Carbon Materials and Manufacturing
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Lecture - 05
Isotopes of Carbon

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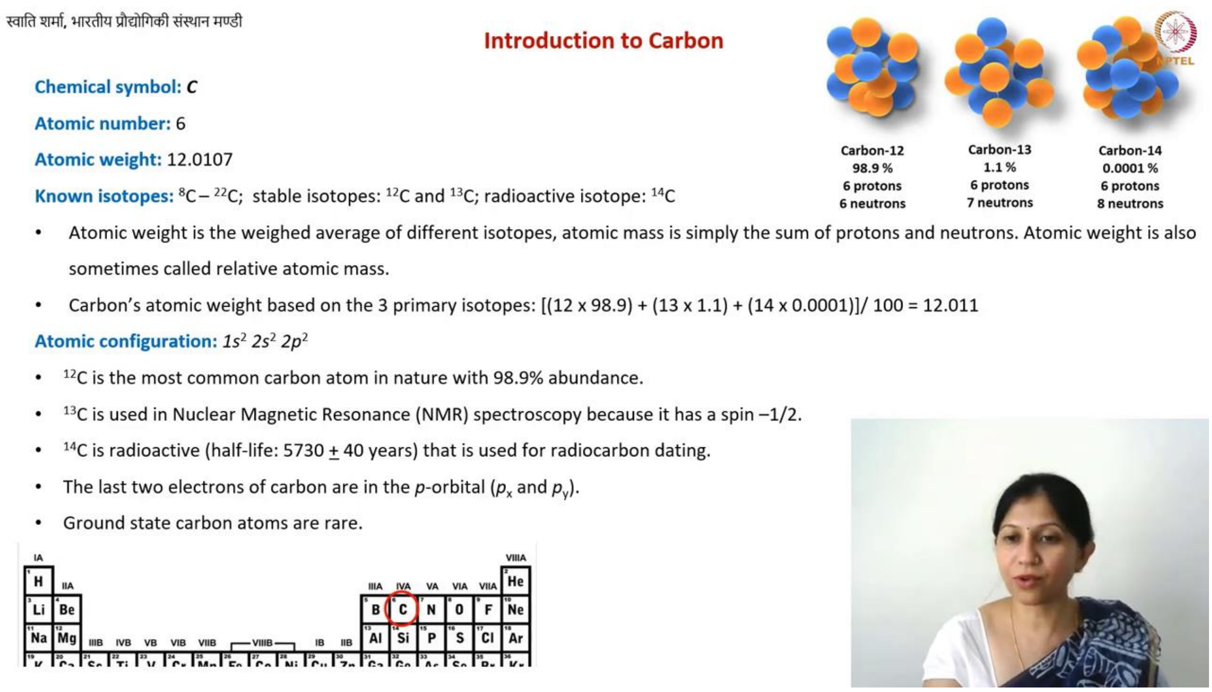

Hello everyone. In this lecture, we will start talking about the technical details of carbon. So, this is the first lecture on Introduction to Carbon. Before we go into making our own carbon materials and finding the application, let us see what you know about carbon in nature.

So, many of you probably already remember that where does carbon belong in the periodic table, you probably also remember that its chemical symbol is C and its atomic number which means the number of electrons in carbon that is 6.

Now, the atomic weight of carbon and I have written weight here not written atomic mass for a reason, that is 12.0107. Now, before we go further let me also tell you about carbon isotopes, do you recall the definition of isotopes? Basically isotopes are different forms of the same element, where you have the same number of electrons; but the number of protons and neutrons varies. So, I have shown it in this picture; carbon-12, carbon-13 and carbon-14, these are the three very well-known isotopes of carbon.

Now, in the case of carbon 12, you have 6 protons and 6 neutrons. I have these as spherical particles for easy representation. In the case of carbon-13 which is about 1.1 percent in nature, we have 6 protons and 7 protons. In the case of carbon-14 which is only 1 ppm Hertz per million in nature, you have 6 protons and 8 neutrons.

