Carbon Materials and Manufacturing
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Lecture - 36
Carbonization of Polyacrylonitrile (PAN) Fibers

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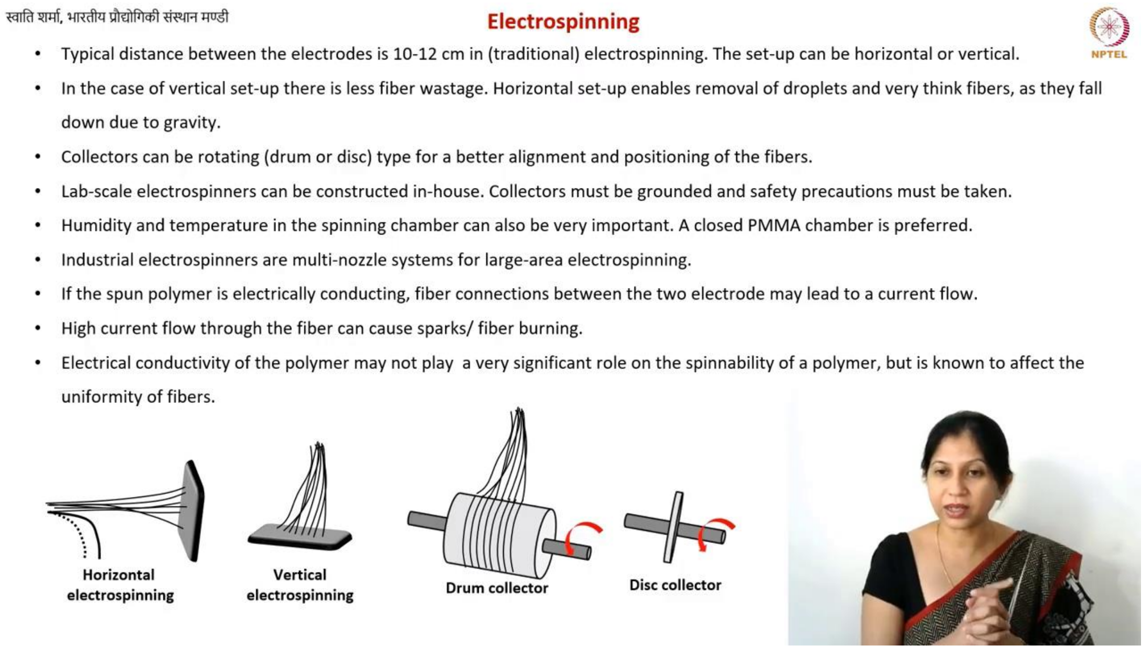

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Electrospinning

- Typical distance between the electrodes is 10-12 cm in (traditional) electrospinning. The set-up can be horizontal or vertical.
- In the case of vertical set-up there is less fiber wastage. Horizontal set-up enables removal of droplets and very think fibers, as they fall down due to gravity.
- Collectors can be rotating (drum or disc) type for a better alignment and positioning of the fibers.
- Lab-scale electrospinners can be constructed in-house. Collectors must be grounded and safety precautions must be taken.
- Humidity and temperature in the spinning chamber can also be very important. A closed PMMA chamber is preferred.
- Industrial electrospinners are multi-nozzle systems for large-area electrospinning.
- If the spun polymer is electrically conducting, fiber connections between the two electrode may lead to a current flow.
- High current flow through the fiber can cause sparks/ fiber burning.
- Electrical conductivity of the polymer may not play a very significant role on the spinnability of a polymer, but is known to affect the uniformity of fibers.

Hello everyone. In this lecture, we are going to discuss a few more things about electrospinning and the electric spinning setup. And, then we will talk about specifically electrospinning of PAN, because that is our important carbon precursor. Let us start with some more parameters, you remember how your electrospinning setup looks like.

And you remember that some of the things that we talked about there are two electrodes. There is a certain distance between the two electrodes, this distance in the case of the traditional far-field electrospinning you will have 10 to 12 cm.

