

**Carbon Materials and Manufacturing**  
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**Lecture – 17**  
**Kish Graphite and PVC-Derived Graphite**

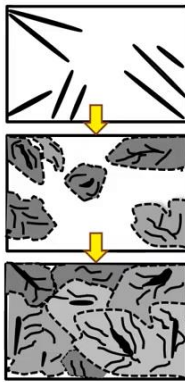
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**Method II - Kish Graphite**



- Kish Graphite (KG) precipitates (along with other residues) during steel manufacturing on the melted iron surface.
- It is refined using sieving, flotation, milling, magnetic separation etc. Up to 99% purity and *mm*-scale large flakes can be achieved.
- It grows as dendrites which form plates (may span up to several *cms*; thickness: 0.01 to 0.1 *mm*).
- Fast-cooled KG has thinner plates but longer dendrites; slow-cooled has thicker plates/ less spread.
- Exists in the form of small platelets that are powdered or directly used in various applications.



Kish Graphite Formation

**Mechanism of formation of Kish graphite:**

- When carbon-iron alloy melt is cooled below the liquidus temperature, carbon precipitates as graphite.
- This is atomic deposition of carbon (although in a large surface).
- If the deposition is layer-by-layer under sudden changes in temperature, graphite is formed.
- The growth mechanism involves nucleation, growth and spread of the crystal in a rapid manner.
- KG is used directly or after pulverization in batteries and related applications.
- KG is similar to natural flake graphite, but industrially the term KG is more common.

**Liquidus line** in an equilibrium phase diagram is the line between liquid and liquid + solid phases.



Hello everyone. In this lecture, we are going to discuss another method of synthetic graphite production or artificial graphite production. This type of graphite is known as Kish graphite. Now, I am not 100 percent sure if it is pronounced Kish or Keesh, because I know that this word is taken from German word which is Keesh.

And Keesh basically means all the impurities like dust particles and stone and things like that which are mixed with your food grains. Now, the term was borrowed because of the fact that this is sort of the waste material from your steel manufacturing industry. What would come out as a waste of steel manufacturing? You have iron, you have carbon, and you also have some other minor quantities of other elements depending upon the exact composition of your steel.

When you mix all of these elements and when you rapidly cool this entire mixture down, then what happens is the excess elements from iron like excess carbon or other elements.

whatever did not participate in steel making, it precipitates out and it deposits on top of the surface of your ingot that you are making.

So, from that waste material, we collect that waste or the film of that waste that gets deposited, and then we extract graphite from it. How will you do that? Typically, you will use methods which are rather similar to what you do for graphite ores. You will initially do some sieving or some basic filtration methods, but after that the primary method would still be floatation.

You remember the froth floatation methods, this always works for graphite because graphite is hydrophobic and it is also light material. So, it can easily float. And often the other impurities are more like heavy metal impurities and salts and so on, so they are either hydrophilic or they are heavier. So, they get precipitated. So, we will do a floatation.

And then of course, afterwards we can also do milling. We can also do a little bit of milling or powdering of the mixture beforehand. And then we will also do magnetic separation because this material came out of iron, it was a steel making by product. So, it will have certain iron. And that is very easy to remove because you can always do magnetic separation to get rid of your iron. By doing this, you can actually get up to 99 percent purity of your graphite.

And this graphite is in the form of flakes. In fact, it is similar to the flake graphite that you get naturally. And sometimes in the literature you might also find the word flake graphite which is used for this kind of material. Now, how does it grow? I have shown it here in this picture. You have a new creation of certain dendrites. And dendrites are like these crystal structures which grow in two dimensions.

Most of the flakes grow in this form. You will have nucleation and then growth of your dendrites. And then at some point, these dendrites grow so much that they sort of overlap each other, and then you will have a complete film. This is basically similar to film formation. Often you will have this nucleation and growth and then the complete area is covered. This is how the graphite flakes grow on top of the surface of steel.

