Carbon Materials and Manufacturing
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Lecture - 25
Pyrolysis Mechanism of Polymers and Other Solid Hydrocarbons

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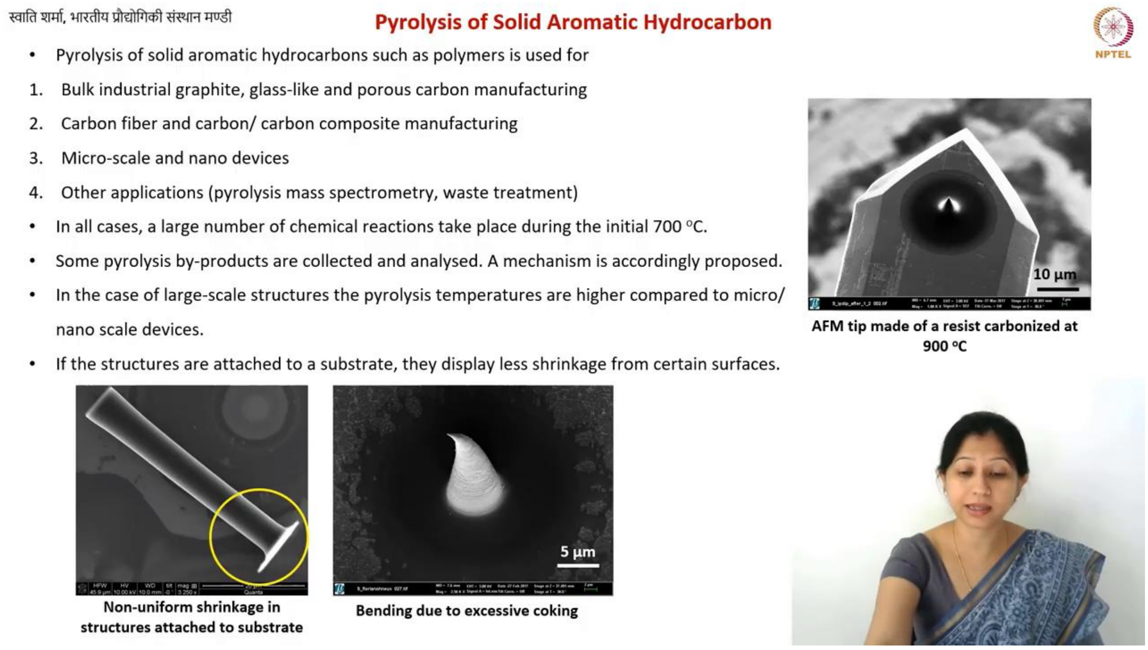

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Pyrolysis of Solid Aromatic Hydrocarbon

- Pyrolysis of solid aromatic hydrocarbons such as polymers is used for
1. Bulk industrial graphite, glass-like and porous carbon manufacturing
2. Carbon fiber and carbon/ carbon composite manufacturing
3. Micro-scale and nano devices
4. Other applications (pyrolysis mass spectrometry, waste treatment)
- In all cases, a large number of chemical reactions take place during the initial 700 °C.
- Some pyrolysis by-products are collected and analysed. A mechanism is accordingly proposed.
- In the case of large-scale structures the pyrolysis temperatures are higher compared to micro/ nano scale devices.
- If the structures are attached to a substrate, they display less shrinkage from certain surfaces.

AFM tip made of a resist carbonized at 900 °C

Non-uniform shrinkage in structures attached to substrate

Bending due to excessive coking

Hello, everyone. In this lecture, we are going to again discuss the pyrolysis process and the mechanism of pyrolysis, but this time that of aromatic solid hydrocarbons and also the ones that are used in their pure forms and not as mixtures. For example, petroleum pitches are carbonized, they also contain a lot of aromatic hydrocarbon compounds, but these are mixtures of aromatic compounds.

We are now going to talk about pure polymers. For example, polyvinyl chloride can give you graphite or graphitizing carbon or phenol-formaldehyde resins which are going to give you glass-like carbon. These are well-defined polymers and we also know the properties or what to expect in the carbon that comes out of these polymers.

So, let us talk about the mechanism of these. I do, however, recommend that you go through the lecture on pyrolysis of gaseous hydrocarbons because there is one important concept of the enthalpy of formation of certain especially that of light hydrocarbons.

That also remains important here because in the case of gaseous hydrocarbon pyrolysis we were more concerned about when will this light hydrocarbon decompose, for example, methane.

But, now we are concerned about when and within which temperature range methane formation is highly likely because of the fact that it is a very stable organic compound. So, I will say that please go through the other lecture. Let us talk about solid polymers.

What do we use them for? You already know that we use them for making graphite, for glass-like carbon, porous carbons from cellulosic materials and then these porous carbons are further activated using chemical or physical activation and then they are converted into activated carbons. So, these are the applications. What else? We also make carbon fibers.

We are going to have a few lectures on carbon fibers. We are going to have a separate section, there we will also discuss the mechanism of those polymers which are used specifically for making fibers, but the idea is still the same. We make fibers using polymers and then we convert them into carbon.

Now, we also make micro and nanoscale devices. Here what we use is photosensitive polymers because in the case of micro and nanofabrication you need to use certain lithographic techniques for patterning for your manufacturing and these lithographic techniques utilize photoresist which is nothing but a similar type of resins. For example, phenol-formaldehyde resin has been used for making glass-like carbon for a very long time, but now if you also induce some photosensitivity to it, how do you induce photosensitivity? Either by adding some materials known as photoinitiators.

These are basically additives and or you can also induce a certain functional group into your polymer which is photosensitive or you can use the combination of both of these things. So, that is how you make the polymer photosensitive.

However, the important thing is that when it comes to their pyrolysis when it comes to their thermal decomposition does not depend on the photoinitiator but on the skeleton of your primary polymeric structure.

Actually, the byproducts that you get from the pyrolysis of phenol-formaldehyde resin at large scale, if you use the same or very similar resin at small scale with the photo initiative still the pyrolysis mechanism will be guided by the chemical structure and not by the photo initiative structure.

