Nature and Properties of Materials Professor Bishak Bhattacharya Department of Mechanical Engineering Indian Institute of Technology Kanpur Lecture 16 Polymers: Introduction and Classification

Good morning everybody, in the domain of materials so far we have covered metals and ceramics. So now we will go to a new domain of materials, which is the polymer. So we will 1st start with a basic introduction to the polymers and then we will gradually see what are the very specific mechanical properties of polymers are and what is the mechanical behavior, what is so interesting about the behavior of polymeric materials?

But as an introduction today, we will $1st$ have a discussion on the basics of polymers and then we will also try to characterise the polymers based on different types of classification criteria and some application we will keep in our mind. So this will just give us kind of overview of the world of polymers.

> **Polymer Basics** $\text{poly} = \text{many}$ $mer = parts$ degree of polymerization = DP \bullet \bullet 68 **Monomer** Monomer Dimer $DP = 1$ $DP = 1$ $DP = 2$ $Monome$ \bullet 888 Dimer Trimer $DP = 1$ $DP = 2$ $DP = 3$ 88-88 88-88 **00-00** n-mer $(n+m)$ -mer m-mer $DP = n$ $DP = (n+m)$ $DP = m$ Laboratory $5a$

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Now, the word polymer has the Greek part in it, where the "poly" means many and "mer" means part. That means whatever polymers you see, it is essentially made of many individual parts, each one of these individual part is actually called a Monomer a single part. Now once I considered to monomers together, if they join their hands then they become a Dimer.

So a Monomer also by definition it has a degree of polymerization or DP which is one. Now if there are 2 monomers, then the degree of polymerisation becomes 2, so for dimers it will be degree of polymerisation, which is 2. If you add a monomer with a dimer, you will get a trimer and the degree of polymerisation will become 3.

Of course, this 1 unit 1 unit adding together or such kind of very small number of units happen for materials like silicon in which there is a term called Oligomer, so that means there are something like 5, 6 or 10 of the monomers join their hands together. But for carbon on which the entire life in Earth has developed, it does not bind only 10 numbers or 15 number or 100 numbers, but of millions or millions of such carbon molecules can easily get bonded with each other.

So specifically keeping carbon in mind in the polymer, our definition is something like N number of degree of polymerisation or n-mer with a m-mer if such polymers when they add together concatenate, then you get something like $n + n$ mer with a degree of polymerisation of $n + m$, so that is the kind of a very big scale polymer that we are talking about. Now how do we classify the polymers?

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There are various ways in which we classify the polymers, we will discuss them one by one today. For example, you can classify the polymers on the basis of their molecular structure. If you try to do that, I will show you that its start with the simplest molecular structure, where it is completely linear then it can be branched that means some branching coming out of the linear, then it can be cross-linked that means the branches are chemically linked and then it can be networked, so that is the molecular structure wise.

IF you look at it from the origin point of view, you can very simply divide polymers into 2 types, one is the which is having natural origin, so natural polymers and synthetic polymers, so that is this group. And then from the polymerisation reaction point of view that means how the polymer is developed, if you look at it then 2 most important types are Chain polymerisation and Step polymerisation, so that is from the polymerisation reaction point of view.

Then from the thermo physical behavior point of view, we generally classify the polymers into 2 groups; one is the techy so called polymers, which can actually you can give it many kind of forms so that is Thermoplastics and the other group which with respect to temperature, you can give it a set form that is the Thermosets, so that is another way of classifying the polymers.

Then in terms of the applications, there are End use of applications of polymers that is also another way of looking at polymers and there are some polymers which are actually advanced polymers, so these advanced polymers okay so that is like UHMWPE or liquid crystal polymers that is like some of the advance versions of the polymers, so let us try to look at them one by one.

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Now, from the origin point of view if you look at the polymers, I told you that you can divide into 2 groups; natural polymers and synthetic polymers. Natural polymers are Shellac or bioadhesive okay say for example, you can consider some of the latex of the tree that comes out, the cotton, or the silk okay, natural rubber, okay, shellac of course I told you and then the starch, which you get from potato okay, or the cellulose that you get from some of the plants.

These are all some of the examples, our bone itself some of the examples of natural polymer. And some of the examples of synthetic polymer our world today is actually surrounded by all sorts of synthetic polymers like synthetic rubber, Bakelite, neoprene, which is also form of rubber, nylon for example, polystyrene, polyethylene, PVCs, so there are so many of them, the synthetic polymers okay so that is as per as the origin of the polymer goes.

