INDIAN INSTITUTE OF TECHNOLOGY ROORKEE NPTEL NPTEL ONLINE CERTIFICATION COURSE Structural Analysis of Nanomaterials LECTURE – 09 Basic Properties: Polymers With Dr. Kaushik Pal Department of Mechanical & Industrial Engineering Indian Institute of Technology Roorkee

Structural Analysis of Nanomaterials

Lecture- 09 Basic Properties: Polymers



Hello, today we are going to discuss about the basic properties of polymers, previously we have already discussed about the metals and their alloys and the ceramics, so today we are going to discuss the third part of this particular lecture series that is polymers. So this we have already



shown in our previous lectures that we have already done the metals and their alloys, we have done the ceramics, and today we are going to discuss about the polymers.

Polymers:

- The word 'polymer' is coined from two Greek words: 'poly' means 'many' & 'mer' means 'unit' or 'part'.
 It is defined as very large molecules having high molecular mass (10³-10⁷ u) & referred to as macromolecules.
 These macromolecules are formed by repeated linking of small units called monomers.
 Monomers are linked to each other by covalent bonds.
- A single polymer molecule may consists of hundreds to a million



Process of formation of polymers

So before going to start first let us know that what is polymers, so what polymers it is generally divided into two parts, one is called the poly, another one is called the mer, poly means as we know its many, and the mer means unit that means there is some repeating unit generally we are using or maybe some repeating units are present that's why it is called the polymer. Generally it is defined as a very large molecules having high molecular mass generally 10 to the power 3 to 10 to the power 7 unit, and referred to as macromolecules, the macromolecules are formed by the repeated linking of small unit called the monomers. As I told already so small small monomers they are attaching each other and then after that they are making one polymers. Monomers are linked to each other by the covalent bonds, so generally in polymer we can see the covalent bonds, a single polymer molecule may consist of hundreds to a million monomers and may have been linear, branched and the network structure.

So the example of the polymers like transformations of the ethane to the polythene, so ethane here is a single monomer, then we are doing the polymerizations then that means same monomers is attaching ethane altogether and then after that they are making the polythene polymer.



So what are the classifications of polymer? So generally we can do the five broad classifications of the polymer, first one is that based on source, then based on structure of polymers, based on mode of polymerizations, based on molecular forces, and based on polymerization mechanism. So first based on source it is also divided into three parts, one is called the natural polymers, semi-synthetic polymers, and the synthetic polymers, when you are talking about the structure of polymers it is also divided into three parts one is called the linear polymers, branched chain polymers, and the cross linking polymers.

When we are talking about the, how we are preparing the polymers then that means the mode of polymerizations it is called the addition polymers and the condensation polymers, and then when we are talking about the molecular forces it is also divided into some parts that is elastomers, fibres, thermoplastic polymers, thermosetting polymers, and polymerization mechanism it is also divided into two parts that is addition or chain growth polymerizations and the condensation polymerization.

Classification Based on Source:

Under this type of classification, there are three sub categories:

1. Natural polymers:

- · They are derived from plants and animals.
- Examples include wood, rubber, cotton, wool, proteins, enzymes, silk etc.

2. Semi-synthetic polymers:

· Cellulose derivatives as cellulose acetate (rayon) and cellulose nitrate.

3. Synthetic polymers:

- · These polymers are synthesized in the industry from chemical substances.
- They are manmade polymers extensively used in daily life and industry.
- Examples:
 - Plastic (polythene)
 - ✓ Synthetic rubbers (Buna-S) and synthetic fibres (nylon 6,6).

So first we will discuss all one by one, so we will start with the based on the sources, so under this type of classifications there are three subcategories, one is called the natural polymers, natural polymers means which we are getting from the environment that means they are derived from the plants and animals, what are the examples? Example is like wood, rubber, cotton, wool, proteins, enzymes, silk etcetera, so this all are we are directly getting from some plants or maybe some animals.

Now semi-synthetic polymers, generally cellulose derivatives such as cellulose acetate which is known as the rayon and the cellulose nitrate, there are some synthetic polymers also, so synthetic polymers, this polymers are synthesized in our industry or maybe the lab from the chemical substances, so mainly we are preparing this kind of polymers as per our requirement, they are manmade polymers, extensively used in daily life and industry, what are the examples? Examples like plastic, polyethylene, or maybe polythene and synthetic rubbers like Buna-S and the synthetic fibres like the nylon 6, 6.







Rayon



Now we are going to discuss about the classifications based on structure of polymers, so first it's called the linear polymers which consist of a long and straight chain like high density polythene, polyvinyl chloride, so in this particular case you can find that there is a long chain of all the mers, then we are talking about the branch chain polymers contain linear chains having some branches, in this particular image you can see there is certain branches has been attached with the main chain like example is low density polythene, and when we are talking about the cross linked or maybe the network polymers, so from this you can find they are forming some kind of bi-functional or maybe the tri-functional monomers and the contains strong covalent bonds between the various linear polymer chains, so it is one polymer chain, it is another polymer chain in between that they are making some linkage or maybe the cross linking, examples, bakelite and the melamine.

Classification Based on Mode of Polymerization:

Polymers can also be classified on the basis of mode of polymerization into two sub groups.

1. Addition polymers:

Formed by repeated addition of monomer molecules possessing double or triple bonds.



Now we are going to discuss about the classification based on mode of polymerizations, so polymer also can be classified on the basis of mode of polymerizations into two subgroups as I already told you, one is called the addition polymers, from the name itself we can understand that it can be formed by repeated addition of monomer, molecules possessing the double or maybe the triple bonds, so two types of addition polymers one is called the homopolymers, another one is called the copolymers.