I mentioned that when you cool the alloy, only then you get this graphite film. So, by controlling the cooling rate, you can have slightly thicker graphite flakes, but in that

case, the spread of the dendrites may not be long. Depending on the condition, you can have either long but thick flakes, or short but thick. When you want a thick flake, you want larger  $L_c$ . What is  $L_c$ ?  $L_c$  is your stack thickness. If that is more important for your application, in that case you would slightly choose the condition accordingly.

But remember that this is a byproduct of steel manufacturing. You will rather optimise process depending upon what kind of steel you want. You may not have the control over all the parameters. But these are the conditions that will give you different types of Kish graphite.

Of course, for various applications this can be used. You can use it directly as flakes. So, the flakes are typically 0.01 to 0.1 millimeter size. They can also be larger though as I mentioned depends on how you are preparing it. But you can have a reasonable flake size and also reasonable flake thickness. So, depending upon your application, you can then post-process it and then use it.

Now, what is the mechanism of the formation of this? Why do we have? What happens? Why do we get this graphite out of it? If you think about it, you have carbon particles which are distributed throughout your alloy. Let us assume that they are uniformly distributed inside your steel alloy. And now there is a sudden quenching or sudden cooling. In that case, they just all want to go out. However, on top of the surface of your steel, you have a lot of carbon atoms, millions of carbon atoms, and they do have the energy that is required. So, very suddenly they form a carbon material.

What is interesting is that this carbon material could have been anything. Why graphite? Because graphite is the most stable form of carbon. Whenever you have atomically deposited carbon, and you also have these very sudden cooling conditions, it will try to go into its most stable state. The carbon will try to go into its most stable form, which is graphite.

We have discussed the phase diagram of elemental carbon. Graphite and diamond phases were more important for us. And we did not discuss so much about the solidus and liquidus lines.

But if you have learned the iron carbon phase diagram before you know that liquidus line is the line that is between the solid plus liquid state, and the completely liquid state ok.

Basically above this line, your material, element or alloy will always be liquid. However, as soon as you go below the liquidus line, that means, now some solid may also exist along with the liquid, and that is when you have the Kish graphite forming.

Whenever your cooling is done below the liquidus line and the solid particles start to precipitate and coexist with the liquid that is the time when you get these graphite flake formations. So, this is an atomic deposition. Although it is a very large surface, it is a very sudden atom by atom deposition of carbon. And this is done in layer by layer fashion. And since we have these very sudden changes that is why we get graphite which most stable form.

We already learned that we have a nucleation growth and spread of the crystal structure, but in a very rapid manner. You can use this material directly or you can then pulverize and then use it for various applications. Basically this is all about the Kish graphite.

The good thing about this material is that we get it from the waste. So, it is graphite, it is crystalline, it is actually similar to the flake graphite that you can find naturally. Because we extract it from the waste, it is relatively inexpensive. And it has a reasonable crystal size and crystal structure, so it is usable for a lot of applications, it also has a very high purity.

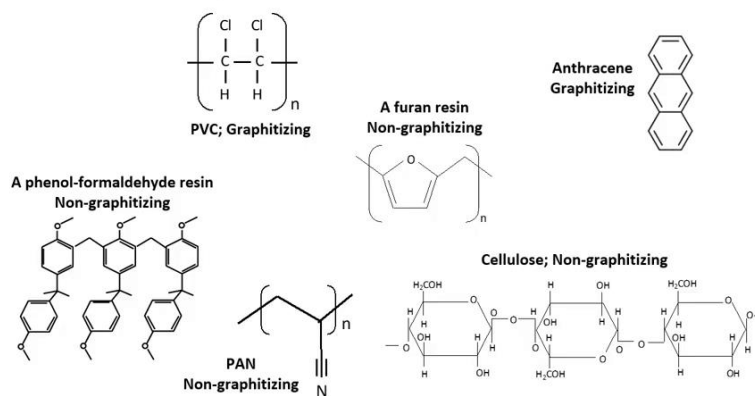
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### Method – III: Graphite from Heat-Treatment of Polymers



