Physics of Functional Materials and Devices
Prof. Amressh Chandra
Department of Physics
Indian Institute of Technology Kharagpur

Lecture – 04, Week 1:
Polymers

Welcome back. This is the fourth lecture in the course Physics of Functional Materials and Devices. We have seen what are solid state materials, how are they classified, we have seen what are ceramics and then we have gone to discuss about composites. While we were discussing about composites, I had introduced to you the requirement of flexibility while we make composites and how they are going to be useful in modern day. The flexibility is mostly introduced by having a phase which is made up of fiber or polymers. So, let us today understand what are polymers and how do we use them in composites and what are the individual properties of these polymers.

So, just like the previous three lectures, we will first define what are polymers, what is the process of getting a polymer that is called as polymerization and based on polymerization you can have different types of polymers. Finally, once we have different types of polymers, we will talk about the applications of these polymers. The word polymer actually is derived from a Greek word poly which means many and thus a polymer is a large molecule which is also sometimes called as macromolecule built up by the repetition of small chemical units. So, you if you want to make a polymer you will have a building block and then you will go on joining many such building blocks together and you will make a large molecule and that is called as macromolecule.

So, sometimes people coming in from chemistry background use macromolecules, people coming from chemical or physics background they call it as polymer and nowadays these two terms are interchangeably used. So, you should understand what a word polymer means and what is macromolecules. So, it is just a repetition of small chemical units to get a large molecules. For example, you can take styrene and then you can go on at adding styrene monomers. So, the building block is called a monomer.

So, one styrene molecule that is a monomer is then added n number of times and you get a polystyrene polymer. This is what the word poly comes from that you are having n number of repeating units. So, once again what is a monomer? It is a molecule that can be converted to a polymer by combining with other molecules of the same or different type. So, it is not that you can you have to only put styrene styrene styrene monomers. You can combine two different types of building blocks and then make a polymer out of it.

The polymerization is the process where you bring these monomer molecules together in a chemical reaction to form a polymer chain or a three-dimensional network. So, if you have this pen then when I add this pen to another pen then it can grow in this direction, in this

direction as well as in the third direction. There what will you get? You will hence be getting a three-dimensional network by having the combination of monomers for n number of times. Usually at least 100 monomer molecules must combine together to produce certain unique physical properties. So, if you have very few number of monomers adding then the properties may be similar to that of monomers.

But if you want to have some unique properties which are different from that of monomers then you must have 100 monomer molecules or more than 100 monomer molecules coming together. So, you can see that sometimes you mention a polymer with 1 lakh molecular weight. That means, there are 1 lakh molecular units which have come together to form a polymer. These unique physical properties can be elasticity, tensile strength or you can have any other form of mechanical strength being introduced to these polymers. Those are different from the building block.

Hence polymerization is important because it gives you a strategy to create new chemicals. So, you can have new chemicals by polymerization. So, you can add two or three different monomers arrange them in a certain order and then repeat that order up to a large number of units and you will get unique properties from these new chemicals. The polymers can be classified based on origin. What is the origin of polymers? So, sometimes you will see that they are naturally occurring polymers.

So, these are natural polymers. Some you will synthesize certain polymers those are called synthetic polymers or you can have semi synthetic polymers that you have natural polymer and on using that you can have certain additional component attached to those natural polymers then you can have semi synthetic polymers. Based on the structure of the polymers what do we mean? Suppose this is the main chain what main chain is the direction in which the monomers are adding. So, if this is the main chain suppose this is the side chain. So, you can put another molecule on the sides of the main chain.

So, based on the structure of the polymers you can have linear polymers, you can have branched polymers or cross linked polymers. You can also have polymers which are amorphous or crystalline in nature. So, you can have crystalline polymers. These semi synthetic polymers can have different type of structures and therefore, you can also have them classified in the form of structure. And finally, you can have homo polymer or co polymer which have different structures.

Based on the force of attractions which are there between the monomers or the molecules which are forming the polymers you can have fibers, plastics or lastomers. Now, you can have different synthesis protocols to make these polymers. Therefore, based on the synthesis protocols which are utilized to make these polymers you can classify the polymers into different sub headings. So, that is under the heading of polymerization. So, you can have polymers which have been obtained by addition process which was followed in the synthesis or ring opening or condensation process of polymerization.

There can be many more processes of polymerization, but I have mentioned only a few just to explain to you how do we classify various polymers. Based on the thermal properties of these polymers mostly these polymers are classified as thermoplastic or as thermoset polymers. So, these are the ways you classify the polymers. The first one which we mentioned was the natural polymers. So, what are natural polymers like enzymes, nucleic acid, proteins, carbohydrates these are all polymers which are naturally occurring and their structures are normally very complex.