Now if you try to divide it in a different way, more like a fundamental point of view, then you can actually characterise polymers in terms of their molecular structure. So that is something that is little more advanced than in terms of instead of dividing them in terms of the origin of the polymers.

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So here, what you will see is that the polymers are essentially of 3 types that is the Linear polymers, then the Branched polymers and then those which are chemically linked in fact, out of them there are 2 types we call it. One is actually when there is a cross-linked structure and another is when there is a network structure. So to begin with, we will $1st$ see the linear structure polymers.

So some polymer units are just like monomers joining their hands together and building up the longest chains okay. Something like polyethylene, polyethylene from single units of ethylene you just add them all together, you get a long chain polyethylene. These are the each one of them of course along their axis because of covalent bonding, they are very strong okay.

But if you think of the transpose direction between the 2, then there is not much of a bonding force there. This will be either very weak Vander Waals bonding or hydrogen bonding kind of things. So as a result, they have $1st$ of all directionality, in one direction they will be exceptionally strong and high modulus of elasticity on the other hand, in another direction they would not be, so they will be weaker.

And they are soluble; they are fusible because of these kinds of structures and they are green also, you can use them many a times, so polyethylene the films you can actually reuse them or recycle them very easily. So the examples are like high-density polyethylene, low-density polyethylene, et cetera, and then PVCs, polystyrene, nylon, PMMA, all of them are good examples of the linear structure.

The other point is that linear structure so are generally they have actually good crystal structure okay. So because their repetivity is generally very good and as a result, many of the linear structures not all but many of them are actually highly crystalline. So the degree of crystallinity if it increases that also improves the mechanical property of the system.

Now, some of them the linear structures are not just linear, but they are branched type of structures. So that means there are fights branches or chains that are connected to the main ones chemically okay, but with another such link, there may be only once again hydrogen bond or Vander waals bond, etc. So they are more soluble and fusible and this is like lowdensity polyethylene is one of them, so that is a linear but there are some branches of it.

Now, if the branches kind of get cross-linked, so that is what the cross-linked structure is. Then what you are getting is that the adjacent linear chains are joined one to another at various positions by actually covalent bonds and they become insoluble and infusible, so that is what is the cross-linked structure.

If this degree of cross-linking increases so much that they form a network structure with high cross-linking and 3D network, then that is the extreme form of cross-linking and this will become insoluble and infusible like rubber, polyurethane, phenol formaldehyde or what we normally called epoxy okay epoxy resins. So that is the ultimate example of network structure.

So this also is important in the sense that cross-linked network structure are actually mechanically more rigid than the linear and branched structures and there is a co-relationship between this kind of the from the in terms of the growth of the polymer from the molecular structure point of view and the thermo physical point of you how we categorise it, there is a co-relationship between them.

And that is, if you see that the polymer is if you find it to be Linear or Branched then there is a high degree of probability that it is a thermoplastic polymer. On the other hand, if it is cross-linked or if it is network then it is more possible that it is a thermo set polymer. Now thermoplastic polymers because of their nature that they are linear or branch, they are heat sensitive, they soften and they actually flow upon heating, it is very easily one chain can smooth over the other.

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And I told you that they are soluble and fusible and this under many cycles of heating and cooling pass, they are recyclable, so thermoplastic polymers are greener in comparison to Thermo set polymers. Most linear polymers and those having some branched structure I told you already that these are actually thermoplastics. Now, individual polymer molecules are held together by weak secondary forces like Vander Waals force, hydrogen bond, dipoledipole interactions, these are the general type of weak bonds between the 2 chains.

So I have 1 chain and I have another one, between them the force that actually works between them is either Vander Waals force or hydrogen bond or dipole-dipole interaction and these are all weak bonds these are all weak bonds and that is why they are mechanically also they are weaker particularly in the transpose direction. Easy to repair by welding, solvent bonding, et cetera if there is a crack because they are formable, so you can actually apply a little bit of heat and then you can repair it.

And also very interestingly, they have unlimited shelf life, this is commercially important. Suppose today I buy some monomer okay and then later on I think of polymerizing it, now for these monomers to polymerize and form a thermoplastic polymer is something in which at least it will not get set, it will not be completely useless if the polymerisation suddenly starts. But you imagine that you have purchased that superglue from the market and you just forgot switch to close the tip of it.

