Carbon Materials and Manufacturing
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Lecture - 33
Activated Carbon: Industrial Manufacturing

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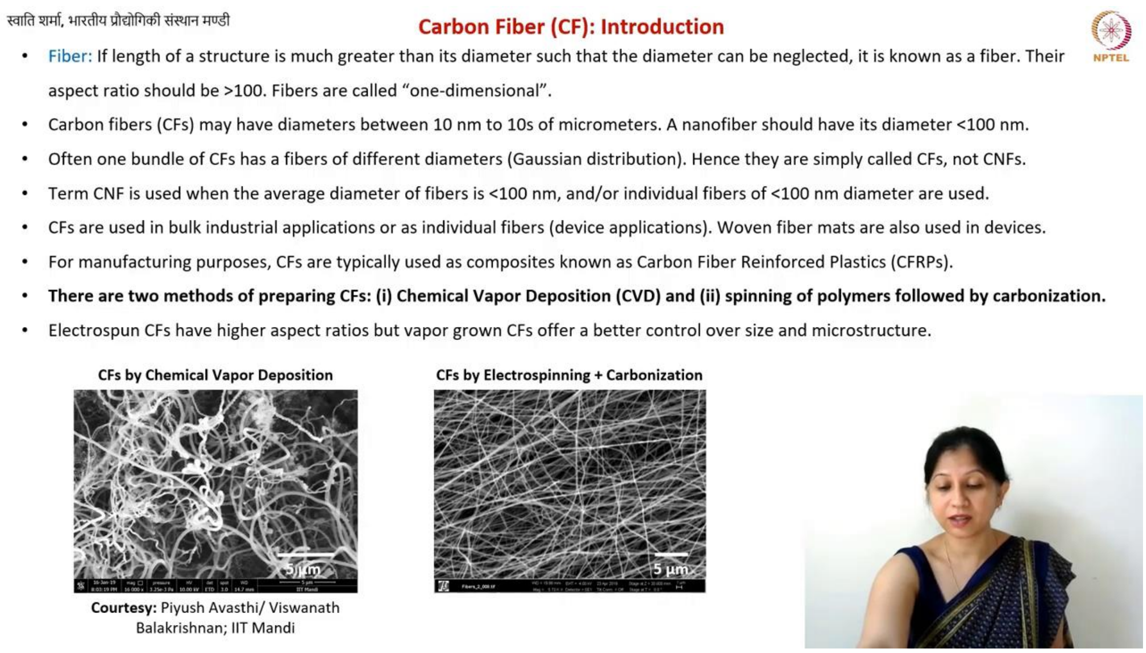

Hello everyone. In this lecture, we are going to move on to Carbon Fibers. Carbon fibers are very important industrial carbon materials that you know already. You know that there are various applications of carbon fibers and carbon fiber-based, composites. For example, aircraft parts manufacturing, car parts manufacturing, you also make different sensor devices like sensor devices and filtration devices, there are various applications of carbon fibers. We can also activate the carbon fibers and then we can get activated carbon fibers that offer a very high surface to volume ratio and they also show very good adsorbance.

There are so many different applications of carbon fibers. What is interesting and the reason why I decided to teach it now at this point in our course because carbon fibers are a good interface between the bulk industrial carbons and the micro and nanoscale carbons. So, afterward we are going to learn more about nano-scale carbon materials.

You know that carbon fibers are manufactured in bulk, because obviously, you need a lot of fibers. then you will perform braiding of these fibers or you weave cloth-like structures out of these fibers. Now, these woven carbon fiber mats are used as sheets when we prepare laminates and that is how we make composite materials. So, these are prepared in bulk, bulk quantities, large-scale applications, large-scale structures.

But we also have the diameters of individual carbon fibers in the micro or sometimes even in the nanoscale. So, that is why I am saying that these can be very important interfaces. You can also use them for micro nanoscale devices when you are making a sensor. For example, if you have individual nanofibers then they can offer much higher surface area and that is why it has higher sensitivity.