What else? There are also some other applications. Let us see if we have time, then we might discuss some of these things and because these are very interesting things and waste treatment is also a very socially relevant topic. Let us see if we can discuss. One more thing that I do not think I have mentioned till now is Pyrolysis mass spectrum spectrometry. This is also one very interesting application of pyrolysis. At least the chemistry students might know that mass spectrometry is performed when we want to analyze a certain molecule, typically these are heavy molecules for example, heavy hydrocarbons.

What do we do? We somehow let them undergo fragmentation there can be various methods using which we can fragment these molecules and obviously, every molecule has its own unique fragmentation patterns, but they are unique to that molecule. However, by understanding those patterns we can guess what is the chemical structure, what type of bonding is present in that kind of hydrocarbon.

However, now how do we analyze these fragments? So, one way by measuring their mass. This is what is known as mass spectrometry. Now, in the case of pyrolysis mass spectrometry what you are doing is you are utilizing the pyrolysis process for the fragmentation of your heavy hydrocarbons and this kind of this technique is used for analyzing fossils. Fossils contain organic matter and also they are extremely valuable.

You just find one fossil, you cannot have several grams of it. What do you find? They are very smaller quantities are available, they are very valuable materials. All of these reasons it is very important that we can just guess their molecular structure using very small quantities.

Often, we are making a wire or at least traditionally that is how it was done, you make a metal wire which can be joule heated, coat your metal wire with whatever material you found. And, then heat that wire, that material will then pyrolyze fragment and then you can analyze the fragmented parts. So, these are some of the applications of the pyrolysis process, pyrolysis of solid polymers.

Now, how do we find out the mechanism of pyrolysis for a certain given material? What you can do is you can analyze the by-products. This is what is also the fundamental principle of mass spectrometry. You can analyze the by-products and then based on that you can guess what happened.

But, this is not the only thing. When we understand the pyrolysis mechanism of a polymer we need to understand two things; what are the chemical structures that are being formed, so, how chemically it is breaking apart. But, we also want to know whether it is undergoing coking or charring. Whether it is going through a semi-solid phase or not, because that decides that determines a lot of things for the type of carbon you obtain. One thing you will definitely do is analyze the by-products. What you will also do is you will see what kind of pattern you get when you carbonize something.

Here I have taken an example of microfabricated carbon structure. You know that in the case of large structures you use a slightly higher temperature and in that case also you need to do multiple times, you need to do resin impregnation for example, to get rid of the porosity.

But, in the case of micro nanoscale devices, because the structures are extremely small, they offer a very high surface-to-volume ratio. So, the defects, as well as by-products, can anneal out easily and that is why you can work with slightly lower temperatures.

The point is that one interesting thing that microfabrication also offers is a platform to study the mechanism of pyrolysis. How? Because you can make structures and then see what is a shrinkage pattern. And the shrinkage pattern tells you about coking or charring also.

In this particular structure that you see here, this is Atomic Force Microscopy tip that we fabricated on top of a silicon cantilever. So, you can see this structure is a silicon cantilever and using two-photon lithography, we pattern this tip, the conical shape and then this was carbonized at 900 °C.

And you can see here and I showed this picture here, there is a big black circle if you see at the bottom. This was the circle, this was the region where we had the polymer tip and after carbonization we had shrinkage. It has become so much smaller which was actually also in the case of microfabrication; this is very useful.

You can convert a micro-scale structure into a nanoscale structure by using the idea of shrinkage. But, you can see that this black footprint actually is a region where your polymer could not have the same shrinkage as it would have in the rest of the structure because of the fact that it had good adhesion to the silicon substrate. This tells you that it undergoes coking because these kinds of patterns would exist mostly for something that undergoes a semi-solid phase if you had a polymer that undergoes charring which means, it remains rigid. It might even have some softening, but still the skeleton would remain rigid. In that case, you cannot get these kinds of shrinkage patterns. In fact, too much shrinkage would cause cracks in these kinds of structures.

If you remember this particular image of a pillar, I had shown it to you in the very first class, when I was telling you the difference between micro-scale structures and microstructure.

So, in this image, if you see there is something very interesting. Llet me tell you this was a pillar we tried making very high pillars and then because it was too high accidentally it fell and then we took the pictures of the fallen pillar.

Now, this was fabricated on top of a silicon wafer. So, it had a substrate. There was a boundary condition. This is your silicon wafer and then on top of that, you have your pillar. So, this is how it was. Now, when the shrinkage took place during pyrolysis you see at the bottom of this picture you can see that there is still a certain region where the material could not shrink.

Because of the fact that it was attached to the silicon wafer and you can see what are the shrinkage patterns. This is yet another interesting structure. So, when we were making these AFM tips, at that time initially a lot of optimization was going on because of the fact that this was a polymer and we did not know much about its chemical structure.

If you purchase a lot of polymers nowadays especially for lithographic purposes, you may not know all the details of their chemical structure because companies selling their specialized inks and have their intellectual property rights protected. We respect that, but we need to find out whether or not the material is useful for carbonization. In that case, you need to here and there perform certain trial and error experiments, also for when you fabricating the structure. So, we made a tip and then we also placed it like this inside the furnace(refer to video at 11:28).

What would that do? Well, if the material is going through a liquid-like or semi-solid type of phase then you will get certain bending which you can actually clearly see in this structure. And, what is the solution to that well, next time you place it like this inside your furnace, there has to be some support base so that the tip is not broken. But, the point is that in that case, you need to optimize the shapes for every single polymer that you work with. You will play with all these parameters to find out whether or not your material goes through undergoes coking. So, this is how we come up with some mechanism of pyrolysis.