In principle, you can go between 5 and 20 cm, but 10 to 12 cm is most commonly used distance between the two electrodes. Now, what is important here? That your setup can be both vertical or horizontal. So, the one that I had shown you, I told you that, you had one needle from the side, one electrode here and then the flow of fibers and over here you had your screen or your collector (refer to video at 1:12).

So, basically the fibers were fabricated horizontally. They were collected horizontally. Why cannot we have a setup like this where you have your needle on top and you have your collector in the bottom? The answer is yes, we do have indeed both kinds of setups and both have their own advantages and disadvantages.

In the case of vertical electrospinning, what is your advantage the fact that you will have less wastage of fibers. So, whatever is coming out, you are able to collect all of those particles, all of those fibers. But, there is also a disadvantage of the vertical setup. I have shown you this schematic when you have this horizontal electrospinning setup. In that case, you are only collecting the good fibers let us say the thin fibers.

And if you have slightly thicker fibers or sometimes you may even have droplets because polymers solution may not always be perfectly uniform. So, if sometimes you have lumps of polymer, you may end up getting droplets. Because of that, those things will then fall on the way and they will not be collected because of the gravity; they will already fall.

But in the case of vertical electrospinning, you will have all of these things collected on top of your substrate.in general when people are conducting research or they are doing experiments with certain new polymers, they will use horizontal electrospinning. Because, you do not know what the optimum conditions are and when do you get droplets and when do you get good fibers.

In the case of industrial processes or well-established processes, you will use the vertical electrospinning setup. Because there what is more important is that you do not end up wasting too much material.in any case, both of these setups are widely used. Now, what you can also do? You can change the size or shape of your collector.

Till now whatever I have shown you in the name of collector has been a plate and you can also attach a silicon wafer on top of this plate. Basically, you have a conductive plate. But, what you can also do is, you can change the shape and size of this collector. How will that make a difference and why should you do that?

Drum collector, this is indeed a very common collector nowadays, if you buy an electrospinning setup you can actually buy these drum and disc collectors along with it. Drum collectors basically they are rotating. They are cylinders of metal and also they are connected. They are your electrode number 2. And they are rotating at reasonably high speeds, let us say 2000 rotations per minute.

What happens now? Now you are like winding the fibers. And when you are winding it especially when your drum is rotating with that speed then, you also end up aligning the fibers which do not happen in the case of a simple plate collector. Now, if you want to position your fibers in a very thin, or very narrow space, then you can use this disc collector.

So, disc also rotates, but you see it's more like a CD a Compact Disc and you are just collecting the fibers at its edge. So, now you have this very thin rope like structure; however, again these kinds of things you will only do for research purposes or for a small-scale fabrication, not for industrial application. There you use the simplest geometries because your process is very much optimized.

there are many other types of collectors, but these are the ones that are rather commercially available. You also can design your own collectors, you have various types of stages. Nowadays all you need to do is sort of play with the electric field.

Wherever you have your conductive collector, then the fibers will go and attach there. They will get attracted to it. you can have collectors as simple as aluminum foil. If you just want a large fabric-like sheet then you can just collect them also on any conductive foil.

So, all kinds of collectors can be prepared. Now, I have also written here and probably I said it in the previous class that you can make your own electrospinner. So, I have nothing against the companies who are selling electrospinning setups, but at the same time whatever you need for research purposes, a small-scale device can indeed be prepared at the lab scale.

What do you need to do? You need a high voltage power supply, you need a good stage. You may or may not need a good stage, you can sometimes also just have two electrodes, one needle syringe and then any conductive substrate connected to the power supply and maybe you need a syringe pump; that is all you need.

You can actually prepare your own electrospinning setup; however, please take care of all the safety precautions, because you are working at very high voltages. And you may get shocks and I have myself learned it the hard way. I think what is a good idea which I should have done also is that you place your entire setup inside a good closed chamber.

And these chambers can generally be prepared using a PMMA sheets. PMMA is Poly Methyl Methacrylate, you get these thick plastic transparent sheets. And you can just do some laser cutting and make your own box, and make sure that the doors are closed when you are running the electrode.

Because you are working at pretty high voltages. And especially if you are working with conductive polymers you may have some sparks here and there especially when you are performing optimization for a new polymer. In that case, there is a possibility of accidents.