So what is homopolymers? They are made by single monomeric species polymerizations, example formation of polythene from the ethane, the same group we are attaching altogether like a mer, monomer and then we are getting the polymer itself, so from ethane we are making the polythene and in this particular case when you are talking about the copolymers they made by addition polymerizations from two different monomers, so there are two species generally we are adding and we are making this polymers like if we add the styrene with 1, 3 butadiene, then we can get the Buna-S.

2. <u>Condensation polymers:</u>

- Formed by repeated condensation reaction between two different bi-functional or trifunctional monomeric units.
- In these polymerization reactions, the elimination of small molecules such as water, alcohol, hydrogen chloride etc., takes place.



Next we are going to discuss about the condensation polymers, so form by the repeated condensation reactions between two different bi-functional on with the tri-functional monomeric units, in this polymerization reactions the eliminations of the small molecules such as water, or maybe alcohol or maybe hydrogen chloride etcetera takes place, so what is the examples of the condensation polymers, like nylon 6, terylene nylon 6, 6, so how generally we are making? We are adding adipic acid with the hexamethylene diamine and then we are making the nylon 6, 6 and the water, and then after that we are removing this water and we are getting the nylon 6, 6.

Classification Based on Molecular Forces:

On the basis of magnitude of intermolecular forces present in them, divided into four subgroups:

- 1. <u>Elastomers:</u>
 - Rubber like solid with elastic properties.
 - Polymer chains are held together by the weakest intermolecular forces.
- Rubber

Example: Neoprene, Buna-S, Buna-N

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Weak binding forces causes polymer stretching.

Vulcanization - crosslinking process in which rubber molecules are converted into 3-D network of interconnected polymer chains through chemical crosslinks of sulfur.

2. Fibres:

- · Thread forming solids which possess high tensile strength and high modulus.
- - Example: polyamides (nylon 6,6), polyesters (terylene).

Then classification based on molecular forces, so on the basis of magnitude of the intermolecular forces present in them, divided into four subgroups, what are those? First one is called the elastomers, elastomers is nothing but the rubber, so it's a rubber like solid with elastic properties, polymer chains are held together by the weakest intermolecular forces, weak binding forces causes the polymer stretching, so we can stretch it up to certain limit, what are the examples? Like Neoprene, Bono-S, Bono-N generally when we are using this kind of elastomers we are adding with some fillers or maybe some kind of additives, say for example of the tire we are adding natural rubber with the styrene butadiene rubber, then how generally this is taking place, so this is the taking place that term is called bi-vulcanizations, what is vulcanizations? Generally cross linking process in which rubber molecules are converted into 3D network of interconnected polymer chains through chemical cross linking of sulfur, here we have given only the sulfur generally we are doing the vulcanizations by the hydrogen peroxide also, so simple in between the polymer chains we are making the cross linking of that and we are making this kind of materials.

Then, next is the fibres, thread forming solids which possess high tensile strength and high modulus, have strong intermolecular forces like hydrogen bonding which leads to close packing of the chains and crystalline in nature, what are the examples? Like polyamides, nylon 6, 6, polyesters are maybe known as the terylene.

Classification Based on Growth Polymerization (Mechanism):

Two broad types of polymerization reactions

Addition polymerization
 Condensation polymerization

1. <u>Addition polymerization or chain growth polymerization:</u>

- Polymer is formed from monomer, without loss of any material.
- Product is exact multiple of original monomeric molecule.
- Proceeds by initial formation of some reactive species like free radicals or ions and by the addition of reactive species to other molecule, with regeneration of reactive feature.

Free radical mechanism:

- ✓ Alkenes are polymerized in presence of free radical generating initiator (catalyst).
- ✓ Initiator (catalyst) Benzoyl peroxide, Acetyl peroxide, Tertiary-butyl peroxide etc.

Next we are going to discuss about the thermoplastic polymers, so generally this polymers are linear or maybe the branched long chain molecules, capable of repeatedly softening on heating and hardening on cooling possess intermolecular forces of attractions, intermediate between elastomers and the fibres, so in a basic idea I can tell you that thermoplastic polymers is something like that, that if we give a shape and then after that we can give it heat and it can again melt and again we can give it the heat, so it is not the permanent one, but when we are talking about the thermosetting polymers its like a, if we give a shape, particular shapes after that we cannot change it, so cross linked or branched polymer molecules which on heating undergo extensive cross linking in moulds and again become infusible, these cannot be reused that is the

vital point for the thermosetting polymers. So what are the examples? Examples like bakelite, urea-formaldehyde resins etcetera. So generally if we see the whole order of strength of this kind of materials so first thermosetting, then after that fibres and then after that thermoplastics and last is the elastomers and the strength point of view.

Next we are going to discuss about the classification based on growth polymerizations, means mechanisms, so there are two types of polymerizations reactions generally taking place, first one is called the addition polymerizations, second one is called the condensation polymerizations. What is addition polymerizations? Sometimes it is known as the chain growth polymerizations also, so in this particular case polymer is form from monomer without loss of any material, product is exact multiple of original monomeric molecules proceeds by initial formation of some reactive species like free radicals or ions and by the addition of reactive species to other molecule with regeneration of reactive features.