- Polymers (synthetic and natural) can be heat-treated under inert environment to produce carbon.
- Type of resulting carbon strongly depends on the precursor. **Many polymers do not yield graphite or even graphitic carbon.**
- Polymer must have a high carbon content and a carbon backbone to carbonize.
- Polymers with a high oxygen content typically do not carbonize well due to internal burning.
- If a polymer is semi-crystalline (e.g. Polyvinyl Chloride) there is a higher probability to obtain graphitic carbon.



The third method of graphite production is the heat treatment of polymers. The first method was heat treatment of petrochemical products such as coke and pitch. The heat treatment of polymers is done for making a lot of carbon materials, not just graphite. In fact, it is rather used more for making what is known as non-graphitizing carbons. And then there are fewer polymers, however, that will also give you some graphite.

At some point, I must have mentioned to you that when people were actually trying to prepare graphite from the polymers, they ended up making other types of carbons. So, what happened was you know in the 1940s and 1950s, graphite became very important for nuclear reactor applications and in batteries and so on. And at that time, people did not use other forms of carbon, they rather prefer to use graphite. So, it was needed in very large quantities. And then people ended up trying out different things; one of them was to convert polymers into carbon.

People initially thought that anything when it is heated to up to  $3000^{\circ}\text{C}$  then it will converge into graphite. So that was the initial impression people always thought that maybe at  $1000\text{-}2000^{\circ}\text{C}$ , we still get some sort of disorder in the material.

But the material will continue to get more and more order which sounds obvious because if you keep on heating it, at some point before its sublimation temperature which is about three  $3500^{\circ}\text{C}$ , it should convert into graphite completely.

But it turns out that does not happen. In fact, there are certain types of carbon materials, no matter how high you will heat them, they do not convert into graphite. So, they never have this anisotropic crystal structure and never have the single layers properly arranged in AB AB A fashion. We will learn about those materials known as non-graphitizing carbons in our next couple of sections, but now we will talk about graphite. So, not all polymers give you graphite as I mentioned.

You should have certain anisotropy which helps or you can have an aromatic backbone. But this may not always work. What aromatic backbone means you have aromatic structures, ring-like structures. And the backbone of a polymer means, this is the primary structure of the polymer. You can have something else on the sides, but this is sort of the backbone that is what is called the primary structure of the polymer.

Aromatic means you already have these 6 membered rings. But of course, when it is a polymer you have hydrogen in like CH and CH. And you want to get rid of all hydrogen, and of course, all other elements as well. Since it was in the ring-like geometry, you will get these kinds of graphitic regions.

But graphitic does not mean it is graphite. When we say graphite, that means, you need to have 3D structures also at larger scale. It should not be a disordered carbon. It should be more of polycrystalline graphite. So, for that purpose, extremely few polymers can be used.

You should have high carbon content that is a very general thing to say. Even though you have a high carbon content that does not really determine the crystal structure. It just determines whether or not you will get carbon at all. Because some molecule polymer molecules, for example, they contain a lot of oxygen. When the polymer chain itself contains a lot of oxygen in form of CO bonds and so on. Now, you keep it in the furnace, you keep it under the inert atmosphere. You have nitrogen or argon flowing inside your furnace. However, the polymer itself contains so much oxygen that it will burn. It will get oxidized if not all of it but a lot of it.

So, what you get at the end? You will get just some bits of powder of the carbon and a lot of mass loss will take place and that is what you do not want.

Also, there are certain other oxidizing materials like chlorine. Typically, you do not want these in your polymers. But again there are no hard and fast rules. Sometimes you need to just try things out. Nowadays you have a lot of new polymers in the market. And there is actually a lot of research in the field of polymer chemistry.

