Introduction to Biomaterials
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Module No. # 01
Lecture No. # 31

Structure and Properties of polymers

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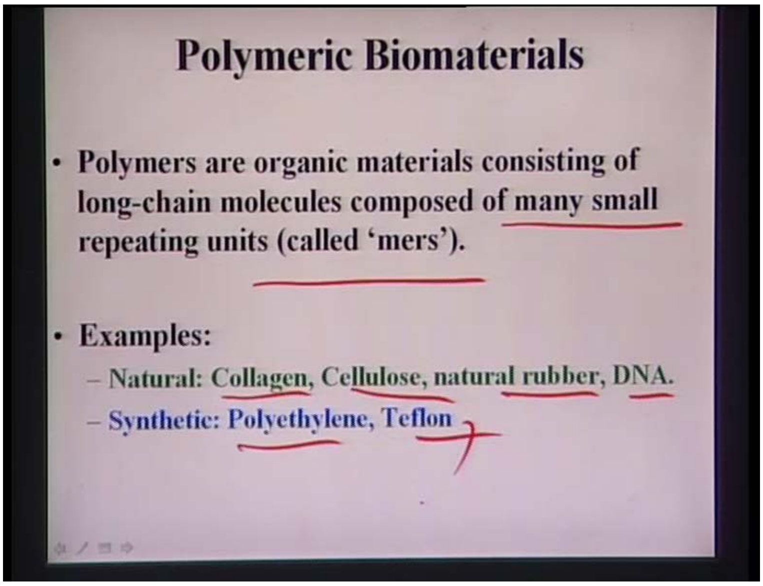

Polymeric Biomaterials

- Polymers are organic materials consisting of long-chain molecules composed of many small repeating units (called 'mers').
- Examples:
  - Natural: Collagen, Cellulose, natural rubber, DNA.
  - Synthetic: Polyethylene, Teflon

Now, I will move on to the discussion on these polymeric materials. Now, this polymeric biomaterials also, I will show you the experimental results later, but before that, I will quickly go through the basics, or fundamentals of the polymeric biomaterials. Now, polymers, as the name suggests, they are essentially organic materials and these organic materials are made of the several mer units and these mer units are repeated in the form of a long chain. So, examples of the natural polymer is that, natural biopolymer is that like collagen, cellulose, natural rubber, DNA and synthetic polymers is the polyethylene, Teflon and then PEEK and lot of other polymers, which are used commonly in structure and biomedical applications.

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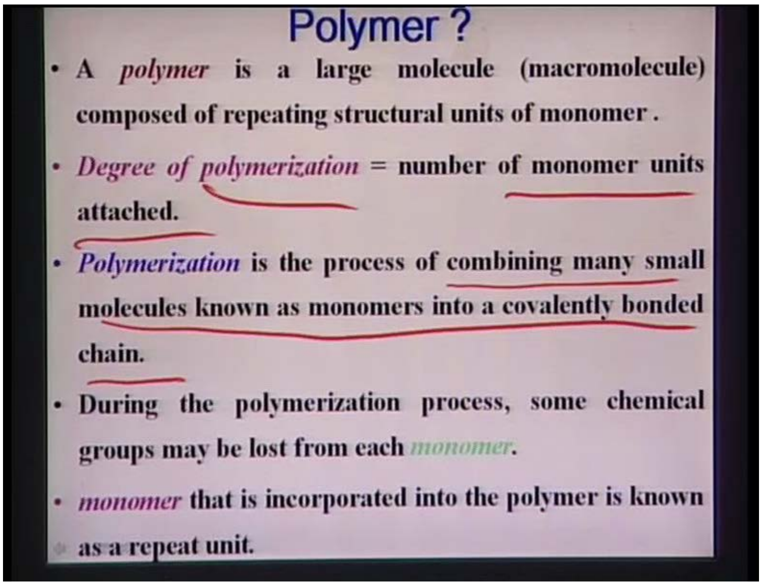

Polymer ?

- A *polymer* is a large molecule (macromolecule) composed of repeating structural units of monomer .
- *Degree of polymerization* = number of monomer units attached.
- *Polymerization* is the process of combining many small molecules known as monomers into a covalently bonded chain.
- During the polymerization process, some chemical groups may be lost from each *monomer*.
- *monomer* that is incorporated into the polymer is known as a repeat unit.

So, degree of polymerization essentially tells you that, how many number of monomer units, that are attached to each other and polymerization, what is the definition of polymerization, that is the process of combining many small molecules known as monomers, in a covalently bonded chain, and during the polymerization process, some chemical groups may be lost from each monomer; and this is like the definition of the homo-polymer.

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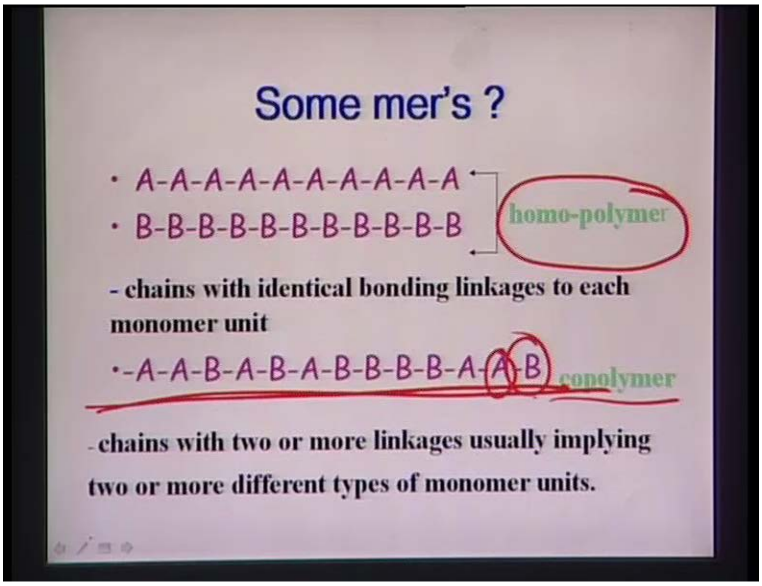

Some mer's ?

- A-A-A-A-A-A-A-A-A-A
- B-B-B-B-B-B-B-B-B-B-B

homo-polymer

- chains with identical bonding linkages to each monomer unit

- -A-A-B-A-B-A-B-B-B-B-A-A-B

copolymer

- chains with two or more linkages usually implying two or more different types of monomer units.