So take care of all the safety precautions. And in the commercial electrospinners typically if you open the door then the voltage supply or the power supply will turn off automatically. So, these kinds of precautions must be taken care of. Industrial spinners also have a multi-nozzle system. Multi nozzle means, you can imagine the nozzle is your spinner edge or your needle.

if you want to perform or if you want to make really large sheets of electrospun fibers, you can have 10 nozzles and 10 syringes and 10 pumps connected to it. So, this is what indeed happens in the case of large-scale industrial fiber especially for carbon fiber fabrication, because you need to then prepare really large, massive laminates in many cases.

Or you need to also braid the fibers, for that you need a lot of quantity of the fibers.in that case you have one single collector, but you have multiple nozzles. So, this is also a variation of it. So, we already talked about the electrical conductivity of the polymers, you also know that if your fiber connects the two electrodes you may have some sparks. So, this is generally about the electrospinning setup. And, now let us specifically talk about the electrospinning of PAN.

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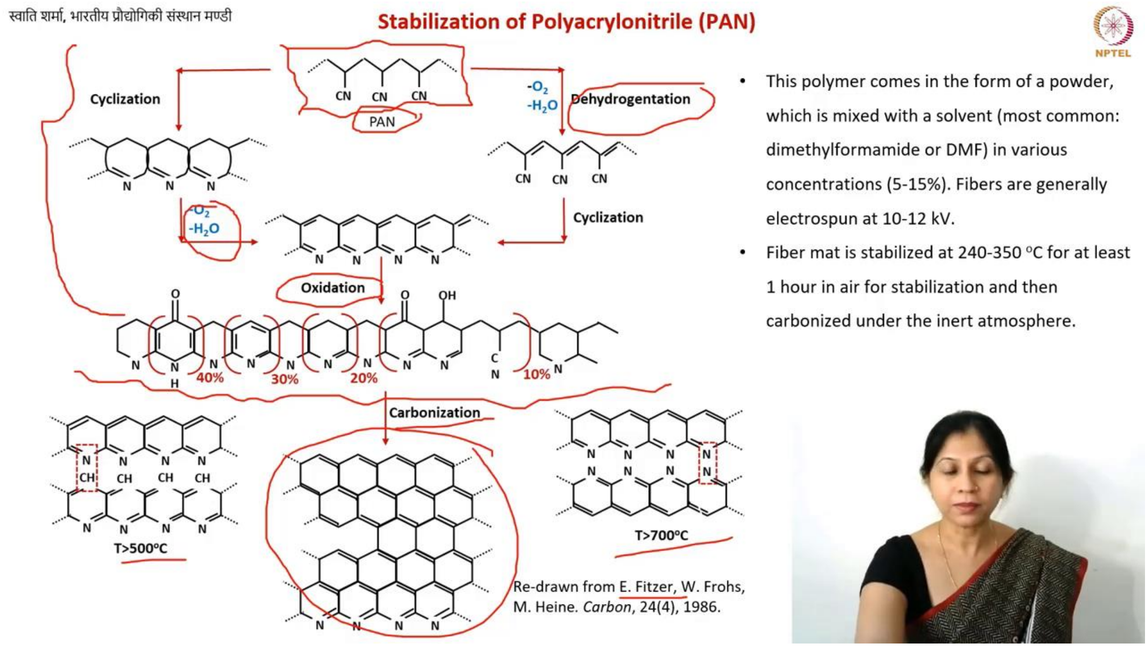

Stabilization of Polyacrylonitrile (PAN)

- This polymer comes in the form of a powder, which is mixed with a solvent (most common: dimethylformamide or DMF) in various concentrations (5-15%). Fibers are generally electrospun at 10-12 kV.
- Fiber mat is stabilized at 240-350 °C for at least 1 hour in air for stabilization and then carbonized under the inert atmosphere.

Re-drawn from E. Fitzer, W. Frohs, M. Heine. *Carbon*, 24(4), 1986.

On this slide I have shown you a lot of chemical structures. These are actually several steps that take place at several stages of the carbonization of PAN. But, before the carbonization, we also perform one more step in the case of PAN. This is known as the stabilization step, and this is what we are going to talk about.