When you have any new material, you can guess whether or not if it's a carbon backbone polymer, for example, you have PDMS which is mainly a silicon-based polymer. In that case, you can already say that there is very little possibility that this will give me any carbon. And even if it does give me a very small fraction of carbon, definitely the shape that I have made will be lost. I will just get some residual carbon.

But in the case of some polymers, you can say that I will get some carbon, but whether or not it will be graphite that is hard to say without any experiments. But in principle, if your polymer is already semi-crystalline, which means it already has some layered

arrangement, and if it has reasonably high aromatic content, then you might be lucky and you might get graphite out of it yeah. So, all these things I have already mentioned.

This polymer is known as polyvinyl chloride or PVC. You must have heard, this polymer is used for making a lot of things. For example, the plastic pipes that you see for you know agricultural purposes or for in any tubes. When you see these plastic pipes, grey colored, they are PVC pipes. And there are also a lot of composite materials that utilize PVC. You have various elastomers rubber-like structures also sometimes they are you know based on PVC. So, there are a lot of PVC, even there is carbon-reinforced PVC that you have in car seats. There are a lot of applications of this polymer.

And this polymer is actually a graphitizing polymer which means this polymer gives you a carbon material that is graphitizable or graphitizing which means it can be converted to graphite when you go to very high temperatures, unlike some polymers which will even at 3000°C only give you non-graphitizing carbon.

On this slide, now I have a few structures of the chemical structures of polymers. For example, anthracene will give you graphite on heat treatment. But there are also some other structures that I have drawn here, for example, a phenol-formaldehyde resin or a furan resin, we will discuss these materials, especially the polymers which will give you non-graphitizing carbon that we will discuss in the next section.

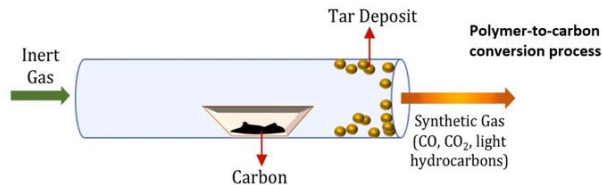
PAN or polyacrylic nitrile is actually a polymer that is used for making carbon fibers. And this typically gives you non-graphitizing carbon. However, under extreme conditions like under 3000°C and with very thin fibers, it has also been reported to provide graphite crystallites.

What we do for fibers, again we will talk about that in the fiber section. Cellulose gives you non-graphitizing carbon. If you take a piece of wood, that contains a lot of cellulose. So, you can actually try to put it in a furnace under an inert atmosphere, and what you will get will not be graphite.

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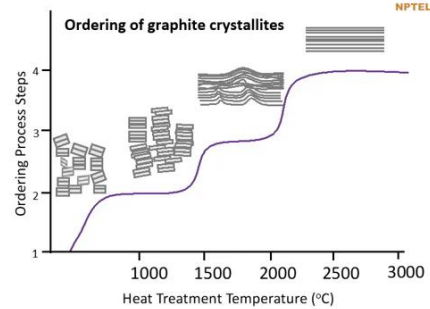
**Heat-treatment of polymers:**

- Must be performed under an inert atmosphere (e.g. under nitrogen flow).
- Temperatures must be  $>2500\text{ }^{\circ}\text{C}$  for graphitization in the case of bulk material.<sup>5</sup>
- All byproducts (tar or gaseous hydrocarbons) should be continuously removed.
- Heating rates should be slow ( $1\text{-}10\text{ }^{\circ}\text{C}/\text{min}$ ) and the material should be allowed to stay at the highest heat-treatment temperature for at least one hour.



- PVC is a common graphite precursor.
- It is heated at  $250\text{-}400\text{ }^{\circ}\text{C}$  for several hours to remove HCl.
- Graphitization is carried out up to  $3000\text{ }^{\circ}\text{C}$ .

<sup>5</sup> Lower temperatures used for smaller sample sizes.