What is free radical mechanisms? Alkenes are polymerized in presence of free radical generating initiator or which is known as the catalyst also, initiator like benzoyl peroxide, acetyl peroxide, tertiary butyl peroxide etcetera are acting as an catalyst, there are three states of free radical mechanisms, first one is called the chain initiation step, second one is called the chain propagation step and third is called the chain terminating step. So what is chain initiation step? In this particular case we can see that involves addition of phenyl free radicals found by peroxide, then benzoyl free radical we are making, then phenyl free radicals, and then we are using with the ethane as a monomer. When we are talking about the chain propagation step, chain propagation step means whatever product we have prepared, now we are try to increase the growth of that particular mars, so what is that? Repetition of this sequence with new and bigger radicals, so like ethane so repeating unit then again we are going to increase the same repeating unit, and then last thing is called the chain terminating steps, means after certain time, after certain reaction we are going to terminate the whole process, so product radicals thus form reacts with another radical to form the polymerized product, so ultimately we are making the polythene.

Preparation of Some Important Addition Polymers:

a) Polythene: It is widely used polymer and of two types:



Now we are going to discuss about the some important addition polymers, how we are going to prepare? Say suppose we are going to discuss about the polythene, it is widely used polymer and of two types, one is called the low density polythene, another one is called the high density polythene, low density polythene sometimes we are calling it as a LDPE, so what is that? Have numerous branches so hard to compress, polymer chains packed loosely together, more flexible and light weight, has low crystalline and high amorphous regions, has weaker intermolecular forces and tensile strength, it is less chemically inert, so like example like the squeeze bottles generally we are using for the chemical reactions, because it should not be very hard so that we can squeeze it and the water will come out, when you are talking about the high density polyethylene in short it is called the HDPE, so it is having some linear structures so can be compressed, polymer chains packed more tightly so strength is more, less flexible and stronger has high crystalline and low amorphous regions, has stronger intermolecular forces and the strength and it is chemically inert also, what are the examples? Examples is the pipes, this pipes generally we are using for the wiring applications in our household.



Next we are going to give the examples of the polytetrafluoroethene, so polytetrafluoroethene is also known as the Teflon, it is manufactured by heating tetrafluoroethene with a free radical or maybe the persulphate catalyst at high pressures, what are the properties? Generally its chemically inert, its resistant to attack by the corrosive reagents, so uses in generally making oil seals and gaskets, we are using for the nonstick surface coated utensils generally we are using, so nowadays in our kitchen we are using all the nonstick utensils where we are using the coating of this Teflon materials. So tetrafluoroethene in the presence of catalyst and high pressure we are making it the Teflon, we are using it for the nonstick pan.

Then we are going to discuss about the polyacrylonitrile, so addition polymerizations of acrylonitrile in presence of a peroxide catalyst leads to the formation of polyacrylonitrile, what are the uses? Used as a substitute for the wool in making commercial fibres as orlon or maybe the acrilan, so sometimes it is called the synthetic wool also, so acrylonitrile in the polymerizations, in the presence of peroxide catalyst we are making the polyacrylonitrile.

2. Condensation polymerization:

- It involves a repetitive condensation reaction between two bi-functional monomers.
- · Results in loss of some simple molecules as water, alcohol, etc.
- It leads to formation of high molecular mass condensation polymers.
- It is also called as step growth polymerization.



Next we are going to discuss about the condensation polymerizations, what is that? It involves a repetitive condensation reactions between two bi-functional monomers, results in loss of some simple molecules like water, or maybe the alcohol etcetera, it leads to formation of high molecular mass condensation polymers, it is also called as the step growth polymerizations, so sometimes condensation polymerizations is also known as step growth polymerizations, what are the examples? Formation of terylene by the interaction of ethylene glycol and the terephthalic acid, so ethylene glycol terephthalic acid it is making the terylene or maybe the dacron, so here other examples of the condensation polymers are melamine polymer, so generally we are using for some crockery or maybe some cups, we are using some kind of bakelite polymer, we are using polyamide like nylon 6, 6, nylon 6 and we are using some polyester like terylene or maybe the dacron.

Preparation of Some Important Condensation Polymers:

- a) Polyamides:
 - Possesses amide linkages, and an important examples of synthetic fibres as nylons.
 - Product of condensation polymerisation of diamines with dicarboxylic acids and also of amino acids and their lactams.



Next we are going to discuss about the preparation of some important condensation polymers, so what is that? It is called the polyamides, which possess the amide linkages and an important example of the synthetic fibres as nylons, product of condensation polymerizations of diamines with dicarboxylic acids and also of amino acids and their lactams, so how we are preparing the nylon? So first nylon 6 6, we are preparing, so product of condensation polymerization of hexamethylene diamine with adipic acid under high pressure and the temperature is almost 553 kelvin, so we are making nylon 6 6 as a byproduct, H2O means water is also generating, so what are the uses? In making sheets, in bristles for brushes and in the textile industry, then how we are making the nylon 6? Obtained by heating the caprolactum with water at high temperature, so caprolactum in the presence of water, at temperature varies from 533 to 543 kelvin, so we are making the nylon 6.



What is the uses? Generally in manufacture of tyre cords, fabrics and the ropes we are using the nylon 6. Then another example is the polyesters, so polyesters from the name itself we can assume that generally poly condensation products of the dicarboxylic acids and the diols, so its manufactured by heating a mixture of ethylene glycol and the terephthalic acid at 420 to 460 kelvin in presence of zinc acetate antimony trioxide catalyst, what are the examples? Like dacron or maybe that terylene, terylene is some kind of materials generally we are using for our suites or maybe dress materials and it is crease resistant, what is the use of that materials? In blending with cotton and the wool fibres, and glass reinforcing materials in the safety helmets.

