Medical Biomaterials
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Lecture – 29
Polymers

Hello everyone. Welcome to the course on medical biomaterials. We will continue on the topic of polymers. As I said polymers are widely used as A Bio material polymers are made up of repeat unit is of the one single monomer or it could be multiple monomers 2 monomers. So, there are wide range of polymers available which can be tuned for any desired application and with different properties. So, we will look little bit on the structure of these polymers also.

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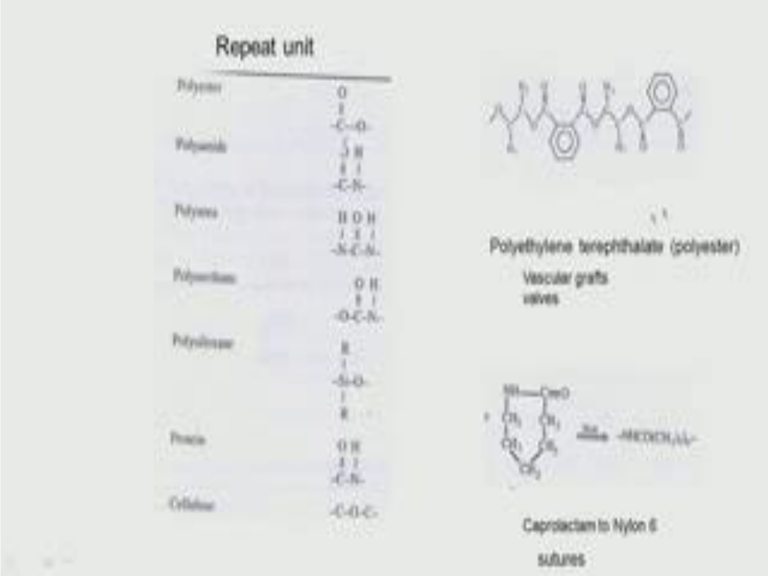

Repeat unit

Polyethylene terephthalate (polyester)

Vascular grafts
valves

Caprolactam to Nylon 6

sutures

For example, look at this polyethylene terephthalate, it is polyester. It is it is originally invented for making fabrics. So, it is called polyethylene terephthalate. So, it has got a terephthalic acid unit here. Then the ethylene glycol that is how they are condensed terephthalic and ethylene glycol condensed as repeat unit is it is called polyester it is also called dacron. It is used in manufacturing vascular grafts large diameters vascular grafts 2 mm type it is also involved in valves patches. So, many other applications it is called polyester and the ester bond as you know can be degraded with the esterase type of enzymes look at this nylon 6 this is called nylon 6.

When we put n; that means, there could be N could be very large number. So, it is like this. So, it starts with caprolactam converted into nylon 6 it is used in stitches and these stitches are not degradable they are very strong nylon is used in applications, where we read very high tensile strength. So, here those days they used to use it as stitches, but then they do not degrade. So, nowadays they are switched on to other bio degradable material.

So, in a polymer you are going to have repeat unit is; that means, same unit gets repeated hundreds thousands of times. And depending upon the number of repeat unit is the molecular weight also changes. For example, polyester will have this particular repeat unit C double bond O C double bond O. This is called ester bond and of course, ester is type of enzymes can degrade this bond polyamide it will has C double bond O N H and this this is the repeat unit. So, it can have many of these. Actually please note the amide bond in the protein that also has got a C double bond O N H to or N H and some other functional group like aliphatic and so on. Polyamide protein polyurea look at this. So, you have C double bond O in the middle of 2 nitrogen amines here. Polyurethanes these are very strong polymers not degradable we have C O on this side C double bond and then we have nitrogen here. Polysiloxanes look at this silicon is here oxygen is here and you can have different groups cellulose C O C and so on.

So, these are the repeat unit is you will find in some of these polymers no it keeps on repeating many times more of this structure. This is called poly para phenylene because you have the nitrogen N H para phenylene terephthalate.

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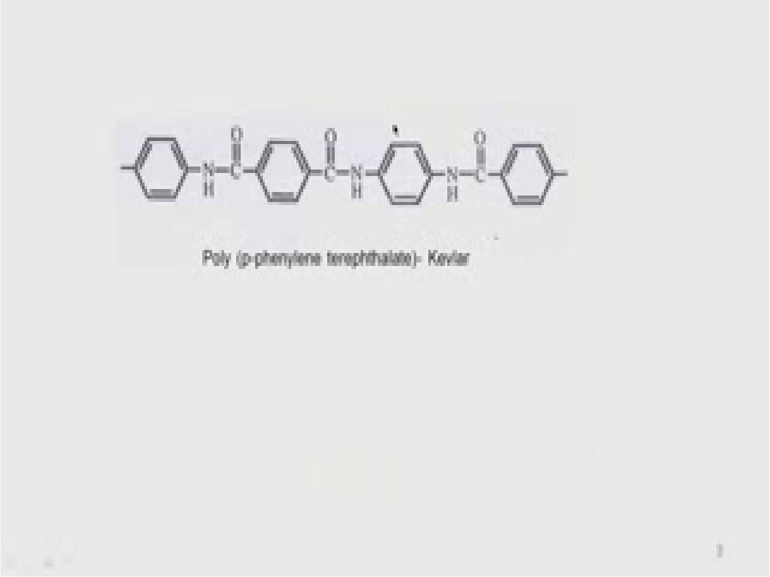

Poly (p-phenylene terephthalate)- Kevlar

If you remember this looks like this right terephthalate, here it is phenylene because you have the nitrogen. It is extremely strong it is called kevlar commercially and they sometimes make A Bulletproof vest with this, they are extremely strong and they have very high tensile strength you can make in to fibres. So, we can make it like younts and then we can spin it to make fabrics out of this. So, that is called poly para phenylene terephthalate. So, this is the para groups this is the terephthalate group and then phenylene nitrogen is there.

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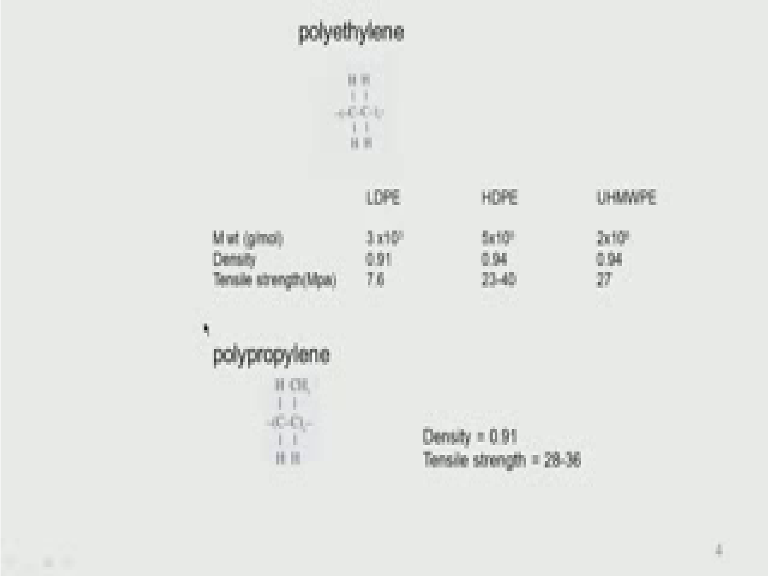

polyethylene

	LDPE	HDPE	UHMWPE
M wt (g/mol)	3×10^3	5×10^5	2×10^6
Density	0.91	0.94	0.94
Tensile strength(Mpa)	7.6	23-40	27

polypropylene

Density = 0.91
Tensile strength = 28-36

Polyethylene, polypropylene all these are very ubiquitous polyolefin, polyethylene is very simple see H 2 here C H 2 here keeps on repeating. So, depending upon the number of repeat unit is they N number of small N we can have low density polyethylene high density polyethylene ultra-high molecular weight polyethylene like that you know. So, if you look at the molecular weight low density around 10 power 3 high density 10 power 5 ultra-high molecular weight 10 power 6. So, these are used some of sometimes in drain cubes. These are used in knee joints when they have a total knee replacement surgery to prevent metal on metal contact you have this.