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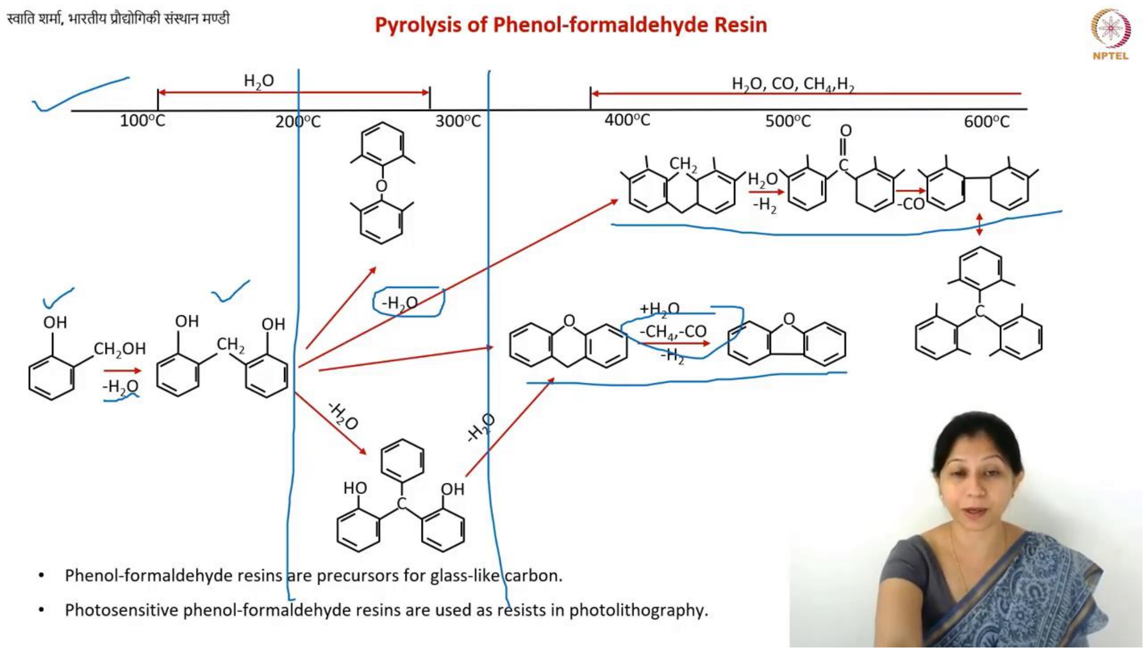

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Pyrolysis of Phenol-formaldehyde Resin

- Phenol-formaldehyde resins are precursors for glass-like carbon.
- Photosensitive phenol-formaldehyde resins are used as resists in photolithography.

Now, we will let us see some examples. So, the first example we have here is that of phenol-formaldehyde resin. Phenol formaldehyde resin, why? Because they are very common precursors for glass-like carbons for microscale as well as large industrial scale. Remember that, the phenol-formaldehyde resin is not just one chemical compound, it is a class of compounds. So, you basically have phenol and formaldehyde and you mix them together you get these kinds of resins. However, you can have different ratios of phenol and formaldehyde, you can also have certain functional groups for example, induce epoxy group.

These functional groups will also slightly change your pyrolysis mechanism. But, some basic compounds are often found in the pyrolysis of phenol-formaldehyde resin. So, you analyze the pyrolysis product and this is what I am going to show here.

You see there are a lot of chemical reactions here and I have taken some of them from certain books which I recite at the end of this lecture. You see that you have a phenol structure and you have a formaldehyde molecule and then you add these two together and then certain water will come out and alcohol will come out as a by-product. Once you heat so, there is also a temperature axis this is where I have shown the pyrolysis temperature and you also see that we are only talking about the region which is within 600 °C because this is the region 600 700 °C where you have most of the important chemical reactions of fragmentation reactions taking place.

After that you basically lose hydrogen and then at some point carbon-carbon bond formation starts or pretty much starts also at the same time, but the chemical reactions when you losing non-carbon atoms is what is happening during your pyrolysis region.

If you increase the temperature, from room temperature let us say you go to 200 °Cand then you go to 300. These are some of the compounds that have been found in the analysis of the pyrolysis, you can see that there is not just one type of molecule but you will get different types of molecules, but these are some of the primary products.

As you keep on increasing the temperature then you see there are different chemical structures, they are all connected with each other as well, of these reactions are also secondary reactions. You also see what is very important is that you have water molecules being produced, you also have methane and carbon monoxide being produced remember that carbon monoxide, carbon dioxide and methane are very stable hydrocarbons.

Whenever they get a chance, they will be formed and when I say they are stable; that means, they have a very negative enthalpy of formation. This is also a very important for us to understand, but you will see that hydrogen also being produced. All of these gases, you will find in your synthetic gas that comes out of pyrolysis of phenol-formaldehyde resin and the tarry byproduct.

You can find some of these chemical structures which do not undergo secondary reactions and these gases are volatile. So, they just escape the material. Now, some of them will also be mixed inside your synthetic gas if they are very volatile and if they are not so volatile, but they do not want to undergo secondary reactions, then you will find them in your tars.

Tar is basically this mixture of a lot of different small hydrocarbons, but not too small. So, this is phenol-formaldehyde resin. What do we use it for? For making glass-like carbon, and photosensitive are used in photolithography, and that you can use for microfabrication using glass-like carbon.