Here you see, this is your starting material PAN. What is interesting about it? If you remember in some of the lectures, I said that if you have aromatic rings, if you have these 6 membered rings already in the polymer, then it is it will yield good graphitic carbon. But in the case of PAN you see you do not have that cyclic structure, it is aliphatic polymer.

However, you do get good quality carbon out of it. And the reason for that, is why I am showing all these chemical reactions. There is a certain cyclization that takes place where your nitrogen atom behaves more as an intermediate structure or even you can call it a catalyst. And, then you have these cyclic structures forming at a certain time point, and then you get good carbon which is, which has graphitic content.

Now let us first think about what a PAN is. when you want to start working with PAN, it looks like a white powder. When you purchase it the typical molecular weights that you buy is around 150000. But, you can also get higher molecular weights PAN; higher molecular weight will have a longer chain length that would change the visco-elastic properties.

in case you need it then you can buy that anyway. The typical parameters for the electrospinning of PAN are mentioned here. You take this powder and you make a solution. And the most common solvent for a dissolving PAN is dimethylformamide or DMF. You may have to heat it up to 70 °C for a while to get a good solution.

Now, you get this solution of PAN and then for electro spinning the parameters that you would typically use is 10 to 12 kV that is your voltage. And, the concentration of the polymer solution generally varies between 5 and 15 percent, but you may also use 10 to 12 percent solution weight by volume in DMF for industrial purposes.

These are some of the parameters that you will use for PAN carbonization. As I mentioned before about carbonization, you will heat it in air between 240 and 350 °C centigrade. Why are you doing this? This is the step which is known as the stabilization step. And over here now, if you look at this diagram or these reactions, you will see that you lose some water and oxygen, there is dehydrogenation at various steps.

This entire thing is actually happening during your stabilization. So, you do need some oxygen. Here this dehydrogenation takes place during its during the initial stabilization step. After that you need oxygen.

Once you get this kind of cyclic structure or you can call it further polymerization. But, then also you are changing the chemical structure a little bit, but you get these kinds of large structures, then you perform the carbonization under the inert atmosphere.

Here you see at 500 °C you have this kind of chemical reaction and at 700 something like this and then you get. Finally, you get these large carbon structures where you have some nitrogen atoms. Maybe even at 900 °C, you will still have nitrogen atoms in it and that is why in order to get rid of the nitrogen all the nitrogen PAN fibers for making the carbon fibers, you will heat them to a much higher temperature rather than 900 because you will still have some nitrogen there.

This entire strategy was suggested by Fitzer. This is still the most extensively studied paper in this regard. So, this is a proposed mechanism of the carbonization of PAN. And, this is where you see what happens during the what is it stabilization.

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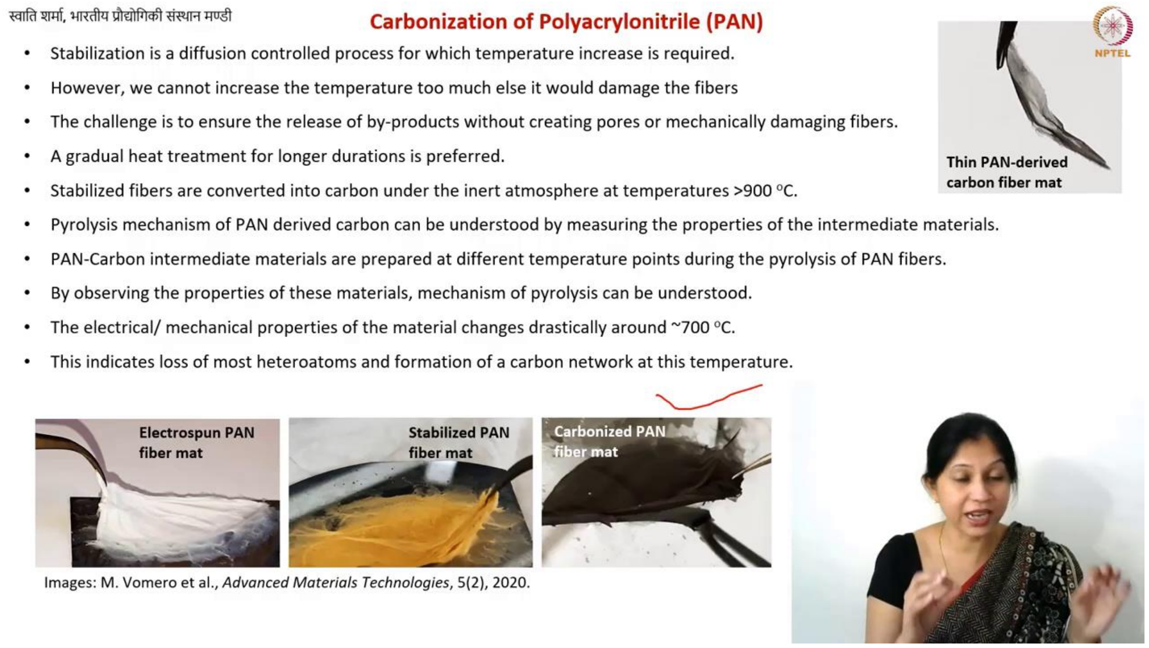