So, in the low density polyethylene sometimes instead of being linear, we can also have side chains; that means, during polymerization you can have lot of side chains coming in so; obviously, it will not be very compact. So, the molecular weight is low the density is also low here. So, as you can see density increases tensile strength also increases from LDP to STP to ultra-high molecular weight polyethylene. And they are very hydrophobic material because we have only carbon we do not have anything else we do not have oxygen nitrogen. So, it is extremely hydrophobic type of material polypropylene. So, there is a C H 3 here that is why it is called polypropylene density is low because the C H 3 is A Bulky group. So, you cannot pack it up too much, but the tensile strength is also high. So, polypropylene there are different types of polypropylene where the C H 3 and the next C H 3 can be in the same direction or same side or in the opposite and so on. So, they are called atactic syndiotactic isotactic. Depending upon how they consecutive C H 3 are located. So, this called polypropylene again this is also very highly hydrophobic, because we have only carbons we have nothing else no oxygen or nitrogen or sulphurs. These polymers are used quite a lot because they very cheap easy to fabricate we can make it in to different shapes, and sizes moulded and so on actually. So, and they are very strong. So, they are used in many applications as well, but remember they are very hydrophobic.

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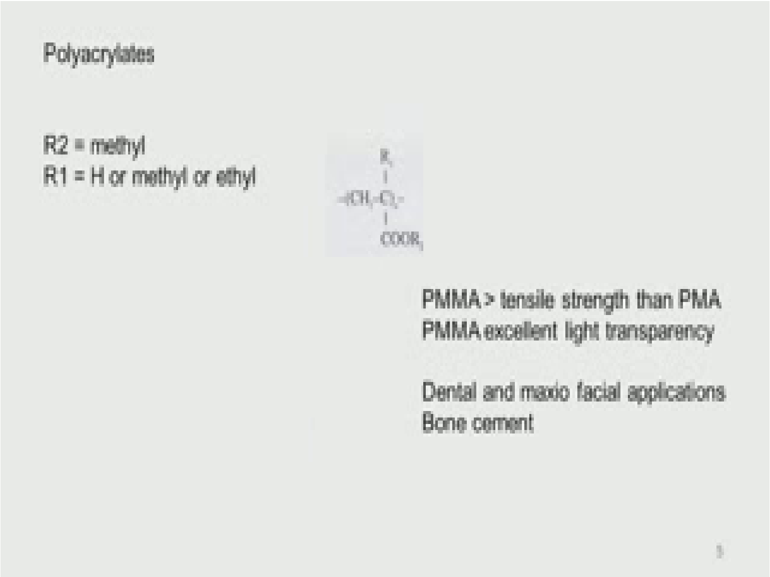

Polyacrylates

R2 = methyl
R1 = H or methyl or ethyl

PMMA > tensile strength than PMA
PMMA excellent light transparency

Dental and maxio facial applications
Bone cement

So obviously, there could be biofilm formation bacterial contamination and so on. Polyacrylates this is the general structure C H 2 C there is a C O O R. So, this this the ester part of it and there is a R 1 here if R 1 can be H or methyl or ethyl R 2 can be methyl. So, we can have methacrylate, when we have methyl here methacrylate that is an ester if you have a methyl here methyl methacrylate. Otherwise we can have just methacrylate if R 1 is H or we can have methyl acrylate, but ethyl methacrylate. So, we can have different types of polyacrylates by changing this R 1 R 2 group, but the most common is poly methyl methacrylate; that means, you have a C H 3 here and a C H 3 here. It is used quite a lot in dental applications maxillofacial applications bones cement acryl, and then it is got fantastic light transparency. So, it is used many places where we need transparent observations and PMMA has higher tensile strength than poly methacrylate; that means, when R 1 is H that is called a poly methacrylate.

So, PMMA is the polymer which is consumed a lot in biomedical applications maxillofacial surgeries dental applications. So, it goes days back to a very long time and it is easy to make polymer starting from the monomer, when we apply a u v the polymerization happens. So, it is very simple to make and we can have different types of polyacrylates.

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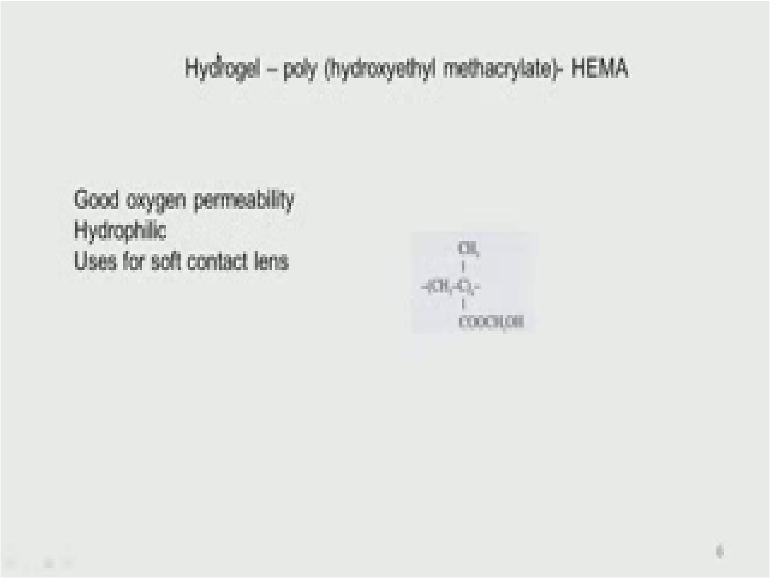

Hydrogel – poly (hydroxyethyl methacrylate)- HEMA

Good oxygen permeability
Hydrophilic
Uses for soft contact lens

Next hydrogels, hydrogels are poly hdyroxyethyl methacrylate hema hydroxy ethyl methyl acrylate. So, look at this structure here. So, we can have a hydroxy then we can have ethyl then methacrylate then methacrylate and so on. Actually they are extremely hydrophilic they are hydro gel; that means, hydrogel is something which can take a lot of water hydro is water right. So, it can take in lot of water they can swell a lot. So, it is used in soft contact lenses they got good oxygen permeability. So, it is used in soft contact lenses. So, the person can wear it for very long period of time.

Whereas you look at PMMA it is used in hard contact lenses, because it is got very transparency, but it does not take in as much water as this particular hema is called poly hydroxy ethyl methacrylate. So, hydrogels not only used in soft contact lenses they are also used in wound dressing surface wound dressing we can even encapsulate drugs and so actually.

