Carbon Materials and Manufacturing
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Lecture - 38
Defects in Carbon Fibers

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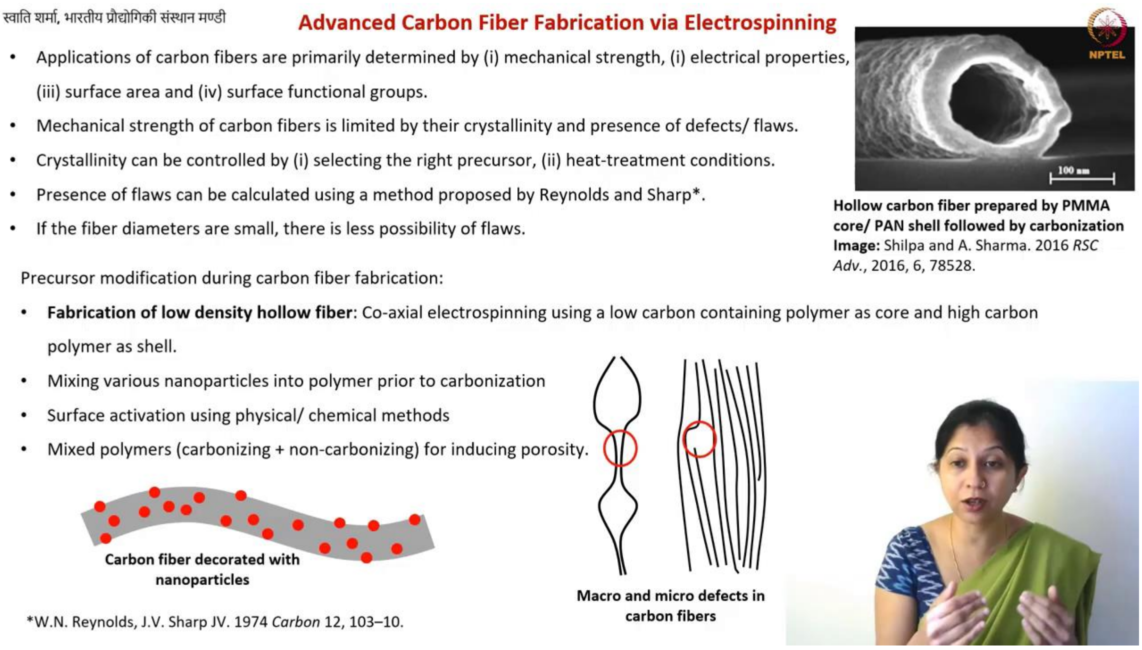

Hello, everyone. In this lecture, we are going to briefly discuss some of the Applications of Carbon Fibers. Now we already know how do we fabricates carbon fibers. We either perform melt extrusion or we perform electrospinning and then we heat treat this polymer or pitch fibers to get carbon fibers.

Now, after that we will also perform certain characterization tests, we will also learn about the mechanical characterization of carbon fibers, but let us first talk about some modifications that you can do during the electrospinning or melt spinning process and then why do people do these modifications? Because there are certain applications associated with them or there are certain applications that require certain type of fiber, not just a simple carbon fiber.

So, I will talk about some of the applications. I cannot cover all the details because there are actually many carbon fiber applications, in both manufacturing industry as well as micro nano device fabrication. You can also make a membranes and filtration columns with carbon fibers.

So, there are so many applications, you can easily do an internet search and look for a variety of application.in fact, every day something new is coming up. But, we will talk about like the fields where we have these applications. So, what are the possibilities with carbon fibers.

The next lecture is going to be about carbon fiber-based composites. A lot of manufacturing related applications actually do not utilize carbon fibers directly but in the form of a composite material. Composite is when you have another material mixed into it a binder or a matrix phase, we are going to talk about all of that.

We are not discussing manufacturing applications for now in this lecture. First of all, as I told you there are certain properties of carbon fibers that make them so interesting for us. So, I told you that these are lightweight and strong materials and they are electrically conductive and they have also similar electrochemical properties like other advanced or graphitic carbon materials. So, these are some of the properties that we are going to utilize.

Now, once we fabricate our carbon fibers, what test do we need to do? What are the property that we need to immediately see? You know what are the applications of this particular type of carbon fiber because each carbon fiber can also be different depending upon the crystallinity, heat treatment conditions and the nature of precursor and also the diameters of course.

