SBS at three different dosages, SBS is styrene-butadiene-styrene, a type of modifier.

So, more details about this, we will be discussing when we talk about modifiers for bitumen. So, you can see what we get from the unmodified bitumen in the case of fluorescence microscopy, it is just completely black. We do not get any useful information about this material in the case of base bitumen. But when we add 2% of SBS to it, we can see the white specs here right? You can see the white specks, bigger ones and the smaller ones also.

This is how SBS is distributed in the base bitumen. So, when we increase the dosage of SBS to 3 %, we can see it clearly; lot of white particles here which are distributed in the base bitumen and at 4 % it is even more clear. So, this fluorescence microscopy is successful in the case of modified bitumen, which emit florescence particles.

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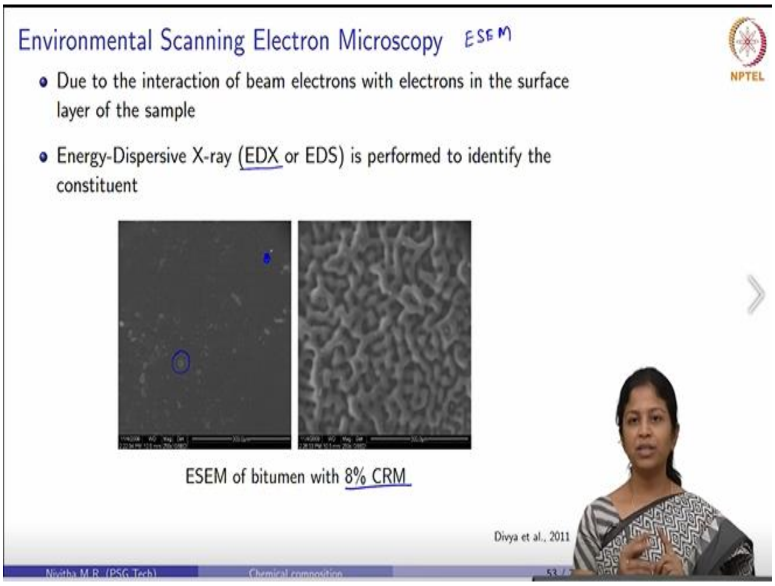

The next technique is environmental scanning electron microscopy or ESEM, right? So this environmental scanning electron microscopy is because of the interaction of a beam of electrons with electrons in the surface layer of the sample. So we have an electron gun, which emits electrons onto the surface of sample. So, these electrons interact with the electrons in the outer shell, and depending upon how they replace these electrons, they emit back and this emitted information is used to get information about the morphology.

So here we can see an image which is captured for 8% crumb rubber modified bitumen. So, we see an image here where crumb rubber is distributed in the bitumen matrix. And here we can see when it is allowed to focus for a sufficient amount of time we can see how the intertwined networks are formed in crumb rubber modified bitumen. So, this is very useful in base bitumen, it can provide us some information, but again more useful in the case of modified bitumen.

In the previous case when we performed fluorescence microscopy, we get only an image of the surface features of the material. But in this ESEM, we can also perform EDX which is called us energy dispersive X ray. So, what this EDX does is, I can choose a particular point here and I can do EDX at this point and I can identify the elemental composition of the material which is present in this particular location.

So, this is very advantageous because, when we add modifier to bitumen, we want to see which is the bitumen phase, which is the modifier phase and if we see some difference in the morphology, we will be able to identify what is the particular material which is present there. So, this is an additional information which we get from ESEM, which is not obtained from fluorescence microscopy.

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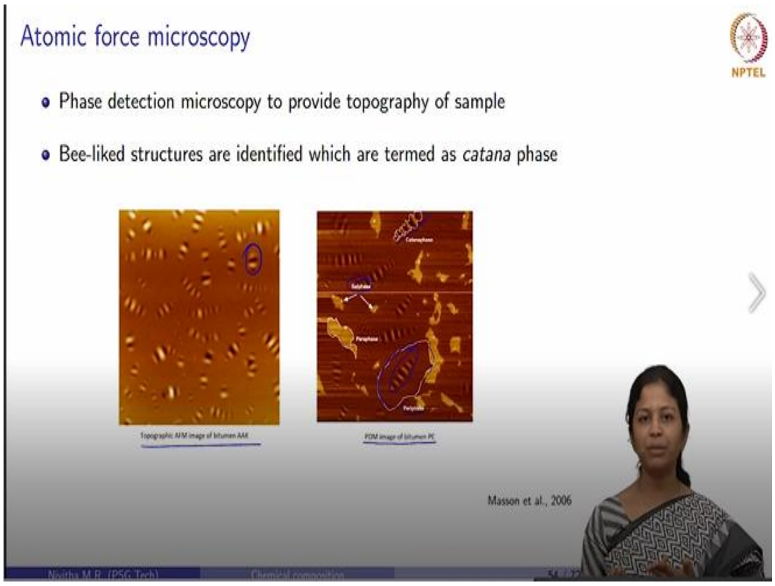