Sometimes we also use individual carbon fibers, sometimes we use them as these cloth-like mats, sometimes we even use the tips of the fibers for sensing purposes. So, there are a lot of interesting applications of carbon fibers. Let us first start by learning what is fiber? You know fiber is a very long structure. When we say long, what does that mean? Long means you can basically neglect its diameter compared to its length.

So, that is your basic definition of fiber that the aspect ratio of these structures should be such that you can neglect the diameters. Aspect ratio is the ratio between the length and the diameter. So, that should be higher than 100 that is when you call it a fiber whether it is a carbon fiber or it is a polymer fiber irrespective of that.

But what are carbon fibers? Well, they are fibers from carbon, but you know that carbon is hard and brittle you cannot directly pull fibers out of it. You also know that there is one more method that we use also for making industrial graphite structure, we also use it for making industrial bulk glass like carbon materials. We shape the polymer and then we carbonize it. We do the heat treatment.

In this particular case, you can pull fibers out of any polymer which has a high carbon content or petroleum by-products such as pitch. So, because pitch is this highly viscous material that can actually yield nice fibers. So, you will use these kinds of materials for making fibers and then you will perform the heat treatment that is the most common method of making industrial carbon fibers.

And we use the term carbon fiber; we do not say carbon nanofibers typically for industrial carbon. Carbon nanofiber or carbon microfiber are not the terms that we use. We call them carbon fibers. Because you know you do not have just all the fibers that are in the nanoscale diameters.

You may still find a few fibers that are smaller than 100 nanometer in diameter, but many of them will be even up to 10s of micrometers. So, you have this gaussian distribution of their diameters and that is why you do not really use the word carbon nanofiber or microfiber, you just rather say carbon fiber.

One more important thing is that you say carbon fibers and not graphite fibers or glass-like carbon fibers. What is the reason for that? Because the carbonization mechanism of fibers is quite different from that of a bulk material because you have a very high surface to volume ratio.

even certain polymers, if you make a large-scale structure from them then those structures might be non-graphitizing, but in the case of carbon fibers it is easier for the defects to anneal out, and that is why there is always a possibility that you can get graphitizing. You can get graphite out of polymers where you do not expect that. If you make other structures from those polymers then you may not get the graphitizing carbon. And that is why the safest terminology is carbon fiber.

You will often see carbon fibers in a bundle. And these bundles as I mentioned bundles are something like a rope, and rope at a very small scale is what you call fiber. Even when you have a certain fabric, you have these rope-like structures, and then you do the weaving from them that is what you also do with the carbon fiber bundles. You make rope-like structures.

Even when each fiber is very long, but if you make a rope then you can get these kinds of very long thread-like structures and then you do the weaving and then you can make different structures. You can also just cut that rope and use the tip of it for sensing applications. So, we will also discuss that in some lectures.

You know that if there is something which is smaller than 100 micrometer, we call it a microstructure and something that is smaller than 100 nanometer, then only then we call it a nanostructure. So, this is also valid. For fibers of course, we are going to measure the diameter and not the length, because length can be several millimeters or even centimeters.

Now, we come to the manufacturing of carbon fibers. in the next couple of lectures we are going to talk about how do we make carbon fibers themselves. But then we will also discuss how do we make things out of carbon fibers. the manufacturing of carbon fibers and then manufacturing using carbon fibers we are going to discuss both.

Manufacturing using carbon fibers especially at bulk industrial scale is typically done in the form of composite materials. Composite materials basically would mean that you do not have just the carbon fibers, you also have a resin. And why do we need the resin? In most cases, when you are doing this weaving of carbon fibers, you need some sort of lubricant. Otherwise, you may end up damaging the surface of the fibers, you may even end up breaking a lot of fibers because they are after all made of carbon, they are hard and brittle.

But once you have a lubricant, once you have a resin then the weaving is sort of easier and that is why we often use these resins. An easier method of giving a shape to carbon fiber-based structures is to use them with the resin; more and more quantitative resin will make it make different types of composite materials.