First of all, we test the mechanical strength of our carbon fibers. for manufacturing applications, you will typically not test the mechanical strength of individual fibers because you are almost always using them as bundles or ropes. So, these threads or ropes or bundles whatever you call them of required diameter of our bundle, then we take that bundle and then test its tensile strength; compressive strength also becomes important but primarily tensile strength.

Then we also want to understand the electrical properties of these fibers. Electrical measurements can be done when you take the fiber and pass current through it. This also for individual fibers or you can do it for the bundle of fibers depending upon your requirement.

What is also very important for a lot of applications and what we use in the case of carbon fibers is their surface area. You know that for different applications for example, electrochemical and also for sensing applications, surface area becomes very important. This was something we also learnt in our porous carbon lectures. In fact, we induce porosity; we increase the surface area because that also increases the absorbance of these kinds of carbons.

Now, if you already have fibers; fibers already exhibit a very high surface to volume ratio, if you further induce porosity then you can have a very high surface to volume ratio and this is also one property that can be used when it comes to carbon fibers and of course, something very much related to this is the addition of surface functional groups.

So, if you want to use these carbon fibers as adsorbance, then you can also chemically induce certain functionalities on their surface. So, they become for example, more hydrophilic which is important for electrochemical application so your entire electrode gets wetted properly.

So, these are some of the properties of carbon fibers that you can play with if you want to use them, especially for device applications.as I said that the large-scale manufacturing applications, we will talk when we talk about the composite materials. Now, if we think about the mechanical strength of the fibers what do you think limits the mechanical strength?

Why do we not have all carbon fibers which have the same exact same strength? Similar to all carbon materials, even in the case of carbon fibers one thing that determines the mechanical, also electrical properties is the crystallinity.

Heat treatment temperature increases, then the graphitic content increases then the stiffness of the material increases, then you have higher modules carbon material. So, that is something that is also valid in the case of carbon fiber. So, as you increase the crystallinity you get higher stiffness, but also there will be some other things and that will be sort of important. You will have a critical diameter of your fibers because fibers bigger or thicker than that may contain more what is known as defects.

So, what is defect? What is the microstructure of carbon fibers? Carbon fibers as I had shown in one of the previous slides, I think when we were talking about melt extrusion; that you have different possibilities depending upon the fabrication parameters, you have different possibilities of arrangement of crystallites in the case of carbon fibers.

So, it is different slightly from the bulk carbon materials, also the effect annealing patterns are different compared to the other bulk like graphite or glass-like carbon or char-like carbons for that matter. So, what happens is these defects or voids we also call them flaws because defect is something which we are typically talking about atomic level, but here we are talking about bigger and larger voids or regions of non-crystalline material. So, these kinds of materials can actually limit the properties of the mechanical strength of your carbon fibers because this is where you have slippers.

This is where you can actually break the fiber when there is strength. So, whenever you have these kinds of sort of voids or flaws and when you pull the fibers, this is where the fracture takes place. So, for example, when you fabricate polyacrylonitrile carbon fibers then sometimes you will have these lumps of polymer.

At the end of the day you have chains in the polymer, you have chains of polyacrylonitrile and then you are preparing the solution in DMF. You may not have the perfectly uniform solution and you may end up having here and there certain lumps or non-uniformities in the solution that is why you may end up getting these kinds of bulges in your carbon fiber.

So, now, I have a circle this region you can see that this is your this is where the necking takes place. So, this is your weaker region when you pull the fibers there is a higher probability that it will break from there and also these bulges will not they may contain some of these flaws or defects, large scale defects because they do not have the same surface area as the rest of your fiber.

And, that is why also the defect annealing pattern, the byproduct annealing pattern, everything is different in that bulge. Even the purity of the bulge if you just compare it with thinner region of the fiber you may even have different purity because now the byproduct annealing patterns are also different in that bulge.

These kinds of bulges which you will see very often especially if you have certain humidity in the chamber or if a solution is not unifor epecially when you have more viscous solutions, you are going to higher concentrations of PAN, in that case, you will see these kinds of bulges a lot and these are macro defectors, you can actually see them.