Next we are giving the examples of phenol formaldehyde polymers, which is nothing but known as the bakelite, so condensation product of phenol with formaldehyde in presence of an acid or maybe the base catalyst. Novolac is the best example, which is nothing but a initial and linear product, so novolac nowadays it is using in paints, on heating with formaldehyde undergoes cross linking to form an infusible solid mass called the bakelite, it is used for making the combs, phonograph records, electrical switches and handles of the various utensils, it is very, very hard and it is also the temperature resistant materials. So how we are making? We are taking the phenol formaldehyde and then we are adding with the bakelite, and then we are making the bakelite product, so simple phenol formaldehyde by doing the condensation methods we are making the bakelite and water is coming as a byproduct materials, and here we can see the several examples of the bakelite products.

Next we are going to discuss about the co-polymerizations, so co-polymerizations, polymerization reactions in which a mixture of more than one monomeric species is allowed to polymerize and to form a copolymer. Copolymer can be made not only by chain growth polymerizations, but by step growth polymerizations also, so in a different step one by one following, if you follow and then we can make this kind of polymerizations, it contains multiple units of each monomer used in the same polymeric chain, so what are the examples? Like mixture of 1, 3 butadiene and styrene can form a copolymer, so 1, 3 butadiene with styrene with some conditions we are making the butadiene styrene copolymer, copolymers have properties

quite different from the homopolymers, what are the examples? Butadiene styrene copolymer its quite tough, good substitute for the natural rubbers, sometimes we are using it for some other applications, used for manufacture for the autotyres, floor tiles, and the cable insulations.



Next we are going to discuss about the rubber, so rubber generally its two types one is called the natural rubber, another one is called the synthetic rubber, so natural rubber its generally, directly what we are getting from the plant itself, so natural polymer and has coiled structure called as elastomer due to the elastic properties, linear polymer of isoprene which is nothing but the chemical name is 2 methyl 1, 3 butadiene also called as cis 1 4 polyisoprene, cis polyisoprene molecule consists of various chains held together by weak Van der Waals interactions, because inter forces are very very less over there, as I told already so vulcanizations of rubber means when we are adding two or more rubbers and then in between that we are using some cross linking materials like the hydrogen peroxide or maybe the sulfur, and then we are making one kind of polymeric chain over there, so generally natural rubber becomes soft at high temperature, the temperature is more than 335 kelvin and brittle at low temperatures generally its less than 283 kelvin, it's improve the physical properties shows high water absorption capacity, vulcanizations also improves the soluble in nonpolar solvent, and its nonresistance to attack by the oxidizing agents, so here as I told already we are adding the sulfur as a vulcanizing agent and then we are making the vulcanized rubber over there, and here you can see that sulfur has been making a cross linking in between the polymeric chains.

2. Synthetic rubber:

- It is any vulcanisable rubber like polymer, capable of getting stretched to twice its length.
- It returns to its original shape and size as the external stretching force is released.
- They are either homopolymers of 1,3-butadiene derivatives or copolymers of 1,3-butadiene.



Next we are going to discuss about the synthetic rubber which I have already told that generally we are making it in some by chemical reactions in our lab or maybe the industry, so it is any vulcanisable rubber like polymer capable of getting stretched to twice its length, it returns to its original shape and size as the external stretching forces released, it's elongations is high, they are either homopolymers of 1, 3 butadiene derivatives or maybe the copolymers of 1, 3 butadiene. So there are two types of techniques by which we can prepare this synthetic rubbers, first one is or maybe the examples is like that, one is neoprene, so formed by the free radical polymerizations of the chloroprene, so chloroprene we are using the polymerizations and from that we are making the neoprene, where we are using this neoprene, generally we are using it for the conveyor belts, gaskets, and hoses, and another example is that Buna-N generally obtained by copolymerizations of the 1, 3 butadiene, and acrylonitrile in presence of peroxide catalyst, already I told either generally we are doing the vulcanizations by the sulfur or maybe the hydrogen peroxide catalyst.

So resistance to the actions of petrol, lubricating oil, and the organic solvents, that's why this Buna-N generally we are using for oil seals, tank lining and etcetera, so now we are going to discuss about the properties of polymers, so if we divide all the properties, so generally there are four groups, first one is called the physical properties, there are two subgroups, one is the degree of polymerizations and molecular weight, another one is the polymer crystallinity.



Next groups is thermal properties which will tell us the melting point and the glass transition temperature of that particular polymer, and if we talk about the mechanical properties of the polymers it is divided into 5 parts, one is strength, percent elongation to break, Young's modulus, toughness, and another one is that viscoelasticity, and last one is the chemical properties, so we'll discuss all this properties one by one.



So first we are going to start with the physical properties, so physical properties means the first molecular weight will come, degree of polymerizations will come, then crystallinity of polymer

will come and the low density, so these all are together is known as the physical properties of polymer.