Now, let us just briefly discuss how do we do this heat treatment. You will generally have a tube furnace. There are different types of furnaces. A furnace is anything where you can heat something. There are variations called muffle furnaces, and there is a chamber furnace and tube.

You want to use the tube furnace which as the name suggests contains a tube that might be either made of ceramic, alumina, or it is typically made also of quartz glass, depends on how high you want to go how and what is the temperature that you want to use.

Quartz will typically not survive above  $1200^{\circ}\text{C}$ , even depending upon the quality and the defects, it might even melt slightly earlier than that, but up to  $1200^{\circ}\text{C}$  typically it survives. But if you want to use a very high-temperature furnace, for example, you want to go up to  $1600^{\circ}\text{C}$  or in the case of graphitization, typically you want to go to  $3000^{\circ}\text{C}$ , then you will use ceramics.

Up to  $1600\text{-}2000^{\circ}\text{C}$  typically alumina and above that you might also consider using silicon carbide. In extreme cases, you might even use the tube that is made of a certain type of carbon material then it can really withstand very high temperatures.

There is a tube and very basic principle, you want to maintain an inert atmosphere in a tube furnace. So, what will you do? You will have nitrogen or any other inert gas flowing through the inlet and outlet. Nitrogen is used for most lab research purposes



because it is relatively cheaper and easily available, but you can also use argon, helium, you can use other inert gases.

Under the nitrogen flow, you have your polymer slowly heating. Slowly heating is important because now I am going to explain to you when your polymer is heating, you have you, you have certain bond-breaking reactions, and after that certain bond-forming reactions.

And you need to allow enough time for these reactions to properly take place and you want to reduce the loss of your carbon material as well because you will lose some carbon in this process. It is not like only the non-carbon atoms will go. They will take some carbon away with them as well, which you want to minimize.

Here, in this schematic, I have only shown you the tube, not the entire furnace, heating coil, and now glass wool. You will have certain thermal insulation in your furnace because you are using really high temperatures like 1200°C and in the case of graphite up to 3000°C. You do not want to touch it.

So, you will have good thermal insulation, so that the surface temperature is always maintained below 150°C or 100°C is good. So, this is a schematic. Now, you see carbon in that little sample holder. This was not initially carbon. This is a polymer. When it was heated, then some of the non-carbon atoms will be removed. How? Oxygen took some carbon with it. So, some oxygen was there and that took some carbon with it and formed carbon dioxide and carbon monoxide and left.

What happened to hydrogen? Hydrogen also took some carbon with it, formed methane and left. During the initial stages, you also had the polymer fragmented into smaller polymer molecules. So, smaller fragments smaller hydrocarbons. If they were too volatile, they also left without completely degrading.

Now, you are left with heavy hydrocarbons, something that is not so volatile that it can just mix into your nitrogen and go away. It is like this oily tarry material. It is also not going to be a part of your solid carbon material. It is volatile enough that at 1200°C, it will be removed from your solid material. But then it is also not going away, often it gets deposited onto the walls of your furnace, you will see some tarry deposits.

When you are doing this process on a large scale, then you can also collect these tarry deposits separately. Again this is a very fundamental schematic. Industrially you will have a lot of different pipes connected to it from where you are constantly removing your tar and constantly removing these gaseous hydrocarbons that are coming out of it. And then the heating and cooling everything is very well controlled. Cooling is controlled in the case of industrial processes. This is the fundamental thing. After everything is left, then you have is the solid carbon material that will be 30 percent of your original material, which depends on the mass loss that depends on the chemical structure of your polymer.

Again I have already mentioned in the case of graphitization for bigger sizes precursor or when you want to make graphite, you will use about 2500°C, typically 3000°C temperature to get good graphite.

And if the sample size is very small or you have a very thin film, in that case, a you may use lower temperatures because then you are providing a lot of surface area for these tars and gases to be removed and that is why you can use slightly lower temperatures. But if you can use 3000°C, then you will most likely do so.