Homo means, that is the same type of mer units, which are repeated; there is no mix of the two mer units. Copolymer means, that A and B, two different type of mer units, which are joined together by covalent bonds in the main chain, or the back bone chain. So, these chain is called the main chain, back bone chain of the polymeric structure.

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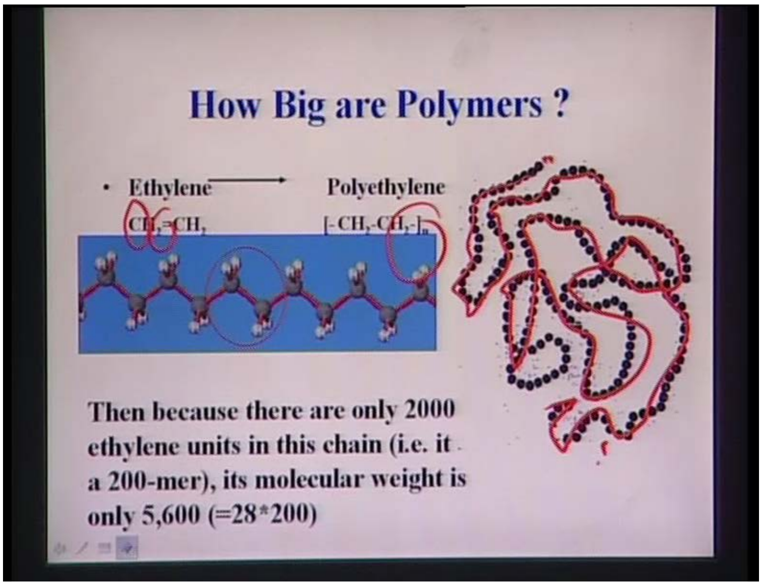

How Big are Polymers ?

- Ethylene → Polyethylene

$CH_2=CH_2$ $[-CH_2-CH_2-]_n$

Then because there are only 2000 ethylene units in this chain (i.e. it a 200-mer), its molecular weight is only 5,600 (=28*200)

Now, one of the important things of the polymers is that, since it is typically made of carbon, hydrogen, nitrogen, oxygen, this kind of very light elements and large number of this mer units are, you know, bonded together, then, these materials they are extremely flexible; like, you can see, this polymeric molecules, now, they can take any shape, the way they want, and they can be squeezed also; and essentially, these looks more like a typical shape of a snake, right; that, how the snakes are squeezed. And, you have, if you remember well that, you know, some of the protein structure also, that time, I have mentioned categorically that, protein structure also, they can take shape of the, like a snake shape, or very squeezed kind of shape. Basically, again, because, why, because proteins are the polypeptides, and polypeptides are again the many peptide units, they are (( )) together, they are joined together and therefore, the proteins being biopolymeric molecules, they can also be squeezed.

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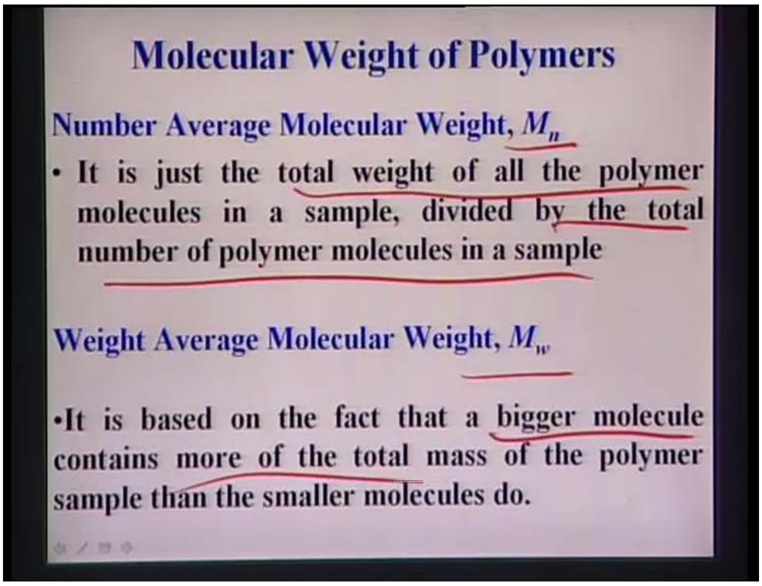

Molecular Weight of Polymers

Number Average Molecular Weight, M_n

- It is just the total weight of all the polymer molecules in a sample, divided by the total number of polymer molecules in a sample

Weight Average Molecular Weight, M_w

- It is based on the fact that a bigger molecule contains more of the total mass of the polymer sample than the smaller molecules do.

Now, this polymeric molecules, as I will show you later, if you stretch it, it can be stretched easily, and it can be given large amount of elastic deformation. Now, how to define, because, there is two way to define the physical properties; one is the density and one is the molecular weight of polymers. Molecular weight, that you can measure by either the number average molecular weight, that is M n, and the another one is the weight average molecular weight. So, number average molecular weight is defined as the total weight of the polymeric molecules divided by the total number of polymer molecules in the sample; and, the weight average molecular weight is that, it is basically defined as the bigger molecule contains the total mass of the polymer sample, than the smaller molecules do.

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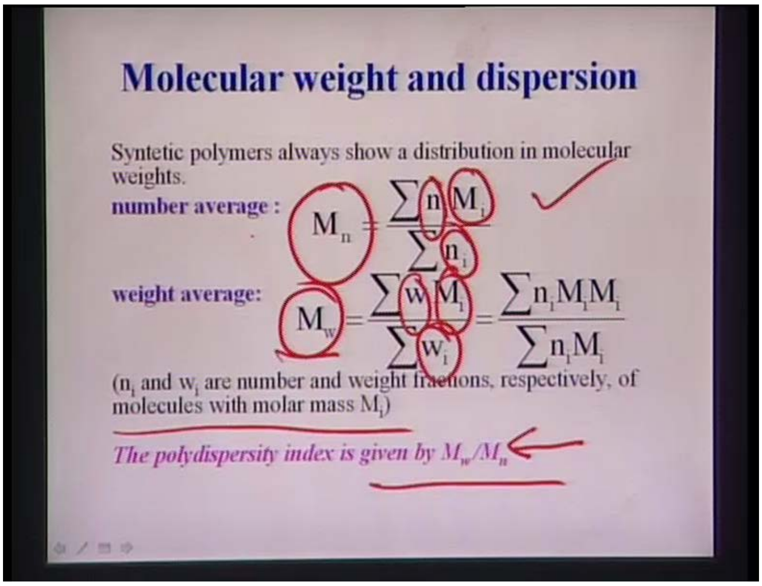