- I. Degree of Polymerization and Molecular Weight:
 - Degree of polymerization: The number of repeating units in the polymer chain.
 - Molecular weight of a polymer molecule: It is Product of the degree of polymerization and the molecular weight of the repeating unit.
 - Molecular Weight Averages: The polymer molecules are not identical but are a mixture of many species with different degrees of polymerization, that is, with different molecular weights.

$$\sum_{i=0}^{\infty} P_i X_i \cdots \cdots \cdots (i) \quad \begin{cases} \text{where,} \\ \text{Set of values} = \{X_1, X_2, \dots, X_n\} \\ \text{Probability of occurrence} = \{P_1, P_2, \dots, P_n\} \end{cases}$$

- Number-Average Molecular Weight:
 - ✓ If N_i is the number of polymer molecules having the molecular weight M_i , then the "numberaverage" probability of given mass is given by:

$$P_{i} = \frac{N_{i}}{\sum_{j=0}^{\infty} N_{j}} \cdots \cdots \cdots \cdots (ii)$$
$$M_{n} = \sum_{i=0}^{\infty} \left[\frac{N_{i}}{\sum_{j=0}^{\infty} N_{j}} \right] M_{i} = \frac{\sum_{i=0}^{\infty} M_{i} N_{i}}{\sum_{j=0}^{\infty} N_{j}} \cdots \cdots \cdots (iii)$$

So first degree of polymerizations and the molecular weight, so first we have to know what is the degree of polymerizations, so the number of repeating units in the polymer chain is known as the degree of polymerizations, what is the molecular weight of the polymer molecule? It is the product of the degree of polymerizations and the molecular weight of the repeating unit, then what is the molecular weight averages? The polymer molecules are not identical but they are a mixture of many species with different degree of polymerizations, that is with different molecular weights, so how generally we are giving the, mathematically we are giving it so it's generally the summation over I from 0 to infinity PI XI, what is the number average molecular

- ✓ Physical properties (like transition temperature, viscosity, etc.) and mechanical properties (like strength, stiffness, and toughness) depend on molecular weight of polymer.
- ✓ Lower the molecular weight, lower the transition temperature, viscosity, and mechanical properties.
- ✓ Due to increased entanglement of chains with increased molecular weight, the polymer gets higher viscosity in molten state, which makes the processing of polymer difficult.
- Weight average molecular weight:



weight? So if NI is the number of polymer molecules having the molecular weight MI then the number average probability of given mass is given by generally PI = NI/summation of J, from 0 to infinity NJ, what is MN? Generally it is summation over I = 0 to infinity into NI/summation over J 0 to infinity NJ into MI that means is equal to summation over I = 0 to infinity, MI, NI/summation over J, 0 to infinity NJ, so this is the another equations.

So what is the physical properties? Like transition temperature viscosity and the mechanical properties like the strain, stiffness, and toughness depend on the molecular weight of polymer, lower the molecular weight, lower the transition temperature, viscosity and the mechanical properties, this is the generally the standard rules we are following. Due to increased entanglement of the chains means that the cross linking in between the chains with increased molecular weight, the polymer gets higher viscosity in the molten state which makes the processing of the polymer difficult.

Now we are going to discuss about the weight average molecular weight, so the weight average probability generally it is given by PI = NI MI/summation over J 0 to infinity NJ MJ, the weight average molecular weight is given by MW = summation over I to, 0 to infinity x NI MI/summation over J 0 to infinity NJ MJ x MI which is nothing but the summation over I, 0 to infinity NI MI square/summation over J to infinity NZ MZ, so what is the degree of polymerizations? The degree of polymerizations can be calculated using the number average molecular weight which is nothing but number average molecular weight by the molecular weight of the repeating unit.



Now we are going to discuss about the polymer crystallinity, from this particular slide we can get the informations about the crystalline and the amorphous polymers, so generally polymer chains are very large as I already told you and found in the polymer in two forms as the lamellar crystalline, another one is called the amorphous, what is lamellar crystalline? In which the chains folds and make lamellar structure arranged in the regular manner, and what is amorphous? In which the chains are in irregular manner, so lamellar are embedded in amorphous part and communicate with other lamellar via tie molecules. Polymers having high degree of crystallinity are rigid and have high melting point but their impact resistance is too low, amorphous polymers are soft and have lower melting points, so generally if we going to calculate the percentage crystallinity it is, the formula is PC x PS – rho C x rho S – rho A/rho S x rho C – rho A x 100 means when we are going to calculate the percentage, so where rho C is the density of the completely crystalline polymer, rho A is the density of the completely amorphous polymer and rho S is the density of the sample.

2. <u>Thermal Properties:</u> <u>Melting Point and Glass Transition Temperature:</u>

- Glass transition temperature is the property of amorphous region of polymer, whereas the crystalline region is characterized by the melting point.
- Glass transition temperature is the second order transition, where as melting point is the first order transition.
- The value of glass transition temperature is not unique because the glassy state is not in equilibrium.
- Its value depends on several factors such as:
 - ✓ Molecular weight
 - ✓ Measurement method
 - On the rate of heating or cooling
- Semi-crystalline polymer shows both the transitions corresponding to their crystalline and amorphous regions so have true melting temperatures (T_m) at which the ordered phase turns to disordered phase, whereas the amorphous regions soften over a temperature range known as the glass transition (T_g) .



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Now we are going to discuss about the thermal properties of the polymers, so when we are going to do the any thermal characterizations generally we'll get two informations, first one is the melting point, another one is called the glass transition temperature, this is the unique properties of the polymers or maybe any kind of elastomer materials, so glass transition temperature is the property of amorphous regions of polymer whereas the crystalline region is characterized by the melting point, so that's why generally for the rubber or maybe the elastomers we are getting the glass transition temperature or maybe any kind of polymer we are getting the melting point, so glass transition temperature is the second order transitions whereas the melting point is the first order transitions, the value of glass transition temperature is not unique because the glassy state is not in equilibrium, so generally the glass transition temperature for natural rubber is -70 degree centigrade, it's value depends on several factors such as molecular weight, measurement methods on the rate of heating or cooling.