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Carbonization of Polyacrylonitrile (PAN)

- Stabilization is a diffusion controlled process for which temperature increase is required.
- However, we cannot increase the temperature too much else it would damage the fibers
- The challenge is to ensure the release of by-products without creating pores or mechanically damaging fibers.
- A gradual heat treatment for longer durations is preferred.
- Stabilized fibers are converted into carbon under the inert atmosphere at temperatures >900 °C.
- Pyrolysis mechanism of PAN derived carbon can be understood by measuring the properties of the intermediate materials.
- PAN-Carbon intermediate materials are prepared at different temperature points during the pyrolysis of PAN fibers.
- By observing the properties of these materials, mechanism of pyrolysis can be understood.
- The electrical/ mechanical properties of the material changes drastically around ~700 °C.
- This indicates loss of most heteroatoms and formation of a carbon network at this temperature.

Images: M. Vomero et al., *Advanced Materials Technologies*, 5(2), 2020.

What else happens during stabilization? This is what we are going to learn now, but before that let me show you some pictures? This is how your electrospun PAN mat looks. I think I had also shown this picture earlier. If you stabilize it looks something like this, it looks a little bit of little brown. So, if your mat becomes brown do not worry you have not burnt it yet. This is alright this is how the stabilized mat looks. And, then when you carbonize it under the inert atmosphere, in this particular case this was carbonized at 900 °C, so this is how now your mat. Now it converts into this carbon, carbon fiber mat.

You would say that this looks stiffer structure, and it is not as flexible as the PAN fibers. Yes, in fact it is not as flexible, but it is still flexible enough. Right now it looks a little bit stiff in this particular picture, number 1 - because you are comparing it with the PAN fibers, number 2 - also there is no solvent and there is at least a little bit of shrinkage. So, the structure is not able to move as freely as before. But, if you take one little part of this mat, then you will see that it is indeed flexible enough. And, it depends on how you fabricate your structures. how many layers you want in your fibers, then you can also control the flexibility of your overall structure.

So, I was talking about the stabilization step and what else happens there? Now you have certain oxidation and dehydrogenation steps that are taking place and there is also some water molecule and oxygen being produced as well because you have both of the certain reactions taking place and also certain byproducts are being formed. This is a diffusion-controlled reaction. When it is diffusion-controlled reaction, that means if you increase the temperature, the diffusion increases in general.

If you keep on increasing the temperature during your stabilization, then you will have a faster and better stabilization. But, you are limited by the stabilization temperature, because if you go above 350 °C, then you may end up either burning your polymer or you may end up melting it. You may end up also deforming your fiber structure. Even 350 °C is pretty high people would keep it below 300 °C in general.

So, what is a good idea? In order to avoid damage to the fibers. What you could do is? You could just heat it, not at very high temperature. So, it has to be above 240 °C, but you can keep it let us say at 270 or 300 °C. You can keep it for an extended duration rather than trying to do it quickly. So, if you do it, slowly and for a long time then you will get better stabilization of your carbon fibers of your stabilized PAN fibers.