I did not tell you the fact that we want these synthetic gases to be removed that is being produced, which is the mixture of all of these gaseous hydrocarbons. Now, all of these things when they are produced as soon as they are produced they should be removed, they should be pushed and that is why we have the tube.

If you have a chamber furnace or something where these things can circulate, they may end up redepositing on top of your sample, then you want to avoid that. So, that is why you need the tube furnace. This process is done slowly like 1 to 10°C centigrade per minute, the slower the better.

And also once you reach this highest temperature, let us say for your process it was 3000°C, you will leave your material at 3000°C for a while. At some point, we will also learn that this entire process is a combination of both thermodynamics and kinetics. Thermodynamics in the sense that you have various reactions and every reaction has a different energy.

Why am I saying various reactions? Because when your polymers are broken into smaller hydrocarbons, each hydrocarbon also might be breaking into further smaller hydrocarbons. There is one reaction going on where you have carbon radicals, that are attaching with each other and forming a carbon solid carbon material.

So, it is very complex mixture at any given temperature, let us say at 500°C, if I look at that material it is it has so many reactions and so many different aspects of it that it is really difficult to study. Let us say if you want to model it, this is also very difficult. However, all of these reactions have their own Gibbs free energy. They have their own thermodynamically possible.

So, that you need to calculate for every individual reaction. Also at the same time, if you keep a certain temperature for a very long time what happens to a certain reaction because some reactions will only take place at a certain temperature. But they might take place. What happens to them if you maintain that certain temperature for a very long time or not.

So, the final temperature is typically what you will maintain for at least 1 hour, you can maintain it for several hours as well.

The PVC is one of the common graphite precursors. And there is another thing with PVC that it contains chloride, it is polyvinyl chloride, and chloride is not good. We already learned that oxygen and chloride are not good.

Interestingly we can remove this chloride from PVC in the form of hydrochloric acid, and that is typically done between 200 to 400°C. And that is done for several hours which will basically form this hydrochloric acid, and the acid will be then removed. Around 300°C something or below 400°C, the PVC becomes liquid because it does degrade.

Our goal is to make sure that most of the chlorine is removed. And after that, the longer you do this process more chlorine you can get rid of. And after that, the material that you actually get is very similar to the needle coke that we were talking about.

So, if you do this heat treatment up to 400°C you get rid of the HCl, and then you also heat it a little bit more and you get coke-like material which can then be processed in a

similar way that we processed coke. If you want to make certain shapes out of it, and then you can heat it up to 3000°C in order to graphitize it or in order to get the graphite.

Over here you can see what happens at different temperature points. Why am I always saying that we need to go to 3000°C. So, you see this is across-section of a graphite crystal in the graph. If you see at the top one, where you have 3000°C, that is a crystal which is your side view. So, if you saw these TEM images, these are the crystal planes. This is a cross-section.

Now, if you go little bit down in terms of temperature around 2000°C, you see a little randomness. It is still not perfect graphite crystallite. You go a little bit to even lower temperatures above 1000°C, say 1100-1200, then you have the crystallites start to form.

Now their  $L_a$ , the crystalline diameter, is also much smaller. And of course, before that, the material is practically disordered. This is the reason that you need to go for higher temperatures when you want to get good crystals of graphite.

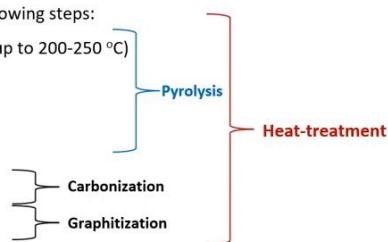
Otherwise, let us say if you stop your process at 2000°C, what you have is then graphitic material. You can say highly graphitic material, highly is basically also a relative term. So, compared to what you have at 1000°C, you can say the 2000°C material is highly graphitic.