•	Amor	phou	s p	olymers	do	not	posse	ess th	ne mel	ting
	point,	but	all	polymers	s p	osses	s the	glass	transi	tion
	temper	ratur	e.							

- The polymer melting point Tm is increased if the double bonds, aromatic groups, bulky or large side groups are present in the polymer chain, because they restrict the flexibility of the chain.
- The branching of chains causes the reduction of melting point, as defects are produced because of the branching.

Glass transition temperatures of some polymers

Polymer	T _g (°C)
Polytetraflouroethylene	-97
Polypropylene (isotactic)	+100
Polystyrene	+100
Nylon 6,6	+57
Polyethylene (LDPE)	-120
Polyethylene (HDPE)	-90
Polypropylene (atactic)	-18
Poly(vinyl acetate) (PVAc)	+28
Polyester (PET)	+69
Poly(vinyl alcohol) (PVA)	+85
Poly(vinyl chloride) (PVC)	+87

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Now we are going to give some examples of the semi-crystalline polymers which shows both the transitions correspondence to their crystalline and amorphous regions so have true melting temperatures at which the ordered phase turns to disordered phase whereas the amorphous regions soften over a temperature range known as the glass transaction temperature, so generally the semi-crystalline polymer, example is that liquid crystal polymer or maybe sometimes we are calling it as a LCP, so in this particular case this is the temperature, this is the glass transition temperature TG, this is the melting temperature TM, so glass transition, glass for glass materials generally it varies up to the glass transition temperature then it is rapidly increasing the volume, when you are talking about the semi-crystalline it is quite less and for the crystalline solids its totally increasing in a rapid manner.

So amorphous polymers do not possess any melting temperature, as I already told you but all polymer possess that glass transition temperature, yes of course, generally as a thumb rule the glass transition temperature of the polymer is around 10 to 15 degree, so the polymer melting temperature point TM is increased if the double bonds, aromatic groups, bulky, or maybe the large side groups are present in the polymer chains, because they restrict the flexibility of the chain itself.

Continued...

Factors Affecting the Glass Transition Temperature:

a) Intermolecular Forces:

Strong intermolecular forces cause higher T_g.

b) Chain Stiffness:

✓ The presence of stiffening groups (such as amide, sulfone, carbonyl, *p*-phenylene etc.) in polymer chain reduces the flexibility of the chain, leading to higher glass transition temperature.

c) Cross-Linking:

- ✓ The cross-links between chains restrict rotational motion and raise the glass transition temperature.
- ✓ Hence, higher cross-linked molecule will show higher T_g than that with lower cross-linked molecule.

d) Pendant groups:

✓ The presence of pendent group can change the glass transition temperature.

- e) Plasticizers:
 - Low molecular weight and non-volatile materials added to polymers to increase their chain flexibility.
 - ✓ Reduce the intermolecular cohesive forces between polymer chains, which in turn decrease Tg.

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The branching of chain causes the reduction of melting point as defects are produced because of the branching, so generally glass transition temperature of some polymers as I told like polytetrafluoroethylene it is -97 degree centigrades, polypropylene 100 degree centigrade, polystyrene 100 degree centigrade, nylon 6 6 is 57, polyethylene LDPE is -120, so these all are the different glass transition temperature for the elastomers and the polymers. So what are the factor affecting the glass transition temperatures, so first is intermolecular forces, so strong intermolecular forces cause the higher glass transition temperature. Next one is called the chain stiffness, so the presence of stiffening groups such as amide, sulfone, carbonyl, p-phenylene etcetera, in polymer chain reduce the flexibility of the chain leading to higher glass transition temperature.

Next is cross linking, the cross links between the chains restricts the rotational motions and raise the glass transition temperature, hence higher cross linked molecule will show the higher glass transition temperature than that with lower cross linked molecules.

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f) Molecular weight:

- ✓ The glass transition temperature is also affected by the molecular weight of the polymer.
- ✓ Tg is increased with the molecular weight.
- ✓ The molecular weight is related to the glass transition temperature by the Fox-Flory Equation:



Where, $T_{g,\infty}$ is glass transition temperature at the molecular weight of infinity, *K* is empirical parameter called Fox-Flory parameter related to free volume inside the polymer.

✓ It is observed that Tg is increased up to the molecular weight of approximately 20, 000, and after this limit, the Tg is not affected.



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Next is pendant groups, means what are the groups are attached, so the presence of pendant group can change the glass transition temperature. And last one is the plasticizers, low molecular weight and non-volatile material added to polymer to increase their chain flexibility, reduced the intermolecular cohesive force between the polymer chain which in turn decreases the glass transition temperature. And another one is the molecular weight, so the glass transition temperature is also affected by the molecular weight of the polymer, TG is increased with the molecular weight, the molecular weight generally is related to the glass transition temperature by the Fox Flory equations, so what it tells? Generally glass transition temperature = TG up to infinity – K/MN, where TG infinity is the glass transition temperature at all molecular weight of infinity, K is the empirical parameter called the Fox-Flory parameter, so this one related to the free volume inside the polymer, it is observed that the glass transition temperature is increased up to the molecular weight of approximately 20,000 and after this limit the glass transition temperature is not affected.

3. Mechanical Properties:

Mechanical Strength:

Strength is the stress required to break the sample.