Among these three primary isotopes, we have carbon-12 and carbon-13 which are stable isotopes. Stable means they do not naturally decay and the third one carbon 14 is the radioactive carbon isotope.

So, often you hear about radiocarbon dating, for that, we are going to use carbon-14. We will discuss a little bit about radiocarbon dating as well. Now, I said that I use the term atomic weight and not mass. If you think in terms of general physics, what is the difference between mass and weight?

The definition of weight is m×g. So, which means that you are factoring in the gravitational constant. Mass remains the same and weight varies. For example, if I go on the moon, then my mass will still remain the same, but my weight will change because the value g will change.

But in the case of atoms are we really factoring in the g? Are we really weighing atoms on a balance or we are saying that an atom on the moon will be different compared to an atom on the earth? The answer is no. Then, why are we using these two different terms; atomic mass and atomic weight? The answer is as follows.

Atomic mass is simply the summation of the protons and neutrons for any particular atom. So, if I take C13: 6 protons + 7 neutrons = 13 which is the atomic mass. But you will never say atomic weight for carbon 13 or carbon 14 or carbon 12 for that matter. You will say atomic weight is for carbon. Why do we say that? Because atomic weight basically takes care of all the isotopes.

So, it is the weighted average of the atomic masses of different carbon isotopes and then, we get one value which we call atomic weight. So, briefly or quickly, you can also calculate this by yourself just take these two, these three values here 12 multiplied by the abundance of carbon 12; 13 multiplied by the abundance and so on and then we divide it by 100 to take weighted average and then, we get a number 12.011 in this case.

Carbon atomic weight: $(12 \times 98.9 + 13 \times 1.1 + 14 \times 0.0001)/100 = 12.011$

12.0107 is what I had written and the reason for that is because all of these values are approximate. In fact, they might even sum up to more than 100. These are approximate values and also, we have omitted many isotopes here. So, approximately when you have these exact numbers and you calculate with the exact 4-5 digit up to that, then you will get the number 12.0107.

So, that is your atomic weight. Atomic weight is something that varies, but the atomic mass remains the same. However, in some elements, mass and weight might be the same. Why? Because these elements might not have different isotopes. If they are naturally found only in one form, in that case, their atomic mass and weight are the same. Now, the atomic configuration of carbon is very easy, you probably know it is $1s^2\ 2s^2\ 2p^2$ when we are talking about the ground state of carbon. Of course, when it hybridizes, then things change fine.

So, now we said that carbon-12 is the most abundant form of carbon and there is also an application of carbon 14. What about carbon-13? Does that also have an application? Yes, there is something called Nuclear Magnetic Resonance spectroscopy or NMR spectroscopy.

Definitely, chemists who are attending this class, know what NMR spectroscopy is. Now, what do we detect in this NMR spectroscopy? I will not go into the technical details, but we can actually measure the relaxation times of those nuclei that have a nuclear magnetism.

So, if you think in terms of electronic magnetism, there are unpaired electrons. For example, in iron, then you will have magnetism and that is actually correct. But nuclear magnetism is when you have an odd number of particles inside the nucleus, so it has nothing to do with the electrons.

So, now, when you have ^{13}C, then you see there is an odd number and that is why the spin value of the spin quantum number is -1/2. So, this particular atom of carbon is NMR active. This is very extensively used in NMR spectroscopy.

The third one as I already mentioned is radioactive ^{14}C and radioactive materials also have a half-life. So, the half-life of radioactive carbon is 5730 ± 40 years. Because when we are talking about the age of a fossil, something that is maybe 5000 years old, then 40 or 50 years does not make so much difference. So, ±40 years is your error.

The last two electrons of carbon are in the p_x and p_y, the p_z orbital remains empty in the case of ground state carbon. But as I already mentioned that in nature it's rather rare to find ground state carbon because it always would form another carbon atom or some other atom and try to try to form a bond and get into a more stable stage.