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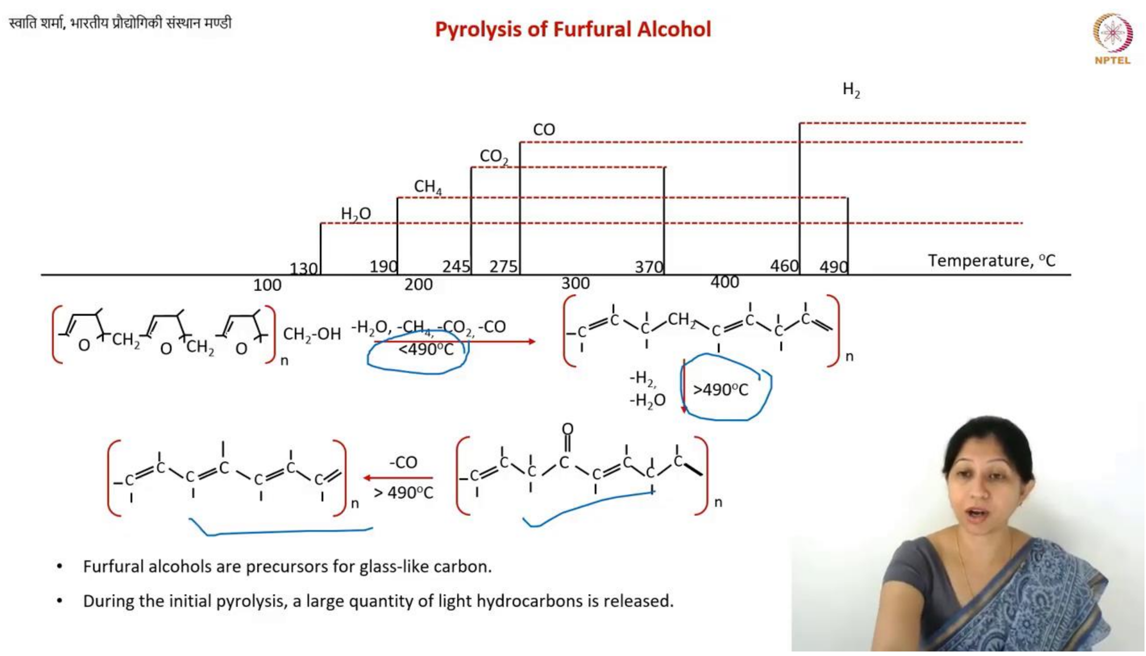

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Pyrolysis of Furfural Alcohol

- Furfural alcohols are precursors for glass-like carbon.
- During the initial pyrolysis, a large quantity of light hydrocarbons is released.

Second example is that of poly furfural alcohol. So, this is a type of furan resin. Furan is basically this ring which contains oxygen. Here also I have shown the pyrolysis temperature and you can see now here, I have made these different steps where which gaseous product is most prominent at which paralysis temperature.

You can also see what happens above 490 °C. Here I have only shown it up to 490 just because of the lack of space, then I went down here. So, you can see these reactions take place below 490 degrees, this again can be 500. 490 is not the exact value depending upon the furan resin structure the poly furfural alcohol.

They do have very well-defined structures, but still the variation can be there slight variation, but let us say above 490, you get these kind of compounds. This is the standard fragmentation pattern for a furfural alcohol. Again, what do we use it for? This is also a precursor for glass-like carbon and this is relatively inexpensive compared to phenol formaldehyde resins. So, we utilize that. Now, you will see that during the initial pyrolysis, you do have a lot of weight loss in the case of furfural alcohol. You see that there are a lot of gaseous products being they are being released from this kind of chemical molecules.

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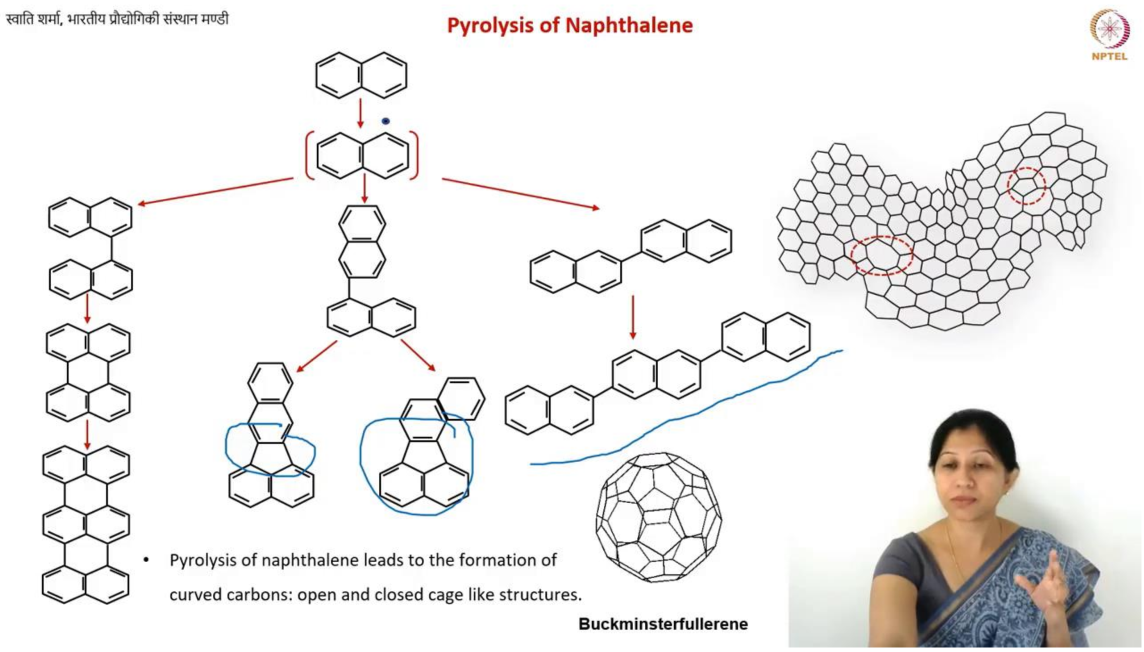

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Pyrolysis of Naphthalene

- Pyrolysis of naphthalene leads to the formation of curved carbons: open and closed cage like structures.

Now, let us also talk about pyrolysis of naphthalene. Naphthalene is not a resins, it is not a polymer. It is just an organic material and at room temperature it is in solid form. Why did I choose the example of naphthalene? Because there is something very interesting about it.

Number 1; it is a very simple molecule. You can see that this is one of the simplest bicyclic structures and so it is easy for us to understand. Also, we can theoretically predict a lot of chemicals that might be produced when you heat treat naphthalene.

But when you actually perform the pyrolysis, it has also shown to yield some fullerene molecules, completely spherical Buckminsterfullerene like molecules. So, here you can already see when you pyrolyze your naphthalene, you get cyclic structures, but you also get these 5-membered rings here and there, not all of them by the way. Some of them are also very highly planar kind of structures, but some of them will contain non 6-membered rings especially 5-membered rings. So, they do have a tendency to bend. And, when you have massive sheets of such structures where you have e 5 or 7-membered rings, and there is a possible bending and what do you get?