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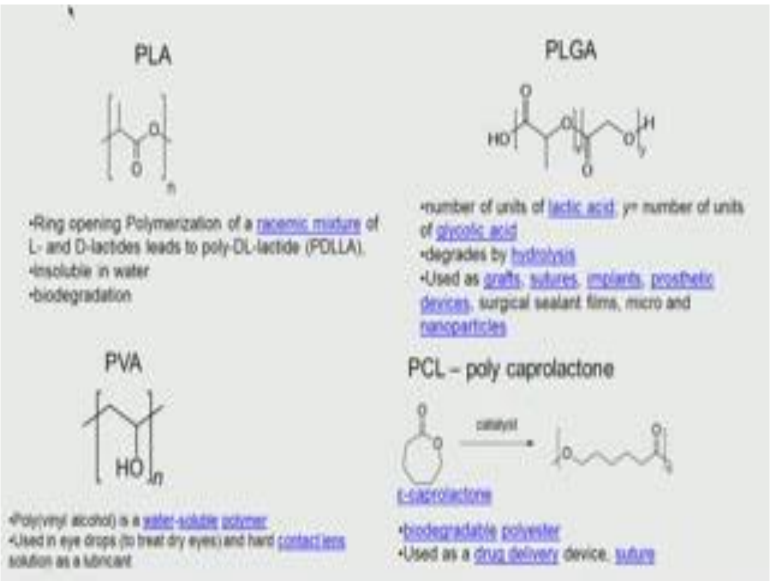

PLA

- Ring opening Polymerization of a racemic mixture of L- and D-lactides leads to poly-DL-lactide (PDLLA).
- Insoluble in water
- biodegradation

PLGA

- number of units of lactic acid, y= number of units of glycolic acid
- degrades by hydrolysis
- Used as grafts, sutures, implants, prosthetic devices, surgical sealant films, micro and nanoparticles

PVA

- Poly(vinyl alcohol) is a water-soluble polymer
- Used in eye drops (to treat dry eyes) and hard contact lens solution as a lubricant

PCL – poly caprolactone

- biodegradable polyester
- Used as a drug delivery device, suture

Now, other polymers these are some polymers which have been approved by the food and drug administration in USA poly lactic acid PLA. So, we have this type of structure lactic acid. So, how does it is biodegradable it is FDA approved, but it is in soluble in water. Now how is it made ring opening polymerization of a resimic mixture of l and d lactase to produce poly d l lactic acid, but if I take only l lactide then I will get PLA poly l lactic acid. So, there insoluble in water and so, we can tune their properties by either taking a d l resimic mixture of a lactides or just l lactide and so on actually.

PVA poly vinyl alc OH ol, it is a water soluble polymer this is also approved by the FDA and it is also very hydrophilic. So, it is used in eye drops and also it is used in hard contact lenses solution as a lubricant. So, PVA is a very good lubricant because it is water soluble, it is hydrophilic in nature. So, it is used in such applications and sometimes when I am mixing a hydrophobic polymer with hydrophilic polymer we use PVA to enhance the mixing properties. PLGA poly lactic glycolic acid poly lactic. So, we can have different combinations of lactic and glycolic.

So, the structure is like this this is the lactic part of it. You can see this this is lactic part of it and this is the glycolic part of it. It degrades by hydrolysis because we have the ester bond it is also used quite lot in medical applications grafts sutures. So, nylon sutures are not degradable. So, after the wound heals surface, wounds a doctor has to remove it pull it out, whereas PLGA type of sutures are biodegradable. So, automatically they will get bio reabsorbed they can be used in implants prosthetic devises surgical sealant making nano particles and so on. So, PLGA is also widely used and beauty is we can change or modify their biodegradable properties by modifying lactic to glycolic acid. So, glycolic is faster biodegradable then lactic. So, we can tune that.

Then is poly caprolactone poly caprolactone, this also biodegradable polyester. So, how is it made you take epsilon caprolactone, with a catalyst like a tin we can make this poly caprolactone. This is also approved by FDA it is A Biodegradable it is used in drug delivery devise sutures. So, we can make PCL based sutures. Remember there is something called poly caprolactum that is almost like nylon it is very strong not degradable. This poly caprolactone is degradable it is approved by FDA. So, do not confuse between lactum and lactone is biodegradable polymer.

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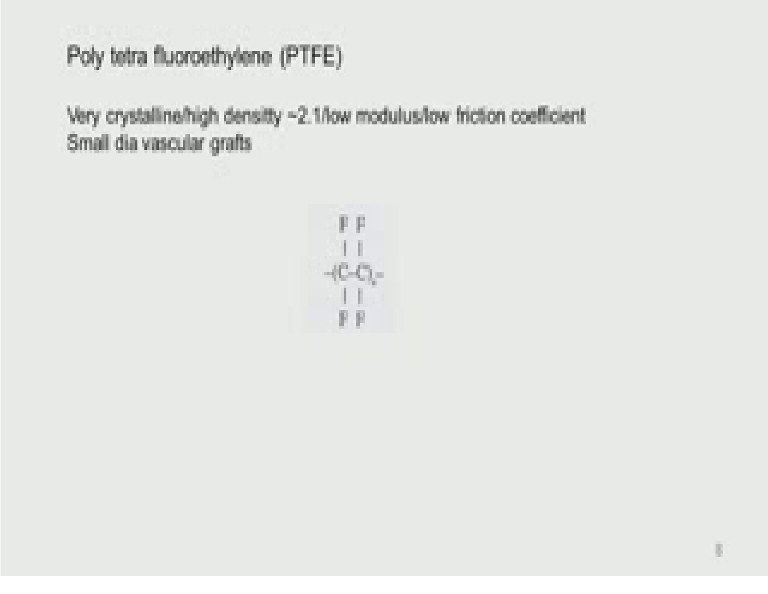

Poly tetra fluoroethylene (PTFE)

Very crystalline/high density ~2.1/low modulus/low friction coefficient
Small dia vascular grafts

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So, lot of polymers then comes PTFE poly tetra fluoroethylene it is a very, So, you can see fluoro, lot of fluoros here very crystalline high density low modulus low friction coefficient. So, it is used quite a lot it is very inert so small diameter vascular grafts. So, if I am looking at large diameter 2 mm, I may go for polyester if I am looking at small diameter vascular grafts I will go for PTFE. So, PTFE we used in vascular grafts PTFE is used in b t shunts. So, this also has quite a good set of applications.

So, we looked at lot of structural features of different types of polymers used and of course, PVC polyvinyl chloride is another polymer where we have one chlorine 3 hs hydrogen one chlorine there. So, polyvinyl chloride it is also very inert it is used for short duration applications. So, maybe drain tubes and so on, and because it is very inert and it is not used for many other purposes especially if you are looking at tissue engineering type of application.

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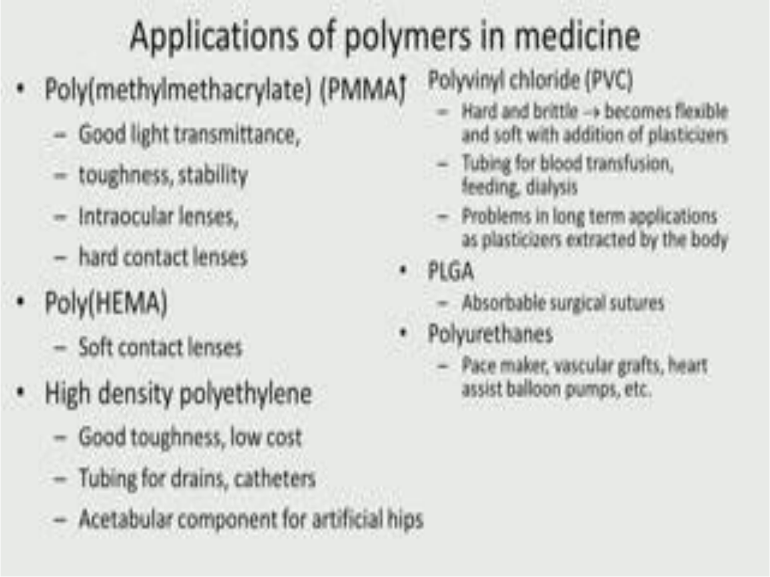

Applications of polymers in medicine

- Poly(methylmethacrylate) (PMMA)
  - Good light transmittance,
  - toughness, stability
  - Intraocular lenses,
  - hard contact lenses
- Poly(HEMA)
  - Soft contact lenses
- High density polyethylene
  - Good toughness, low cost
  - Tubing for drains, catheters
  - Acetabular component for artificial hips
- Polyvinyl chloride (PVC)
  - Hard and brittle → becomes flexible and soft with addition of plasticizers
  - Tubing for blood transfusion, feeding, dialysis
  - Problems in long term applications as plasticizers extracted by the body
- PLGA
  - Absorbable surgical sutures
- Polyurethanes
  - Pace maker, vascular grafts, heart assist balloon pumps, etc.