In fact, that is the reason people often use this horizontal electrospinning set up because these are heavier fibers, at least most of them will fall before reaching the collected electrode. If you look at look inside a transmission electron microscope you look at the macrostructure of your fibers. In that case, I have shown again with the circle, you can have these kinds of regions where you do not have any graphitic planes. You can call it an amorphous region, you can call it a region with randomly oriented and random bond lengths of the atom, but you do not have sp2 type hybridization or you also do not have any graphite crystalline.

Now, overall when you look at a fiber-like this, this is a very small region, altogether the fiber will look uniform and you will also even call it graphitic carbon fiber if you are able to observe the peak for graphite in your study. So, you still will be able to call it a good fiber and this is a graphitic fiber.

But when there is any tension or fatigue or whenever the deformation takes place, this is where you are going to have your cracks and breakage. So, these are the possible defects in the case of carbon fibers.

Some of them, we can avoid and some of them we can actually not avoid, but that is also the reason we are not using single fibers and we are rather using bundles of fiber. So if one of your fibers breaks you still have others and in a rope, if one fiber breaks others can still hold the structure. So, however, this is where you have the problems with the mechanical properties.

As I mentioned already crystallinity can be controlled, number 1 - by heat treatment temperature and number 2 - by choosing the right precursor. In the case of fibers, we are relatively limited because we also need to see the spinnability, manufacturability of the fiber of the polymer, but we can choose at least the right concentration.

We can choose our precursor in such a way that we get good fibers out of it. These crystallinities, we know how to control. Now, flaws are something that is not easy to control however, as diameter of the fibers gets smaller then there is a lower probability of getting the flaws because these flaws are often larger like they are for example, in size 50 to 70 nanometer.

In that case, if the diameter of your fiber itself is 100 nanometer then there is a very small probability then that you will have a defect that is 50 or 70 nanometer. So, you can do one thing that you can reduce the diameter of these fibers. Now, how do we calculate the approximate size of these flaws? There is a method proposed by Reynolds and Sharp which we will briefly discuss.

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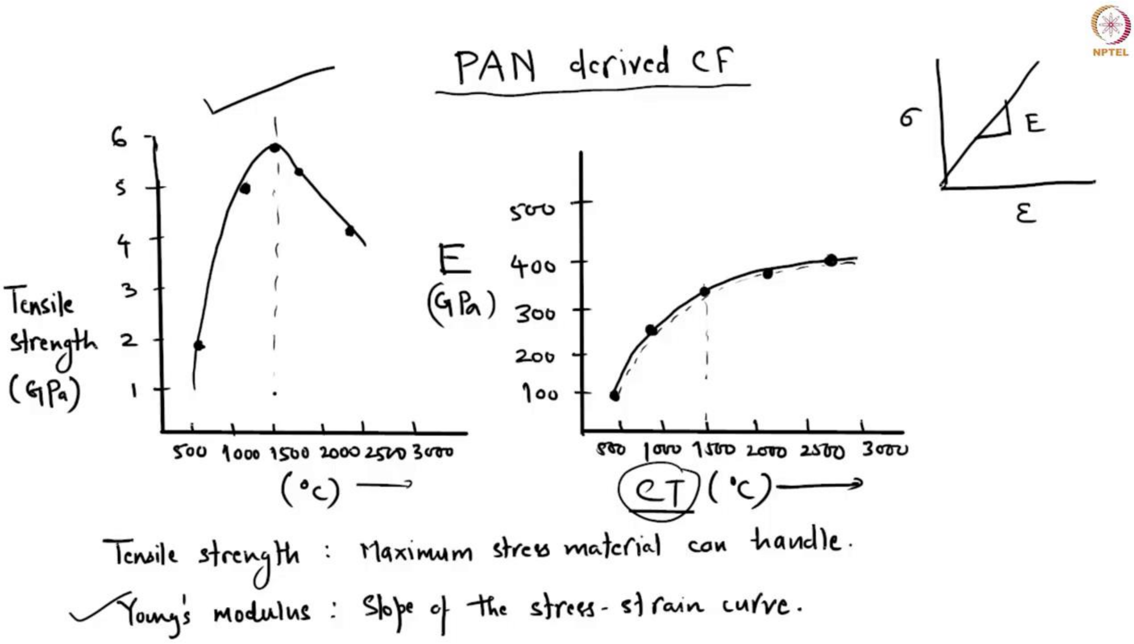

When we talk about the mechanical properties of carbon fibers especially PAN derived carbon fiber. So, it is interesting that they do not necessarily show an increase in their overall value when we increase the carbonization temperature why?