And the third technique is atomic force microscopy; this atomic force microscopy is again another advanced level, which provides us two information, the first one is morphology related information; it also provides information about elasticity of the constituents which is present on the surface. So, how this technique works is, we have a cantilever probe, which keeps scanning this material in a particular linear fashion.

So, this cantilever probe keeps moving along the surface of this material. So, depending upon the indentations in the surface, it will move down or up and that provides information related to the morphology. The second one is a phase detection mode. So, what happens here is light of a particular wavelength is input on the sample. So, the input signal is of a particular wavelength now, this input signal reaches the material and depending upon the elasticity of the material, the time taken for this input signal to reflect back and the phase angle between the input signal and the output signal is calculated to obtain the elastic properties of the material.

So, here the first one is a topographic image which we see here, we can see a lot of bee-like structures which are present here. So, these bee-like structures are identified which are termed as Catana phase and there are also other phases which are defined here. This is a phase detection microscopic image of a particular bitumen PC. Here we can see there are four phases which are present here. The first one is a catana phase, which we had defined earlier, a bee-like structure. And then we have a periphase, which is surrounding this catana phase, so we have this catana phase here and we have a periphase which is surrounding this catana phase right?

We have few other phases, which is apara phase, which is present here and we have few specs which are called as Salphase. So, few researchers were able to associate the chemical composition of bitumen to each of these four phases. So, research is now underway to interpret this atomic force microscopic image which we obtain for bitumen. So, these are some of the currently used techniques as far as bitumen is concerned.

I will not get into more details about this technique as they get into the research level, so for this particular course, let us just stop with identifying what are these techniques and what is the information that we get from each of these techniques.

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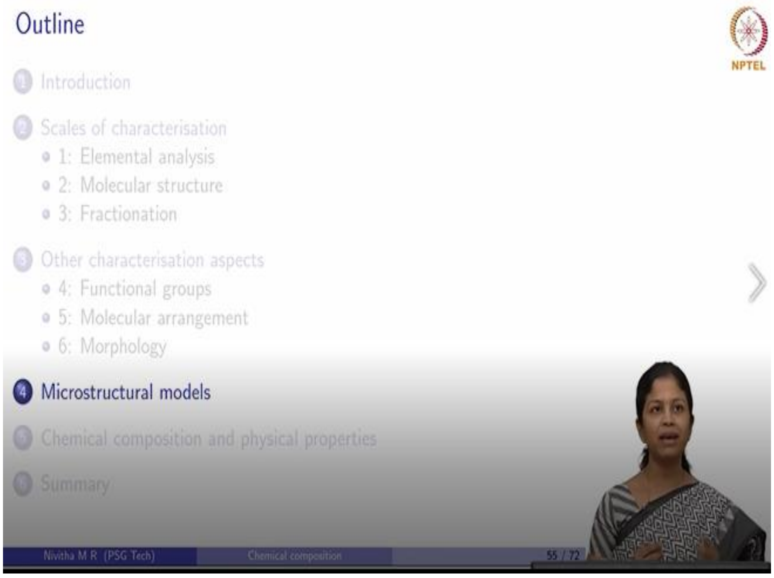

So, in this lecture, we have seen what are the different techniques which are available for fractionation of bitumen and then we also focused attention on few other techniques. We have seen how functional groups in bitumen can be specifically identified and how they are used. We also saw how molecular arrangement of bitumen is characterized using amorphous and crystalline fractions and how DSC is used to capture the thermal events in bitumen.

And we also saw few microscopic techniques which are available for bitumen and we focused on fluorescence microscopy, environmental scanning electron microscopy and atomic force microscopy. So we will stop this lecture here. In the next lecture, we will discuss about the micro structural models available for bitumen and what is the link that is created between the chemical composition and the physical properties of bitumen. And what are the various attempts that are currently progressive in this regard. So I thank you for your time.