So, what are the applications I have been telling PMMA good light transparency. So, it can be used for hard contact lenses intraocular lenses. It is very stable hema hydroxy ethyl methyl acrylate soft contact lenses polyethylene high density polyethylene tough low cost tubing drain catheters acetabular components for artificial hips knee joints polyvinyl chloride, it is hard and brittle, it becomes flexible by adding plasticizers used in tubing for blood transfusion feeding dialysis. So, it is not used for long applications because the plasticizers present may come out PLGA absorbable reabsorbable surgical sutures. Polyurethanes pace makers vascular grafts heart assist balloon pumps, it is almost like rubber it is very flexible. So, polyurethane is also finding quite a lot of applications.

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- Advantages
  - Ease of manufacturability to produce various shapes
  - Tailorable properties
  - Reasonable cost
  - Availability with different mechanical and physical properties
- Disadvantages
  - Leachable
  - Wear and breakdown
  - Difficult to sterilize

So, polymers they eases of manufacturability to produce various shapes tailorable properties, I can change I take PLGA, I can change an amount of lactic to glycolic, I get different properties reasonable cost. It we can make it in different mechanical and physical properties, we can make it in different shapes later on I am going to do some experiments and show you disadvantages.

Leachable there could be some monomer like for example, lacrylic acid present in PMMA may leach out which could be toxic; for example, any other monomers or leachants. For example, if you take PVC the plasticizers like thalates are added to make it is soft and flexible that may leach out over a long period of time. Wear and break down. So, they can wear out they can also break down there could be some oxidation reaction or hydrolysis difficult to sterilise. So, if I use for example, steam sterilisation some polymer may observe moisture, if I use some chemical ethanol or something some there could be some reactions in some cases. So, we need to be very careful what type of sterilisation method do I follow when I have a polymeric material.

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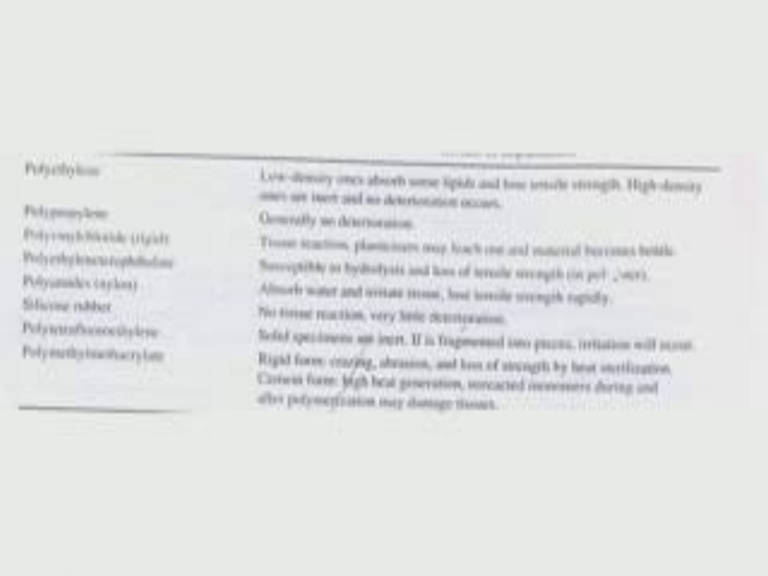

Polyethylene	Low-density ones absorb some lipids and lose tensile strength. High-density ones are inert and no deterioration occurs.
Polypropylene	Generally no deterioration.
Polyvinylchloride (rigid)	Tissue reaction, plasticizers may leach out and material becomes brittle.
Polyethyleneterephthalate	Susceptible to hydrolysis and loss of tensile strength (in polyester).
Polyamides (nylon)	Absorb water and irritate tissue, lose tensile strength rapidly.
Silicone rubber	No tissue reaction, very little deterioration.
Polytetrafluoroethylene	Solid specimens are inert. If is fragmented into pieces, irritation will occur.
Polymethylmethacrylate	Rigid form: crazing, abrasion, and loss of strength by heat sterilization. Cement form: high heat generation, unreacted monomers during and after polymerization may damage tissues.

So, some other problems polyethylene it absorbs lipids LPDE. So, tensile strength becomes poor high density ones are inert. So, no deterioration occurs polypropyline. Generally, no deterioration polyvinyl chloride, tissue that is rigid ones, tissue reaction the plasticizers like thalde present means leach out material may can become brittle polyethylene terephthalate. So, hydrolysis because they have ester bond hydrolysis is. So, strength can come down polyamide nylon they can absorb water irritate tissue loose tensile strength silicon rubbers no reaction, but and very little deterioration PTFE solid specimens, are inert if it is fragmented into pieces it can cause irritation poly methyl methacrylate rigid form crazing abrasion loss of strength heat sterilisation, when I heat it for sterilisation, it will lose strength cement high heat rigid heat generation. We can even make the polymer unreacted monomers may leach out and damage tissues. So, each polymer has some problems or the other it is happening.

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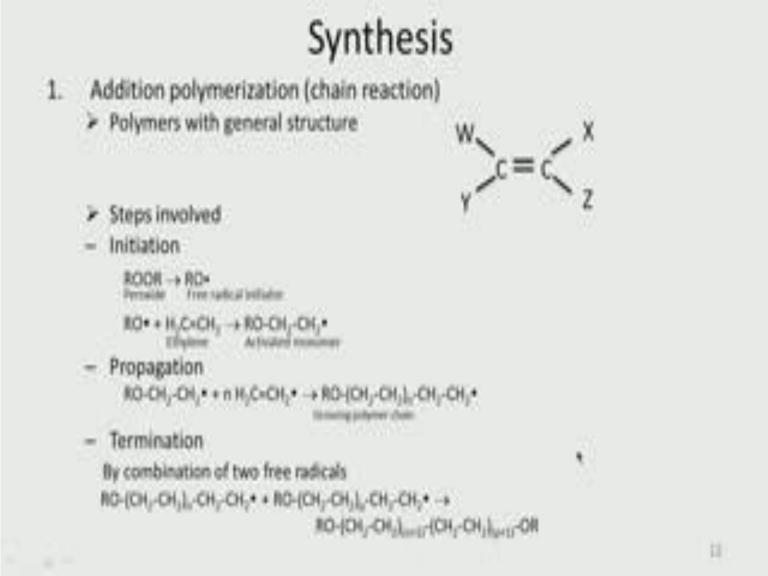

Synthesis

1. Addition polymerization (chain reaction)
   - Polymers with general structure
   - Steps involved
   - Initiation

     $ROOR \rightarrow RO\bullet$

     Peroxide Free radical initiator

     $RO\bullet + H_2C{=}CH_2 \rightarrow RO\text{-}CH_2\text{-}CH_2\bullet$

     Ethylene Activated monomer
   - Propagation

     $RO\text{-}CH_2\text{-}CH_2\bullet + n\,H_2C{=}CH_2\bullet \rightarrow RO\text{-}(CH_2\text{-}CH_2)_n\text{-}CH_2\text{-}CH_2\bullet$

     Growing polymer chain
   - Termination

     By combination of two free radicals

     $RO\text{-}(CH_2\text{-}CH_2)_n\text{-}CH_2\text{-}CH_2\bullet + RO\text{-}(CH_2\text{-}CH_2)_m\text{-}CH_2\text{-}CH_2\bullet \rightarrow RO\text{-}(CH_2\text{-}CH_2)_{(n+1)}\text{-}(CH_2\text{-}CH_2)_{(m+1)}\text{-}OR$

Let us look at how they are synthesised there are 2 ways one is called the addition another is called the condensation in condensation is called also call stepwise. So, we can stepwise grow the polymer.