Molecular weight and dispersion

Syntetic polymers always show a distribution in molecular weights.

number average : $M_n = \frac{\sum n_i M_i}{\sum n_i}$

weight average: $M_w = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum n_i M_i M_i}{\sum n_i M_i}$

(n_i and w_i are number and weight fractions, respectively, of molecules with molar mass M_i)

The polydispersity index is given by M_w/M_n

So, basically, if you see that, mathematically, number average molecular weight is defined as that sigma n i M i by divided by sigma n i. So, M i is that molecular weight of the individual short chain containing n i number of mer units, divided by what is the total number of mer units, like all those small chains. So, that way, you can get this M n value. So, similarly, M w, that is the weight average molecular weight, again, sigma W i M i divided by sigma W i and W i and M i is the molecular weight of the i th chain of the polymer, and which has the weight of W i. So, these things are written here that, n i and W i are the number and weight fractions respectively, of molecules with molar mass of M i. Now, polydispersity index also is an important things, like, it also shows the characteristics of the polymerization of that given polymer and typically, it is defined as the ratio of M w to M n.

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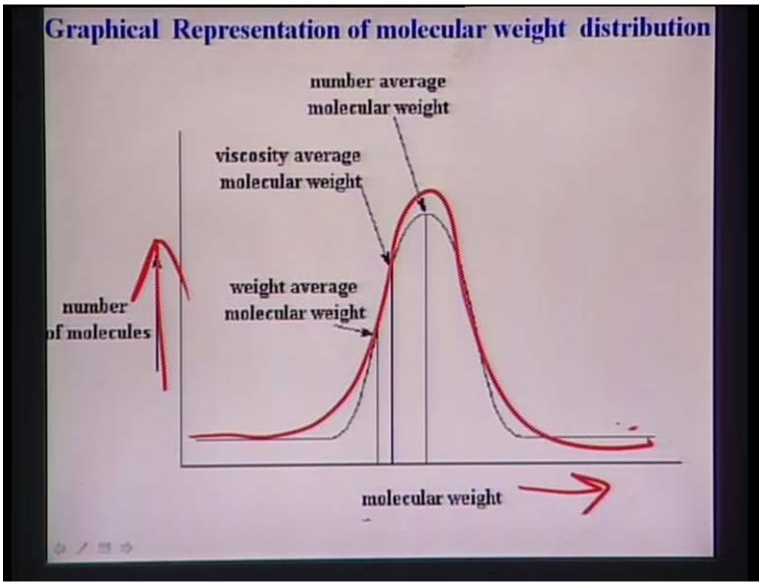

Graphical Representation of molecular weight distribution

This is a typical molecular weight distribution curve. So, number of molecules, if it is plotted along y axis, molecular weight if it is plotted on x axis, so, this is the molecular weight distribution. You have this number average molecular weight, that is the M n, and you have the weight average molecular weight, that is the M w; and there is another, another way you can define the molecular weight, by the viscosity average molecular weight; but largely, this is, the M n bar, M w bar, these are like, widely used in text book, as well as in research.

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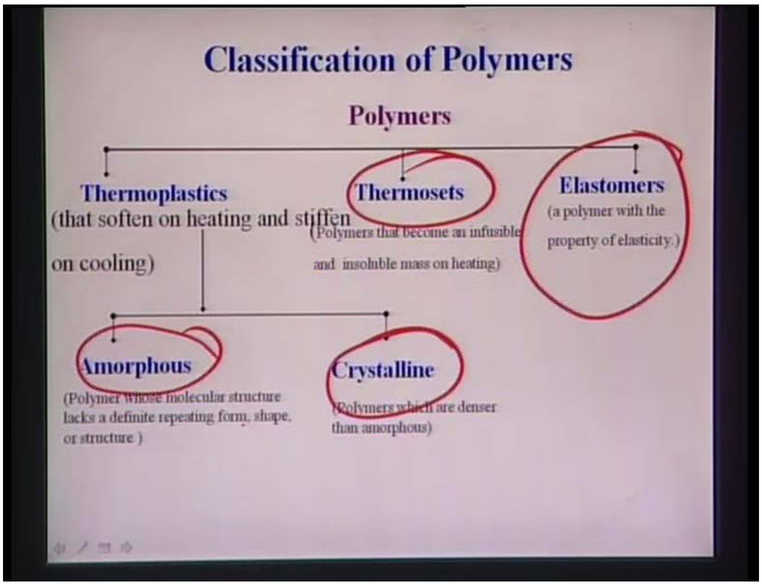

Classification of Polymers

Polymers

Thermoplastics
(that soften on heating and stiffen on cooling)

Thermosets
(Polymers that become an infusible and insoluble mass on heating)

Elastomers
(a polymer with the property of elasticity.)

Amorphous
(Polymer whose molecular structure lacks a definite repeating form, shape, or structure)

Crystalline
(Polymers which are denser than amorphous)

Now, how these polymers can be classified? They are broadly classified into 3 classes: thermoplastics, thermosets and elastomers. So, thermoplastics means, it sounds like that, if you heat this polymers, thermo means thermal, means heating; plastics means it becomes more plastic; so, that means, it softens on heating and stiffens on cooling; means, it will act like a soft rubber kind of things, if you heat it up. Now, it will contract and it will stiffen, then, when you cool it to room temperature; that is the typical behavior of thermoplastic. The advantage of the thermoplastic is that, when you heat it up, then you can give a particular shape, or you can give a desired shape, the way you want. In contrast, thermoset means, that you know, once you heat it up, that polymer itself kind of goes to a frozen state; like, you cannot do any kind of working, you cannot give any mechanical shape, or you can, you cannot do any mechanical working to give it a desired shape. So, that is the fundamental difference between the thermoplastic polymers and thermosetting polymers. Elastomers, elastomers is another kind of polymers, which has a large, which can, which can exhibit large amount of elasticity, or large amount of elastic deformation, which is close to 800 to 900 percent. Typically, polymers, their strain to failure, or strain to fracture is roughly around 100 percent, but elastomer can goes to, can go to 700 to 900 percent.