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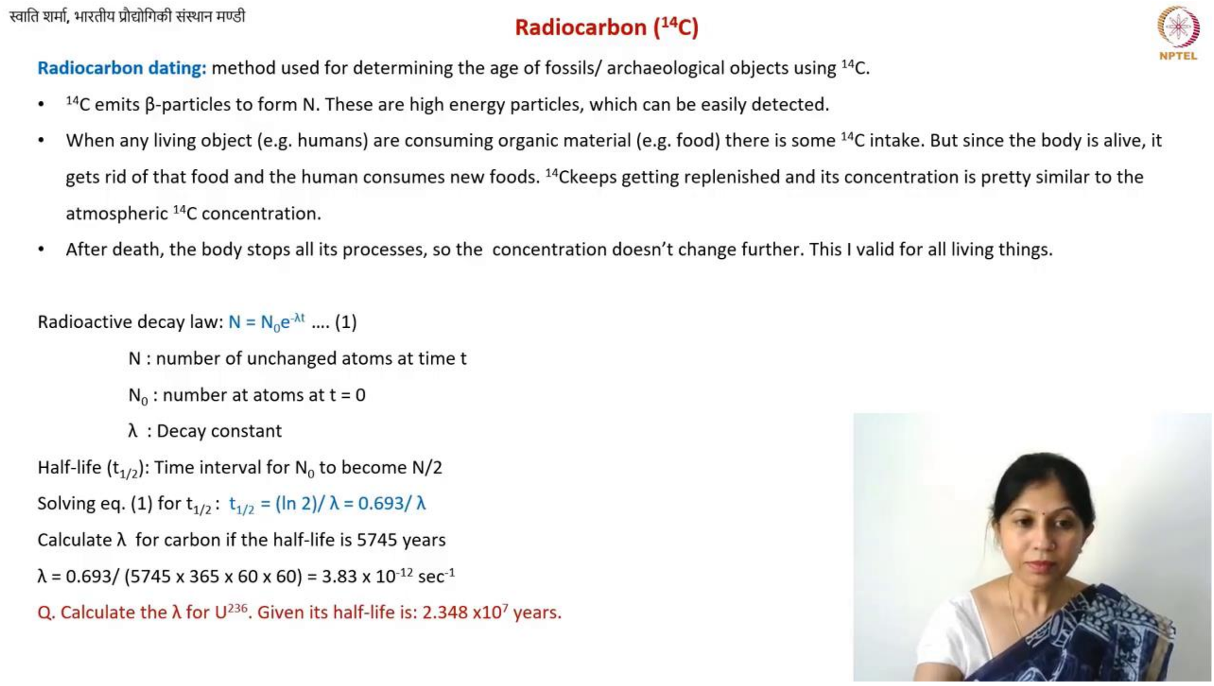

So, let us talk a little bit more about radiocarbon. You know that radiocarbon dating is used for dating very old objects, for example, you find some spider sticking on top of a stone; something like this would contain some carbon. The reason is that because these are organic materials. So, after a long time, after several thousands of years when you have all the non-carbon materials or non-carbon elements have left the material, then some carbon is always there, we can detect it.

Now, if you find some carbon, that means, there is also some natural abundance of carbon-14 in it and that is why you can do radiocarbon dating. But exactly how is it done? So, when there are any living objects whether it is humans, animals or even plants, let us take an example of a tree. So, a tree would take some carbon dioxide from the atmosphere. But as long as the tree lives, it will keep on using that carbon dioxide for making things whatever it needs and then, there will be some waste from the tree, that will go back into the atmosphere and then new carbon dioxide it will keep taking. So, basically, it will reach a steady-state with the atmosphere.

So, the concentration of carbon-14 or carbon in that tree would be then equal to the concentration of carbon-14 in the atmosphere. Now, we can guess what this concentration in the atmosphere at various time points was and then, we match the concentration from the value that we found in the experiment and that is how we measure or that is how we kind of guess the age of that particular object.