But you can always improve the graphitic content and at around 3000°C, you can get a good graphite crystal, and that is why we go to those temperatures. However, this is not valid for all polymers. Right now we are talking specifically about PVC.

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Inert heat-treatment of polymers consists of the following steps:

1. Removal of water/ solvent/ volatile impurities (up to 200-250 °C)
2. Cleavage of C=O, C-X (250-350 °C)
3. Cleavage of C≡N (350-500 °C)
4. Cleavage of C-H (500-700 °C)
5. Formation of C-C bonds (700-2000 °C)
6. Increase in  $L_s$  and  $L_c$  (up to 3000 °C)



- Since the first step of the process is pyrolysis, often the entire heat-treatment is called **pyrolysis**.
- The exact temperature values for different segments can vary depending upon the precursor
- Heating rate (ramp rate) and environment also influences pyrolysis chemistry
- During pyrolysis of polymers, multiple reactions take place; several radicals form, dissociate and re-form; new hydrocarbon and carbon fragments (generally curved) are generated.
- **Micro/ nano scale structures may graphitize at temperatures as low as 900 °C.**



In this context, there is one more term that you need to understand very well and it is known as pyrolysis. This entire process where you are performing a heat treatment under an inert atmosphere, what do you call it and what are the various stages of this process?

Let us try to understand what is happening chemically? This is a more general form, I am talking about all the different polymers because most of the polymers are organic materials. So, what are they made of? They are made of carbon, hydrogen, nitrogen, oxygen, sulfur, and other elements.

But the primary components will always be carbon, hydrogen, nitrogen, and oxygen. Some of the reactions will remain common. Some of the bond breaking temperatures will remain common, because there is a certain strength, for example, of the carbon-oxygen bond.

Depending upon your polymer, you may go a little bit above or a little bit below the temperature. But depending upon the energy of your bond, it will not differ too much. You may sometimes also have some catalytic elements inside. Let us define some very fundamental rules for all the polymers. So, not just for PVC.

What happens up to 200°C, you have a polymer, you may have some water in it. You may have some standard volatile impurities, those things will go away up to let us say 200-250. And nothing really chemically changes. In most cases, depending upon the degradation temperature of your polymer.

Now, interesting things start to happen. The carbon-oxygen bond cleavage takes place at about 250. So, this is a range 250 to 350°C centigrade. So that will depend upon the exact chemical structure. But as I said that let us define some general rules. After that your carbon-nitrogen bonds break. Nitrogen does some interesting things and that is why I have written 300 to 500.

There is a larger range for nitrogen also because nitrogen sometimes serves as a chemical catalyst, which actually helps in forming aromatic structures even though the material may not have aromatic structures to begin with. But then you have the carbon-nitrogen bonds breaking.

The last one to break is carbon-hydrogen. Why last? Because it is a single bond and so stronger especially in the case of aromatic structures. This is the one that is the strongest, and that is removed at the end. This is between 500 and 700°C for most polymers.

There may be some exceptional cases like some bonds might not have complete degradation even up to very high temperatures, but for most polymers, this is what works. Up to 700°C, you will have most of the hydrogen bonds broken which means that your polymer will break into smaller and smaller fragments.

Some of these smaller fragments without further bond breaking will just leave your material because you have this nitrogen pushing them anyway. They are out as soon as they form a smaller hydrocarbon.

Around 700°C, you will have an almost complete decomposition of your polymer. And most of the non-carbon atoms are now ready to leave or have already left.

Now, when the non-carbon atoms leave? So, my carbon and hydrogen had a bond and now hydrogen just went outside in some form. Now, what happens to this carbon? This carbon is radical now. It has an unpaired electron. The electron which was previously participating in bonding depends upon the polymers that had  $sp^2$ ,  $sp^3$ , or all kinds of bonding. So, whatever was the bonding, these carbon atoms were bonded to one or more other atoms. Now, it is just a radical which means it is ready to form a bond.