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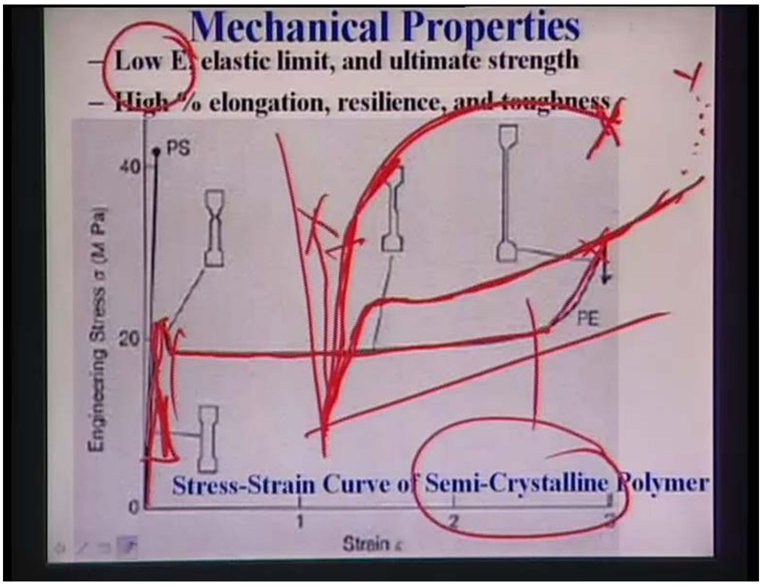

Mechanical Properties

– Low E, elastic limit, and ultimate strength
– High % elongation, resilience, and toughness

Stress-Strain Curve of Semi-Crystalline Polymer

Now, thermoplastic polymers can be further classified to amorphous polymer and crystalline polymer; I will come back, I will come to this term, so that, I, you can understand it better with the help of some schematic; that, what is meant by amorphous polymer, or what is meant by crystalline polymer. This is a typical stress-strain curve for this, engineering stress-engineering strain curve for the polymeric, thermoplastic polymeric material. Now, what you see, this is for the polyethylene. So, initially, you have elasticity behavior, or elastic behavior; the slope of this part will give you the modulus of elasticity, right; that is the value of E. Now, finally, after this, it goes to some peek value; then, it has a broadly, it is a kind of...So, this part, essentially tells you that, at a constant stress, polymer is getting more and more amount of strain, without even going to the fracture; and, prior to the fracture, for polyethylene, it goes to little bit increase in stress, before it goes, it reaches the fracture strain, and then, it fractures completely. So, this is the kind of, typical behavior of a thermoplastic polymer and this is the case for the semi-crystalline polymer.

Now, remember, like the way I have mentioned to you for the ceramic materials, there is no ceramic, which is known to mankind, which is like 100 percent covalent and 100 percent ionic. Ceramics have always a mixture of ionic and covalent bond. Similarly, there is hardly any polymer, which is like 100 percent amorphous and 100 percent crystalline. You always get, kind of, mostly semi-crystalline polymer; that means, some volume fraction of the polymers have crystallinity and rest of the volume fraction shows like a amorphous matrix. Now, one of the important things for the polymeric materials that I must highlight, when I, when you compare with the ceramic based materials, or polymer based materials, now, polymers have a low elastic modulus. Low elastic modulus, that means, it has a much more compliant behavior. The slope, if you compare, on the plot, you can, you want to plot like ceramic materials, ceramics have a very high elastic modulus; that means, the slope will be very steep; that is, like a very steep curve, for the stress strain curve; unfortunately, ceramics goes to failure, without undergoing any kind of deformation.

For metals, metals have intermediate values of elastic modulus; that means, initially, it is straight, that is, linear elasticity; it goes to non-elastic behavior, plastic behavior, it goes to fracture; that is the case for metals. Now, on the same plot, if you want to plot it for polymeric materials, like high density polyethylene, then, it goes, keeps on going, dotted, dotted, and then, it goes to fracture. Now, what you are trying to get, the message from this plot that, ceramic is the extreme left; intermediate values is the metals, because metals have the intermediate elastic modulus and metals have a typical elastic behavior, then goes to non-linear plastic behavior, then goes to fracture; polymers they have further right, because the polymers have a low elastic modulus. So, slope also will be much and much less. So, that is, it means, it is a more compliant behavior; however, this polymers, they go like this, then, it goes to some increasing strain and at constant stress, the polymers can be strained to a large amount of strain. So, this dotted means that, actually, the strain to fracture of polymers will be much higher compared to that of even the most ductile metal that you know, like aluminum, or copper. So, aluminum, copper can have, let us say, strain to fracture is, let us say, 40 to 50 percent, let us say; high density polyethylene, if it is well made, or if it is well processed, they can undergo strain around 100 percent, or little higher than 100 percent. So, large amount of strain can be given to polymeric materials.

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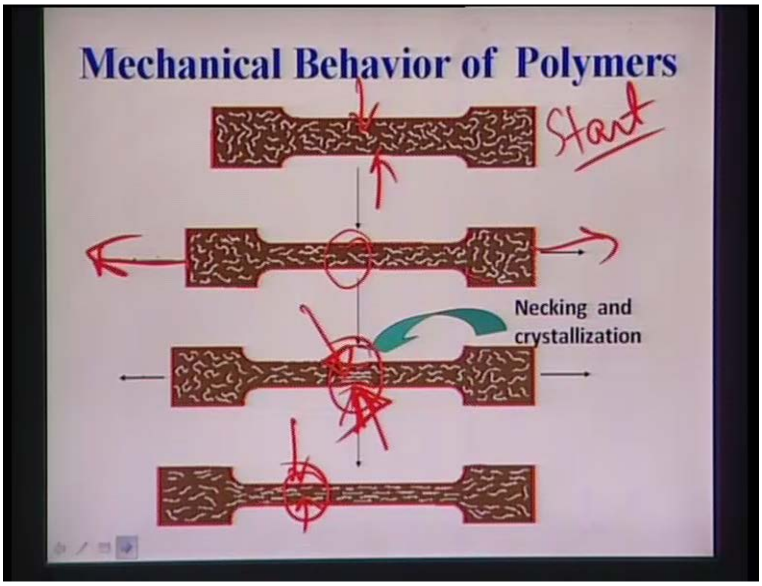

Mechanical Behavior of Polymers

Now, the reason is that, why these polymeric materials can be given such a large amount of deformation? Now, if you start with that, this is your starting point. So, you start with the material, where this short chains of the polymer, or the polymeric chains, like, you know, this is like a dog bone type of geometry; this is like a typical tensile bar, like a dog bone type of geometry; and, in this dog bone type of geometry, this, all this chains, which are appearing is that, you know, white in color, or bright in color, they are randomly oriented. So, there is no orient, no specific, or preferred orientation of the chain. Now, you start pulling in tension, then, what will happen? When you start pulling in tension, then, what you slowly try to see here that, some chains here, it is trying to get aligned, and you see, this point; you keep on pulling in tension, at this point, your polymeric, some chains are getting aligned perfectly along the tensile stress axis; and, that means, this part of this polymeric test samples, they have, kind of orientation, which is parallel to each other and therefore, there is some regularity, or repeatability in the orientation of the polymeric chain; and, that shows that, these material has kind of crystallinity, that has taken place here. And then, this region, also called the neck region, neck means that, this is like a, there is certain contraction that you can see; because, if you can see the width of this area, and then, width of this area, certainly, you can see, the width here, is much less compared to the starting sample dimension; however, the lengthwise, it has increased more, compared to the starting sample dimension.