You can have starch, cellulose as other examples of natural polymers, but their structures are simpler than that of enzymes or proteins. Why did I mention the structure? The reason is if you go back to the third lecture you will see that we have seen that the structure plays an important role in deciding the properties of ceramics or ceramic matrix composites. Hence, as you change the structure of the polymer the characteristics of these polymers also change. The second classification which we had discussed was the synthetic polymers. These are what? These are man-made polymers polyethylene, polyvinyl chloride, nylon etcetera.

Can you name a few polymers which are man-made, but you use them on daily basis. If you just concentrate and think on the daily activities which you have then you will find that you are surrounded by man-made polymers. Finally, you have semi synthetic polymers. These are polymers that are derived from nature itself but then they are made to undergo certain chemical processes so that you find enhancement in their quality as well as the performance in terms of chemical or physical properties. You can have rayon, you can have vulcanized rubber, you can have guncotton or you can have many more semi synthetic polymers.

Now, if you want to list the applications of these natural, synthetic and semi synthetic polymers you will find that natural polymers are used to make papers, they are used in pharmaceuticals, foods and imaging agents. The synthetic polymers are used in plastic bags, the film wraps, the pipes, the water pipe which is used to water the plants in the garden for packaging purposes or they can be used as electrical insulators or for coating purposes. The semi synthetic polymers are extensively used in tire industry. So, where do you get this polymer? You have this rubber plant and you get the fluid out of this rubber plant, modify this fluid which is collected from the rubber plant and then you get the polymer which is used in tire industry. Similarly, the other application of these semi synthetic polymers is also in explosives.

Based on the structure you have linear, branched or cross linked polymers. A linear polymer is what? It consists of a single continuous chain of repeating units. The atoms are bounded to each other covalently. So, it is not ionically it is covalently which forms the backbone of the polymer. So, this is the backbone of the polymer.

The examples are polyethylene, PVC, polystyrene, polyamides and many more. Whereas, a branched polymer so, you can see there is some branching occurring over the main chain. A branched polymer is a macromolecule. So, you have large number of repeating units which extend and give you a polymer. These macromolecules are made from the polymerization of polymers and has a branch like structure.

The properties of these polymers are mainly affected by the amount of branching. You can clearly see that these two are not similar. And suppose I now add many more branches to this example. Will the example of the branched polymer which I had before I started putting these extra branch will have the same properties as the next branched polymer where you have seen you are seeing so, many more branches. Obviously, they would be different because the weight which is being which is being felt by the backbone would be different and therefore, the frequency of vibration of these backbone would be different.

And hence, you will see different kind of properties. If you have more number of branches, but the branches are made up of dissimilar polymers then you will have different properties. You can go on talking about the effect of branching and you will see that the branch structure will have different properties from linear polymer. In addition to that, the branch polymers will also have different properties by the amount of branching. Examples are low density polyethylene LDPE, high density polyethylene HDPE and polypropylene PP.

This is the common terms which are used. And finally, what are cross linked polymers? These are the polymers where the monomer units are cross linked together to form a three dimensional polymer. So, you cross link these polymers to get a three dimensional network. You have examples such as polyester fiberglass, you have polyurethanes which are commonly used in coatings, adhesives or you can also have vulcanized rubber based on these cross linked polymers. Then we had discussed about amorphous and crystalline polymers.

Obviously, what would be the amorphous polymers? These are polymers that have no crystalline regions or they have short range ordering. So, there is no uniformly packed molecules. So, you will have short range ordering. Instead, the amorphous regions of a polymer will have randomly packed molecules which will mean that there is no sharp melting point. The examples are the polymethyl acrylate, the polystyrene, you can have polycarbonates, polysulfones, you can have polyvinyl chlorides and many more.

This is one of the most common polymer which is surrounding us. Can you please find out the applications of PMMA? You will be amazed to see that the application of polymer which is polymethyl acrylate stretches from the bathroom sink to floor tilings to biomedical applications to an application which is called as lithography where they are used as photoresist. This polymer is one of the most used polymers in today's world. Then if you have a crystalline polymer, what would that mean? That would mean that it has long range ordering or well organized structure. We have seen what a crystalline material means and those same definitions stand good for crystalline polymers.

