Carbon Materials and Manufacturing
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Lecture – 20
Polymer-derived Carbon: Coking and Charring Mechanism

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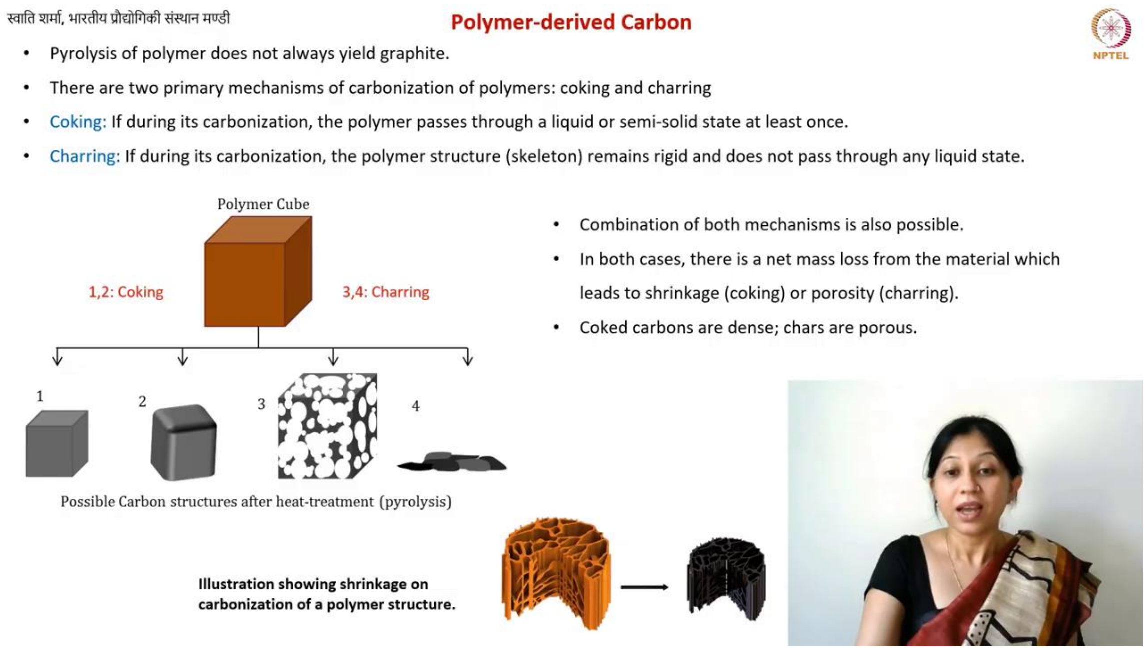

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Polymer-derived Carbon

- Pyrolysis of polymer does not always yield graphite.
- There are two primary mechanisms of carbonization of polymers: coking and charring
- Coking: If during its carbonization, the polymer passes through a liquid or semi-solid state at least once.
- Charring: If during its carbonization, the polymer structure (skeleton) remains rigid and does not pass through any liquid state.

Possible Carbon structures after heat-treatment (pyrolysis)

- Combination of both mechanisms is also possible.
- In both cases, there is a net mass loss from the material which leads to shrinkage (coking) or porosity (charring).
- Coked carbons are dense; chars are porous.

Illustration showing shrinkage on carbonization of a polymer structure.

Hello everyone. Now we move on to other forms of industrial carbon materials, bulk industrial carbon materials. We discussed a lot about graphite and there are various methods of preparing graphite. You can make graphite from the pyrolytic carbon that you get from gaseous hydrocarbon precursors and you can also convert polymers into graphite, not all polymers, but some polymers via heat treatment.

And you can also call it pyrolytic carbon because this is obtained after the pyrolysis of a polymer, which is also an organic material, not necessarily gaseous. I told you before that not all polymers give you graphite. In fact, extremely few polymers yield graphite; most of them would yield what is known as non-graphitizing carbon.

And these non-graphitizing carbons are also then further classified or further divided into various forms of industrially important carbon. And this is what we are going to start learning now and then individually we will talk about each one of these materials.