Addition means we take 2 units is and add them. So, polymers you can make like this with general structure like this no. So, how do you do it in the addition the radicals are formed initially you add generally you add some free radical initiators that is R O dot means, it is a radical now this radical reacts with this portion of this it produces the activated monomer. Now this keeps on growing this is called propagation. So, long grows that is why it is called stepwise addition grows and then you terminate it. You add some terminating agent or radical scavenging agent. So, the polymerization stops and the chain growth stops.

That’s called addition polymerization. So, here generally it is through radical. So, you had radical initiator which produces radical of the monomer. And which keeps adding stepwise. So, the polymer grows and when there is a radical scavenger the radical stop. So, the polymerization gets terminated it is called addition polymerization.

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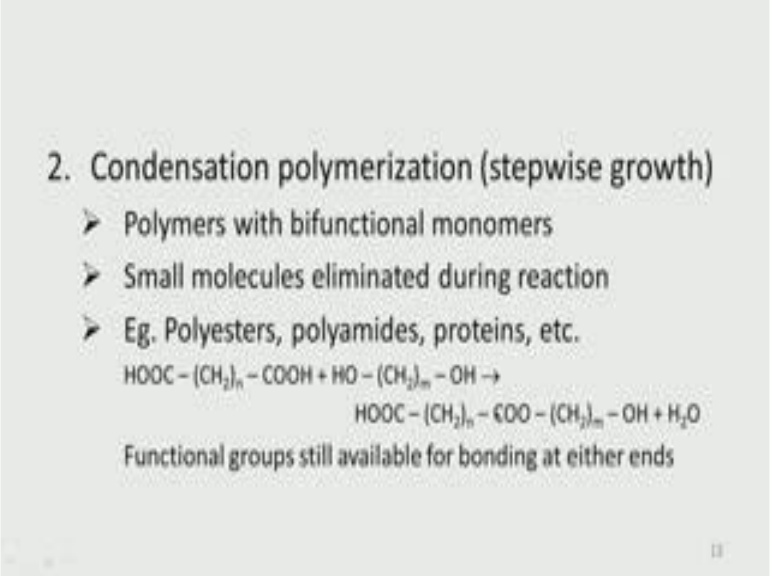

2. Condensation polymerization (stepwise growth)

- Polymers with bifunctional monomers
- Small molecules eliminated during reaction
- Eg. Polyesters, polyamides, proteins, etc.

$$HOOC-(CH_2)_n-COOH + HO-(CH_2)_m-OH \rightarrow$$
$$HOOC-(CH_2)_n-COO-(CH_2)_m-OH + H_2O$$

Functional groups still available for bonding at either ends

The next one condensation. So, we add 2 units is get condensed together. And generally you throw out water or methanol which is removed by using vacuums. That is how polyesters are produced like I said terephthalic acid and ethylene glycol. So, you get when you use terephthalic acid, you get methanol it is produced similarly polyamides proteins. So, all these are called condensation polymerization. How when you have functional groups on both sides you can have condensation say for example, C O O H is a functional group O H. So, we can keep an adding one unit with another unit and so on. So, polymmonomers which have functional groups on both sides can be done through this condensation polymerization where as in the other one stepwise we need to generate radicals which keep on adding and the chain growth takes place. So, 2 basic methods by which most of the polymerization reaction happen we will not go too much in to in, but it is good to know.

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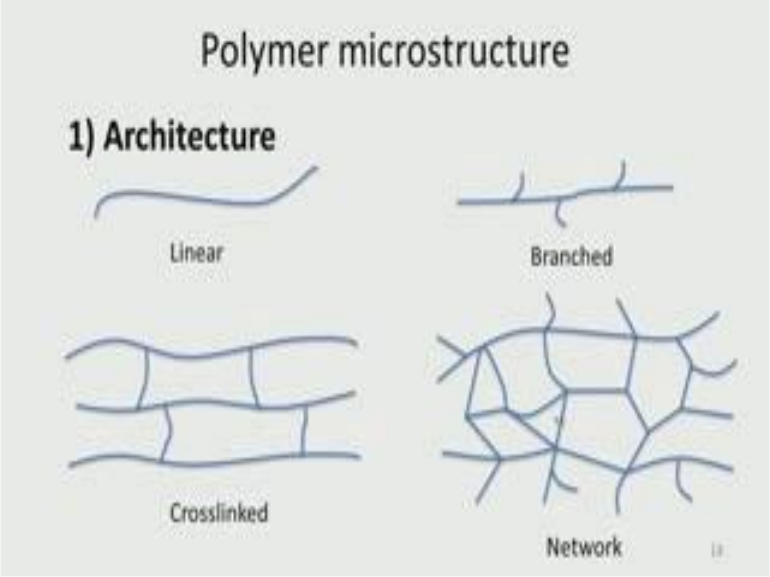

Polymer microstructure

1) Architecture

So, we can have different type of architecture linear branched like low density polyethylene starts getting branched that is why the densities are low whereas high density will have less branch. So, they get packing better. So, the densities are high cross linked. So, we have one unit one unit one branch chain. So, they are all cross linked like this sometimes, we add a cross linking agent network. So, we can have polymerization taking place like a network dendrimer. They call it star polymers there are. So, many types which are in that fashion the network type of polymer. So, different types of structures are possible and they all have different melting points different face change temperature and so on actually the property is also change because of these architectural features.

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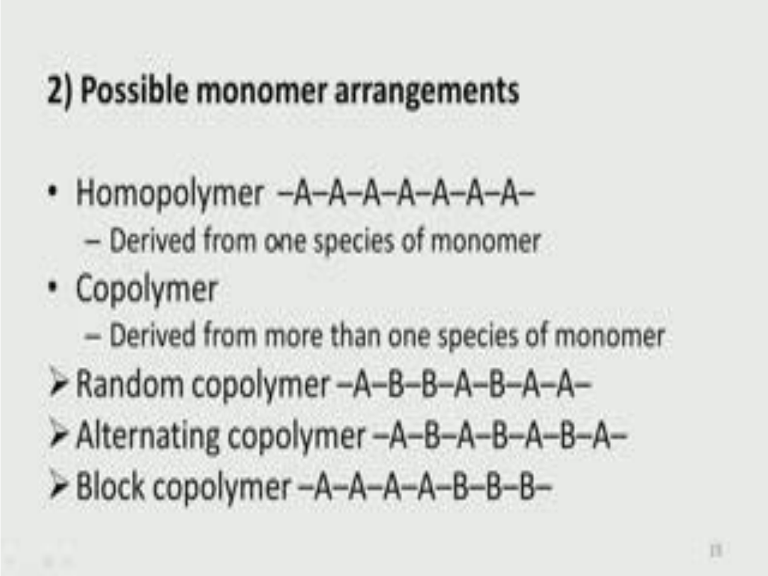

2) Possible monomer arrangements

- Homopolymer –A–A–A–A–A–A–A–
  - Derived from one species of monomer
- Copolymer
  - Derived from more than one species of monomer

➢ Random copolymer –A–B–B–A–B–A–A–
➢ Alternating copolymer –A–B–A–B–A–B–A–
➢ Block copolymer –A–A–A–A–B–B–B–

And the monomer arrangement says suppose I have one unit another another this is homo polymer. Co polymer is when I have more than one monomer A B. So, I can have random co polymer alternating co polymer as you can see A B A B A B this is random or block copolymer A A A B B B then again A A A. So, each of this will have different set of properties change dramatically whether it is block or whether it is random finally, it is it is possible to tune their reaction. So, that we can get either random or alternating or block copolymer. Of course, in homo polymer you will always have A A A. Of course, you may have branches like polyethylene LPDE, but this type of monomer arrangements will happen only when you have more than one monomer.