What will happen that there will be a polymerisation reaction instantly as it comes out and get in contact of the air with oxygen, reaction starts, so there it will constantly get thermo formed, so it will become a thermo set and as a result that particular glue will be useless very soon, so then it has a very limited shelf life from the Thermo set polymers. But thermoplastic do not suffer from this kind of problems that is why it is almost like unlimited shelf life it is having.

What is the disadvantage, it is prone to creep. Now that you can easily see that they since the chains can actually slip over each other with a little bit of course because the force that holds them together in a weak force like Vander Waals force or hydrogen bonding hands, a little bit of force you can easily move one over the other. For the example of like polyethylene, polystyrene, okay, PET that you see many a times for using some of the bottles, etc, PVCs, nylon, polypropylene, PMMA.

PMMA one of the use is in your dentist for example if you go, they actually make the artificial teeth or such kind of things using PMMAs, so it is also known as dentist's powder, so that is the thermoplastic polymers. Now let us look at the Thermo set polymers okay.

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Before we do that, what are the typical applications suppose nylon, about the nylon wires okay and you also know that the nylon wires creep and the creeping happens because of the thermoplastic nature.

Then PVCs, polystyrene, which is used where there are more complex shapes for example. PMMA also is known as there is a common name of it its call it some people call it acrylic actually, so you can you will get it in the market as artificial glasses for example, they are transparent, then polypropylene which is used in the chairs for example and then PET, which is used in the bottles.

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Now let us look at the thermosetting polymers. Thermosetting polymers are actually network polymers. They are creep resistant, they are less sensitive to temperature quite naturally because unlike the linear polymers, here you have cross bonding or you have chemical bonding, so that means the individual chains are not very free to loop with respect to each other as a result they are creep resistant, as a result they are less sensitive to temperature.

And they attain permanent hardness due to cross-linking, and once they attend that, once again I want you to recall the superglue example that once it gets network then it do not soften and flow upon heating that is a good part of it. But then that also means that it is nonpost formable okay. So that means obtained in soluble or fusible stage in early or intermediate stage, but once they get cured, they will be infusible and insoluble, so as a result their shell life is actually very limited.

And but the good part is that they have excellent thermal and chemical stability once it is polymerized. The mechanical disadvantageous part is that they are brittle, they are nonrecyclable, so that is the flipside of it and the examples are like Bakelite, epoxy, Urethane. Urethane is like the foams that you use in your sofa for example. So that these are poly urethanes PU we call it PU foams. PU foam is a very common name and that is used in your sofas, etc, so that is the thermosetting polymers.

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Now in terms of applications you can try to visualize that it is used in the magazines, it is used in the Bakelite, hair dryer okay or so of course the glues of epoxy A, epoxy B, there are sometimes you will see in market that there are 2 glues, you will need to mix them together to actually initiate the polymerisation reaction because they are so sensitive, the heat sensitiveness and the shelf life is so limited so its special care is taken that they do not automatically get networked like the superglues.

So you would get them in 2 parts, epoxy A and epoxy B, you mix them in a particular isometric ratio, the polymerisation starts and you will get a good hard thermoset polymer, which is used in composites.

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Now, thermosets that mean it has to undergo a particular process called curing in order to get set. So the process to this from a monomer stage, $1st$ you are starting the process, so in liquid state itself the branching is occurring and then the gel is forming, so some are branched, some are already chemically linked so there is a solvent in gel phase. And from there the amorphous glassy phase will start as you increase by the addition of heat and sometimes pressure.

The gelation, vitrification will start and we will get a fully cured thermoset okay. So over the time as this gelation is happening, viscosity of the system will continuously increase and in between you will get that intermediate phase of gelation, where you get a gel phase and a sol phase as I told you. And with respect to time, this sol phase will gradually decrease and the gel phase will increase so that basically you get all interlinked phases and then the hardening or the vitrification is going to occur in the system.

The machine with which we generally do it, I will just want to mention it to you at this point is called an Autoclave machine okay, is used say for example, when you make the aircraft wheels okay, so this is composite these days and in that composite that matrix is nothing but a thermoset polymer, so that thermoset polymer is to be cured, so what you do is that you actually make this whole thing out of or thermoset polymer and then put it on the temperature and pressure so that it gets cured, the vitrification occur and you get that beautiful wing shape.

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Now, what happens in the polymerisation process, we have told many a times the polymerisation process from monomer to polymers? Now, now there are 2 types of polymerisation process; one is called Chain or Addition polymerisation. So in this process, the monomer units are attached to one at a time in a chain like fashion to form a linear macromolecule okay.