Not all polymers give graphite that you know already. Why does that happen? The question is why? You know that, if the polymer has some sort of chemical structure, let us say it has semi-crystalline kind of layered arrangement; then there is a higher probability that you will get graphite out of it. But sometimes even with certain layered arrangement, you do not really get graphite.

So, why does this happen? Why do you get graphitizing or non-graphitizing? Sometimes you will see certain forms of carbons; they have a very flat structure. They have a shiny surface almost. And on the other hand, you have something like coals and charcoal, there you will have more porosity. They do not have any shine; they rather look like z-black, they absorb as much light as they can. There are two mechanisms that are responsible for this. Now, remember that graphitizing and non-graphitizing are more related to the chemical structure of the polymer, whether or not you have semicrystallinity. And the flatness and certain other properties that we are going to discuss, that is more determined by these coking and charring mechanisms. But now, we are basically talking about the mechanism of polymer to carbon conversion, and then we will learn about other carbon materials.

What is coking? You know already about needle coke which is a common precursor for industrial graphite, but needle coke does have graphitizing. So, it has already certain graphite crystallites although but they have impurities, they can lead to graphite formation.

However, there is also some coke. Coke is not just one thing, coke is a range of materials. Cokes can also yield non-graphitizing carbon. So, that depends on what is the precursor you used for making the coke; even within the petroleum coke, you may not always have all same kind of coke, for example, in the case of pitch, you learnt that there is an isotropic pitch and there is a mesophase pitch. One has graphitic crystallites and the other does not. One gives you an isotropic carbon and other gives you isotropic carbon

The same thing happens with coke, not all of them will give you the same type of carbon then why do we call them coke? Because they are formed by the coking mechanism and what is this coking mechanism? You know that your carbons are made from organic materials and if these organic materials, especially in the case of polymers, after its complete degradation which typically would happen at 300-400 degrees or even before that in some cases; after its complete degradation, if this polymer undergoes a semi-solid or liquid-like phase. If it softens, in that case, the carbon that how will it be? If you melt something, then it becomes very soft liquid-like, and then what will happen? It will try to minimize its surface energy and try to settle down.

And now when it is settled down and when the carbon is obtained from this material then that will have a very flat and shiny surface. On the other hand, if this does not happen as in the case of charring, your entire material structure is rigid, it is standing there, whatever mass loss happens, has to happen through the same surface, but your skeleton of that polymer it is like very rigid.

In that case, you will rather get porosity in your material than a flat shiny surface. This is how you divide and classify your materials. On the next slide, I am going to give you a chart. Here are just some of the possibilities when you carbonize any polymer.

Let us take a cube of a certain polymer and put it inside the furnace. You have nitrogen flow, argon flow or any inert atmosphere in your tube furnace. Now, what did you do? You heated it up to 900 °C; let us say 900°C is the minimum temperature for at which you will get any reasonable carbon, before that you will have a lot of impurities.

Let us say you heat this cube, now what will happen; there is more than one scenario. You are converting it into carbon, but what type of carbon? If you perform an experiment like that, this is what you will get. If you have the shape intact, then that is scenario number 1.

When your shape slightly got modified or distorted. It is not even distorted, but it became slightly flattened or became more smooth and corners disappeared, you can see here in structure number 2. So, this is the second scenario.

The third scenario would be that your cube does not really shrink, or even if it does shrink but not very much. In this picture, I have shown the exact same size, but you may have some shrinkage but not very much, why? Because all the mass loss that had to happen created pores. The mass loss did take place. Let us say whatever carbon you obtain is lower than 30 percent between the original mass.

The structure will shrink if anything of the gaseous and the tar-like things are uniformly annealing out throughout your material, then it will create shrinkage. But if you have pores being created then the structure is very rigid.

Now there is also this fourth scenario, where you completely have a rigid structure. It is not shrinking and becoming smaller. You do have the rigid structure, but at some point, the porosity is so much that, the structure cannot just remain intact anymore. Then you get something like flakes and powders, maybe a very small fraction of your carbon would left. So, these are the 4 scenarios that will take place.