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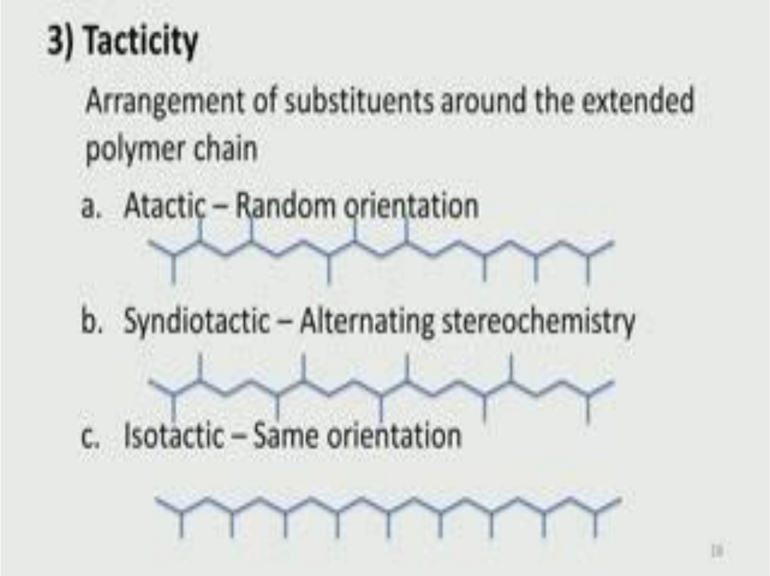

3) Tacticity

Arrangement of substituents around the extended polymer chain

a. Atactic – Random orientation

b. Syndiotactic – Alternating stereochemistry

c. Isotactic – Same orientation

There is something called tactility. That is the arrangement of substituents around the extended polymer. For example, you take polypropylene. So, there is a C H 3 there right that the pined end. So, the C H 3 of one and the C H 3 of the next repeat unit if they are all in the same side that is called isotactic same orientation. If they are alternating they can be syndiotactic and if they are in the random fashion, it can be atactic this happens especially when you have this type of extended functional group. So, pendent groups for example, let us look at this let us look at this PVA they all the PVA O H of the next they all could be in the same direction or they could be alternating or they could be in a very random fashion. Same thing with polypropylene look at this C H 3 of the next could be in the same direction and so on or they could be in the alternating or they could be in the random. So, these are typical examples. So, we can have all in the same direction isotactic alternating syndiotactic and this could be atactic. So, polyvinyl alc OH ol the OH groups or polypropylene the C H 3 groups. So, all in the same direction. So, the again the properties change dramatically depending upon how the tacticity look like. So, you can see we that is why polymers are become very useful in bio material applications there are. So, many variations that are possible the arrangement of the monomers the 3 dimensional feature which gives you the tacticity. So, all these that is the arrangement of the substituents.

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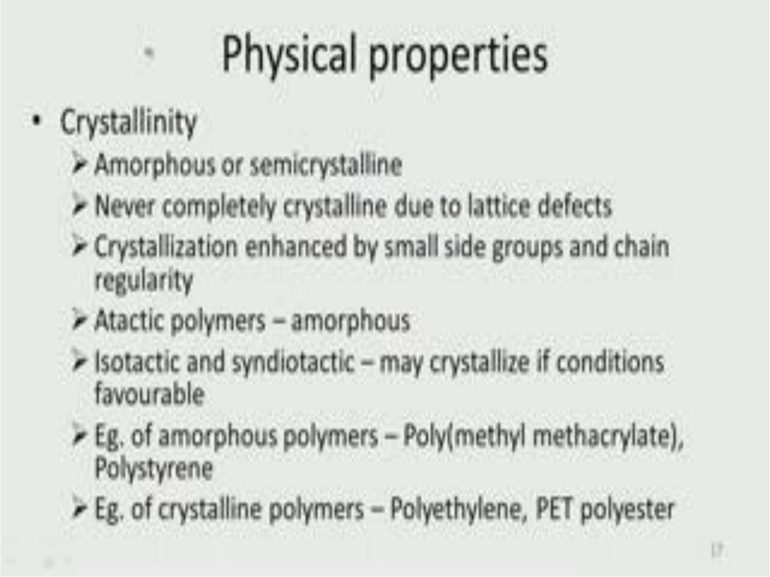

Physical properties

- Crystallinity
  - Amorphous or semicrystalline
  - Never completely crystalline due to lattice defects
  - Crystallization enhanced by small side groups and chain regularity
  - Atactic polymers – amorphous
  - Isotactic and syndiotactic – may crystallize if conditions favourable
  - Eg. of amorphous polymers – Poly(methyl methacrylate), Polystyrene
  - Eg. of crystalline polymers – Polyethylene, PET polyester

So, all these make a lot of difference in their physical chemical property polymers also have some crystallinity they could be amorphous or semi crystalline, they can never be completely crystalline un like your metals. So, they will be amorphous semi crystalline. So, there could be some amorphous regions some crystalline regions. So, if there is degradation amorphous region may get degraded crystallization enhanced by small side groups and chain atactic polymers are always amorphous as you can see and they cannot pack well. Hence they are always amorphous isotactic may crystallize if conditions are favourable poly methylene methacrylate polystyrene they are all amorphous polymers.

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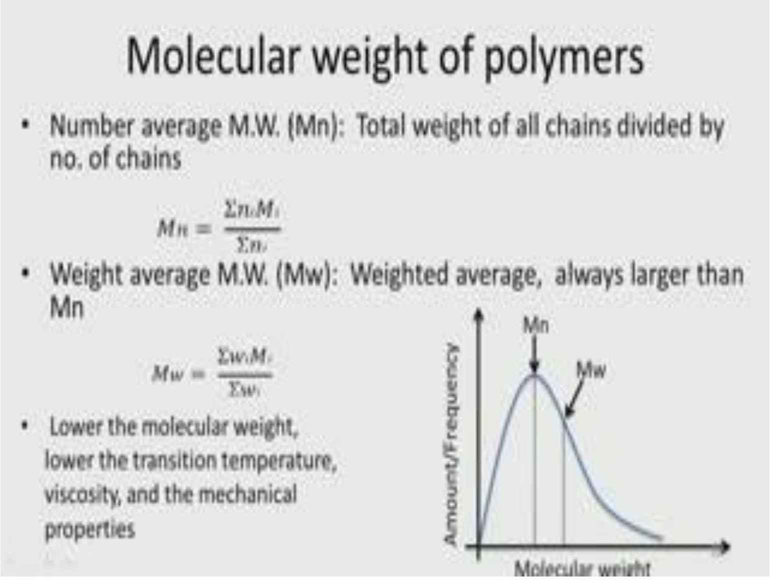

Molecular weight of polymers

- Number average M.W. (Mn): Total weight of all chains divided by no. of chains

$$M_n = \frac{\Sigma n_i M_i}{\Sigma n_i}$$

- Weight average M.W. (Mw): Weighted average, always larger than Mn

$$M_w = \frac{\Sigma w_i M_i}{\Sigma w_i}$$

- Lower the molecular weight, lower the transition temperature, viscosity, and the mechanical properties

Polyethylene polyeh, ethylene terephthalate that is the polyesters, they can have crystalline properties polymers have 2 types of moleculararation factor. They can also have 3 types of molecular weights mostly one is called the number average molecular weight, this is represented as Mn other one is called the weight average molecular weight number average molecular weight total weight of all chains divided by number of chains Ni Mi; that means, some chains have certain molecular weights some chains have another molecular weights. So, you multiply and sum it up divided by number of chains that gives you the number weight average molecular weight; that means, we do not look at the number we look at the weight of chains which have certain molecular weight. So, w i Mi divided by w i understand. So, we here we look at number of chains which have certain molecular weight here we look at the weight of chains which have certain molecular weight and number average is always less than weight average. So, look at this suppose you have because polymers will have a mixture of molecular weights that is mixture of length there could be some chain length smaller some chain length longer some of them very long.