So there are only a few active sites in this case from where this polymerisation will start like this is one active site and then one after the other the process of polymerisation is happening. Only very few such active sites are there in fact, this will come as a catalyst is getting broken, then they decompose then the active initiator or R star will come. This R star, the moment it is going to react with a monomer, you get the $1st$ active unit that is the RM 1 star.

Then as a chain we propagate this RM 1 star, with another monomer to get RM 2 star. Then that process will continue like one RM n - 1 star will give you an RM n star, then that process will stop, then one of this RM n star is going to react with another of the RM n star, then there will be a RM $m + n$ R formation.

So as both the sides are now of the polymers is having two R, it will lose its cutting teeth that means the chain polymerisation will stop at that instant, so that is what is the addition of the chain polymerisation. Much like that there is another type of polymerisation where you do not have to really depend on one or 2 sides, but you can have simultaneous process of polymerisation in many places.

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So like everywhere this is happening and this is like it can involve more than one monomer species and monomer will react with any nearby monomer, they will not wait for some other active area to come and make them ready for reaction would not happen, they will readily react, so no special activation is needed to allow a monomer to react and a small molecular weight byproduct such as water that will be eliminated, that is why sometimes the Step polymerisation is also called Condensation polymerisation.

A typical reaction is like you have this OH element and then the this thing HO here, so $H +$ OH react with each other and you get the new one and similarly you get in another case, this OH + HO and you get a new one every time you are getting some water or condensation out of the system, so that is what is the Step polymerisation. And this you will find in polymers like phenol formaldehyde, nylons, polycarbonates, okay, these are all produced by the condensation polymerisation.

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Now we talk about some of the advanced polymers, one of them is ultrahigh molecular weight polyethylene like UHMWPE, this is becoming very important today because these are linear polyethylene, but it has very high molecular weight okay. What is the significance of high molecular weight? That means you have the each monomer itself is so long that actually it gives you a high melting point, high mechanical it gives you a high modulus of elasticity, et cetera.

So there are 2 trade names of it, one is Spectra, another is dyneema and both of them have extremely high impact resistance, high resistance to wear and abrasion, very low coefficient of friction, they are self lubricating and they have nonstick surface, very good chemical resistance to normally encountered solvents, excellent low-temperature property and outstanding sound damping and energy absorption characteristics.

Only thing is that their mechanical properties diminish rapidly with increased in temperature because they are the linear polymers, so they are susceptible to as I told you to creep like problems, but at if the temperature changes not very high then they work, they have excellent properties, they are used in Femoral implants, pipes, light gears in lagos, et cetera, that is what one of the examples of the advanced polymers.

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The another example of advanced polymers is the Liquid crystal polymers. So some of these aromatic polyester based on p-hydroxybenzoic acid and related polymers, they come into this category. Now, why they are liquid crystal we call it because in the liquid state generally, any material is supposed to be in a very amorphous state, but these materials in a liquid crystalline state you will get them that means they will be neither purely crystalline nor purely liquid, so you can consider it to be a new state of matter.

They are capable of forming regions of highly ordered structure while in the liquid phase, but regularity will be lower than the completely solid crystal. They are extremely unreactive and inert and highly resistant to fire. So something like the LCDs, the liquid crystal displays on digital watches or flat panel computer monitors, television and other digital displays, they are actually made of these liquid crystal polymers.

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Now let us try to categorise the polymers on the basis of the end use of applications. Let us see what the end uses of a polymer are. The first end use it in terms of the films, polymeric films you will get in various sizes in the market from 25 micron, we also call it in terms of micron, 25 micron to 125 micron meter thin films that are used for packaging food products.

And their important properties, they are low-density, high degree of flexibility, high tensile and tear strength, they are resistance to moisture and other chemicals that is why we generally wrap it up, for examples are polyvalent wrappers, polypropylene, cellophane, et cetera. So that is one of polymers where it is mostly used as films.

Then the other group I told you about this foams right, the sofas for examples which has the foams. So there you have the polyurethane foams, so foams are another very important categories of polymers, they contain relatively high volume percentage of small pores and trapped gas bubbles, they are commonly used as cushions in automobiles and furniture as well as in packaging and thermal insulations you get the polymeric foams, so that is another end use so films and foams.

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What else you will see? You will see polymers in coatings for example, in paints, varnish, enamel, lacquer and shellac you will see them. And they are used on to protect the surface and so that to protect it from corrosion and for electric insulations, to improve the appearance of an object you apply the polymeric colour, but that is for the coating.

