Carbon Materials and Manufacturing
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Lecture - 31
Carbon Black: Introduction and Properties

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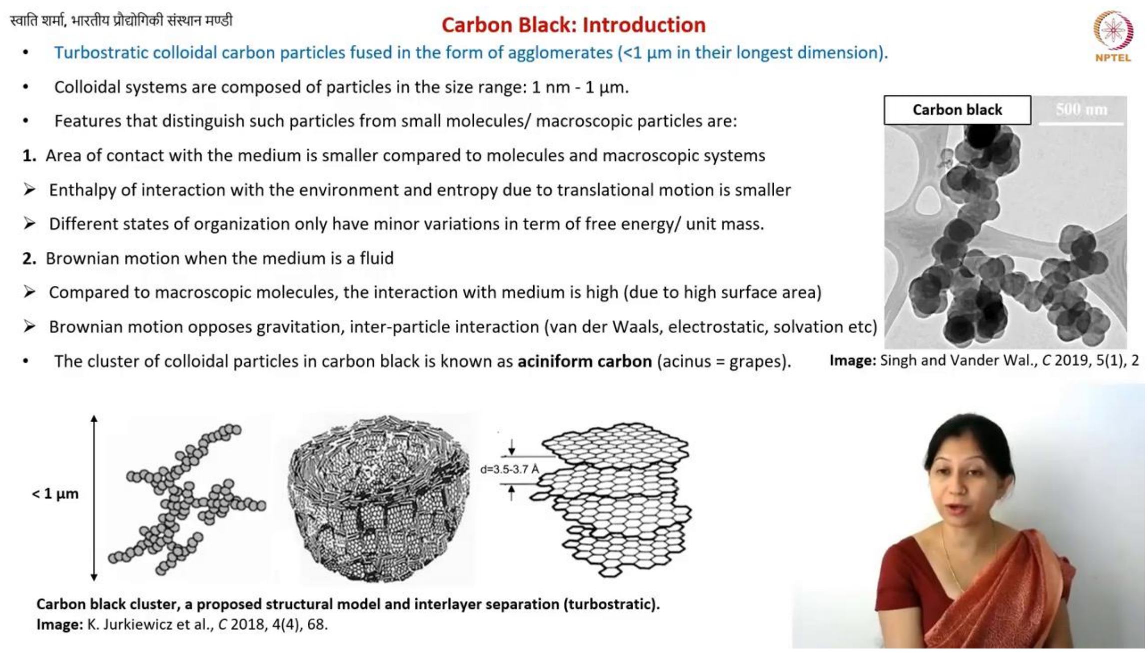

Hello everyone. I hope you are enjoying your industrial carbon section. Now, we will move on to a very important industrial carbon material, which is known as Carbon Black. Carbon black is actually something that has been industrially manufactured for over 50 years. We already have well-defined optimized scaled-up processes for the manufacture of carbon black.

This material is very important because this is used for reinforcement of rubber in the case of tyre industry. You can imagine that tyres have been very important in the last 50 years. There has been so much development in the automobile industry. You often hear that you have now more advanced tyres which last longer, all thanks to carbon black.

In fact, it is the properties of carbon black that have been improved and also of course, of the rubbers, but this is the material that is used for the reinforcement. Of course, there are many other applications as well, you can reinforce other polymers, and you can make them electrically conductive. The standard properties of graphitic carbon materials, they are also valid for carbon black.

What is the definition of carbon black? Well, it is a turbostratic colloidal carbon particles. So, it is a particulate material. There are multiple things here; turbostratic you understand, turbostratic is nothing but if you have these graphene-like sheets in any carbon material. They are randomly rotated on top of each other rather than in the A B A B A fashion, then you call it a turbostratic material.

Often the materials that have a strong curvature or curved carbon structures tend to be turbostratic. Because it is difficult for them to have these flat geometries and A B A B A graphite-like crystalline order. So, that is something you understand. This is also a material with short-range order.

Now, what do we mean by the colloidal carbon materials? Whenever you think of a colloid what comes to your mind is a suspension. If you have these particles, you put them inside a solvent then you are going to get a suspension. This is basically what we have here. But these are carbon particles. So, we are still talking about solid carbon particles, not the solution.

However, if you did make a solution or tried to dissolve it, they will not get dissolved. You already know carbon does not get dissolved easily. But the point is that the particles are not so large that they will settle. So, you will have sort of a suspension; these are the colloidal carbon particles.

Here is an image, this is a transmission electron micrograph of carbon black. You see this is like a cluster of nano-scale particles. The particle size should be 1 μm or smaller than 1 μm. I am talking about the entire cluster and these are called particles, but they are not necessarily spherical.