So, it will theoretically sort of follow not exactly a Gaussian distribution, but this sort of distribution. So, the this will be the number average the weight average. So, weight average will always be larger than the number average. So, if you divide weight by N number of weight average by number average that is called polydispersity; that means how disperse the system is it can be 1.2 or 1.3. And so on because weight average is always larger than the number average. Lower the molecular weight lowers the transition temperature viscosity and mechanical properties. So, lower the molecular weight. So, small molecular weight polymers will have lower viscosity lower mechanical properties.

I said there is third molecular weight that is called viscosity average molecular weight that is based on viscosity of different chain lengths we will not go in to that. So, generally everybody follows number average weight average number average tells you the number of chain which have certain molecular weight. Here the weight of chains which have this molecular weight, that is how it is calculated and I said weight average is always larger than number average if you divide this Mw by Mn we get a term called polydispersity that is generally 1.2 or 1.3 or 1.4 and so on actually.

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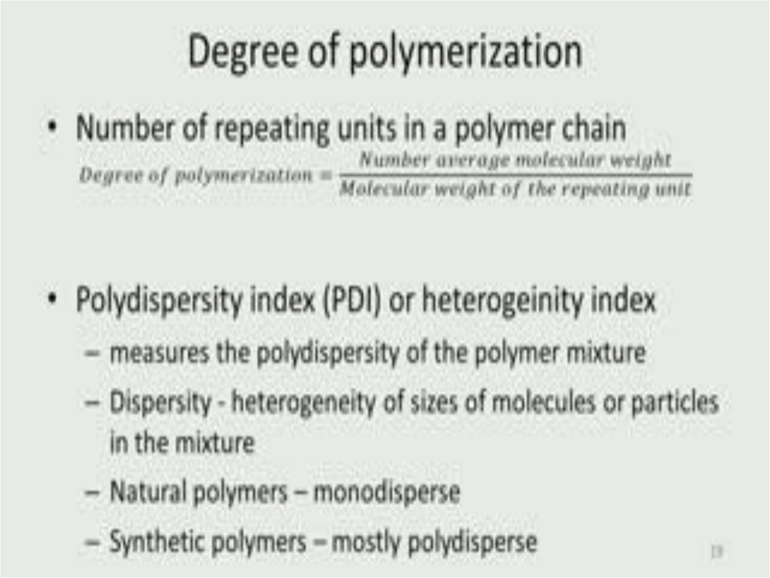

Degree of polymerization

- Number of repeating units in a polymer chain

$$\text{Degree of polymerization} = \frac{\text{Number average molecular weight}}{\text{Molecular weight of the repeating unit}}$$

- Polydispersity index (PDI) or heterogeinity index
  - measures the polydispersity of the polymer mixture
  - Dispersity - heterogeneity of sizes of molecules or particles in the mixture
  - Natural polymers – monodisperse
  - Synthetic polymers – mostly polydisperse

Then there is something called the degree of polymerization that is number of repeating unit is number average molecular weight divided by molecular weight of the repeating unit, that is called the degree of polymerization. This is obvious right. So, one repeating unit this total molecular weight. So, if I divided this by this it will tell you how many this unit is are there, that is why it is called degree of polymer as I said polydispersity or heterogeneity that is Mw by Mn sorry, measures the polydispersity heterogeneity of sizes natural polymers are monodisperse synthetic polymers are mostly polydisperse.

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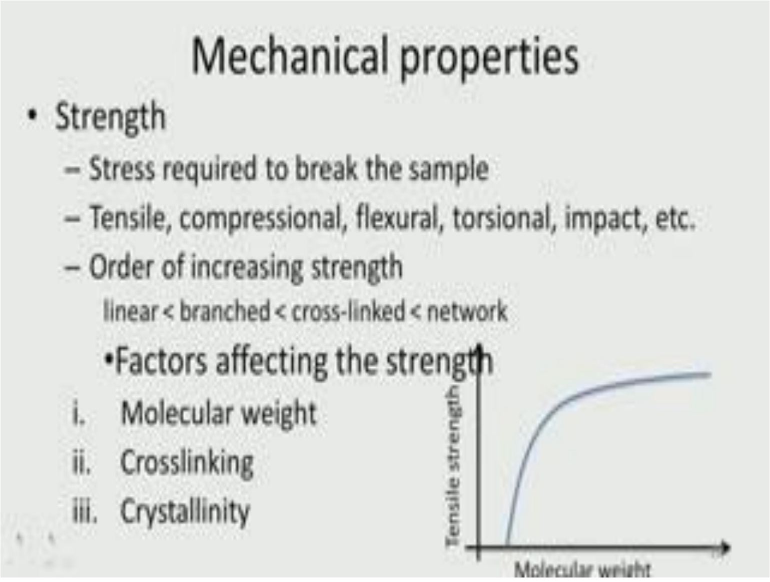

Mechanical properties

- Strength
  - Stress required to break the sample
  - Tensile, compressional, flexural, torsional, impact, etc.
  - Order of increasing strength

    linear < branched < cross-linked < network

•Factors affecting the strength

i. Molecular weight
ii. Crosslinking
iii. Crystallinity

Mechanical properties we have the strength, stress required to break the sample we have studied long time back tensile compression flexural torsional impact when you have linear lower than branch cross link network. So, when you cross link they will have higher strength there are network they will have much higher mechanical properties. So, what are the factors which effect strength the molecular weight, cross linking if they are very highly cross linked they are going to be very strong, and tough crystallinity if they are crystalline then you have certain better mechanical properties as against very amorphous. So, molecular weight tensile strength increases increase, in molecular weight increase in tensile strength.

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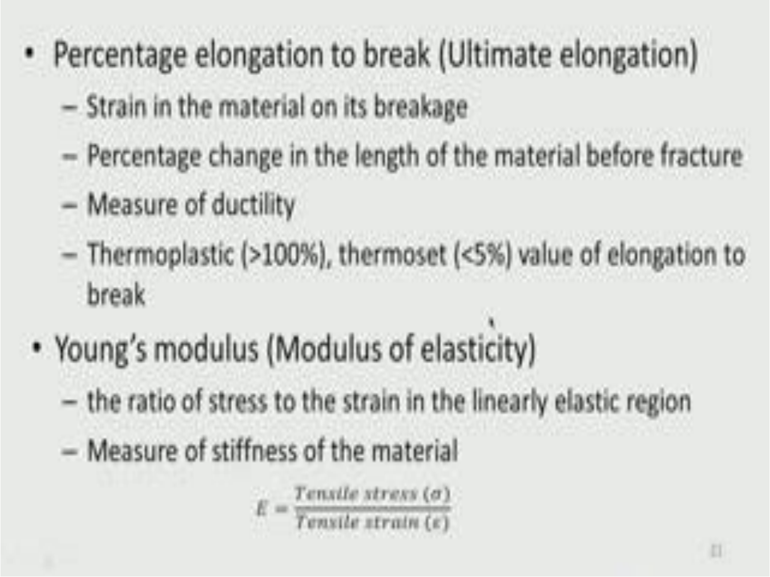

- Percentage elongation to break (Ultimate elongation)
  - Strain in the material on its breakage
  - Percentage change in the length of the material before fracture
  - Measure of ductility
  - Thermoplastic (>100%), thermoset (<5%) value of elongation to break
- Young's modulus (Modulus of elasticity)
  - the ratio of stress to the strain in the linearly elastic region
  - Measure of stiffness of the material

$$E = \frac{Tensile\ stress\ (\sigma)}{Tensile\ strain\ (\varepsilon)}$$

Percentage elongation to break that is the ultimate elongation. Originally I talked about thermoplastic thermoset right. So, elongation to break tells you about the ductility percentage change the length of the material before fracture. So, if you keep on increasing the length by pulling it reaches certain length and then it breaks that is the elongation to break it is a measure of ductility. So, thermoplastic greater than hundred thermoset less than 5 because thermoset is very rigid it breaks. Young's modulus this you know long time back we studied tensile strength by sorry tensile stress by strain, it gives you a stiffness of the material. So, polymers also will have a young's modulus, but of course, they are much lesser than metals like stainless steel.