Then also the resin that you are using can change the properties of that. You may have biocompatible resins, you have some thermosetting plastics which can harden and some may not. So, these are the things, we are also going to learn in the next section of our lecture which is carbon fiber composites.

Let us now talk about just the manufacturing process of carbon fiber. I already told you one thing, you can make fibers from polymers and you can carbonize them. This process of making fibers from a polymer is known as spinning. Spinning is just the term used for pulling fibers from any polymer or any petrochemical product or any high carbon containing material. So, this process is known as spinning.

Now, when we make fibers using polymers or pitch then, of course, you need to perform the heat treatment step. And the heat treatment step remains the same as it is for other types of carbon materials and again depending upon the kind of crystallinity you want in your final fibers and that would be determined by the application.

Do you want good stiffness in your fibers or what is more important for you is the surface area or the flexibility? Depending upon that you can tune the manufacturing parameters; you can tune the heat treatment temperature and the heat treatment environment. And of course, you can also tune the diameters of your fibers by changing the viscosity of your polymer. These are the things we are going to discuss.

Spinning can be further divided into two types of spinning; one is melt spinning or known as melt extrusion and the second one is electrospinning. So, as the name suggests we are also using some electrostatic forces to perform the spinning operation. here I have mentioned as number 2. And the number 1, I have written as chemical vapor deposition.

So, there are two types of fibers, one is these spun fibers. The second type of fibers is vapor-grown fibers. you will also hear the term VGCF. These are Vapor Grown Carbon Fibers. These are the type of fibers which are prepared by chemical vapor deposition techniques. We briefly talked about CVD, we will also talk about it again when we talk about graphene and carbon nanotubes.

But the idea is the pyrolysis of gaseous hydrocarbons on top of a catalytic surface. We learned before there was a copper sheet and you were doing pyrolysis of hydrocarbons and then getting the graphene-like flakes which were then hot-pressed and we ended up getting pyrolytic graphite which was then converted into highly oriented pyrolytic graphite.

The process remains pretty much the same with some variation in the parameters. What importantly changed here is the shape of your catalyst. This is also a process that we will discuss for carbon nanotube fabrication because tubes and fibers both can be fabricated using this method. Fibers are basically not hollow, tube is hollow. There is a certain critical size of your catalyst after which you will rather get fibers than tubes.

Also, this is also very interesting, we will learn about the history of carbon nanotubes. The tubes were actually observed already in the 1950s. They are reported in the literature, but at that time people called them hollow carbon fibers. They did not call them tubes, they just called them hollow carbon fibers. So, fiber and tube are very closely related.

This is the method number; getting the fibers directly from the pyrolysis of hydrocarbons. And the second one as I have already mentioned is spinning and here, I have shown you the picture of carbon fibers fabricated by electrospinning. Now it is easy for you to understand that in the case of CVD type carbon fibers, you directly get carbon fibers but in the case of electro-spun fibers you need one more step, heat treatment step.

So, there are advantages and disadvantages of both processes. Actually, you just will decide depending upon your application and what kind of fibers you need. Often it happens that you have better control over the microstructure of the fibers. So, the graphitic structure that you have, you will have better control in the case of CVD because this is a bottom-up process.

So, you are doing atomic deposition of carbon. there you have a better control. you can also control the type or the structure of your catalyst. You can change the CVD parameters there. You have a better control over the microstructure. But as you can see in this picture that you have this forest sort of thing growing. in terms of length, these fibers are not as long as you get from electrospinning, but there are advantages of that. Plus of course, you do not need to perform any further heat treatment unless you want to further graphitize the carbons. You can do the heat treatment again to improve the crystallinity if you need that otherwise you get directly carbon fibers.