Examples are polyethylene, polypropylene, polyesters, nylons and many more. What was the third? You had homopolymers or copolymers. Homopolymers are the ones which are composed of only one type of repeating unit. So, if this is a repeating unit, you will just go on adding it one after the other and you will get a chain of these repeating units, but only one type of repeating unit. What would be copolymers? If we extend from homopolymers, this would be simple.

Polymers composed of two different repeating units in a polymer molecule will be defined as a copolymer. And then you can say, there could be different kind of copolymers. One could be random copolymer. You can immediately understand what would be random copolymers. There would be that at least there are two different types of repeating units, but they are not distributed along the polymeric chain in a well-defined order.

The distribution is random. So, two red balls coming together, then two green, but if it would have been ordered copolymer, then it should have been two red, two green, two red, two green, but then you start seeing one red and one green in the chain. So, it is a random copolymer. Then you can have alternating copolymers, very simple. You have red, then green, then red, then green. So, there is an ordered arrangement of the two repeating units along the polymer chain.

Now, rather than having only one unit that is in the alternating copolymers, you can have block copolymers. That this means you will have more than two or more than two blocks of each repeating units alternating. So, you can have three red balls or two red balls, then two green or two red balls and this behavior will extend throughout the polymeric chain or you can have graft copolymers. You will have grafting on the backbone. So, if this is the backbone of the polymer, then what will you do in the graft polymer? You will graft the second unit on this backbone.

So, you can put green, two green balls at different places of this backbone of the polymers. These are called as graft copolymers. We had discussed based on the classification of the force of attraction, you can have different types of polymers. So, you can have chemical bonds which can be primary or secondary chemical bonds.

First, we should understand that. Primary bonds are what? The ionic bonds, the metallic bonds and the covalent bonds. What are the secondary chemical bonds? The van der Waal forces, the hydrogen bonds and the dipole bonds. The secondary forces have attraction which are responsible for cohesive aggregation between individual molecules and they are weak in nature compared to the those of the primary chemical bonds. So, based on the force of attractions, the polymers are classified as fibers, plastics or elastomers. Fibers are linear polymers with high symmetry and high intermolecular forces.

They result in high modulus, very large tensile strength, but they have moderate extensibilities, that they can be extended to a certain number of repeating units. But they are finding applications in aerospace, automotive, marine or construction industries. Examples are nylon, the lysosil or modal diacetate fibers. What would be elastomers? Elastomers have irregular structure. So, we are moving from high symmetry to a lower symmetry.

They have weak intermolecular attractive forces, if there are weak intermolecular attractive forces that means, I will be able to move easily because my neighbor is not going to disturb me too much by for making a certain motion. And therefore, they are very flexible polymer chains. The chain segments of elastomers can undergo high local mobility. Why? Because the intermolecular forces are weak and therefore, I can have independent or nearly independent

motions with respect to my neighbor. Hence, elastomers exhibit high extensibilities which they can recover rapidly on removal of imposed stress.

So, once you remove the stress, they can come back to the original shape because still there are intermolecular attractive forces. It does not mean that there are no intermolecular attractive forces. There are forces, but they are weak and therefore, if I put a stress, the motion can be independent. But once I remove the external force, then these weak forces bring the structure back to its starting point. So, they as are natural rubbers, polyurethanes, the neoprimes and silicones.

Then you have the applications of these fibers, elastomers and plastics. You will find that they are used in textiles, carpets, ropes, seat covers, the dashboards in the cars, the insulating and the roofing purposes. Elastomers are used in gloves, seals, gaskets, the swimming suits, plastics you already know, packaging, automotive parts, toys, medical devices. These are only a few. Can you list equal number of more examples where fibers are being used, the elastomers are being used or plastics are being used.

If you can list them, then you can be sure that you are understanding difference between a fiber and elastomer and a plastic. Because you can say that this is a polymer, so it is being used in a given example. But which type of polymer is being used, if you can identify that, then you are understanding the difference between the polymers. Then we had talked about the polymerization based classification. So, you have different types of polymers which are obtained using different synthesis protocols.

So, you can have condensation polymers which are formed by a series of condensation reaction types, where any two species can react anytime leading to a larger molecule and in addition to that where the small molecule usually a water or ammonia is eliminated. So, it is taken out of the whole polymeric chain. Examples are polyamides, polyesters or urea formaldehyde. Then you have addition polymers. These are polymers which are obtained by reactions such that monomers are added one after the other to a rapidly growing chain.

This process is actually involving three additional steps. These are initiation, propagation and termination. So, you initiate the polymerization. So, what you have? You have monomer, then another monomer, then another monomer and they are getting longer in the chain.