So, essentially, what I am trying to say here that, with increasing amount of stress, the more and more amount of load you are actually applying, externally, the more number of chains will try to align themselves, with respect to the tensile stress axis; however, since polymers, they behave like a viscous solid, it is not like elastic solid, this orientation of the chains along the tensile stress axis, will take some time; and that is what is reflected here, in this tensile stress axis - strain axis, that you can see, at the constant stress level, polymers are undergoing large amount of strain; and, that is reflected, what I am trying to show you in the next slide that, you know this chains, they are, kind of, orienting themselves, along the tensile stress axis and that is taking time, because, it is a viscous solid and therefore, this polymers, they have the unique capability of undergoing large amount of strain prior to fracture.

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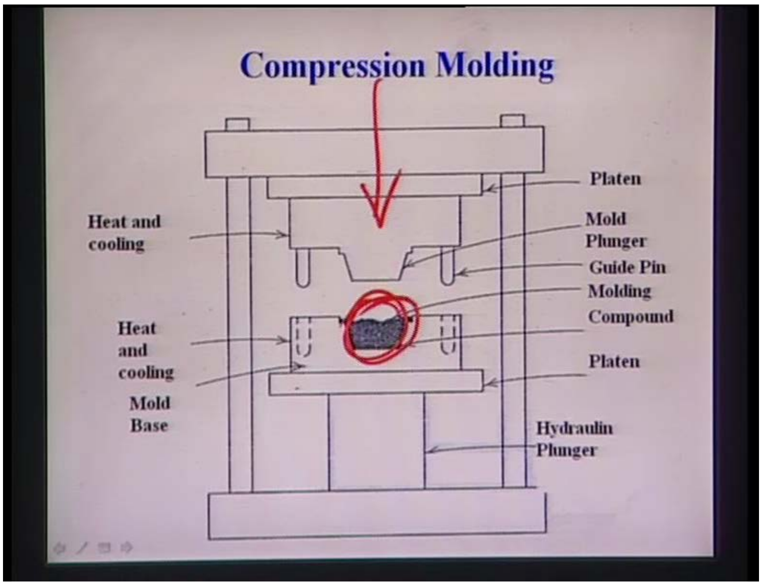
Compression Molding

Now, coming to the, some processing techniques that, the way this polymeric materials can be made, now, you know, ceramics, they can be fabricated by sintering. So, it starts from the powder. Now, polymers also, essentially a powders-based method. So, you start with the powders, but, because of their unique properties of the low melting point, as well as, the thermoplastic polymers can be deformed, when it is in the plastic state; you can put this powders in a particular mould cavity, then, you can pressurize it from the top, and then, you can create a particular shape using the compression molding technique.

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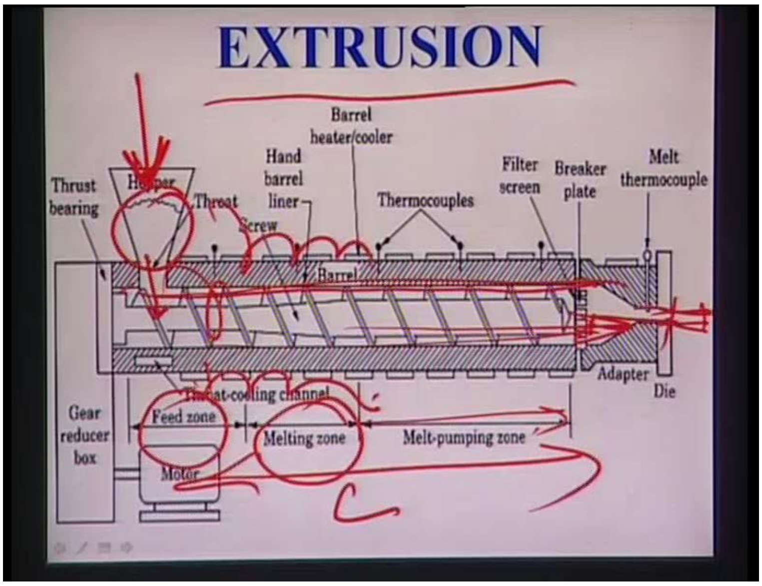
EXTRUSION

And, this is one of the way you can do. Other way you can do that, these fabrication of the polymers, or processing of the polymers, is by extrusion method. Extrusion method means, you put all your polymeric granules, or molecules in the hopper and then, in this, through this hopper, it is fed into this barrel and this barrel is typically much longer. So, this length of the barrel can be divided into 3 distinct zone; one is the feed zone; feed zone means, in this barrel, this polymeric powder particles are fed; melting zone means, here is some heating coils, external heating coils is there, and through this external heating coils, the heat is supplied to the polymer, and then, their melting point of 300 400 degree Celsius. So, you know, you do not need to supply much current to the heating coils and the polymers will be molten; and once it is molten, then, you can push it; that is the melt and pumping zone; there, you can push it, so that, polymeric melt can be forced through this die and subsequently, this can be cut into pieces. So, it will be coming out as an extruded rod, and then, you can cut into pieces, the way you want. So, that is, essentially the entire extrusion process. So, extrusion means, you are essentially first melting the polymeric powders, then you are forcing, so that, this, your allowing this polymeric melt, to push through the particular die orifice.