We rather take an equivalent sphere, when we calculate the diameter of these particles. These are actually very small nano-scale carbon particles, and they are fused together. They form a bunch or a cluster because that provides them a more stable geometry and that is why we have these clusters.

The cluster size in its longest dimension should be approximately of the 1 μm range. So, it is not exactly 1 μm. Often the individual particles are in the 10 to 15 nm range and the bunches, typically are slightly above 1 μm, like 1050 nm. But this is acceptable approximately, so they should be in the 1 μm range. So, this is how the bunches are known as carbon black particles.

Now, let us talk a little more about the colloidal systems. So, what is most important in a colloidal system? It is the size of the particle. If the particle is too large, then it will settle. If it is too small, then that you do not call it a colloidal system. We are going to compare the colloidal systems which both small molecules and the macro scale systems particles.

In the case of colloidal particles, you need to have the size range within 1 nano meter to 1 μm. This is the definition. But if we compare it with two things, first we compare it with the small molecules, and then we compare it with the micro-scale particles.

When we compare it with small molecules, if you put them inside the medium they will have a much larger contact area, but compared to small molecules then you have a smaller contact area.

Although, it is also relatively very large, but compared to small molecules, in fact, from the colloidal particle also if every nano particle was away from each other; it was separated then you will have a much larger contact area, surface area. So, that is how they differ from the small molecules.

Now, why does this happen? Because the enthalpy of interaction is smaller compared to the smaller molecules and also the entropy. So, what is entropy? Inside the solution, how randomly your particles can move, how fast they can move, how much they can go away from each other.

These are the translational motions of your molecules that determine the entropy of the entire overall system. So, for these particles compared to the small molecules the entropy and enthalpy both are smaller. And that is how you will say that there is less contact.

We are talking about these colloidal particles, but they have a lot of small particles, all together, they fuse together. Can we have different organizations of these particles?

So, when we are talking about enthalpy and entropy then probably it is easier for you to understand that if you just switch the positions of these nano scale particles inside your carbon black particle, still you are probably going to have pretty much the same in enthalpy and entropy. Because as long as the overall dimensions are in this 1 μm range you are not going to see much change in the behavior of your particles.

The answer is yes, you can have various organizations of these nano-scale particles and the shape of this cluster is not well-defined. So, it is like a cluster or it is like a bunch of grapes. So, the bunch of grapes can have slightly different shapes, one bunch from another.

We consider these individual 1 μm scale particles as our individual particles. Because these particles are pretty much of the same surface energy and they particularly have the same properties even if there is a small variation in terms of the organization of particles within the system.

So, that is one thing that differentiates it from small molecules. Now, when it comes to comparison with larger or macro scale particles, then we do not call them molecules we call them particles. Of course, the most important difference is that you have the Brownian motion.

So, if you have fluid as a medium then you will have Brownian motion. In the case of carbon black particles or any colloidal particle, which you do not have in the case of large-scale particles because they typically tend to settle down. Now, when we talk about the Brownian motion, Brownian motion is basically something that opposes all the inter particle forces.

Also, it opposes the gravitational forces and that is why the low density is also very important here. The light weight of the carbon is also very important and this entire material, in fact, is also called a fluffy carbon material. Because this is like a very fluffy spongy material altogether. Even individual nano particles because they have short-range order.

So, these are very small turbostratic crystallites that may also contain a lot of defects which may also contain some impurities. And because of the individual particle has a very low weight and of course, when you see a cluster then you can see that there is a lot of empty space in that cluster.

So, altogether you have this kind of Brownian motion because of multiple factors, because these particles are able to oppose the gravitation, the Van der Waals forces other interactive forces between two particles. The cluster of colloidal particles as I already mentioned that it looks like something like a bunch of grapes. And that is why it is also sometimes called aciniform carbon. Now, the word acinus means grapes. I think it comes from Latin. So, because these particles look like a bunch of grapes, so this is also another term that you will hear aciniform carbon when it comes to carbon black. And here is a picture where I have shown the proposed micro structure.

In the second image here, you see you can see that there are very small short-range order, so small crystallites, but these are not again well-defined crystallites. So, you will get only a broad peak if you perform diffraction studies. However, this material is also composed of these hexagonal carbon sheets. But these hexagonal carbon sheets tend to have defects and they tend to have a very small range order.

So, they are just like fused together and this is also one reason that the density of the particles even at it is microstructural level is very low. So, yeah, here I have also mentioned this review article, maybe you could go through that and understand more about this material.