So, the chain is growing. So, this is propagation. But for how long will you let this polymerization process to occur? You have to stop at certain point and that process where you stop the growth of the chain is called as termination. Monomers generally employed in this addition polymerization process are unsaturated and that means, they are usually with carbon-carbon double bond. The examples are polystyrene, polyethylene, polyacrylate nitrile, the polyvinyl chlorides. And finally, you are going to have polymers which are ring opening polymers. They are derived from the cleavage and then the polymerization of cyclic compounds take place.

So, you take a polymer, have the cleavage, you cut it and then allow it to grow in certain order. Finally, based on the thermal properties, they are either thermoplastics or thermosets. The

thermoplastics are what? They are the ones which flow under the action of heat and pressure, but upon cooling the polymers harden and assume the shape of the mold. So, or the container in which they are being forced to expand or soften under heat and pressure. In addition, these thermoplastics when compounded with appropriate ingredient, so you have an additional ingredient there, they can usually withstand several of these heating and cooling cycles.

So, you heat it, you cool it, you heat it, you cool it, one cycle of heating cooling cycle. But if a material can sustain a large number of heating cooling cycle, that is what is the requirement. And these thermoplastics can withstand many number of heating and cooling cycles. Common examples are polyethylene, polystyrene and nylon.

In addition to thermoplastics, we have the second class of polymers. These are thermosets. These thermosets are the polymers which when heated undergo a chemical change to produce a cross link or a solid polymer. So, when heated they will go on chemical change. These usually exist initially in the form of liquids which are called as pre-polymers. They can be then shaped into desired form by the application of heat or pressure, but these thermosets are incapable of undergoing repeated cycles of softening and hardening.

Softening means heating cycle, hardening means the cooling cycles. And the examples are phenol based formaldehyde or urea based formaldehyde or epoxies. The applications of these thermoplastics and thermoset polymers are the aircraft cabins, the medical devices, the pipe systems. Whereas, you can have thermosets which are used in cell tower tops, the heat shields, circuit breakers, disk break pistons or agriculture feeding trucks. So, there are certain well-defined applications for thermoplastics and then for thermosets. There are two types of polymerization reactions, the step growth polymerization and chain growth polymerization.

The step growth polymerization as the name suggests would be what, where a bifunctional or multifunctional monomer reacts to first form a dimer, then a trimer, longer oligomers and eventually the long polymer chain. So, you can have the formation of dimers, the trimers, then a much larger oligomers and finally, a long chain. Then you have chain growth polymerization, where the unsaturated monomer molecules add on to the active site on a growing polymer chain. So, there is an active site on a chain where the monomer would be adding. Thus, the rate of growth of polymer chain is very different in these two cases.

For step growth, the growth is logarithmic whereas, for chain growth it is linear. So, depending upon the type of polymerization, you will get different kind of time scales to obtain a certain polymer. So, the molecular size of a polymer can be quantitatively estimated by the degree of polymerization for how long the polymerization took place and what was the degree of polymerization. So, if you take an example of polystyrene and then see what this subscript n means. This is basically indicating the number of repeating units present in a polymer or the molecule which have been repeated n number of times to get a polymer chain.

This defines the degree of polymerization and it specifies the length of polymer molecule. What would be the case of low molecular weight polymerization? What would be the case?

That means you have n which is larger. So, if you have large n that means you have high degree of polymerization. So, molecular weight would be much higher and that is what the meaning of this term n gives you. A high degree of polymerization is normally required for a material to develop useful properties so that it can be appropriately described as a polymer.

What we had seen earlier where we said that n should be 100 at least 100 or more else you will not get useful properties. This is the same thing which is being written once again here. And I hope now the concept which was mentioned in the initial part of this lecture is clear to you. These are the details of the way you can calculate the molecular weight and the average molecular weight of the polymers based on the polydispersity and heterogeneity index. We will also come back to this bit later when we talk about the synthesis protocols, but I have just introduced these two concepts so that you know what are the terms number average molecular weight and weight average molecular weight means when we start the synthesis protocols.

This brings us to the conclusion slide of today's lecture. In today's lecture what have we talked about? We have mostly focused on polymers. What is the definition of a polymer? How do we classify a polymer or how do we classify polymers? Then we have talked about what are the various processes by which you can get these polymers and finally, for the different types of polymers we have also given the applications of those polymers. These are the references which were followed in today's lecture and you can read more about the field of polymers and polymer science using these references and I thank you for attending today's lecture. Thank you very much.