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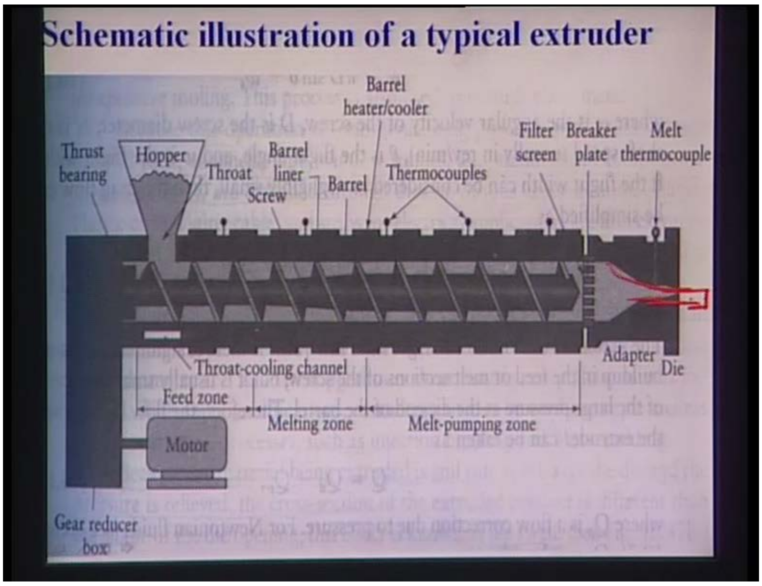
Schematic illustration of a typical extruder

So, this is more, you can see in this extrusion that, you can, this, from this point, so, this die, through this die orifice, this polymeric extruded rod can get out of the system. Now, some of the polymers, which are, which are being used in this different biomedical applications, first one is the polytetrafluorethylene, that is Teflon.

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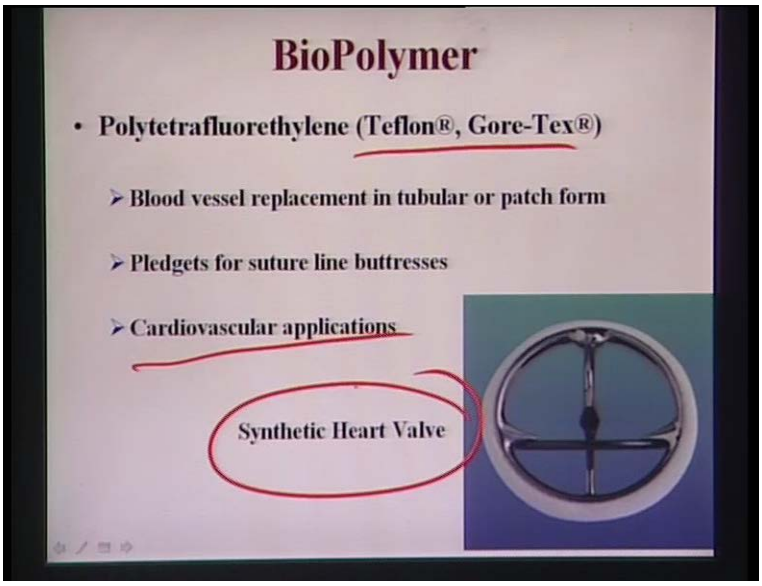

BioPolymer

- Polytetrafluorethylene (Teflon®, Gore-Tex®)
  - Blood vessel replacement in tubular or patch form
  - Pledgets for suture line buttresses
  - Cardiovascular applications

Synthetic Heart Valve

Now, this has got several applications; cardiovascular applications, and like, this is the examples of the synthetic heart valve. Now, therefore, the synthetic heart valve, the property that you require is the haemocompatibility; that is the blood compatibility property; and blood compatibility, if you remember correctly, blood compatibility essentially tells you that, whether the materials will form thrombus, when blood will be flowing, in contact with the material; and if the thrombus forms, then, that means, this biomaterials cannot be used for the cardiovascular applications. Now, thrombus can form and thrombus cannot be, cannot be adherent, or thrombus can be pushed out of the system, by continuous blood flowing dynamic conditions; that way also this biomaterial can be used for cardiovascular applications.

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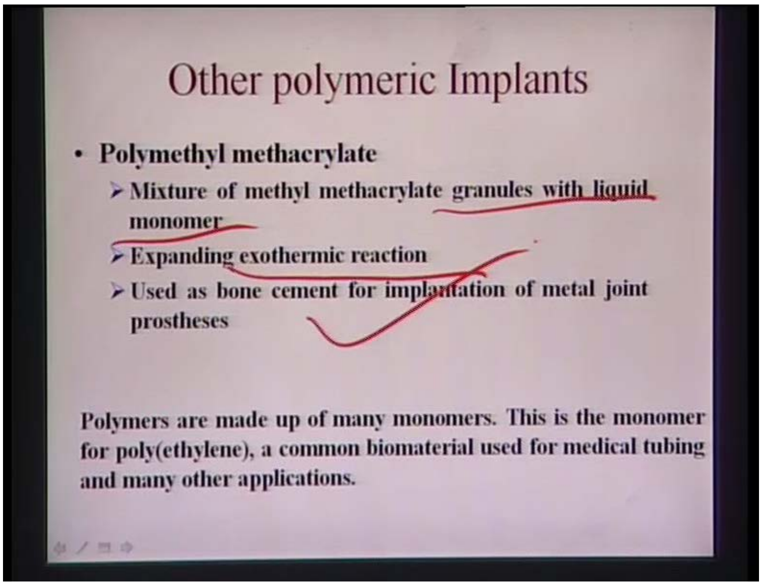

Other polymeric Implants

- **Polymethyl methacrylate**
  - Mixture of methyl methacrylate granules with liquid monomer
  - Expanding exothermic reaction
  - Used as bone cement for implantation of metal joint prostheses

Polymers are made up of many monomers. This is the monomer for poly(ethylene), a common biomaterial used for medical tubing and many other applications.

But if the thrombus can form, they can form a chunky thrombus; they can adhere to the material; you cannot use that material in real applications. The other polymeric materials which are used for biomedical application is polymethyl methacrylate; this is also used as a bone cement applications. So, bone cement means, like, orthopedic surgeons are doing some operation in the OT; now, they are putting some stem, or they are putting some part, or orthopedic, or the bone implant in the human body, and there are some gap which is there, between the natural tissue, or natural bone and that new implant material. So, this is like a cement; you know, the way you have seen that, how a house is built, so that, you are putting bricks together and between two bricks, you put the cement, so that, the two bricks are bonded together. So, similar thing, you can, you can visualize in a much narrow scale that, implant material is, put it inside the body and then, cement you are giving, just to fix that implant material with a natural bone, which is lying outside that implant material. So, this is the mixture of methyl methacrylate granules with a liquid monomer and this expands during the exothermic reaction; and, used as a (( )) bone cement for implantation of metal joint prostheses; that is what, I just explained to you.