What will happen if you have coking and what will happen when you have charring? Maybe when you look at this picture, you can say number 2 is caused by coking. Your polymer must have gone through some sort of semi-solid liquid-like state and that is why you have these smoothening of the corners.

But also number 1 can very well be caused by coking because sometimes the polymer will not really become liquid-like, but it will just become semi-solid and more like rubber-like and gel-like state. So, you do not really lose the shape, but you do not get porosity. You do get shrinkage.

Now, scenario number 3, and 4 that is caused by charring. There you may or may not lose the structure. You may or may not get some shrinkage. But you will get a lot of porosity and that is why your carbon will look very black. And now you can already imagine what are the properties, you can expect from these types of materials.

When you have a very smooth and shiny surface, then, of course, being smooth and shiny itself is a very nice property and you have these very flat structures, which can be used for a lot of applications. We are going to talk about the applications in detail. And if you have porosity, then this kind of material can have a very good absorbance for various gases, various liquids, and impurities that are mixed in water. So, you can use porous carbons for water filtration and for various different filtration applications.

The fourth type of carbon, when you have in very small fraction that, that might be useful, but you will never do that because then your process is too expensive to get very little carbon so you will most likely not do it. So, these are the four scenarios.

For certain polymers, you may even have a combination of both, for example, initially the polymer does not become soft but at certain higher temperature point, because of certain chemical reactions, it goes through some softening. On the other hand, it can also happen that the polymer does go through softening in the beginning, but later on it has a certain charring mechanism. At some point, the structure becomes rigid and then you only get shrinkage or maybe you even may get some porosity. But these cases are rather rare. In general, you will have these 3 or 4 scenarios. Now, as I mentioned, then the mass loss can cause either shrinkage or porosity or in some cases both.

Now, how does porosity relate to density? When something has more porosity, it has less density, which is very clear. When you have coked carbons; coked carbon means, whatever is prepared by coking, then you are going to have it very dense. A very simple experiment, if you have a liquid and you pour a liquid inside any pot, the liquid will take the shape of the pot.

Later on, you are going to get a very flat surface, atomically flat and with high density. But in the case of chars, you are going to get more porosity and therefore, less density. In some cases, you can already make your polymer structure porous, like as I have shown here. There are many things you can in terms of when it comes to manufacturing, we will talk about that.

Then you can play around with these, with the fact that how much does your polymer soften during its carbonization, and does it give you graphitic and non-graphitic carbon? You can also make your structures porous and then you see what happens.

In this case(refer to slides), whether you call it coking or charring? This is actually coking that is happening because the porosity is not because of carbonization. We already had the porosity in the polymer structure itself. In fact, the entire thing shrank and that is why you, even the sizes of the pores changed; they were modified because of the shrinkage of the entire structure.

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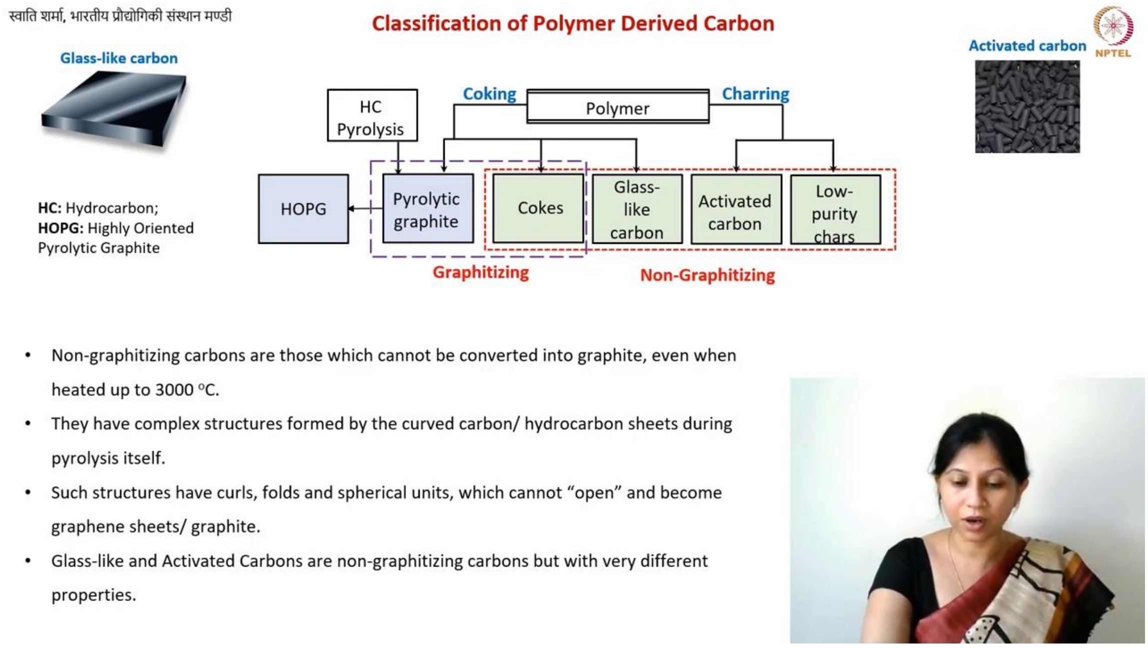