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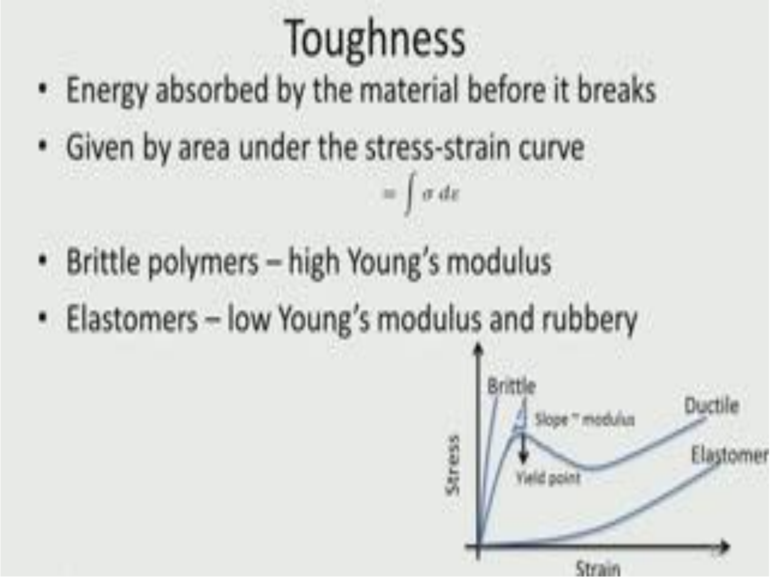

Toughness

- Energy absorbed by the material before it breaks
- Given by area under the stress-strain curve

$$= \int \sigma \, d\varepsilon$$

- Brittle polymers – high Young's modulus
- Elastomers – low Young's modulus and rubbery

Toughness there is energy absorbed by the material before it breaks brittle polymers high young modulus like you, even like your ceramic elastomers low young's modulus ductile materials will have like this. So, you have brittle polymers ductile material elastomers, this is a stress strain diagram. The slop as you know in the elastic region is called the young's modulus you remember all these right long time back. So, the area and the curve gives you an idea about the toughness. So, this elastomer the brittle material ductile material that is toughness before it is breaks right from elastic to plastic region.

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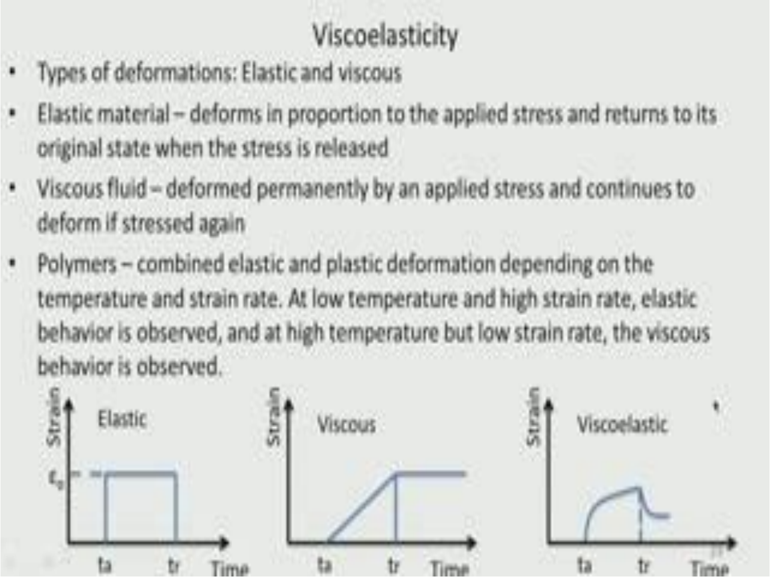

Viscoelasticity

- Types of deformations: Elastic and viscous
- Elastic material – deforms in proportion to the applied stress and returns to its original state when the stress is released
- Viscous fluid – deformed permanently by an applied stress and continues to deform if stressed again
- Polymers – combined elastic and plastic deformation depending on the temperature and strain rate. At low temperature and high strain rate, elastic behavior is observed, and at high temperature but low strain rate, the viscous behavior is observed.

Viscoelasticity we again defined it long time back. We can have an elastic and the viscous. The elastic material deforms in proportional to the stress. So, for example, return to it is original state when the stress is released. So, I give at time certain stress. So, the strain is here until the stress is maintains strain is here, as soon as the stress is released. It comes down when it is viscous material it takes longer for it to reach that value, sorry viscoelastic material it slowly reaches and then it comes down, but it never comes down and reaches the that is called the visco elastic material deforms in proportional to the applied stress and returns to it is original state. Viscous fluid deforms permanently by an applied stress and continuous to deform stressed, again polymers have both elastic and plastic depending upon temperature and strain rate at low temperature high strain rate elastic behaviour is observed and at high temperature low strain rate viscous behaviour is observed. So, we will see the viscoelastic type of nature of polymers.

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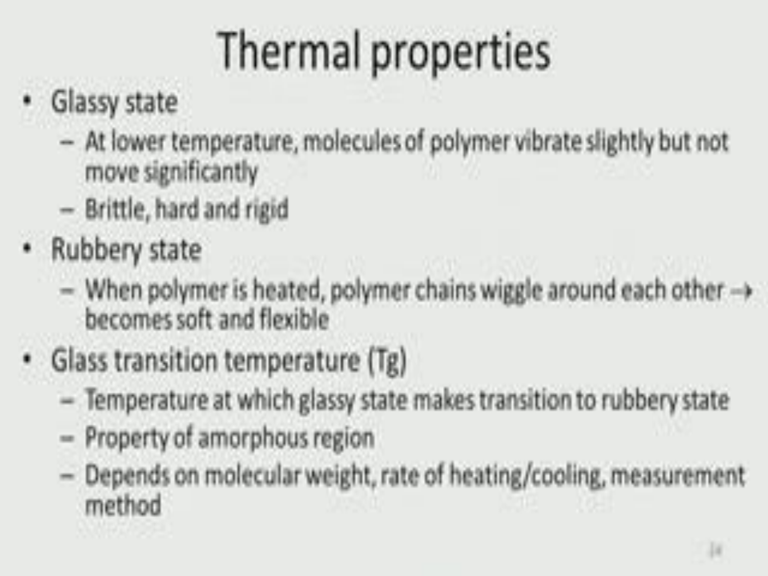

Thermal properties

- Glassy state
  - At lower temperature, molecules of polymer vibrate slightly but not move significantly
  - Brittle, hard and rigid
- Rubbery state
  - When polymer is heated, polymer chains wiggle around each other → becomes soft and flexible
- Glass transition temperature (Tg)
  - Temperature at which glassy state makes transition to rubbery state
  - Property of amorphous region
  - Depends on molecular weight, rate of heating/cooling, measurement method

There is something called thermal properties. Polymers have this glassy state, rubbery sate and also the glass transition temperature. We will talk about all these in the next class.

Thank you very much.