Next we are going to discuss about the mechanical properties, so when we are going to discuss about the mechanical properties first it will come the mechanical strength, so it is the strength is a stress required to break the sample, there are several types of mechanical strength, first one is called the tensile, generally stretching of the polymer, torsional which is related to the twisting of the polymer impact, generally by the hammering, flexural bending of the polymer and the compressional means the compression of the polymer. So what are the increasing strength, so in that particular case the increasing strength is like that network is the highest one, then cross linked, then the branched and linear is the lowest one, so here if we see the stress strain curve of the polymers, so generally for the brittle plastic, then fibre, and elastomer you can see the maximum strain over there, so in terms of stress so fibre is the highest one.

Factors Affecting the Strength of Polymers:

* Molecular Weight:

- Tensile strength of polymer rises with increase in molecular weight and reaches the saturation level at some value of molecular weight.
 - $\sigma = \sigma_{\infty} \frac{A}{M}$ where, σ_{∞} = tensile strength of polymer with molecular weight of infinity, A = some constant, M = molecular weight.

✓ Cross-linking:

Restricts motion of chains and increases the strength of polymer.

✓ Crystallinity:

It increases strength, because in crystalline phase, intermolecular bonding is more significant. Hence, polymer deformation can result in the higher strength leading to oriented chains.

Molecular weight (g/mol)

molecular weight of the polymer

0

So what are the factor affecting the strength of polymers? First one is the molecular weight, where tensile strength plays a vital role, so tensile strength of polymer raises with increased in molecular weight and reaches at the saturation level at some value of the molecular weight, so generally sigma = sigma infinity - A/M, where sigma infinity is nothing but the tensile strength of polymer with molecular weight of infinity, A is some constant, and capital M is nothing but the molecular weight of that particular polymer. Cross linking restricts motions of chain and increase the strength of the polymers, crystallinity it increase the strength but because in crystalline phases intermolecular bonding is more significant, hence the polymer deformation can result in the higher strength leading to the oriented chains itself, so here the variations of the tensile strength, so if we are increasing the molecular weight up to certain time the strength will increase and then after that it will become constant.



Now we are going to discuss about the percentage elongations of break, or maybe known as the ultimate elongations, so it is the strength in the material to its breakage, suppose we are having one polymer we are pulling it, then it will increase and increase and increase after certain time it will fail, so it measures the percentage change in the length of material before fracture, so it is a measure of the ductility, ceramics have very low less than 1%, metals have moderate, generally 1 to 50%, thermoplastic is more than 100% and thermosets is also less than 5% value of elongation to break.

* Toughness:

- ✓ The toughness of a material is given by the area under a stress-strain curve.
- ✓ It measures the energy absorbed by the material before it breaks.

$$Toughness = \int_{0}^{\epsilon_{f}} \sigma \, d\epsilon$$

where, ϵ_f is the true strain at fracture.



Stress-strain curve is shown which compares the stress-strain behavior of different types of materials.
 Rigid materials possess high Young's modulus (such as brittle polymers), and ductile polymers also possess similar elastic modulus, but with higher fracture toughness.

What is the Young's modulus or maybe the modulus of elasticity or maybe the tensile modulus? It is the ratio of stress to the strain in the linearly elastic region, elastic modulus is a measure of the stiffness of the material, so generally it is denoted by capital E which is nothing but the tensile stress, sigma by the tensile strain that is epsila toughness, so the toughness of a material is given by the area under a stress strain curve, its measured the energy absorb by the material before it breaks, what is the toughness? Generally it's the integration of 0 to epsilon F x sigma D epsila, where epsila F is the true strain at fracture, so this is the whole toughness of this particular polymeric materials, so from the stress strain curve is shown which compares the stress strain behavior of different types of materials, from this you can see we have given the examples of the brittle polymer, we have given the examples of the ductile polymer, and we have given the high elastic, so you can see what is the toughness of this particular material. So rigid materials possess the high Young's modulus such as brittle polymers and ductile polymers also possess the similar elastic modulus but with higher fracture toughness.



- There are two types of deformations named as:
- i. Elastic deformation
- ii. Viscous deformation

i. <u>Elastic deformation:</u>

- ✓ Strain is generated at the moment the constant load (or stress) is applied, and this strain is maintained until the stress is not released.
- ✓ On removal of stress, the material recovers its original dimensions completely, that is the deformation is reversible that is:

 $\sigma = E \in$





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Now we are going to discuss about the viscoelasticity, so there are two types of deformations generally we are seeing, first one is known as the elastic deformations, and the second one is called the viscous deformations, so what is elastic deformations? Strain is generated at the moment the constant load or stress is applied and the strain is maintained until the stress is not released, on removal of stress the material recovers its original dimensions completely, that is the deformation is reversible because it will come to again to its original positions, sigma = E epsila, where E is the elastic modulus, sigma is the applied stress, and epsila is the strain developed.



Then we are going to discuss about the viscous deformations, so strain generated is not instantaneous and it is time dependent, when the load is removed material does not return to its original dimensions completely, so there is little bit stress will be present in the material, so deformations is irreversible, so generally sigma = gamma x D epsila/DT, so where gamma is the viscosity and D epsila/DT = strain rate, so but low strain rate polymer should combine behavior of elastic and plastic deformation depending on temperature and strain rate, at low temperature and high strain rate elastic behavior is observed and at high temperatures the viscous behavior is also observed, so combine behavior of viscosity and elasticity is observed at intermediate temperature and the strain rate value, so generally we are having one elastic behavior materials, when we are adding with some viscous behavior materials we are getting the viscoelastic properties of that particular materials, so these behavior is terms as the viscoelasticity and the polymer is termed as the viscoelastic polymer.