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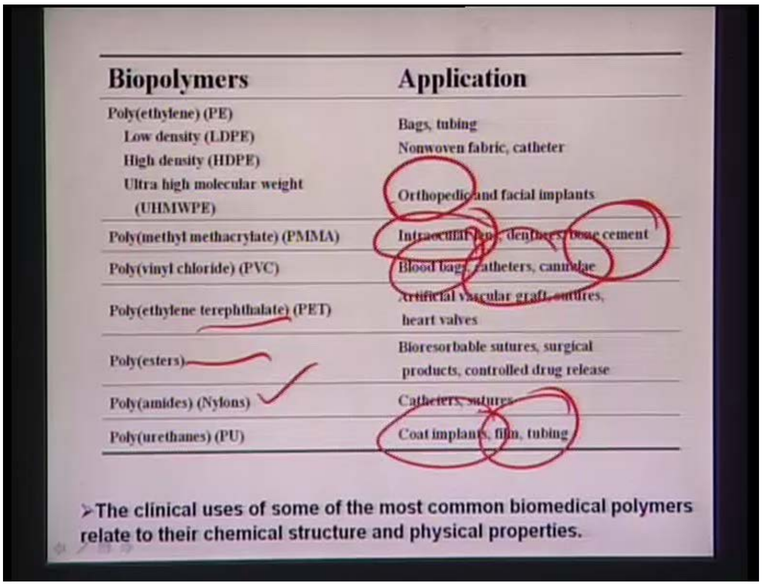

Biopolymers	Application
Poly(ethylene) (PE)	
Low density (LDPE)	Bags, tubing
High density (HDPE)	Nonwoven fabric, catheter
Ultra high molecular weight (UHMWPE)	Orthopedic and facial implants
Poly(methyl methacrylate) (PMMA)	Intraocular lens, dentures, bone cement
Poly(vinyl chloride) (PVC)	Blood bags, catheters, cannulae
Poly(ethylene terephthalate) (PET)	Artificial vascular graft, sutures, heart valves
Poly(esters)	Bioresorbable sutures, surgical products, controlled drug release
Poly(amides) (Nylons)	Catheters, sutures
Poly(urethanes) (PU)	Coat implants, film, tubing

- The clinical uses of some of the most common biomedical polymers relate to their chemical structure and physical properties.

Now, these are like, you know, summary of the different biopolymeric materials, like polyethylene bags, or tubing, or ultra high molecular weight polyethylene like orthopedic applications; I think, I have mentioned it, when I have, I have discussed different components of the T H R, Total Hip-joint Replacement; you have the stem, which is typically made of titanium, or stainless steel; you have the femoral ball head, which is typically made of ceramic, like alumina, or zirconia, and you have that, acetabular cup, which is typically made of ultra high molecular polyethylene. But they have also, problem of, like you know, high wear rate, or large, coarser wear debris particles, which can cause genotoxicity and which can cause some aseptic loosening and because of that, ultra high molecular polyethylene is currently being replaced by other polymer, polymer ceramic composites. Now, coming to the PMMA, that can be used as intraocular lens in the eye, then, dentures, as well as bone cements; polyvinyl chloride, this as a blood bags, catheters and all this things; PET, then polyesters, then poly urethanes, like coat implants, films, tubings, etcetera.

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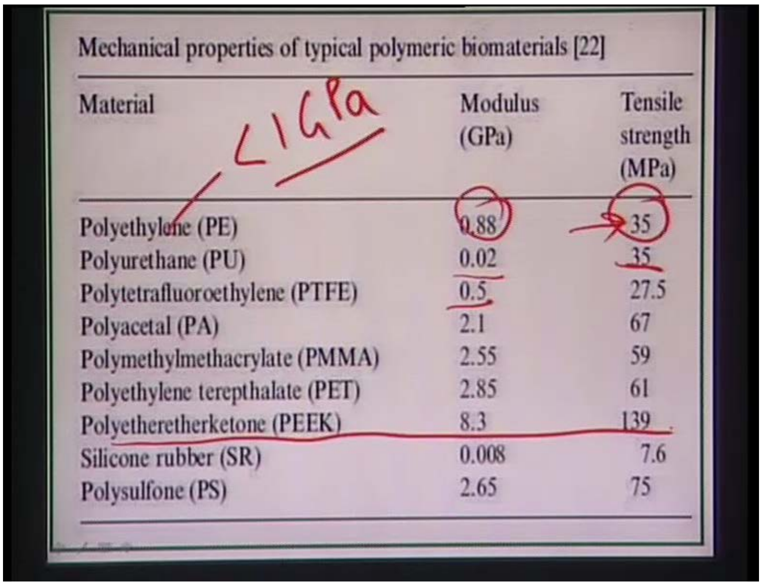

Mechanical properties of typical polymeric biomaterials [22]

Material	Modulus (GPa)	Tensile strength (MPa)
Polyethylene (PE)	0.88	35
Polyurethane (PU)	0.02	35
Polytetrafluoroethylene (PTFE)	0.5	27.5
Polyacetal (PA)	2.1	67
Polymethylmethacrylate (PMMA)	2.55	59
Polyethylene terepthalate (PET)	2.85	61
Polyetheretherketone (PEEK)	8.3	139
Silicone rubber (SR)	0.008	7.6
Polysulfone (PS)	2.65	75

Now, this table, essentially shows you that, what are the summary of the mechanical properties of the different polymeric materials. So, this summary, essentially gives you that, overall idea that, what is the combination of modulus of elasticity, or elastic modulus and tensile strength, that you can obtain in this materials, and that elastic modulus, you can see, this is like a 0.9 gigapascal and this is 35 megapascal. So, 0.9 gigapascal means, it is even less than 1 gigapascal elastic modulus.

Now, if you take the most of the cortical bone, the cortical bone, their elastic modulus is somewhere between 3 to 8 gigapascal. So, even if you use the polyethylene alone, you cannot match with the lower bound of the cortical bone, in terms of the elastic modulus property. Other things is the, tensile strength 35 megapascal, is still low for the use as a cortical bone replacement applications. You need to increase the strain properties of this materials. Coming to the polyurethane PU, which is even less; so, it is like 20 megapascal, or 0.02 gigapascal and 35, again, tensile strength is 35; PTFE is equally less 0.5; the material which is a good combination of the elastic modulus, as well as the tensile strength, is the PEEK; that is, polyetheretherketone. So, PEEK has a modulus, elastic modulus of 8 gigapascal, and tensile strength also, 139 megapascal. So, 8 gigapascal means, it is 10 times higher than that of the polyethylene; 139 megapascal tensile strength means, it is roughly 4 times higher than that of the tensile strength of the polyethylene. So, really, you can get one order higher elastic modulus and you can also get four times higher tensile strength in this materials, by choosing polyetheretherketone, compared to that of the polyethylene.