Now, you should understand there are two important parameters, number 1 is your Young's modulus. Now, Young's modulus you know what is it. This is the slope of the stress strain curve and that is your Young's modulus which keeps on increasing as you increase the as the you increase the carbonization temperature.

Here in this curve, you will see that you have this kind of profile. So, basically this is your carbonization temperature. So, above 1500 °C, you too have increase in the Young's modulus. However, it is not very sharp increase, the curve almost flattens, but there is a certain increase.

There is another property which is known as the tensile strength. What is tensile strength? Whenever you are thinking in terms of a wire or fiber like structure, maximum stress that your wire can handle or your fiber can handle, above that it will break. So, that is your tensile strength.

Now, if you see this curve then the tensile strength of your PAN derived carbon fibers increases up to let us say 1500 °C, but after that it indeed declines, it decreases.in many applications what is more important is the tensile strength rather than the Young's modulus. So, depending upon the application you need to select your fabrication parameters, because it is not necessary that just increasing the modulus is important for your fiber.

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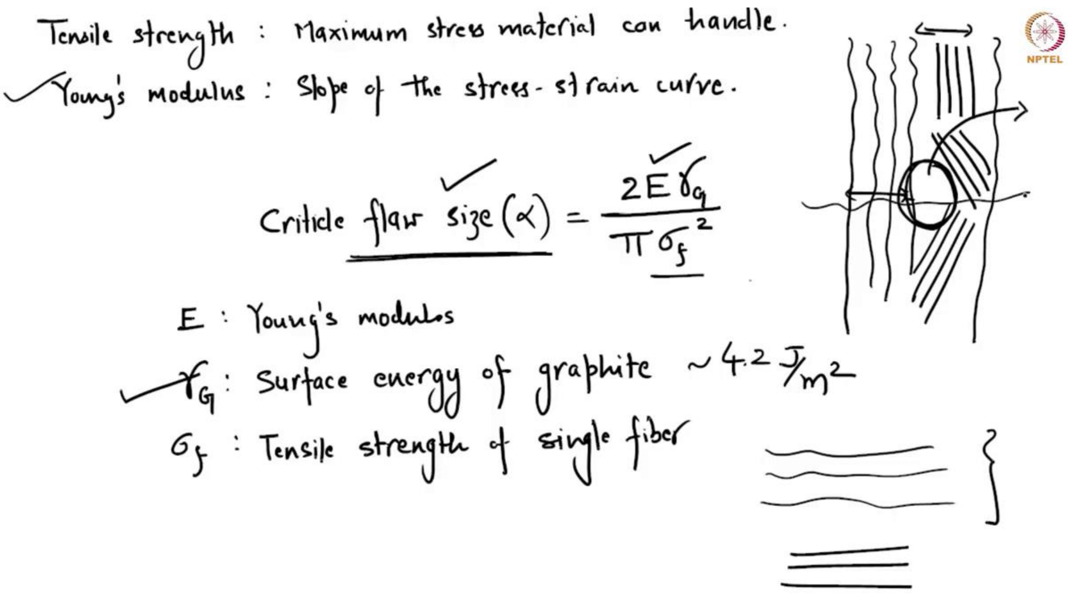

Now, coming to this flaw size that we were talking about, this is the Reynold's and Sharp method or the formula is given by them. What is the flaw size again? This is the size of your trapped defect in a carbon fiber that would limit its mechanical properties and here is the relationship.

This is Young's modulus. γ_G here is the surface energy of graphite which is approximately $4.2 J/mm^2$ and the σ_f is the tensile strength of an individual fiber. There have been certain modifications to this relationship and people have instead of considering the surface energy for graphite, people have also considered the surface energy that is experimentally calculated for a set of carbon fibers or a type of carbon fiber or the ratio of surface energy of carbon fiber to that of graphite.