4. Chemical Properties:

- Different side groups on the polymer can lend to:
 - a. Ionic bonding
 - b. Hydrogen bonding
- Polymers containing amide or carbonyl groups can form hydrogen bonds between adjacent chains.
- Dipole bonding is not as strong as hydrogen bonding.
- Example: Polyesters have dipole –dipole bonding between the oxygen atoms in C=O groups and the hydrogen atoms in C-H groups.
- Generally, polymeric materials are noncorrosive in nature. Because, upon exposure to liquid, they may experience by swelling or dissolution.
- Polymers may deteriorate by swelling and dissolution.

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Now we are going to discuss about the chemical properties of polymers, so different side groups on the polymers can link to ionic bonding, another one is called the hydrogen bonding, so polymers containing amide or carbonyl groups can form the hydrogen bonds between adjacent chains, dipole bonding is not as strong as the hydrogen bonding, examples like polyesters have dipole-dipole bonding between the oxygen atoms C double bond O groups and the hydrogen atoms in CH groups, generally polymeric materials are noncorrosive in nature because upon exposure to liquid they may experience by the swelling or maybe the dissolution. Polymers may deteriorate by the swelling and the dissolution, it is also another properties of the polymers.

Polymer Degradation:

- It is a change in the properties (Strength, colour, shape, molecular weight etc.) of polymer or polymer based product under the influence of one or more environmental factors such as heat, light, moisture and chemical.
- · Covalent bonds in polymer are rupture as a result of environmental factors.
- · Due to the chemical complexity of polymers, their degradation mechanism are not well understood.

Po	lymer can degrade by exposure to		Types of degradation
1.	High temperature	⇒	Thermal degradation
2.	Shear action	⇒	Mechanical degradation
3.	Oxygen, ozone and chemicals	⇒	Chemical degradation
4.	Electromagnetic, ultrasonic radiation	⇒	Light induced degradation
5.	Moisture (Liquid)	⇒	Hydrolysis or swelling & dissolution

Now we are going to discuss about the polymer degradations, so it is a change in the properties like strength, colour, shape, molecular weights, etcetera of polymer or polymer based products under the influence of one or more environmental factors such as heat, light, moisture or chemical, say suppose we are keeping that polymer for a longer time into the environment or maybe buried into the soil or maybe dipping it into the water, so we can see that degradation of that particular polymer, so covalent bonds in polymers are rupture as a result of the environmental factors, due to chemical complexity of polymers their degradation mechanism are not well understood still research are going on. Polymer can degrade by exposure to like high temperature, what will happen? Thermal degradation will takes place, if it is under oxygen, ozone and chemicals, the chemical degradation will takes place, electromagnetic, ultrasonic radiations, light induced degradation will takes place, and if it is open to the moisture or maybe the liquid, hydrolysis or swelling or maybe the dissolution will takes place.

Properties	Ceramic	Metal	Polymer
Hardness	High	Low	Low
Elastic modulus	High	High	Low
High temperature strength	High	Low	Low
Thermal expansion	Low	High	High
Ductility	Low	High	High
Corrosion resistance	High	Low	Low
Resistance to wear	High	Low	Low
Electrical conductivity	Intermediate	High	Low
Dansity	Low	High	Low

Comparison of the properties of ceramics, metals and polymers:

Thermal conductivity

Now we are going to just give a brief idea about the ceramic metal and polymer in terms of different properties, so say suppose if we talk about the hardness, ceramic is having very high, metal is low, and polymer is also low, so generally I'll give you some major examples like elastic modulus, for ceramic it is high, for metal it is high, but for polymer it is also low, if we talk about the ductility, for ceramic materials it is very, very low, for metal it is high, and for polymer also it is high, if we are talking about the electrical conductivity, so generally for the ceramic materials it has intermediate, for metal it is too high, but polymer it is low generally it acts as a one kind of insulator, if we talk about the thermal conductivity for ceramic it is intermediate, metal it is high, for polymer also it is very, very low.

Intermediate

High

Low

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Now what are the characteristics of the polymers? So generally polymer is having low density, low coefficient of friction, good corrosion resistance, good mould ability, poor tensile strength, low mechanical properties and the poor temperature resistance. What are the advantages of polymers? Generally it resist to corrosions and the chemicals, low electrical and thermal conductivity can be made conducting, low density, high strength to weight ratio that is the prime considerations for choosing the polymer. It can reduce the noise, it is a wide choice of colours and the transparencies, ease of manufacturing and complexity of the design possibilities, and also it is very, very cheap.



What are the disadvantages of polymers? So generally comparatively low strength and low dimensional stability, have low heat resistance, high performance plastics have very high cost, some polymers are very, very costly, they are softer than metals and are more susceptible to deformation under load, it is go brittle at low temperature and are also flammable, it can burn easily.

So now we are going to give some common applications of the polymers, so generally for the sports we are using for some helmets, some balls, or maybe medical we are using some kind of tissue scaffolds, some bones, joints, nowadays we are using some kind of orthopedic implants, for industry we are using some automobile parts, for using insulations, for packing materials, for agriculture we are using it for the preventing soil erosions, reducing the irrigation facility and this all are the very, very less, they are n number of applications where we are using the polymer.



So now we have come to the end of this particular lecture and if we summarize this particular lecture, we have already discussed that polymers are organic, macromolecules made of repeating units, material properties controlled by degree of cross linking, different classes of polymers and already we have discussed with their properties, we have discussed about the mechanical properties, thermal properties, chemical properties of those polymers and it is also very easy materials to process and having the low cost. Thank you.

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