This is your curved carbon structure and when you get massive sheets of curved carbon structures often you may also end up getting Buckminsterfullerene or structures that have very high curvature even if they are not completely closed. So, the pyrolysis of naphthalene has actually been reported to yield fullerene structures. So, this is yet another example. Now, we will take also another similar example.

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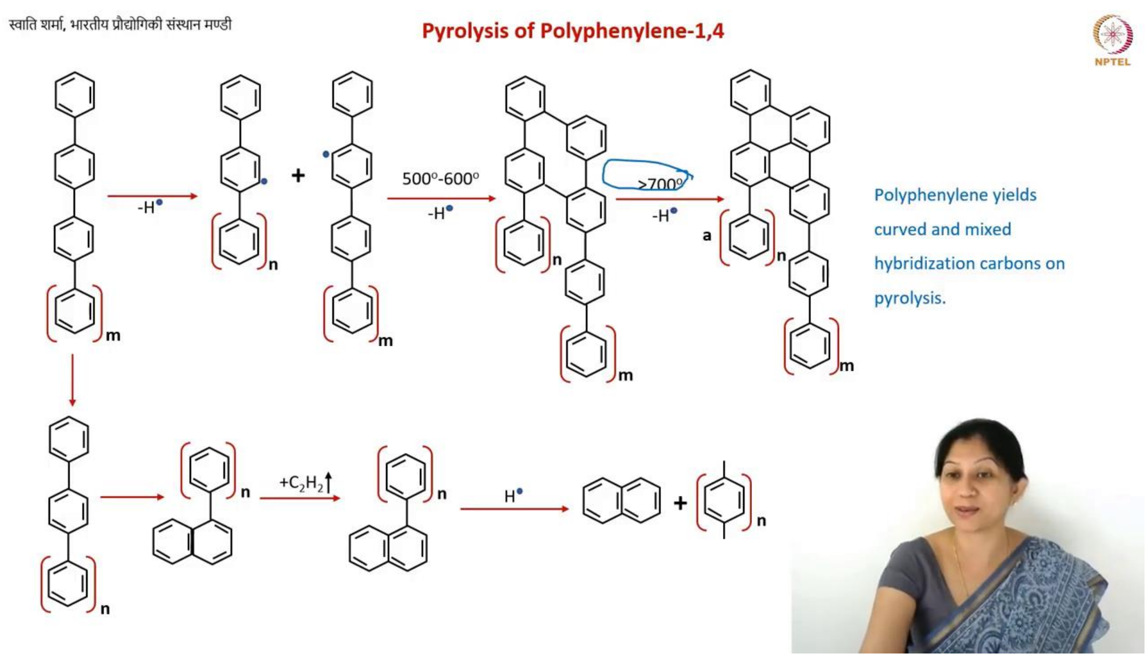

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Pyrolysis of Polyphenylene-1,4

Polyphenylene yields curved and mixed hybridization carbons on pyrolysis.

This is the example of polyphenylene. Again, this is not a heavy hydrocarbon that is why I said similar example because it is not a very complex molecule. But again you have these structures. There is a certain cyclization that is taking place and what is happening above 700 °C also you can say see that.

Now you are getting large sheets of aromatic carbon and this kind of polymers can actually yield very good graphitic carbon. So, this chemical has not been reported, at least I could not find any paper where they say that you will have fullerenes being formed or curved carbons. I also do not see any 5-member rings, but you can try it out and see what do you get.

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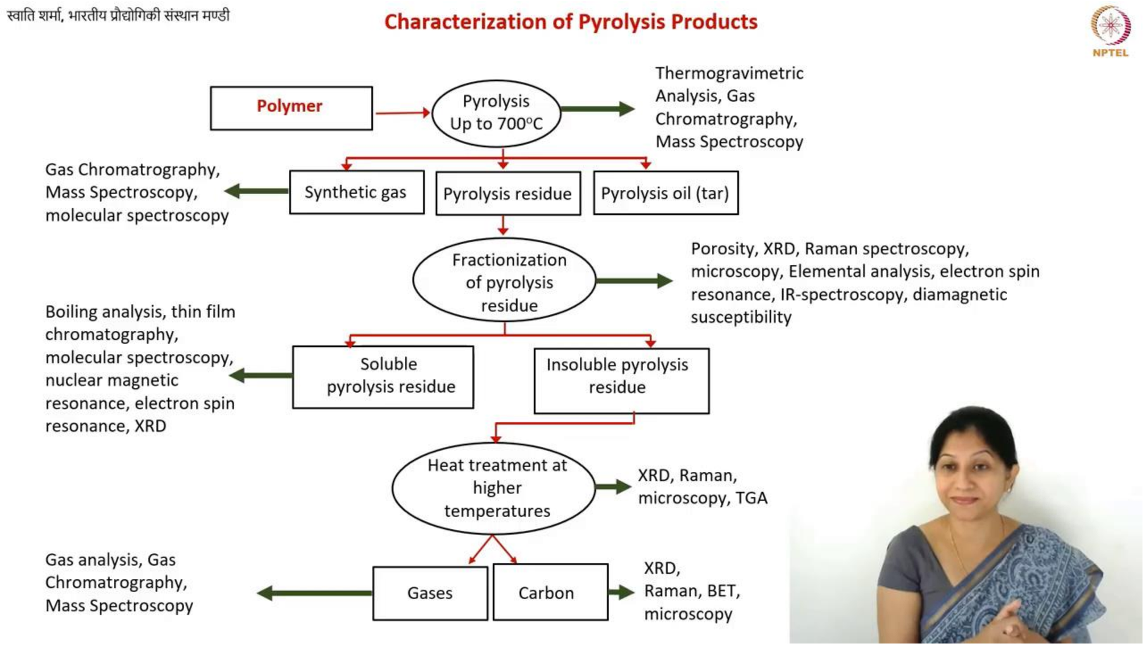