Now, once you have these stabilized fibers, then you would convert them into carbon. And that is done at a minimum temperature of 900 °C. At 900 you have maybe 97 percent carbon content in your carbon fibers if you perform the elemental analysis.

So, we also need to understand little bit of this pyrolysis mechanism. I told you when we were talking about pyrolysis, I told you that typically you will have the pyrolysis taking place up to 700 degrees. And after that, you will have carbon-carbon bond formation and at some point, you will get a reasonably good carbon network around 900. So, you can work with that.

But, then you further increase the temperature, then you get more graphitic content and you get rid of all the impurities. If you want to get pure graphite, you will go all the way to 3000 °C. And, you have to have a graphitizing polymer, not all polymers will give you graphite.

So, what happens in the case of PAN? And can we actually do what do we know about the pyrolysis of PAN, even it is such a common polymer. And also things that we know about PAN can they also be applied to other polymers. So, what we can do is you place these fibers inside the furnace, and as in these pictures you can see you take them out at. So, this is after stabilization.

Then I heat treat it for up to 400 °C, and then I take the sample out then I heat treat it at 500 °C, I take the sample out 600 °C and so on or even I can take the sample out every 50 °C. There will be some rearrangement of bonds in certain chemical reactions, certain annealing of byproducts during the cool down also.

But, ignoring that if I just take these materials and try to understand their properties, their elemental purity, their electrical conductivity, their mechanical properties. Then, we can get some idea about what is happening during the pyrolysis. So, these materials I would call them PAN carbon intermediate materials.

Because, they are neither PAN nor carbon. They are definitely not carbon. Even if you say carbon with high impurities even that is not correct.it is better to not call them carbon. Sometimes people use the term char for these kinds of materials, but we do not want to give the impression that this is formed by coking or charring. So, in order to avoid any confusion, we just call them intermediate materials.

I will show one plot on the next slide, it seems that most of the properties undergo a very sudden change around 700 degrees for polyacrylonitrite. What does that mean? You will have a lower electrical resistance little bit, PAN is insulating. So, the material remains pretty much insulating, maybe the electrical conductivity increases a little bit as you increase the carbonization temperature.

However, at 700 °C you will see a sudden jump in electrical conductivity. So, the materials that are prepared at temperatures higher than 700 °C, you can call them electrically conducted, before that you will still have them in the insulation insulating material range.

Similarly, for the mechanical properties, the material will be very soft, but then suddenly it becomes stiffer at 700 °C. Of course, this stiffness and also the electrical conductivity is not very high at 700 °C. In fact, if you keep on increasing the temperature, you will then get a further increase in crystallinity, and therefore, the properties will also improve.

From this, you can understand that there is some big change is happening in the material at around 700 °C. And what is this change? Most likely this is where you are getting rid of all the non-carbon atoms. Because initially, you lose some atoms, you lose some oxygen, you lose some nitrogen, but hydrogen leaves later around 600 °C. Then hydrogen and remaining nitrogen are also leaving in the case of PAN. Most of the heteroatoms, we get rid of them at around 700 °C, I am saying most of them, not all of them.

You basically have a sudden release of byproducts just before the 700 °C and you now have sort of a carbon skeleton or carbon network you can call it. That is what you now have at 700 °C. Now, you are doing further heat treatment just for getting higher crystallinity and higher purity.