Now, there is also a certain type of instrumentation that is used for radiocarbon detection or measurements, they are basically beta particle detectors. Because carbon-14 nucleus emits a beta particle; the beta particle is nothing but an electron or also it can be a positron. So, these particles when they are emitted, they are also very high-energy particles. So, high-energy particle means if I throw something with very high energy, what will happen? It can travel a long distance. So, this is how these beta particles, because of their energy, they can travel long distances without getting to deviate from their path or without getting damaged.

So, this means that if I want to detect them and I use a detector, they will also reach the detector with very high efficiency. Basically, it is also easier to measure carbon-14 compared to other elements. So, that is how we use carbon 14 for radiocarbon dating.

So, as I mentioned whatever is the process dating with carbon-14, that is valid for also animals, human beings, and anything that is living ok. Now, we just quickly look at it, mathematically. You remember this radioactive decay law.

$$N = N_0 e^{-\lambda t}$$

What are the different terms here? N is basically the number of unchanged atoms; unchanged means radioactively unchanged. So, the number of unchanged atoms at any given time t is N and N_0 was the number of atoms at some point time point t_0. You can see it is an exponential decay and that is why we have the minus sign there and lambda is the decay constant which is characteristic of every particular element or every particular material.

Now, one more thing probably you remember that what is a half-life, which means when you have half of the radioactive material left, which is the time interval when your N becomes N0/2.

So, if you now insert these values into this equation 1, then you will get a value of $t_{1/2}$ for everything. So, the general formula for $t_{1/2}$ is:

$$t_{\frac{1}{2}} = \frac{ln2}{\lambda} = \frac{0.693}{\lambda}$$

Now let us quickly calculate it for carbon-14. So, let us say I am doing some experiment and in that experiment, I found out that the value of half-life is 5745. And I said in the previous slide that the number is 5730 years for the half-life, but also ±40 years.

So, let us say if you take a value 5745 years, then how do you calculate the lambda? So, very simple;

$$\lambda = \frac{ln2}{t_{\frac{1}{2}}} = \frac{0.693}{t_{\frac{1}{2}}}$$

The only thing I have done here is conversion from years to seconds. So, because the unit of lambda or the decay constant is per second. So, this is how you can calculate the radioactive decay constant for any element. For example, for your own self, you can also do it for uranium 36 and you can do it for many other elements if you know the half-life.

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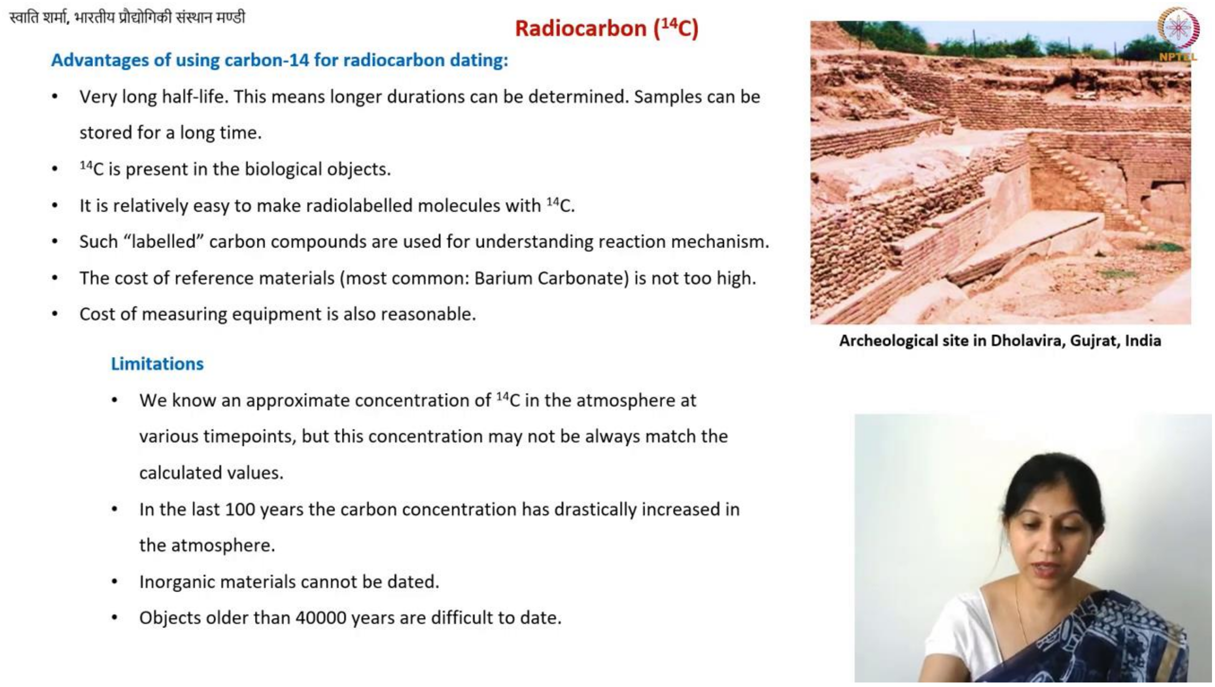