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Characterization of Pyrolysis Products

Polymer

Pyrolysis Up to 700°C

Thermogravimetric Analysis, Gas Chromatography, Mass Spectroscopy

Gas Chromatography, Mass Spectroscopy, molecular spectroscopy

Synthetic gas

Pyrolysis residue

Pyrolysis oil (tar)

Fractionization of pyrolysis residue

Porosity, XRD, Raman spectroscopy, microscopy, Elemental analysis, electron spin resonance, IR-spectroscopy, diamagnetic susceptibility

Boiling analysis, thin film chromatography, molecular spectroscopy, nuclear magnetic resonance, electron spin resonance, XRD

Soluble pyrolysis residue

Insoluble pyrolysis residue

Heat treatment at higher temperatures

XRD, Raman, microscopy, TGA

Gas analysis, Gas Chromatography, Mass Spectroscopy

Gases

Carbon

XRD, Raman, BET, microscopy

Now, coming to the characterization of the pyrolysis products. I told you that all of these things we have decided based on the characterization of your byproducts. At what stage, what kind of characterization technique will you use? That is very important. If you are given an unknown polymer or you do not have complete information about it, then what do you do?

How do you find out, what is going to happen? Number 1; one good idea is to make small-scale structures and then see the shrinkage patterns especially if you have it attached to a substrate. That will give you the very first idea of whether or not it is undergoing coking. Whether or not you are going to get glass-like carbon from it or graphite-like carbon from it or it is undergoing charring.

Most of the synthetic polymers would typically undergo coking as a rule of thumb. So, but still, that is something you could, that is your first experiment, but then you want to understand or analyze the byproduct of pyrolysis. Here is a prepared chart where I showed what techniques can be used, you can also have some other advanced techniques. But, these are often use used techniques. So, you pyrolyze your polymer up to, let us say 700 °C. We are not talking about very high temperatures. What do you get? You get synthetic gas, you get pyrolysis oil or the tarry product and then you get some solid product. If you have performed this process under nitrogen or under a strictly inert environment, in that case, you will often get a lot of solid residue and if there is any combustion also taking place in the process then you will get smaller fraction of the residue solid residue.

Now, what is important for us? All of these things. So, you also need to analyze the gas tars and now what do you do with the residue? First, let us complete the chart here. What do you do with this residue at 700 °C; at this temperature you do not have carbon yet.

If you call it carbon then it has a lot of impurities because it also has these hydrocarbon impurities still mixed. So, what you can do is you can fractionalize this residue. So, you can basically now separate out the soluble products or soluble chemicals and insoluble ones from that thing.

This is going to be a simple fractionalization or simple separation because you can actually try you take this pyrolysis residue and you try to dissolve it into as many organic solvents as possible. Why organic solvents? Because typically all of these are organic compounds for example tar-like materials are soluble only in organic solvents polar, non-polar you can try both.

After the soluble things will be in the solvent, they will come out and then you still have some insoluble pyrolysis residue which most likely contains all of your carbon because carbon is typically insoluble in everything. It is the hydrocarbons that will be soluble.

What do you do with this insoluble residue? Then you further heat treat it. If you want to get graphite you can go for graphitization temperatures or you can stop at a certain temperature let us say 900 or 1500 °C or whatever. You heat treat this residue now, the insoluble part for at further heat further temperatures.

And, at the end again there will be some non-carbon entities. maybe there is still some hydrogen left over. So, you will get some gaseous product and then you will get carbon and if you want to go for graphitization then this carbon is further processed and you want to decrease the d spacing.

This is basically the entire chart of pyrolysis. Now coming to the characterization technique at each step. When you are performing the pyrolysis itself, you can do something known as thermogravimetric analysis, we are going to discuss all the characterization techniques.

When you perform this is commonly known as TGA, you are basically looking at the weight loss. Weight loss gives you a lot of information about what is happening to your material. You can do gas chromatography, similar to mass spectrometry. In gas chromatography basically you are analyzing again the fragments of your fragmented molecules or whatever came out after the fragmentation of your heavy hydrocarbon.

You can analyze them using gas chromatography or mass spectrometry. There can be also some other methods, but these are commonly used methods. So, this is what you do at the pyrolysis stage. Now, when you have the synthetic gas and the pyrolysis oil or tar-like materials, you can you analyze them. Again using gas chromatography, mass spectrometry, and also various types of molecule molecular spectroscopy techniques, for example, you can use infrared spectroscopy and so on.

Also, for the pyrolysis oils, you can use very similar techniques. Here rather than gas chromatography you will use mass spectrometry and you can also use very various chemical analysis techniques. Now, for the solid residue that you further process, you can also do certain analyses. Whether you can dissolve it into a solvent and then take the fraction which has all the hydrocarbons dissolved into it and then you can analyze it using various techniques. Or, you can just take the residue itself. You can measure the porosity of that residue.

You some carbon in it and you already have some sheet-like structures because you see that cyclization does take place before 700 or around 700. So, you will have some sheet-like structures and the d spacing can be analyzed for them.

Of course, that will be higher than that of graphite for sure, but you can measure it to understand how much higher is it; what is the d spacing value. You can also do Raman spectroscopy at this point, maybe you will get a very complicated spectrum.

You can use electron microscopy, optical microscopy. You can do elemental analysis. Actually, elemental analysis is a simple technique, it becomes very important at this stage. Often you will use carbon, hydrogen, oxygen, nitrogen analysis that is also available rather easily. Now, you can understand whether you have 90 percent carbon, 95, 98. Other techniques, electron spin resonance is also a very interesting technique where you can find out the nature of the radicals that are present inside your material.

All of these diamagnetic susceptibilities are often used for understanding the d spacing of carbon materials. So, you can use all of these techniques for analysis. Also, for the soluble part that I was discussing before there, you can do a lot of things. You can do fractionalization boiling analysis, you can use TLC, thin-film chromatography. And you can separate because once you have l some organic materials dissolved inside a liquid then it becomes much easier to perform analysis. You can even perform NMR of course, ESR again. And, you can also then perform X-ray diffraction analysis, you can also perform X-ray spectroscopy rather.