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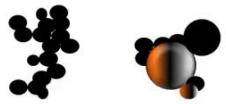
Carbon Black and Soot

- Carbon black should not be confused with soot.
- Both carbon black and soot contain fractions of tars. But carbon blacks have a much higher elemental carbon content.
- Soot may contain larger droplets of tars/ oils/ resins, while carbon black essentially contains clusters of nanoscale particles.
- Soots are particulate materials having variable quantities of organic/ inorganic solids along with tars/ crosslinked resins.
- Soots may be carcinogenic due to the presence of impurities such as aliphatic hydrocarbons, naphthenes, polynuclear aromatics etc.
- Soots can be heat-treated (> 1200 °C) to yield particulate carbon with lower impurity levels.
- Density/ specific surface area of such carbons may be different from typical carbon blacks.
- India is the second largest producer of carbon black globally.
- Indian inks have been known to contain well-defined carbon blacks ~3000 years ago.
- **Applications:** reinforcing agent for rubber, pigment in inks, other coatings and plastic reinforcement.



Carbon black   Soot

Reinforcement mechanism:

- Formation of a physically bonded flexible filler network
- Polymer filler couplings

Further reading: A.I. Medalia *et al.*, A comparison of carbon black with soot. *The Science of the Total Environment*, 1983, 31, 1-22

Another very important thing is that you should understand about carbon black is that carbon black is not soot. In the beginning also, I mentioned that not everything that is black and carbon is called carbon black. There is another term which is called black carbons which is very confusing.

Sometimes when you get these soots. Soot is what? What comes out of your car exhaust that is diesel soot or petrol soot or whatever comes out of the candle that is also soot. So, all of these materials are un-burnt carbon materials. And your carbon black also contains un-burnt carbon particles. And that is why often soot and carbon black are confused.

People think that soot is carbon black that is not the case. There have been several articles published and a lot of studies that have been done where a comparison of soot and carbon black is made and then you can understand what is the difference. So, this is what we are going to discuss.

One important thing about carbon black. So, before we talk about the manufacturing that we will do probably in the next class. The point is that this carbon material is interesting and also different from other carbon materials in the sense that it contains some impurities. It does contain hydrogen and it may even contain some tar-like, little small fractions of tars or moisture, and these impurities are acceptable.

What is interesting about this material, it is not fabricated or it is not manufactured using the pyrolysis process, but rather a combination of pyrolysis and combustion. So, this is probably the only large-scale carbon material that you will hear that is actually prepared in the presence of oxygen.

You are essentially performing combustion, but in a very controlled environment. And that is important to mention here because when we have soot, then the conditions are not controlled. So, what comes out of your car exhaust that these are un-burnt carbon particles.

We also discuss them in the context of environmental pollution that these exhausts, exhaust gases contain not just black but also brown carbon. And that brown carbon is nothing but carbon that contains a lot of tar and these are being formed when there is no control over the process.

But in the case of carbon black, you already saw that we have these grape-like carbon particles structures and these are being fabricated under a highly controlled environment despite the fact that you have oxygen in the system. The quantity of oxygen, in fact, is optimized.

And then the combustion is performed in a highly controlled fashion and the particles, of course, need to have very well-defined size and well-defined geometry. And even the smaller particles, the nanoparticles that form these clusters, their size is also well-defined, that is not the case with soot.

Let us discuss what is soot and what is carbon black. I mentioned that both carbon black and soot contain tars. If carbon black contains tar, then how can you say that you know it is different from soot? Well, the total C/H ratio, the ratio of carbon to hydrogen in the case of carbon black is much higher. This is what is known as the elemental carbon ratio. So, that is much higher in the case of carbon black.

Another important thing is that in the case of soot, you can often have larger droplets of tars. So, when your burning diesel, then there is diesel being sprayed. And then it is getting mixed with the oxygen and then it burn basically some particles remain unburned some even the tar itself goes out. But you may actually end up getting larger droplet us of tar.

So, large means it can also be 5 μm. So, you know that in the case of carbon black the entire particle size is 1 μm. Now, if there is a 5 μm size tar ball that is going out, even if it is partially burnt that is what happens in the case of soot. So, you do not have any control over size, also you do not have any control over the fraction of tar. Often you have a much higher fraction of tar in the case of soot.

Now, there may not be just tars, but also sometimes some sort of resins in the case of your soot. So, that will depend on what kind of soot it is, not diesel soot, but candle soot or other. So, you will also have this large hydrocarbon resin like molecules that are also present which is definitely not the case with carbon black.

So, carbon black looks something like this. We already saw the TEM image and the soot might look something like this. As I said you may have brown carbon particles, which basically contain tar and you can have relatively larger amounts of tar. You can also have some inorganic materials mixed.