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Classification of Polymer Derived Carbon

Glass-like carbon

Activated carbon

NPTEL

Coking

Polymer

Charring

HC Pyrolysis

HOPG

Pyrolytic graphite

Cokes

Glass-like carbon

Activated carbon

Low-purity chars

Graphitizing

Non-Graphitizing

HC: Hydrocarbon;
HOPG: Highly Oriented Pyrolytic Graphite

- Non-graphitizing carbons are those which cannot be converted into graphite, even when heated up to 3000 °C.
- They have complex structures formed by the curved carbon/ hydrocarbon sheets during pyrolysis itself.
- Such structures have curls, folds and spherical units, which cannot “open” and become graphene sheets/ graphite.
- Glass-like and Activated Carbons are non-graphitizing carbons but with very different properties.

Here in this slide, I have a nice diagram for classification. I have not written the names of the polymers, but I have just written what mechanism will give you what. So, while coking mechanism, polymer goes through certain softening. This can give you graphite, we talked about it from PVC.

So, this will give you pyrolytic graphite. What you can do with this? You can make highly oriented pyrolytic graphite after further treatment or you can also just stop at pyrolytic graphite. I have also mentioned here that by hydrocarbon pyrolysis you can get pyrolytic graphite. Although, it is not a part of this particular diagram, because, it is a polymer, but I just showed it because HOPG can also be obtained.

Now, coking will also give you some cokes. But as I said, cokes are a range of materials, it is not one unique material, they will give you different types of carbons. So, you get cokes by coking for example, needle coke will definitely give you graphite. So, I have classified this pyrolytic graphite and some cokes which will give you graphitizing carbon together.

From this process of coking, we get one more very important material which is also used in micro and nanofabrication and that is going to make at least a few of our lectures. This material is known as glass-like carbon commonly known as glassy carbon. Although the IUPAC name is glass-like carbon but commonly it is known as glassy carbon.

This is again another type of carbon that has a very flat surface. And since it is prepared at very high temperatures, it also has very high purity and it has very interesting electrochemical properties, despite the fact that this is not graphitizing. In fact, no matter how high you heat it, it will never convert into graphite. In fact, this is one of the most important non-graphitizing carbon, industrial carbon materials.

This is an image; it looks something like this. It is just a plate of carbon, which looks very shiny and flat, maybe slightly darker in color compared to graphite. So you may say graphite is black but I call it like darkest grey, but this carbon is black.

After seeing so many carbon materials and after reading about them and doing experiments; I can differentiate the shades of black, but you do not need to do that, most of them are black, darker black and lighter black and shinier black and something which is very dark you call it darkest grey color. But basically, glass-like carbon is slightly darker in my mind compared to graphite and it has a very shiny surface and it is a very highly stable material. It is very interesting material, we will talk about that.

Let us come to charring. Charring gives you something called activated carbon. You must have also heard about activated carbon. If you buy activated carbon in the market, you get something that looks like coal. You can say also that you have these cylinders of activated carbon. It has no shine; this is how you recognize it. So, it absorbs as much light as it can, well it looks blacker.