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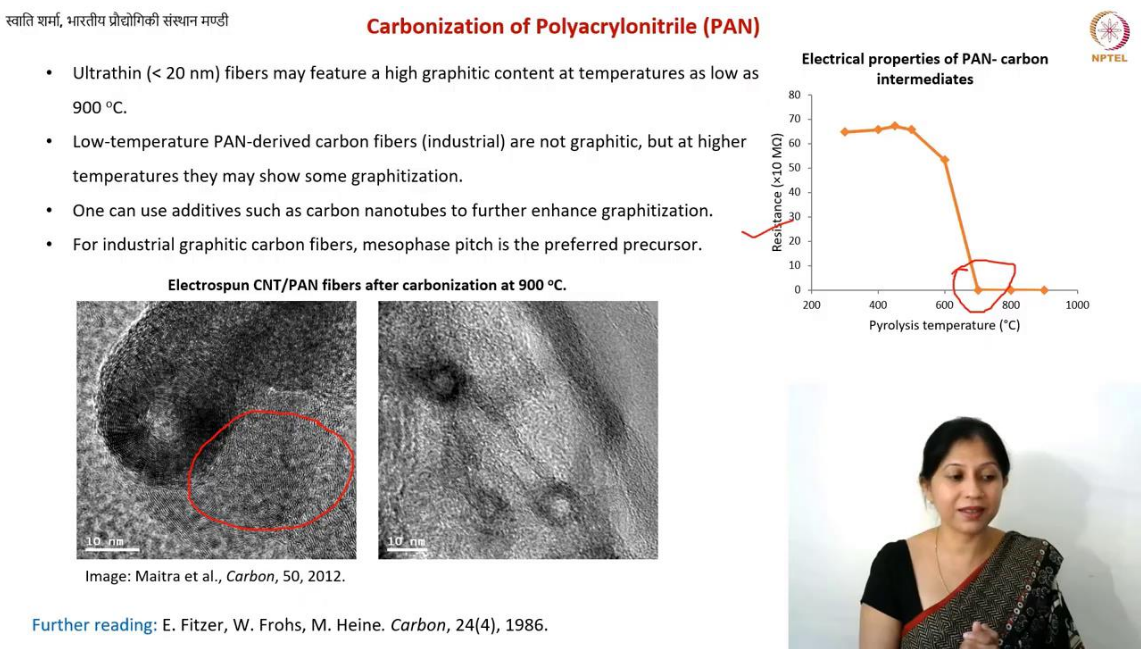

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Carbonization of Polyacrylonitrile (PAN)

- Ultrathin (< 20 nm) fibers may feature a high graphitic content at temperatures as low as 900 °C.
- Low-temperature PAN-derived carbon fibers (industrial) are not graphitic, but at higher temperatures they may show some graphitization.
- One can use additives such as carbon nanotubes to further enhance graphitization.
- For industrial graphitic carbon fibers, mesophase pitch is the preferred precursor.

Electrospun CNT/PAN fibers after carbonization at 900 °C.

Image: Maitra et al., *Carbon*, 50, 2012.

Electrical properties of PAN- carbon intermediates

Further reading: E. Fitzer, W. Frohs, M. Heine. *Carbon*, 24(4), 1986.

As mentioned, this is one plot. You can see here this is approximately 700. And, these are the intermediate PAN carbon materials. And this is electrical resistance and this is pyrolysis temperature. You can also plot mechanical properties and other properties.

What is interesting is for other polymers, maybe the temperature is not exactly 700 maybe, it is 650 °C or in some cases 720 °C. But, for many polymers, this is pretty much what you get. Between 600 °C and 700 °C you will have this sudden change in properties.

Keeping in mind that also these experiments were performed in the lab furnaces, where you even the furnace display 700 °C maybe it is 696 °C something. So, minor error is possible, but this is just to give you an idea. That is number 1, this is what happens for PAN.

And number 2 - this is one method of understanding the mechanism of pyrolysis. In the case of carbonization of PAN, there are few more important things, especially when we talk about the carbonization aspects. If the fibers are ultra-thin; ultra-thin means less than 20 nm thin, often they can be carbonized at a lower temperature. This is not just the case with PAN, but any polymer when you have very small structures. But this effect of structure is only visible or only atleast dominant when you have structures that are smaller than 20 nm. So, extremely small structures if you carbonize them, they can have both byproducts and defects annealing out very easily because of their high surface area. But as I mentioned it does not happen in micro-scale, this is often the case only at the nano-scale and especially fibers that are smaller than 20 nm. So, in this case, you may get higher graphitic content at 900 °C itself. Now, one more interesting question arises, is PAN graphitizing or non graphitizing type of polymer?

What kind of carbon does it give? For the industrial carbon fiber fabrication, if you want to get a higher graphitic content or if you want to call them graphite fibers then, you will still use mesophase pitch and you will not use polyacrylonitrile. In general polyacrylonitrite is a non-graphitizing type polymer.