So, this is another difference in the case of carbon black because you are using a hydrocarbon source. So, we are also performing processes similar to pyrolysis, but the fact is that it is not pyrolysis because there is combustion going on as well because there is oxygen present in the system. But we are sort of optimizing how much of the process should be pyrolytic and how much of it should be combustive.

But that is not the case with soot. So, you will often have these kinds of particles. Now, you may think that these are also colloidal particles and it becomes confusing. Because as I already mentioned people call soot and all of these impurity containing forms of carbon, black carbon and so black carbon is sometimes confused with carbon black.

The point is that if you carefully observe; if you do the particle size analysis or also when you do when you perform elemental analysis you will know that carbon blacks are quite different from the soot. However, soot can be heat treated further to get more purity.

The temperature of the process used for making carbon black is between 1300 and 1500°C. So, if you take your soot particles and anneal them out basically, get rid of your tar that you had in the soot. In that case, you can potentially get a material that is similar to carbon black, but you may still not be able to carbon get carbon black because you may not be able to get these perfect grape-like particles.

One more thing is that please do not confuse soot and do not use them for all the applications because they can be carcinogenic. So, they may cause cancer. They basically have a lot of safety issues. In fact, that is why we are studying all this environmental pollution and everything. Because these brown carbon particles, and also some of the black carbon particles have carcinogenic effects. Esepcially soot but that is not the case with carbon black.

So, soots contain various hydrocarbons, they contains naphthenes, they can contain various polynuclear aromatics. Because of the presence of all of these non-carbon materials or hydrocarbons you have carcinogenicity in the case of soot. As I said you can heat treat your soot and potentially get something which has a high carbon content, but it may still not be carbon black. Because the density of those particles can be different, the size of those particles can be different.

In carbon black, when you have these bunches of nanoparticles, what does that mean? That means that first you are getting these nanoscale particles, then they are fusing together. So, this is a bottom-up process you will not get the same kind of material when you heat treat the soot; or the soot should have been also formed with the nanoscale particles, in that case, heat treatment might lead to carbon black production.

In fact, sometimes in some industrial processes the first initial stages of production when you perform the combustion, at that time whatever material is formed people call them soot. So, that is another confusion in this regard, but you understand that what is the difference.

Coming to a completely different topic. I told you before that India is one of the largest producers of carbon black. What is also interesting is that the history of carbon black has a lot to do with India. In India, we do not know when did printing or large-scale writing started, but we definitely know that India did produce inks even 3000 years ago. And approximately 3000 years ago we actually had well-defined carbon black production in the country and those carbon blacks were used as pigments for these inks and those inks were actually supplied all over the world. They were even called Indian inks. So, carbon black has its history definitely involves India.

Now, the applications, I already mentioned that reinforcements of rubber are the most important application and that is why we have the large scale production. But other than that of course, the pigment in inks. Even today a lot of printing inks contain the black color, inks are often based on carbon black.

And then you can also reinforced plastics and you can perform you can make coatings. Many plastics or polymers, for example, PVC or Poly Vinyl Chloride is often reinforced with this carbon black. And also for research purposes if you add carbon black particles into certain polymers, of course, the mechanical strength increases.

So, this can be used in composite materials, but also the electrical conductivity increases. So, for that purpose also you have to optimize the fraction of carbon black in your polymer, but for multiple applications, these particles are used. When we reinforce the rubber using carbon black, then what is the mechanism of this reinforcement?

Well, there are two things or at least these are two theories; the first one is that there is a filler network. So, this is fillers we will talk about composites in detail, you always have a matrix phase and a filler phase or additive phase. Carbon black is used as a filler. This filler network provides stability and mechanical strength to the material and also the interaction of the matrix phase and the filler phase provides mechanical strength to the overall system.

In fact, there have been several studied studies where people have figured out what is the mechanism because you see this material is a very high surface area material. Surface area is the most important thing when it comes to carbon black and also its lightweight. And because it is fabricated in the presence of oxygen, you can imagine that you will also have certain surface functional groups which will make it hydrophilic.

Also, you may have certain radicals present on the surface. And these radicals can actually enhance the polymerization or the rate of polymerization in a polymer. So, this is also another mechanism by which on the surface of the carbon black particles there is an improved rate of polymerization of your matrix phase. This is how you basically get your rubbers with better properties better mechanical properties.

So, here I have mentioned one article. There are many articles where a comparison of soot and carbon black is made, but this is one of the older articles which you can read and you can actually see both at industrial scale and research scale how soot and carbon blacks differ from each other.