But in the second case, you need to perform the heat treatment now, there is also an advantage to that. Although it is an additional step; it adds to the cost of the fibers. Number 1, the fibers that you are getting are at a very large scale. You know it is kind of continuous manufacturing but in the case of CVD you will have batch manufacturing because you will prepare batches. That we will discuss that on the next slide.

In the case of electrospinning, you can even have continuous operation because you are just pulling fibers from a polymer, you can keep on doing it. And you can control the heat treatment parameters and also determine the crystallinity of your fibers accordingly. So, there are advantages of both of these methods. Now, we are going to go more into the details of how we classify these carbon fiber manufacturing techniques.

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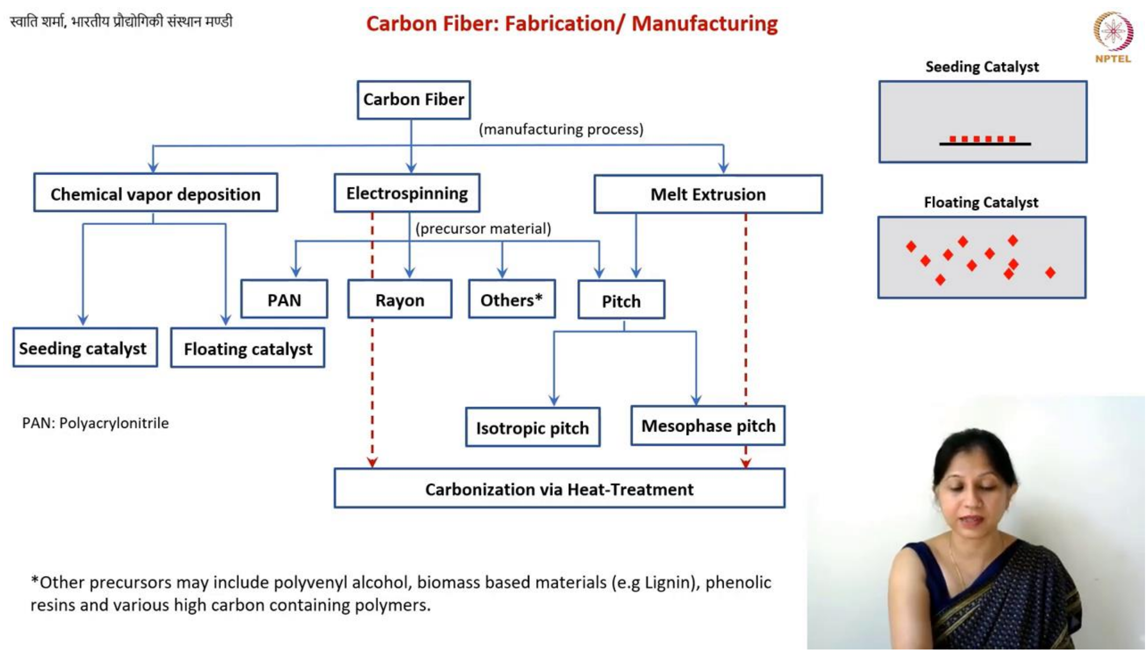

The first thing, based on the manufacturing process as I mentioned one is spinning, one is carbon fiber chemical vapor deposition. But here spinning can be divided into two things, as I said electrospinning and simple melt spinning or melt extrusion is also terminology that is used. Let us first talk about CVD.

Based on how it is performed you can further classify these. one is known as seeding catalyst method and the other one is floating catalyst method. So, for any kind of pyrolytic fiber fabrication, your catalyst becomes the most important thing, the shape of the catalyst, size of the catalyst, and how you distribute that catalyst inside your furnace or your reactor that also becomes very important.

Based on this distribution of the catalyst you can divide it into two types, this one seeding catalyst means you have catalyst attached to a solid substrate. You have the catalyst on top of it. Now, what will happen? When there is pyrolytic deposition, what will happen? You will have these structures growing like a forest, that was the one I had shown you the picture in the previous slide. You will have the structures growing from on top of these catalysts.