But you also can buy pallets, you can also get powder of activated carbon and you can get these kinds of cylinders. The reason of its color and its lack of luster and so on is that, it has a lot of porosity.

And activated carbon is used for a lot of absorbent applications and water filtration columns are one of the most important applications. In fact, if you have a water purifier at home, most probably the column that you have inside it, most likely it has certain form of activated carbon filled, maybe in the powder form.

So, you have these columns of activated carbon, which feature great absorbance. And after that, there may be a lot of these char-like materials, for example, even charcoal you get from the wood. If you do not have very high-temperature heating, in that case you will always have a lot of impurities in it.

When people are performing the waste treatment, so they take a mixture of a lot of things. Whenever you have a mixture of plastics as well as wood and now if you heat them all together; now the wood type materials, cellulosic materials will typically undergo charring so and synthetic polymers will typically undergo coking.

This is also again a rule of thumb. It is not the case with all the materials or all the polymers. Certain synthetic polymers can also have a charring or a combination of coking and charring. But as a rule of thumb, natural polymers like cellulose rather will give you chars.

So, natural polymer will undergo charring mechanism and synthetic polymers coking. But if you urban solid waste, which is a mixture of a lot of polymers; you have a lot of polythenes, plastics you may have some wood or you may have some paper, in that case, you cannot really recognize whether it is coking or charring or what mechanism. When it is like a mixed carbon material, in that case, you will just call it a char.

Whenever there is a sort of low purity carbon or you do not know the exact composition of that polymer, you have any metal impurities in it or not, which can very well happen in the case of waste materials or waste-derived carbon. So, if you do not know much about it or you cannot say a hundred percent the type of carbon then you just call it char. So, low purity chars, we would call it either charring or you can also obtain it with a combination of coking and charring.

Now interestingly these four things in the green boxes, are non-graphitizing. You see that coke I have mentioned in both graphitizing and non-graphitizing because you can have both types of cokes. Glass like carbon and activated carbons are definitely non-graphitizing carbons. And we are going to learn in detail what do we mean at a microstructural level, what do you call a non-graphitizing carbon?

You understand the general definition is that, whatever is not graphite, but it is a high purity carbon then you can call it non-graphitizing carbon. Low purity carbon you will generally, either just call char or you say coke. Coke is also a term that is used for low purity carbons because cokes are more like raw materials for preparing high purity carbon. So, coke and chars are not necessarily very high purity materials or high purity carbons but glass-like carbon and activated carbon do have high purity. And of course, your HOPG or highly oriented pyrolytic graphite has very high purity.

However, at the microstructural level, we are going to learn the difference between these two types of carbons, especially the non-graphitizing carbon.

The fundamental definition is no matter how high you heat, even you can go up to 3000 degrees, you will not be able to convert these non-graphitizing carbons into graphite. Why does that happen? Because from the beginning when they were forming, whatever whether it was coking mechanism or charring; when they were forming from the polymer, some curved carbon structures were formed.

They may be curved carbons, not completely spherical structures, curved structures, tube like or just some very wavy sheets of graphene. The point is that once a completely curved or highly curved structure or a complete sphere is formed, that requires very high energy to open.

So, the energy of formation of fullerene itself is pretty high. Once it is formed, because of whatever reasons, that depends on the chemical structure of the polymer; maybe that was the most suitable structure at that point. So, you got these very highly curved or completely spherical structures at the beginning itself.

And now the energy to open those fullerenes and convert them back into graphene-like sheets is going to be very high. Sometimes it is not just possible to do so and that is why they will never become flat again no matter how high you heat them. They will not make the AB AB crystallites again. They will remain curved.

And that is why you are going to have a very complex microstructure. If you look at these materials or look at non-graphitizing carbons, what are you going to have? You are going to have a lot of curls, a lot of folded structures, a lot of curled structures and some completely closed structures and so on. And they can also be of different sizes; some of them may be very small, some of them may be very large. So, you can never really define a crystal structure for this kind of material.