However, one thing that is clear from this relationship. Your flaw size is indeed directly proportional to Young's modulus. What does that mean? That means if you increase your pyrolysis temperature and you get Young's modulus that is very high so you may actually also get larger voids in it. However, this relationship may not be valid for ultra-thin fibers because there you have defects annealing out very easily.

However, if you have you know 1 micrometer to 5 micrometer diameter fibers which is often the case with industrial carbon fibers, indeed you may get some defects when your when you increase the carbonization temperature why does that happen? What happens is in the beginning when you have you know when you have heated your carbon polymer fibers to above 1000 °C.

At that time, you have these turbostratic carbon sheets; what are turbostratic carbon sheets again? These sheets are also graphene-like but they contain several defects and therefore, they are not organized in an AB AB A fashion as in the case of graphite.

The spacing between these lines is slightly higher than what you would get for graphite structures. These types of carbon structures known the arrangement is known as the turbostratic arrangement and the carbons that have that kind of arrangement are also sometimes called turbostratic carbons.

So, you have turbostratic structures, now you increase the temperature. What will happen? Some of them may actually align and form graphite crystalline. However, now when this space decreases, because the spacing between the sheets is now decreasing, what happens is there may be some voids created.

Because we are not supplying any material from outside while the structure shrinking, and it is shrinking in random ways. It is not necessarily one big graphite crystal that is forming. So, you may end up getting certain voids or certain flaws. Again, if the fiber is very thin there is a high probability that some of these flaws will anneal out.

In the case of thicker fiber some of them will anneal out, but not all of them. Some may remain trapped and these are then your weak points in your fiber, that is why your fiber will break. So, this is just to tell you that just increasing the carbonization temperature is not enough.

By the way one more thing, this relationship is not necessarily valid for fibers that are prepared below 900 °C.in fact, anything that is prepared below 900 we may not even call it carbon fiber, they have a lot of impurities.

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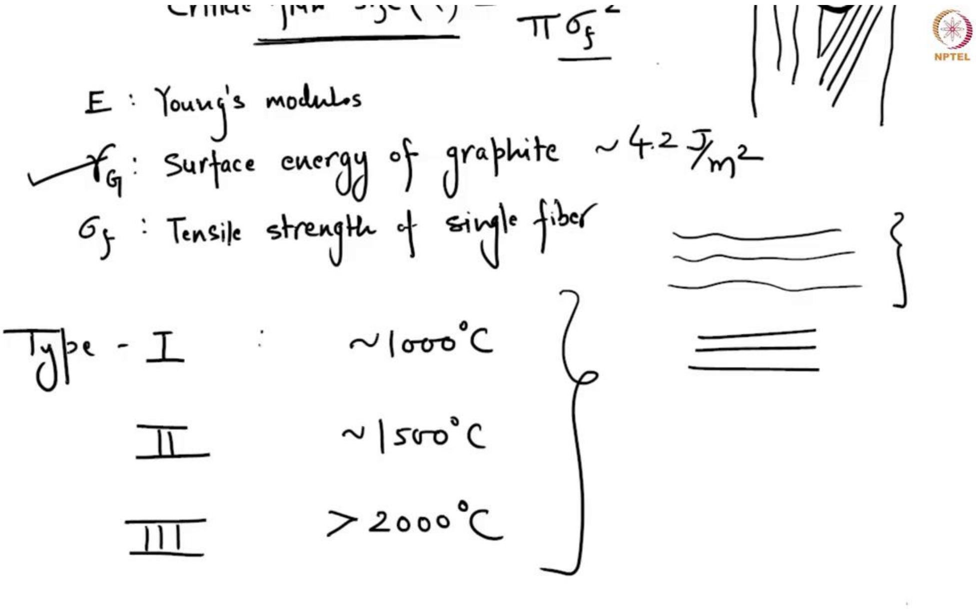


They are like intermediate materials that we had discussed earlier. But, these are only valid for type I type II by the way I don't think I have told you what are type I and II and III fiber? So, type I carbon fiber are prepared at approximately 1000 °C centigrade for industrial need. Whatever is prepared at 1500 °C that is known as type II fibers and type III fibers are those prepared above 2000 °C centigrade.

So, you can decide which type of fiber and what are the conditions that you require for a certain application. Now you already know that if the diameters are smaller, then there is a lower probability of getting the flaws. Now let us talk a little about what we can do to our electro spun fibers. What modifications we can make in the polymer precursor and that is how we can get more what you can call advanced carbon fibers.