And also for the surface analysis and for a fractionalized pyrolysis residue, you can also use XPS which is known as X-ray photon photoelectron spectroscopy that gives you details about the surface functional groups. So, these are the techniques then you can utilize at these stages.

Once you have heat-treated carbon then X-ray diffraction is the most common technique. You want to know the d spacing and that is why you use X-ray spectroscopy. Raman spectroscopy now will give you a good value of the disorder and graphitic content in your carbon.

You can of course, use electron microscopy. TEM nowadays has become very common, you can still use TGA if you want to see what is the weight loss because of the loss of hydrogen if you had any. So, you can still perform TGA at this stage. BET is a surface porosity or surface area measurement technique, you can do all of these techniques again and analyze the gaseous and pyrolysis products. You can also have any other technique for measuring porosity. There are many new advanced techniques nowadays you can perform tomography and so on.

You can use various other techniques as well, but the idea is that these are the stages at which you will analyze your different pyrolysis products and that is how you will come up with the mechanism of pyrolysis for a certain given polymer.

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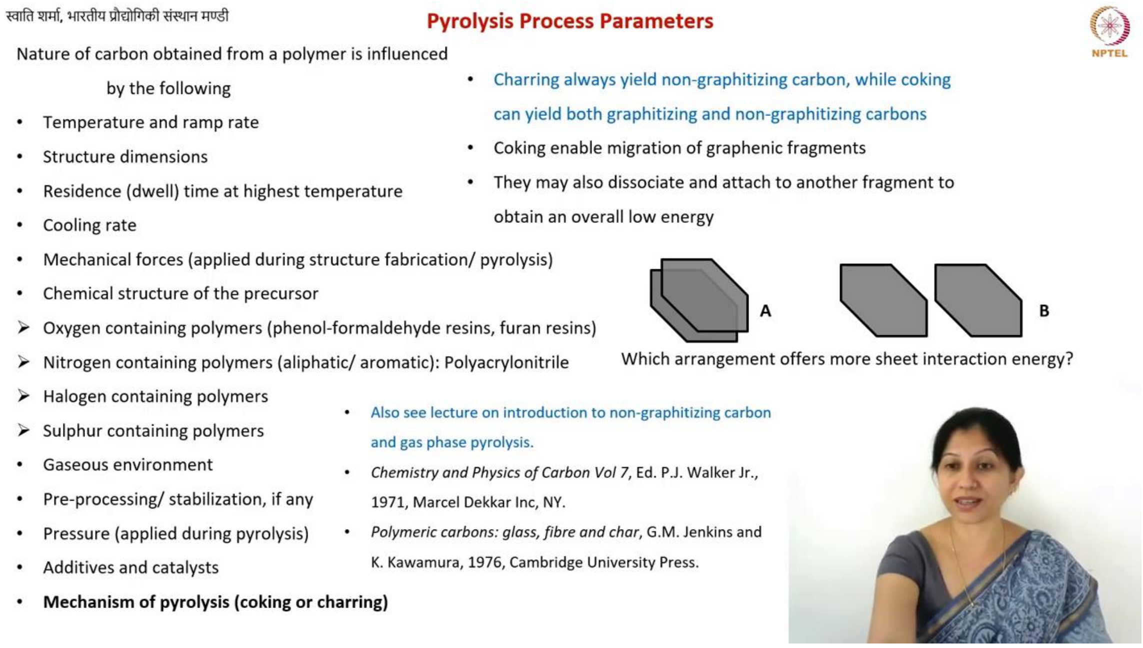

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Pyrolysis Process Parameters

Nature of carbon obtained from a polymer is influenced by the following

- Temperature and ramp rate
- Structure dimensions
- Residence (dwell) time at highest temperature
- Cooling rate
- Mechanical forces (applied during structure fabrication/ pyrolysis)
- Chemical structure of the precursor
  - Oxygen containing polymers (phenol-formaldehyde resins, furan resins)
  - Nitrogen containing polymers (aliphatic/ aromatic): Polyacrylonitrile
  - Halogen containing polymers
  - Sulphur containing polymers
- Gaseous environment
- Pre-processing/ stabilization, if any
- Pressure (applied during pyrolysis)
- Additives and catalysts
- **Mechanism of pyrolysis (coking or charring)**

- Charring always yield non-graphitizing carbon, while coking can yield both graphitizing and non-graphitizing carbons
- Coking enable migration of graphenic fragments
- They may also dissociate and attach to another fragment to obtain an overall low energy

Which arrangement offers more sheet interaction energy?

- Also see lecture on introduction to non-graphitizing carbon and gas phase pyrolysis.
- *Chemistry and Physics of Carbon Vol 7*, Ed. P.J. Walker Jr., 1971, Marcel Dekkar Inc, NY.
- *Polymeric carbons: glass, fibre and char*, G.M. Jenkins and K. Kawamura, 1976, Cambridge University Press.

Finally, what are the parameters that influence your pyrolysis process and why do we need that? Because this is very important for us. This is what will determine the microstructure of the final carbon product that we are going to get. Some of these important parameters, of course, one thing you know is the temperature.

The temperature of pyrolysis and the temperature of overall heat treatment, both are very important. Even if you are getting the graphitizing carbon from a certain polymer, still whether or not you will get graphite that will depend on the further steps of your heat treatment.

So, the entire heat treatment process and the temperature of everything is very important. The temperature ramp rate is also very important. What is temperature ramp rate? That basically tells you how fast or how slow you are increasing your temperature. So, 5 °C per minute or 25 °C per minute will make a lot of difference.

If the pyrolysis process is very fast, in that case, you are not providing enough time for your by-products to anneal out or to gaseous products. So, they end up participating in the secondary reactions or they may end up redepositing on top of your material.

In fact, if you perform pyrolysis inside a closed container or open container even that makes a lot of difference because there is this re-deposition or re-participation of the byproducts in your reaction. So, all of these things will definitely make a difference.