The very important use of polymers, suppose you consider a Silk sari so it has silk fibre in it. And the fibre is very important application of a polymer because it has a very high degree of actually modulus of elasticity, it is isotropic and you can use it for various applications including making jet aircrafts, right. So they are usually long filaments having at least 100 is to 1 length to diameter ratio.

And can subject it to mechanical deformations like stretching, twisting, shearing, abrasion, they are very good to absorb this. They are used in textile industry for fabric Cloths which can be either woven or it can be used to make composites. Our next example of polymers is the adhesives.

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They are used to join a large variety of materials like metals, ceramics, polymers, composites, et cetera. And their advantage is that they are lighter in weight, they have the ability to join the similar materials, they have better fatigue resistance and they have lower manufacturing costs, but limitation is many times in terms of high-temperature or in terms of impact resistance, so these are some of the problems with the polymeric adhesives.

There are natural adhesives like animal glue or casein or protein, starch and resin here. And artificial resins like epoxy, polyurethane, Cyanoacrylate or acrylic polymers. They are used in aerospace, automobile and various types of stationeries, etc, so that has also become very popular use of polymers as adhesives.

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Then there is a good group of polymers, which we called them to be elastomers. Now what does that mean? It means that if you look at this particular diagram will be very clear to you that any brittle material will show a high model of elasticity, but they will fail at very low strain level okay. Now the plastics, they will become non-elastic beyond a certain point, and then the plastics strain will grow until it fails.

The elastomers on the other hand, they actually remain elastic that means if you actually unload it, it will trace the same path, but they can take a very large deformation so they remain elastic even though in a non-linear manner, highly nonlinear, but they can take up a very large strain. So naturally, whenever we talk of elastomers what comes in our mind are the rubbers for example.

So they have very weak intermolecular forces, low Young's modulus and high failure strain, that high failure strain is very important for them. So for a polymer to be an elastomers, it must not easily crystallise because the molecular chain should remain naturally coiled in the unstressed state, the chain bond locations must be free to readily respond to an applied force, delayed plastic deformation should be there.

The examples are silicon rubber, Butyl rubber, nitrile rubber, neoprene, etc. Their applications are like gasket seals, noise and vibration damper, car door seals, et cetera, so that is about the elastomers. The plastics I already told you that this is like it is read between the elastomers and the brittle material.

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They are malleable, can be molded into solid objects of diverse shapes, some plastics are very rigid and brittle and others are flexible, they are used for all general-purpose applications like some wise or very quick rapid prototypes you want to make, you use the plastics and they can be either thermoplastic or thermosetting that is about the plastics. So let us try to keep some names of thermoplastics for reference.

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Like ABS, which is used in what you called rapid prototyping purposes, so this is used mostly for rapid prototyping. Then the acrylics, I told you the Plexiglas is one of the examples, is used in lenses, transparent and aircraft enclosures okay, outdoor signs, et cetera. Fluorocarbons like Teflon group, which is used in anticorrosive seal, chemical pipes and valves because it is very much it is high-temperature resistant anticorrosive material.

Polyamide like nylon, using bearings, gears, cams, brush handles, et cetera. Polypropylene, which is used in sterilized bottles, packaging films, cabinets, etc. Polystyrene, which is used in wall tiles, battery cases, toys, indoor lighting panel, they have a lustre in them typical example is like Carinex, Dylene, etc. Polyesters like this fibres, dacrons, mylar, they are used in recording tapes, clothing, automotive tire cords, beverage containers. And Polyethylene, which is it very well that it is used in flexible bottles, toys, battery parts, tumblers, all sorts of very general-purpose applications. And there are the thermosettings and there are 3 important thermosettings here.

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One is amorphous one that is the Phenol formaldehyde, the trade name is Bakelite, it is used in telephones, motor housings, et cetera. Then the Epoxies, it is also amorphous, the trade name the popular trade name is Araldite, which is used in adhesives, protective coatings, and fibre glass laminates.

And then the polyesters, it can be thermoplastic or thermosetting, which means it can be either amorphous or it can be semi-crystalline. There are many different names like laminac, selectron, et cetera, which is used in helmets, fibre glass boats, et cetera, and chairs. So these are thermosettings, some of the regular thermosetting for your reference. So this is what we have given a brief introduction to the world of polymers. In the next lecture, I will talk about how to calculate the molecular weight of a polymer; I will talk about the polymeric structure and the tacticity of a polymer, thank you.