Basically, they are somehow better or different or more improved compare to our standard regular carbon fibers. So, what are the things I mean? You can already imagine what are the things you can do because we have this flexibility of carbonizing.

So, you can tune a lot of properties by carbonization process and heat treatment process. That is one of the most important things about carbon materials in general that you can tune their properties by playing with the parameters of heat treatment process.

So, one thing here you can do when it comes to carbon fibers you can make a fiber that has a core shell-like structure. What do I mean by core-shell? You have two different polymers. So, there is one polymer that makes the core and the other one makes the shell. How can you do that?

Actually, it is not that difficult, electrospinning setups even come with these what is known as co-axial spinning which means you have two concentric cylinders or your needle. When you have a spinneret, you can have two different polymer jets going out at the same time. So, in that case, you can choose your core in such a way that it does not carbonize very well. So, it is a low-carbon-containing polymer.

At the same time, you can choose your shell as a high carbon-containing polymer such as PAN. What will happen once you carbonize these structures? During the heat treatment, your struck, your material because the core material does not give good carbon anyway, it will disappear to a great extent if not completely and then your shell will remain there as carbon fiber.

And, in fact, these kinds of experiments have been done. This is a very beautiful picture you see. You have a hollow carbon fiber. Hollow carbon fibers will offer a lot of interesting properties for example, first of all, their overall density is so much lower. We always want to have a high mechanical strength but low weight of our carbon fibers.

So, if you have hollow fibers, you can imagine the weight goes down so much, your density of the overall bulk carbon fibers is so much lower. You can also you can use these for a lot of biomedical applications, drug delivery application. Basically you can trap a lot of things inside these hollow fibers, you can also use these structures for supercapacitor electrodes, for battery electrodes and for any application where you require a high surface area.

Now, you open up so much more surface area in the case of these kinds of fibers. So, this is one thing that you can do with your carbon fibers. What you can also do is, you can mix a lot of additives. Any nanoparticles or even other carbon structures, I showed you in the previous slide that you can add carbon nanotubes, you can even add graphene flakes, you can add various nano structures into your polymer solution.

So, when you are making your PAN solution you can already mix these things inside your PAN solution and then spin fibers out of it. Of course, you will have to optimize. The most important thing to optimize is the concentration of your additive because if it is too much then the polymer will lose it is spin ability.

But, once you optimize this concentration now, you get fibers like what you see in this image that you have a lot of these kinds of fibers are known as decorated fibers. You will hear this word in the literature that you have carbon fibers decorated with certain nanoparticles or glass-like carbon electrodes decorated with certain nanoparticles or many other structures whether they are large scale or small scale they can be decorated with nanoparticle.

So, this is also another thing you can do. Why would you do that? Because now your carbon fibers basically serve as the sort of a substrate for these nanoparticles. Maybe there is a certain nanoparticle, you want to utilize the property of the nanoparticle and not that of the carbon fiber or you want to utilize the property of both.

carbon fibers are conductive; if you have high heat treatment temperature, then you can have conductive carbon fibers. Now, you can pass current through these fibers and you can even perform joule heating because if you can pass current through certain fiber.