You can call them graphene sheets or graphene-like sheets. But we call graphene when it is a single layer and when it is defect-free. In this particular case, you are definitely going to have defects like point defects, non-six membered rings. You are definitely going to have them, that is when you are going to get curves and that is the reason for the curvature in these carbon structures.

So, you are going to definitely have these structures. Now, it is a complicated thing, whether or not you should call them graphene because you can say these are sp^2 carbon sheets, but even that is not a perfect way of describing it. Because these are curved carbons have sp^{2+n} type hybridization.

But you understand what I am talking about. It is these graphene-like sheets but with a lot of non-six-member rings and that is why you have the curvature. You may have these sheets in a variety of sizes and you may also have some completely closed structures. And all of these together then will make your non-graphitizing carbon, which is glassy or activated.

Now, when the microstructure is so similar, then why glassy and activated carbon are different in terms of properties and in terms of physical appearance. Their mechanism of formation was so different; one was prepared by coking, and the other one was prepared by charring.

So, one has pores, one does not; that already makes a lot of difference. So, this is what we are going to learn in further lectures.

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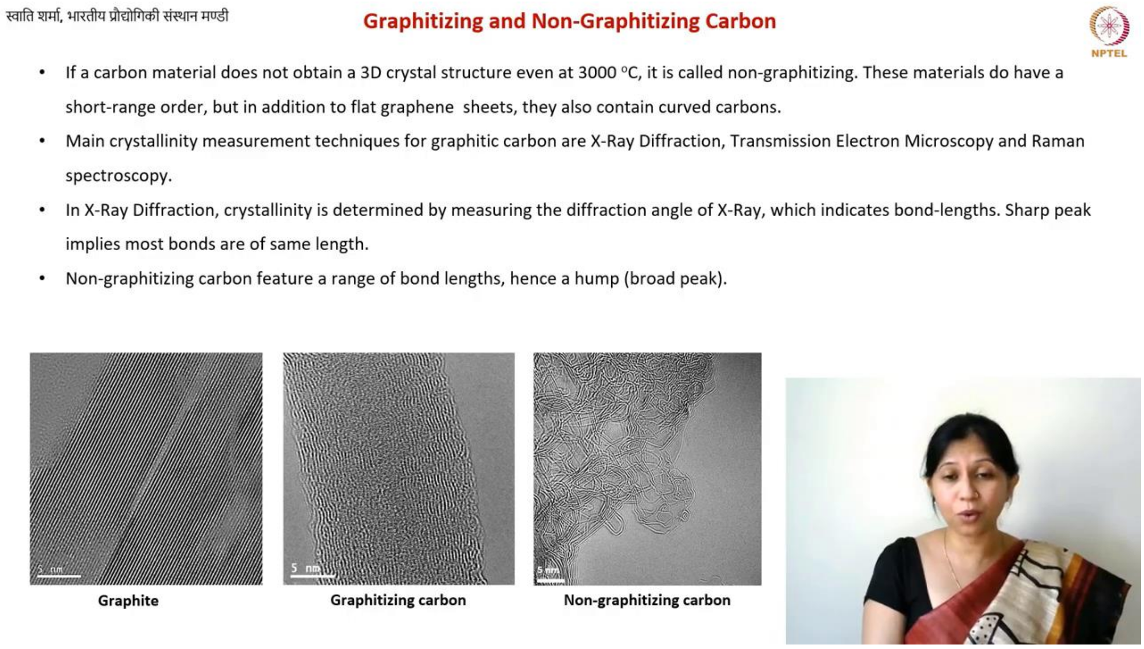

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Graphitizing and Non-Graphitizing Carbon

- If a carbon material does not obtain a 3D crystal structure even at 3000 ^{o}C, it is called non-graphitizing. These materials do have a short-range order, but in addition to flat graphene sheets, they also contain curved carbons.
- Main crystallinity measurement techniques for graphitic carbon are X-Ray Diffraction, Transmission Electron Microscopy and Raman spectroscopy.
- In X-Ray Diffraction, crystallinity is determined by measuring the diffraction angle of X-Ray, which indicates bond-lengths. Sharp peak implies most bonds are of same length.
- Non-graphitizing carbon feature a range of bond lengths, hence a hump (broad peak).