The dimensions of your structure; now multiple times we have talked about whether you have very small structures let us say smaller than 20 nanometers then they may graphitize even at a very low temperature. Because this depends on various factors, one is the annealing out of the defects as well as by-products. Also the idea that the voids cannot really be accommodated in a very small scale structure. So, the voids will have no other option, but to anneal out. Because of these reasons the structural dimension dimensions make a lot of difference. And, this is also important for us because nowadays we often working in the nanoscale.

So, some of the principles of the bulk pyrolysis or bulk industrial fabrication or manufacturing of carbon materials cannot be directly translated to nanoscale because of the structural dimension changes. So, this is an important factor. The residence time also it is called the dwell time is how long do you keep your material at highest pyrolysis temperature or highest heat treatment temperature for that is the residence time. This is important. What else?

Cooling rate; we have not talked about cooling rate, also most of the lab-scale furnaces may not even allow for control on the cooling rate, but large massive industrial furnaces definitely allow, they facilitate water cooling. Then you can also set the cooling rate and that also makes a difference to the microstructure of your carbon.

Mechanical forces: here I am specifically talking about mechanical forces that we apply during the fabrication. If you are pulling fibers and you try to use a rotating drum collector during electrospinning; this you will learn in the electrospinning lecture, in that case you will have these more aligned polymer chains to start with.

This also makes a difference to the microstructure of carbon, but since we are talking about pyrolysis here, even during pyrolysis if you place a certain weight on top of your carbonizing material in that case also can lead to certain chain alignments and that can give you a slightly different microstructure than what you expect.

Chemical structure of precursor; of course, this is the most important thing. It depends upon your precursor and what you are going to get. This has been then further divided. There are different time types of carbon precursors some of them contain oxygen. For example, the examples that we discussed today.

Some of them contain nitrogen then nitrogen can also be either aliphatic nitrogen or aromatic nitrogen. One good example of aliphatic nitrogen-containing polymers – polyacrylonitrile again is used for making carbon fibers and we will separately discuss it during our fiber classes.

Halogen-containing polymers and also sulfur containing. So, all of them can have slightly different pyrolysis mechanisms, and accordingly, you will get slightly different microstructure in your carbon.

The environment in which you perform your pyrolysis. So, you will often perform it in an inert environment under nitrogen, but you can also use forming gas. So, you have 5 percent hydrogen mixed into it or you can perform the pyrolysis also under vacuum. So, the environment in which it is performed also makes a difference because that makes the two things. One of course, it can induce certain chemical reactions, provide a reducing environment, so that will probably change slightly the byproducts that were being found. So, inert atmosphere versus reducing atmosphere can have slightly slight differences in the reaction mechanism. Also if you are performing it under a vacuum maybe your by-products are getting more easily sucked inside. So, these things will also make a difference.

The pre-processing or stabilization of the polymers; for example, in some cases it is required for polyacrylonitrile to do some pre-processing. Many other polymers require some sort of even pitches, not just polymers. You need to do some pre-treatment for stabilization and then the conditions that are used for stabilization also become very important.

Pressure; well we have not talked about pressure-induced pyrolysis, but if you have an autoclave process, you have certain induced pressure during your pyrolysis in that case that can also influence the microstructure of your carbon that you get.

Additives, catalysts; will definitely make a lot of difference that how do we get graphite using metal carbides. So, even in the case of chemical vapor deposition that we will talk about during nanomaterials, catalysts make a lot of difference and they very strongly influence the formation of carbon structures or the type of carbon that you get from that.

Finally, the mechanism of pyrolysis; that is the most important thing, coking and charring we have been discussing that. So, these are all the parameters, maybe there are some more, but these are the primary parameters that will influence your pyrolysis process, the mechanism, and accordingly the microstructure of the final carbon material.

One very important thing that you must remember is that whenever a polymer is undergoing charring, you will never get graphite. You will predominantly get hard carbons or what is known as non-graphitizing carbons. By the way, non-graphitizing carbons are also known as hard carbons because they are hard and brittle.

And, graphite-like carbons although sometimes they can also be hard, often they are called soft carbons because they have this layered structure. So, you can get soft carbons you will typically get or graphitic carbons only when there is coking mechanism.

However, coking does not always give graphite. Sometimes you will have graphitizing carbon, sometimes you will have non-graphitizing carbon, but charring will always give non-graphitizing carbon. So, this is something very important. Now, how does coking help in yielding graphite-like structures?

Well, coking enables the migration of your graphene-like sheets or graphenic sheets which are being formed during the initial stages or even cyclic structures polymeric, they still contain hydrogen, so you do not call them graphene yet, but these large scale cyclic structures can easily float if you have this coking mechanism.

If you want to get graphite-like structures then you need to have sheets organized on top of each other that is when you will get good stacking. Even in the case of glass-like carbon you do have these are non-graphitizing carbons, they contain a lot of curved carbons.

But, even in that case the dissociation of these fragments from larger fragments and then they float and then they migrate and attach to some other. So, they are able to form more stable geometries in a more convenient fashion if you have a fluid-like or liquid-like or semi-solid-like structure during their carbonization.

So, coking is very important for giving any carbon with flat and shiny surface of course, and any graphitic carbon. In charring, if you keep on increasing the pyrolysis temperature or the heat treatment temperature at some point you will get some short-range order.

But compared to carbons that are prepared by coking that is not going to be as good or the electrical conductivity is not going to be as high. So, these are some very important parameters. So also, to show you how does this works with the coking and coking mechanism.

You know the sheets can actually align on top of each other, in the case of charring that will not happen. If there are two sheets next to each other, there is little possibility that they can place themselves on top of each other. So, this is for you to think which of these structures is better in terms of graphitization or which of them enables more interaction between the two sheets.

It is very clear, but this is for you to think. So, now for further reading, so, I already told you that you must look at the lecture on non-graphitizing carbon in the gas phase pyrolysis maybe some other lectures as well. These are two books from where I have taken some of these diagrams especially the diagrams on the phenol-formaldehyde resin and furan resin fragmentation patterns. So, you these books you can also use for further reading.