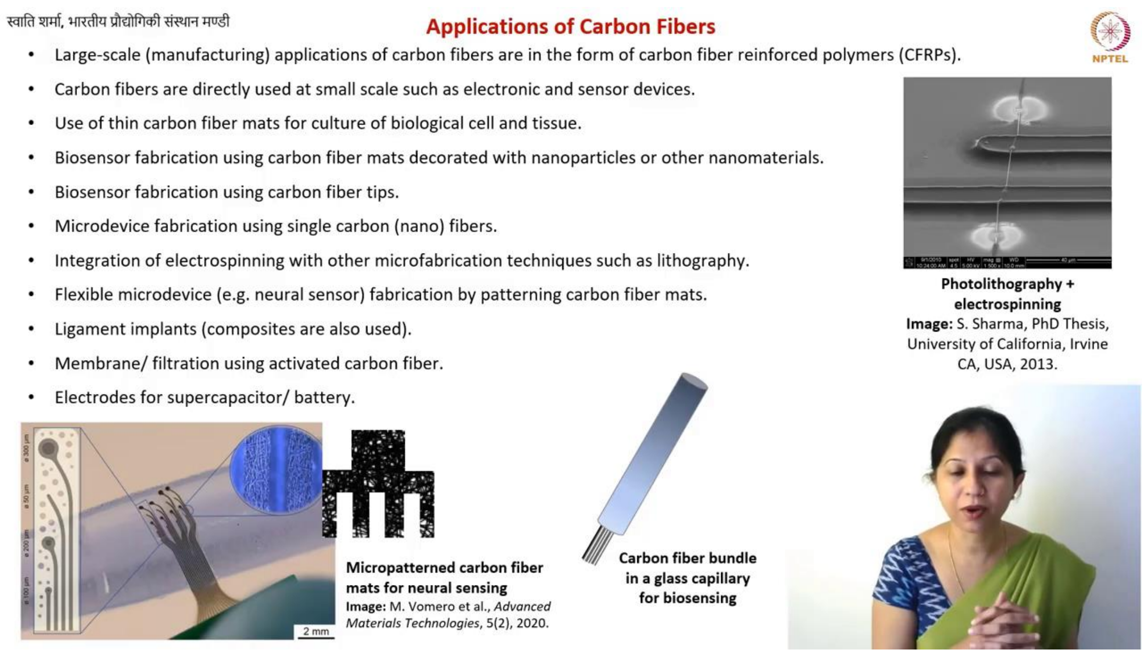
In that case maybe at a certain temperature, your nanoparticles become activated. Those nanoparticles can then perform sensing of different types for a number of biological applications. Biosensors are a class of devices where you are somehow sensing a biological entity.

That biological entity can be a virus, can be a bacteria or can be a lot of things. You can sense certain types of drugs, the concentration of these drugs and so on. So, for a number of these application biomedical applications, you will utilize these kinds of decorated nanoparticles, this is also one possibility that we have.

We can perform surface activation. So, you know that we do physical surface activation using steam and carbon dioxides. You can do that also for the carbon fibers and you can also use certain chemical methods. When you are preparing the fibers in the polymer itself you will add certain chemicals and then carbonize them.

So, whatever you do for porous activated carbons which we learnt in some of our previous lectures, whatever you do for activated carbon porous carbons the same thing you can do for making activated carbon fibers. By the way, polyacrylonitrile divides fibers also can be activated. So, it is not necessary that they have to be derived from cellulose or rayon, different types of carbon fibers can be activated.

So, these are some more possibilities that you have. Of course, you can make different types of mixtures of carbonizing and carbon non-carbonizing polymers like I showed in the hollow cylinder. These hollow fibers had coercion-like geometry. But, if you just make a mixture and then perform the electrospinning then carbonizing, you will get highly porous carbons. Then you go on activating these porous carbons further, then you can imagine how much surface area is available for your application. (Refer Slide Time: 25:31)



Let us now talk about the applications, as I mentioned we will not talk about the composite applications for now in this lecture. Carbon fibers can be directly used for a lot of applications. in manufacturing applications, fibers are used with certain resin because you need some lubricant for braiding them for making the fabric out of them, otherwise you may end up damaging your fiber mechanically damaging your fibers.

Also, they are rough, they are hard and brittle, it is not that easy to process them without a resin. But of course, when you use the resin you will lose some of the surface properties of your carbon fibers. Overall mechanical strength will be reduced because now you also have some polymer mixed into it. So, you do not have 100 percent carbon fiber mass.

So, there will be some loss of property, but in the case of microdevice applications, we directly use the carbon fibers. We do not use them with the resin and for making a biosensor I will come to it. You can use the fiber with a little bit of polymer or a resin in it. But in that case, that polymer must be bio-compatible. So, we will see some examples here.

I have not given any specific example, but there are publications that you can search for. You have these ultra-thin carbon fiber mats that can be used as cell culture substrate. So, in case you do not know cell culture, it basically means you are artificial artificially growing cell of different types cells and tissues.

You are doing it outside of the body which is known as the in-vitro and you are trying to grow the cells to and why do you do that? To see the effect of certain drugs, before we start testing in animals and humans we often test it on the cell lines or these cultured cells.