However, there have been certain publications where people use certain stress from the beginning or certain additives in the material or even very high-temperature special treatments can yield graphite-like crystallites at the end. But, that is only happen when you have specific specialized treatments. In general, PAN is a non-graphitizing polymer, but we do not say that we have our glass-like carbon fibers or graphite carbon fibers or non-graphitizing for that matter.

For a couple of reasons number 1 - in the case of fibers, as I said that the defects can anneal out relatively easy. So, you cannot always say that you never going to get graphite out of it. Although under normal circumstances that does not happen, because there will be some curved carbons that are formed. There may be some fullerene-like structures although in the case of fibers. It is less likely because especially when you have fibers as thin as 20 nm, then it is possible that these defects will anneal out. However, there will be some curved carbon structures.

So, this is more of a non-graphitizing type of carbon and that is why you should not get graphite out of it, but we also do not know exactly what is the mechanism of carbonization, do we call it coking and or do we call it charring? Mostly it is coking process, but you see in the case of PAN you have this cyclization going on. This is more complex compared to most of the other methods.

So, you do not specify whether it is a coking mechanism or charring mechanism. You just called the fibers that come out of it as carbon fibers.one thing we do know is that we do get a high carbon content in your in the fibers that come out of it.

What happens at low temperatures? In the industrial case you will call 900 a low temperature. Because in industrial-scale we are anyway not making fibers smaller than 20 nm or we have large enough fibers and that is why you do not get good much graphitic content at 900 °C and you would typically go for higher temperatures.

What you can do If you want to get some graphitic content? Again, that would be mostly for research purposes rather than for industrial applications, you can have some additives. You can have metal nanoparticles, you can also have certain carbon additives like you can add carbon nanotubes in your polyacrylonitrile solution.

In the case of polyacrylonitrile, it is relatively easy, because you are preparing a solution from a powder.at that time you can also have some additive. Of course, you will have to optimize the concentration. So, that the material does not lose it is spin ability. In these pictures you can see that we added some carbon nanotubes into PAN. And, then we spun fibers out of it and then carbonized this entire thing again.

This material actually becomes sort of a carbon-carbon composite material. What is the advantage of this entire process? I do not know if it is clear in these pictures, but if you see over the regions that are close to the nanotubes, they show more graphitization because of this templating effect.

That is what you can do to improve graphitization. So, we also see them in the transmission electron microscope images. And, we also can do electrical conductivity measurements. So, you will typically if you have higher graphitic content, you will have higher electrical conductivity.

Depending upon your application like for sensing applications or also for gaining more mechanical strength, you can test different properties. One way of increasing graphitic content is also this addition of either graphitic carbon nanomaterials or you can also have catalytic graphitization where you can have metal nanoparticles, for example iron.in that case you will need to get rid of this iron or whatever metal afterward from your fibers. So, you will have to perform certain leaching experiments etc., but there are certain methods of improving the graphitization in PAN fibers.

However, as I have mentioned before that for industrial graphitic or graphite fiber fabrication, Again, graphitic and graphitic are the content of graphitic crystallites, in a disordered carbon material. And as long as you can detect that peak of the graphite, in XRD or any other spectroscopic or diffraction analysis, then you can call it graphitic.

However, graphitic does not mean that there are any given fraction of crystallites. So, it can keep on increasing and that is why you will say that the graphitic content keeps on increasing at higher temperatures, this is valid for all carbon materials not just fibers.

But non-graphitizing would mean that it will never convert into perfect graphite. So, that is what we have in the case of PAN fibers, you have this is non-graphitizing. But, it does get higher and higher graphite content, as you keep on increasing the pyrolysis or heat treatment temperature.

Or if you add carbon nanotubes or induce stress or with other methods. These are some of the articles that you can read, you can find them on the internet. There are ways of getting a very high graphitic content in PAN-derived fibers. As I mentioned you can read more about it, this is an area where you have an overwhelming amount of literature.

You can find several books, several research articles, several review articles on carbon fibers, electrospinning and PAN-derived carbon fiber. this was a paper from where I took that mechanism image. And there are many other papers so, if you are interested you can read more about it.