Now, there are many archaeological sites, where of course, this is a very helpful technique. For example, this is a picture of Dholavira in Gujarat. So, this is one of the Indus valley sites. There were many Indus valley civilization sites, now there is one also in Ropar and you know the Harappa Mohenjo Daro.

So, they are all connected and historians are actually now studying the connection between them and the scripts that are found there. So, there is a lot of work going on. But now, it becomes very critical to find out the age of these sites because the entire history of the country is related to that.

So, you find some tree or maybe you find some ashes or maybe you find some object which may contain some organic matter or some carbon, then you use the radiocarbon dating. So, you can already write many advantages of this technique.

First of all, it has a very long life. Let us say if you want to find out the life of or the age of something which is 10000-20000 years old. In that case, you cannot use an element that has only 10 days of half-life right. Because then, it would have already decayed in 10 days to the half of its concentration and then, further half and further half and today, the concentration would be so low that you would not be able to find out. So, carbon in that sense has an advantage over other elements.

Carbon is present in biological objects and also, it's relatively easy to make reference standards. Reference standards mean if whenever I do some analysis, I need to have a reference, what is the value that I expect. So, because carbon is available in everything, it is easier to make these reference standards using the labeled carbon or labeled carbon means the radioactive carbon.

So, where you have replaced the carbon-12 atoms with carbon-14 atoms that is what you call a labeled compound, radio label compound. In the case of chemistry, these compounds are also used for many other applications. For example, learning the mechanics of a certain reaction. So, if I mix three things a, b and c; in the case of a and b, I have carbon-12; but in the case of c, I have carbon-14 and I can detect it. Also, we can do it with carbon-13; but let us say right now, we talk about carbon-14 which can be traced because it is a radioactive isotope.

Now, when I mix these three things, I want to see what is attaching to which one, at what time, how this material is splitting, and what is new things are being formed? So, I want to trace my carbon-14 atom which I can do, and this is how I can understand the mechanism of a certain reaction. It is also in radio analysis and in chemistry, and it is widely used radiocarbon material.

Altogether the cost of reference materials, also the cost of the instrumentation everything is reasonable for the case of carbon; of course, it can always be expensive compared to something; but altogether this is a very common technique and we all know about it that for dating a lot of archaeological objects, this technique has been widely used.

Everything has certain limitations. So, one big problem with carbon-14 is that we are kind of dependent on our knowledge of the concentration of carbon-14 in the atmosphere at any given point. But that can change locally. For example, in the last 50 years or last 100 years, we all know that the concentration of carbon in general has increased a lot in the atmosphere which also means that the concentration of carbon-14 has also increased a lot. Now, this may have happened 20000 years ago, there was a big fire and that is why the atmospheric concentration of carbon increased or because of meteorite heating and things like that.

So, because of these reasons, the atmospheric carbon concentration may not be exactly what we think, but still it is a good approximation. Of course, when we are doing radiocarbon dating, then it has to contain carbon, the fossil has to contain carbon which is the case with most of the fossils.