Cell culture can also be performed in a liquid because we also need to provide some food to the cells and this food may contain glucose, this food may contain certain antibiotics and also whatever is required for the cells. So, this is what is known as cell cultural medium and nutrients and a lot of things are mixed into the cell culture media.

Now, cells will float in that medium and they will culture directly. However, in the actual biological environment cells are not really floating in our body, they have solid support and to mimic these biological conditions we sometimes use what is known as cell culture substrates or scaffolds. So, substrate you will say when they are 2D and scaffolds are also basically substrates, but 3D substrates.

So, for making these cell cultures substrates as well as scaffolds sometimes the carbon fiber mats are directly utilized. Now, here the property of carbon that it is inert becomes very important because cells will typically not like anything that can react with them you know, then they can have certain chemicals that come out of these substrate materials then they do not like it.

But in the case of carbon, it is so inert that cells it does not bother the cells. So, it works, it functions as a very good cell culture substrate. So, there are various examples where carbon fiber mats or used as substrates. Again bio-compatibility also can make it useful for biosensing application.

There are many things about biosensor. There are many types of biosensors, some of them utilize the electrochemical properties of the substrate material, some of them may not have an actual substrate or even any cells or any biological moiety for example, enzymes attached on to them, but they may just use some kind of nanoparticles which are sensitive to a certain biological entity.

There is a variety of biosensors, enzymatic electrochemical being the most important ones. For biosensing applications also you can directly use carbon fibers. Now, you may use the carbon fiber mat or fabric-like structure or you can also use the tips of your carbon fibers.

Why would you use the tips? Because there you can actually use these nanoscale tips let us say your fibers are nanoscale, then you really are able to sense even very small individual biological entity that you are planning to sense. So, what you do is you take a fiber bundle and then you put it inside a glass capillary.

People occasionally will also mix a little bit of resin again because you want to put it inside the glass capillary, it is like when you put a thread inside a needle. So, you try to make the thread a little bit harder, so that it can go easily so some resin may be used, of course, it has to be bio compatible.

And, now you can also fabricate a number of different micro-scale devices. You can have electronic devices, you can have sensor devices, you can have various different types of devices.it is not like microdevice is one thing. Here I am just trying to show that how you can use carbon fibers for these devices. Of course, one option is that you can use the entire fiber mats.

So, there are lot of examples; these mats have been used as electrodes for supercapacitors and batteries. And, then you can also utilize single fibers as well. Here in this image, you can see that this is a combination of photolithography and electrospinning.

So, the electrode paths you see, there are two lines and then there is a suspended fiber on top of them. So, the fiber was prepared by electrospinning while these electrodes were patterned using photolithography. Now, you already know about photolithography, you have certain phenol formaldehyde resins that can be converted into carbon.

If you also have a fiber suspended on top of them, then this entire assembly can be converted into carbon. So, you have the entire carbon structure and now you can perform your sensing using that individual fiber. You can even perform Joule heating on top of that fiber and you can use it as CVD substrate. So, there are multiple applications where you can combine other microfabrication techniques with electrospinning.

You can also take the electrospun cloth-like fiber or woven or non-woven and then you can perform etching of that fiber and then do the micropatterning and then you can make these ultra-flexible devices that can be used for sensing purposes. So, this is an example where we used it for neural sensing purposes, but there are many other devices that are possible using micropatterning of carbon fiber mats or carbon fabric.

You can also have some biomedical implants which are mainly again fabricated using composite materials because they have to load-bearing and they also need to stay inside your body. The problem with carbon fibers is that they do not degrade.

So, if you make a ligament implant; ligament or tissues can grow nicely on top of it. So, it provides like a template and the tissue can grow nicely on it. But, the problem is that now afterward you will have to surgically remove it because it will not degrade and excrete out of your bodies. So, you have to surgically remove these carbon implants.

So, here the inertness and stability of carbon is also a little bit of a problem, but ligament implants nonetheless are fabricating using carbon fibers, again some resin may be used in that case and you will typically use a woven carbon fiber mat and not spun fiber mat.

Other devices are membranes and filtration devices and again you can activate the carbon fibers that increase the adsorbance and microporosity. Altogether you can use it for a number of applications electrodes I have already mentioned. So, these are some of the applications of carbon fibers. In the next lecture, we are going to learn about carbon fiber composites.