Graphite

Graphitizing carbon

Non-graphitizing carbon

On this slide, I have shown you these images. You see the microstructural difference. These are three transmission electron microscope images, in each case the scale bar is 5 nanometer. The first one indicates graphite. Now, you know what is the layer separation in the case of graphite? It is 0.335 nanometer.

Now, in the case of other carbons which are like, which are graphitizing carbons; they look like this, this is like the second image. So, you can already see that, there is a possibility that this material can become like the first image. It can convert if at higher temperature.

But if you had the non-graphitizing carbon that you see in image number c, you can see already that it is kind of all entangled. Forget about it, it is not going to open and then give you graphite. So, these are the three images that will give you some impression of what is graphitizing carbon from a polymer and what is non-graphitizing carbon.

Now, in the case of non-graphitizing carbons, however, you may have short-range order. So, here it is, I do not know if you can how clearly you can see from this image; you have two or three layers definitely organized on top of each other, you just do not have a larger stack.

You may have a few, in fact as you keep on heating the material and keep on increasing your carbonization temperature, you will also get some increase in these stack thicknesses or La the crystallite size as well. But you will not get complete graphite. So, the entire material will definitely gain more and more order with the temperature. But you will not get complete graphite and that is why they are called non-graphitizing carbon. You may have short-range order means, you can have small crystallites, which can also be measured using X-ray diffraction techniques or in the TEM micrographs that these are the TEM micrograph.

You can definitely also see it here. You can also do Raman spectroscopy characterization techniques which we are going to learn in some other lectures. Raman spectroscopy tells you, what is the fraction of crystallinity or disorderedness.

The point is that as you increase the temperature, you may get more and more crystallinity, more and more order in the material which is measurable. And in fact, these techniques become very important in graphite preparation. That is why the heat treatment temperature becomes very important in the case of all carbon materials.

But if you think of it from the industrial viewpoint, when you increase the heat treatment temperature that also really increases your cost. Just think about it, you are using some coils or you typically using Joule heating process to heat something up to 3000 degrees, that definitely adds to the cost of the material.

And that is why there have been a lot of processes that may or at least people have tried out to reduce the temperature of your carbonization. But of course, the higher the temperature, the better the material. At least as on date that is the status that you have high-temperature carbons are more expensive and you have better crystallinity and better purity.

Because let us say if you want to do catalytic graphitization, you can add some catalyst which may reduce your final temperature a little bit, but then later on you have to remove that catalyst particle from the material. So, you ultimately end up adding one more step and despite that, you may not really get very high purity in your carbon.

So, all these things add to the cost and that is why when it comes to industrial carbon materials, still the good carbons are prepared at very high temperatures. And at every step, we are going to do a lot of characterization to know what is the quality of our carbon. And the quality is always measured in the case of carbons, at least these sp2 type materials or materials which have disorder mixed allotropes and also in the case of curved carbons; the better electrical conductivity, better mechanical properties, etc are all measured based on the crystallinity. Now, if you are doing any characterization. If you get a sharp peak for the X-ray diffraction, that means you have these 00L planes that we talked about.

So, if you get a sharp peak for that, then you know the material is closer to graphite or it has atleast graphitic crystallites. But on the other hand if you get a broad peak, which you would call a hump, that indicates that you do not have any specific crystal plane that indicates that you have variable bond lengths throughout your material.

So, when you have curved structures or when you have certain molecules that are under strain and some of them are very small, some of them are large, some have certain stacking, some do not have certain stacking. So, altogether you will get a range of bond lengths.

And that is why, when you are doing its characterization, you will never get one specific value. You will always get sort of a range of values for everything. And that also influences the properties. When somebody asks you what is the electrical conductivity of glassy carbon, then you will always mention the range because that will depend on the exact heat treatment temperature of your glassy carbon, exact graphitic content and exact fraction of short-range order. All of these things will then determine the properties of these non-graphitizing carbon materials.