But sometimes what happens is you find only the bones of humans or bones of animals and if you then want to detect, for example, the oldest fossil; the oldest human fossil available in the world is of a female, who existed more than 3 million years ago and there is a name given to that fossil, Lucy. So, there are many bones of Lucy that have been found and based on the dating of those bones, then the age of that type of human was detected.

However, because we only had bones and even the bones had gone through 3 million years and that is why there was no organic matter found there. In that case, you need to use more sophisticated techniques. You can also do radio dating with other elements, but that may be very much more expensive. Inorganic materials cannot be detected by carbon dating, that is another limitation.

And lastly, if something is very old like more than 40000 years old, then the technique becomes a little bit weak, because we do not have very good information about the atmospheric carbon at that time and also the concentration of carbon, then becomes so low because you see in 5730 years the concentration of carbon 14 becomes half and then, half of that and then half of that. So, at some point, if something has been decaying for more than 40000 years, then the concentration then becomes so low that you are not able to detect it. But all together, this is a very handy technique.

My goal is to tell you all that radiocarbon dating is based on carbon-14 and not carbon-13 because sometimes people get confused. So, you remember carbon-12 and carbon-14, now there is also something called carbon-13 and that is not radioactive, that is a stable isotope.

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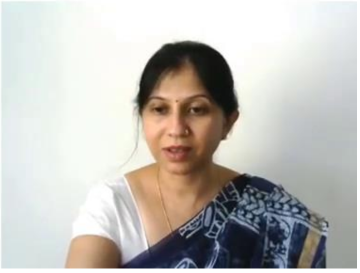
स्वाति शर्मा, भारतीय प्रौद्योगिकी संस्थान मण्डी

NMR active carbon (^{13}C)

Stable isotope that is used in chemical analysis using Nuclear Magnetic Resonance (NMR) and Mass Spectrometry.

- Nuclear magnetism: if an atom has an odd number as atomic mass, it possesses a "nuclear" magnetic moment (spin 1/2 or 3/2).
- This spin can alight itself in an external magnetic field and can then relax depending upon the surrounding environment. Different relaxation patterns can be measured in NMR.
- Magnetic Resonance Imaging (MRI) is also based on this principle. ^{1}H atoms are NMR active.
- ^{1}H present in water or other molecules can be detected.
- ^{13}C is used in NMR but not MRI because it has low natural abundance (1.1%).
- Compounds labelled with ^{13}C can be artificially synthesized but the composition of the human body cannot be changed!
- In general C is considered MRI-silent which means
    - (i) it does not interfere with the electromagnetic field to produce artefacts
    - (ii) C has a low electrical conductivity hence low eddy currents are produced.
- Hence, carbon-based composites can be used for making bone implants (patients can undergo MRI).
- Carbon is also transparent to X-Rays (this property is called radiolucency).
- Carbon composites are also used for making biomedical equipment (e.g. X-Ray plates).



So, this radio the carbon-13 is the one that has an odd atomic mass. It is 13, and when the atomic mass is odd, you will have a spin 1/2 or 3/2 or -1/2 or -3/2. So, you will have one unpaired electron, you will find the spinning quantum number of that nucleus.

Now, the fundamental principle of this NMR spectroscopy is that if you keep these kinds of materials or these kinds of elements in an external magnetic field. Then, in the presence of this external field, these spins can align and then, when the field is removed, they can relax.

And based on these relaxation times and based on this alignment of spins, the number of spins that align and do not align, what kind of relaxation mechanism they have and based on these different elements can be analyzed and this is what we do in NMR spectroscopy.

If you remember the medical imaging technique i.e. MRI is also called Magnetic Resonance Imaging. Why do we call it MRI? This is also actually based on the exact same principle as NMR; this is based on the principle of nuclear magnetism.