The second method is what is known as floating catalyst. floating catalyst as the name suggests, the catalyst particles are floating inside your furnace or the reactor. And while they are floating the carbon is being deposited on top of them and you are getting fibers. So, there will be some differences in both of these methods.

Number 1, in the case of seeding catalyst, you need to ensure is that your catalyst is at high temperature because you need high temperature for the decomposition of the hydrocarbon. So, what is important for you is that just your substrate, only that part must have high temperature. But in the case of floating catalyst you need to have high temperature throughout your reactor on the tube. So, that is one difference.

In the case of seeding catalyst, mechanism is very interesting. The catalyst particles after the fabrication of the fiber, does it stay on top of the fiber or at the bottom of the fiber? In fact, both of these are acceptable mechanisms, and we will discuss them more in the context of carbon nanotubes as well. But in the case of floating catalyst, this does not matter because all of your fibers are floating anywhere.

Also, where do these fibers go? They typically deposit on the walls of your tube. So, both of these have advantages and disadvantages. And also one of them is a batch process and in the case of floating catalyst you can also have a continuous process, you can also have bulk manufacturing. So, these are the two types of vapor-grown carbon fiber manufacturing.

Now, I come to the other one electrospinning. So, electrospinning can be further classified based on the precursor materials, the instrumental setup and the fundamental principles of electrospinning as well.The melt extrusion we are going to learn in the next couple of lectures. Right now, this is just the classification.

So, based on the precursor material you can actually now classify your electrospinning, and this I am talking very specific to carbon fiber. Electrospinning is also used for making a lot of other biological material. You can use biomaterials, nice different biocompatible polymers and you can make a large number of structures.

Now we are not talking about electrospinning in the context of other polymers, but just for the carbonization of polymer. So, here I am taking only those polymers which are most common carbon precursors or carbon fiber precursors at an industrial scale. PAN or polyacrylonitrile is the most common carbon precursor for industrial applications. Almost 80 percent carbon fibers are fabricated using polyacrylonitriles. So, that is our first precursor.

Then we also use what is known as rayon. What is rayon? Rayon is basically treated cellulose or recycled cellulose. Rayon is also a very common industrial carbon fiber precursor. Then we talked about pitch, you already know we have different types of pitches. We have isotropic pitches, and we also have the mesophase pitch. Mesophase pitch is what will give you more graphite carbon.

We can now use both of these types of precursors for getting different crystallinity in the carbon fibers which is also very common precursor. And now there are many other polymers also.

For example, you can have some phenol-formaldehyde resin, you can have many other new polymers that are being designed specifically for carbon fiber production, but because those polymers still would make only a very small fraction of industrial manufacturing, I have not mentioned all the names.

Now, I have written pitch on the right-hand side and the reason for that is that I also wanted to connect it to the melt extrusion box. Pitch fibers can be spun using melt spinning. So, basically, you can imagine what it means. You have melted pitch or you have pitch at a high-temperature. Pitch at room temperature is a semi-solid material. It is highly viscous, but it is still not solid.

So, it is a liquid material, but if you slightly increase the temperature. You can also reduce its viscosity. And at some point, you can get the optimum viscosity where you get the fibers of the right diameter that you want. So, you can also perform this melt extrusion using pitch. Of course, I already mentioned to you that you have isotropic and mesophase pitches. And based on this, now you will make your fibers.

After spinning the fibers, now in both cases electrospinning or melt spinning, you will now perform the carbonization using your standard heat treatment process. Here are some of the names of these other polymers. Of course, electrospin, as well as melt spinning, can be also utilized for making many other structures, not just carbon fibers, but also make glass fibers. Metal spinning is rather indeed used for making glass fibers.

So, you can use these techniques for spinning various types of fibers and as I have already mentioned that not just carbon fibers, you can also you know make different other different fibers. For example, for biological applications, especially for making different types of membranes, the electrospinning is used very extensively in that case.

In the next couple of lectures, we are going to learn about these individual techniques, more specifically.