There are millions of these carbon atoms which are actually ready to form bonds. And what will carbon do in this case? Carbon atoms are happy forming bonds with

themselves. So, all of these carbon atoms will try to come together and they will form a large-scale carbon material.

You will call this formation of carbon-carbon bonds which go on between 700 to 2000°C. It happens because bonds can also rearrange themselves. And then there may be some high-energy bonds, 9 membered rings I do not know. There may be some high-energy structures that will try to get the lower energy state. So, the bond rearrangements will continue to happen up to 2000°C.

Especially after 900°C, you will also have this rearrangement of bonds then you get is more and more graphitic content. What does that mean? That means your  $L_a$  and  $L_c$  or crystallite diameter and the stack thickness both continue to increase as you provide more and more heat.

In the case of graphite, when your  $L_a$ ,  $L_c$  increases, they will have anisotropic crystals. But in the case of other carbons, they will increase but they will still have very random orientation and all together in bulkier material will be disordered that we will discuss in the next section, but these are the general rules this is what chemically takes place.

Now, about the names, whatever happens in the first 4 steps or up to 700°C that we call pyrolysis. To be more specific whatever happens when the bond-breaking first starts. Water removal in the first 100°C, we do not count, but let us say whatever happens up to 700°C in general that process is known as pyrolysis. This process of breaking bonds of carbon and heteroatoms in the absence of oxygen is called pyrolysis. This is purely thermal

Up to 2000°C what happens, we call it carbonization. And then above 2000°C typically is known as the graphitization. This entire process, you can always call it heat treatment. Even if you call the pyrolysis part as heat treatment, it is not wrong, because you are always doing the heat treatment.

We should call this entire process of converting polymer to carbon, heat treatment, but people often end up calling it just pyrolysis or just carbonization or just graphitization because whatever is the most important reaction, whatever is the most important process that people are aiming at then they call it that.

You can say that the polymer was converted into carbon via pyrolysis. Or when you convert something into graphite in order to show that you actually went all the way to 3000°C, you will just say that I have graphitized a carbon. So, sometimes people will use one of these three terms, but you can always use the heat treatment term altogether.

Since the first step is pyrolysis and also a larger portion of it is pyrolysis people often end up calling it pyrolysis. One more reason for that is that during pyrolysis, you can actually make a lot of changes. For example, at a certain temperature, you see that your polymer has a lot of oxygen in it, so you want to get rid of all of that.

You know that this is the window where I have oxygen leaving the material, you may keep your material for a very long time at that temperature in order to get rid of most of the oxygen. So, this is where you basically play with the parameters. Also, you can increase the heating rate or decrease the heating rate. All of these things are done during pyrolysis and that is why often people call this entire heat treatment just pyrolysis.

These were the general rules, the exact conditions which include the exact pyrolysis temperatures for each step that will vary slightly, depending upon the chemical structure of the polymers. This is a very complex reaction that you have from pyrolysis. This pyrolyzing matrix, which means the mixture of all the multiple things. For example, I take in 600°C or some might choose any temperature what do you have in your material at that point? You have some fragmented bigger hydrocarbons and smaller hydrocarbons. Some parts of your polymer still left over; you may have some bubbles forming because you have some gaseous things that are going out that are volatile hydrocarbons.

You may have each of these smaller hydrocarbons breaking into further hydrocarbons. Some carbon atoms maybe some carbon radicals have already formed carbon-carbon bonds. So, you may have some solid carbon also at that point.

So, at any given point, this crazy mixture of materials will be called pyrolyzing matrix. And these reactions for any pyrolysis of any polymer can be extremely complex to understand because you have so many different reactions that are going on. I mentioned it before that when we have smaller structures and we have a higher surface-to-volume ratio then we can sometimes use lower pyrolysis temperatures. This is something we are going to learn when we learn about micro and nano fabrication.