And however, we also technically call this technique nuclear magnetic resonance imaging. So, the actual name of MRI is NMRI. But medically, the term nuclear was removed because people get afraid whenever they think of anything that is nuclear. They think that now something bad will be done to my body. So, that is why for medical purposes, it is called only MRI and not nuclear MRI. But this is based also on the same principle of nuclear magnetism.

But here what we do is we take the protons because there is a lot of water in our body and hydrogen as it has only 1 proton. So actually, proton is also NMR active and since our body contains a lot of protons because we contain a lot of water, that can be then imaged using MRI technique, and based on that, you can find out what is wrong with the body.

Now, this whole thing I am telling you because when we talk about the applications of carbon, carbon is used for a lot of biomedical applications. For example, making the bone implants or also, different kinds of even equipment that are used for biomedical imaging purposes and so on. Carbon is used for manufacturing those things.

And in that context, you will hear a lot that carbon is MRI safe or carbon is X-ray safe. So, why is that the case? So, this is what I am trying to describe a little bit here because it often gets confusing. Now, carbon-13 is NMR active; but importantly, in the case of MRI, it is not important because we are only imaging proton, we are not really doing carbon-13 based imaging.

And why we are not doing it? Because the natural abundance of carbon-13 is only 1.1 percent. In the case of hydrogen, all the protons are NMR-active. So, the concentration of the signal is very high. But in the case of carbon 13, you will never get enough signal to do the imaging.

Then, why are we doing spectroscopy? Because in the case of spectroscopy, we can artificially make something that is labeled, this time labeled with carbon-13 not carbon-14. So, we can always make this kind of material for the purposes. There are some coupling mechanisms between hydrogen and carbon that we want to understand for a lot of organic materials for the analysis.

So, carbon-13 NMR is done; but in the case of MRI, carbon-13 is not quite used. So, do not get confused by why carbon is MRI safe or MRI silent? Well, two reasons because first, it does not really interfere with the electromagnetic field that is used during MRI and that is why there are no artifacts, the images are not distorted. And second, which is actually a more important reason that carbons are electrically conductive, but the conductivity is low enough. And as I also mentioned previously that we can tune the conductivity, just by changing the preparation method. We can also have carbon with a little bit high conductivity or with a little bit low conductivity. The one that we use in biomedical applications has a relatively low conductivity and good mechanical strength, that is why this particular carbon does not have a lot of eddy currents produced in it.

So, you know that whenever there is a conductive material that is kept inside an inactive magnetic field, then eddy currents are being produced inside the material. Now, in the case of metals, you have a lot of eddy currents which also mean that the metal can heat up at some point. So, if somebody has a metal implant, prosthetic arm, for example, somebody has it made of metal and when you do MRI, then the implant itself can heat up.

But on the other hand, when you use a carbon implant, then there is a much lower probability that it will heat up or something will happen to it because the eddy currents compared to metals in general are very low. So, because of these reasons, you can use it for making implants. So, these are not just pure carbon materials, but carbon-based composite or CFRPs, that we will learn about them and how we make the implants?

Typically, we can do 3D printing for making the exact shape of the bone that we want and so on. Carbon is also transparent to X-rays. X-rays will completely pass through the carbon because when some X-ray of your body being taken, then you only see the bones right; you do not see the polymers, you do not see the skin because these are organic compounds that are primarily made of carbon and carbon is transparent to X-rays. It let them through it, not completely, but at least 70 to 80 percent X-rays can go through carbon, which also means that now if you have a bone implant, then that will not interfere with the X-ray.

So, for example, let us say I had an implant here. And then, if you want to see if the implant is actually working properly or the bone has joined properly or not. So, if you want to measure the progress and you want to do the X-ray, then the implant material should not be opaque to X-rays right, otherwise it will hide some of the information.

So, in the case of carbon that is not a problem and that is why we also use carbon for. This is another reason for carbon’s biomedical applications, which also include biomedical equipment like the plates which are used for X-rays and even the tables and a lot of things that are used also in the equipment itself. So, a lot of these things are then made of carbon-based composites and carbon-based composites.