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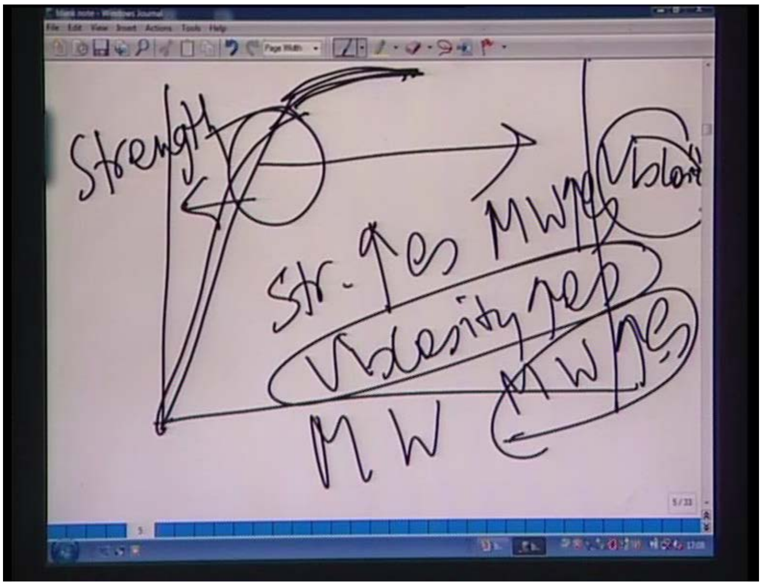

So, one of the important thing in polymeric materials, is that, one need to remember that, if your strength, if you plot and then, other side, if you plot your viscosity, and then, x axis, if you plot molecular weight, then, what will happen, your strength and viscosity, both will actually increase, and that will increase upto certain level of molecular weight and then, it saturates. So, beyond a certain increase in the molecular weight, to get a maximum strength is not advisable; other things is important that, you are, because your strength and viscosity…So, your strength increases, as your molecular weight also increases, and your viscosity increases, as your molecular weight also increases. So, what is the implication of that? Implication of that is that, if your molecular weight increases, if your viscosity increases, then, manufacturing will be very difficult; because then, you cannot use like extrusion process, because if the polymer melt itself is very viscous, or very thick, then, what will happen, you cannot really push the polymer melt in this extrusion chamber, or you cannot do much mechanical working on this viscous solid.

So, if you want to make a material, which you can, which you want to give a different shape, based on the polymeric materials, then, your molecular weight needs to be optimized, so that, you get a polymeric melt with desirable level of viscosity; at the same time, you can get the polymeric material with higher level of strength property, because your strength is important, but strength property should not be increased, or should not be enhanced, at the expense of the difficulty in your processing, or at the expense of the difficulty in your manufacturability of this polymeric materials. So, these things needs to be carefully controlled, and therefore, why I am mentioning these aspect here that, in this polyethylene, and if you go to this polyetheretherketone, in this two materials that we are dealing here, now, these attracted attention because, polyethylene, actually you can give it a different shape, but polyethylene suffers from a combination of poor mechanical properties, like poor elastic modulus, and very low amount of, very low level of strength. At the same time, polyetheretherketone has a one order of magnitude higher elastic modulus and about 4 times higher tensile strength, then after, than that of the polyethylene; however, polyetheretherketone cannot be processed that easily, like that of the polyethylene. So, therefore, you have to compromise between the properties, as well as the way that you can make this materials, using standard manufacturing techniques, like extrusion, injection modeling, or compression molding and so on.

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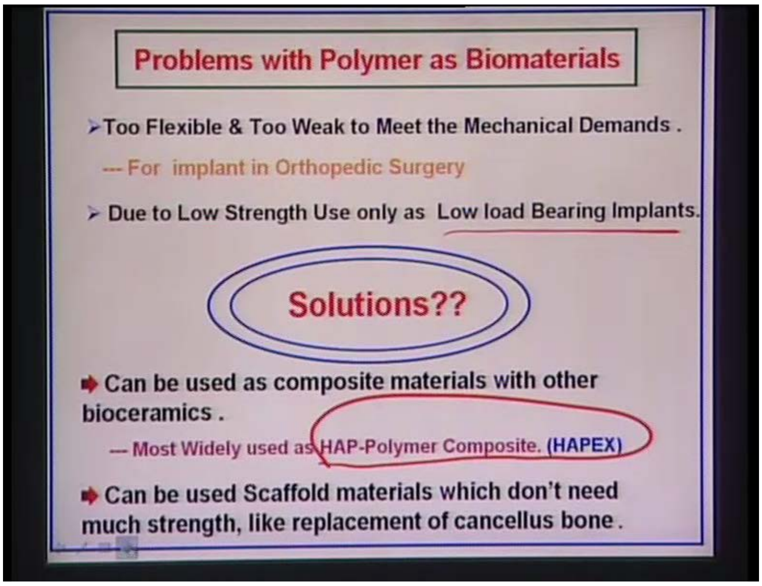

Problems with Polymer as Biomaterials

- Too Flexible & Too Weak to Meet the Mechanical Demands .
  - --- For implant in Orthopedic Surgery
- Due to Low Strength Use only as Low load Bearing Implants.

Solutions??

- Can be used as composite materials with other bioceramics .
  - — Most Widely used as HAP-Polymer Composite. (HAPEX)
- Can be used Scaffold materials which don't need much strength, like replacement of cancellus bone .

Now, problems with polymers as the biomaterials, like polymers are too flexible and too weak to meet the mechanical demands; too weak means, it has very low level of strength and low elastic modulus; and due to low strength, they can be used only low load bearing implants. Now, if you want to use it, this polymeric materials, or improve the mechanical properties, what are the possible routes, or possible avenues? Possible route is that, hydroxyapatite polymer composites, or polymer based other composites, like, with other ceramic reinforcement.

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HAp- Polymer Composite

❖ Why do we care about hydroxyapatite?

- HA can be mixed with various polymers to form biocompatible and possibly bioactive composite materials.
- These polymer composites have been used in High Load Bearing implants.
- HAPEX™ (Bonfield *et al.*) is a composite consisting of HA particle reinforcement in a high-density polyethylene (HDPE) matrix
- Whisker shaped particles improve the mechanical properties of similar HDPE/HA composites (Roeder *et al.*).

Now, why do we require really hydroxyapatite, because hydroxyapatite is a natural choice; because hydroxyapatite is already contained in the natural bone, along with collagen. So, therefore, people always try to use the hydroxyapatite in developing different composites, so that, you can mimic the composition as close as possible, when compared to the natural bone.

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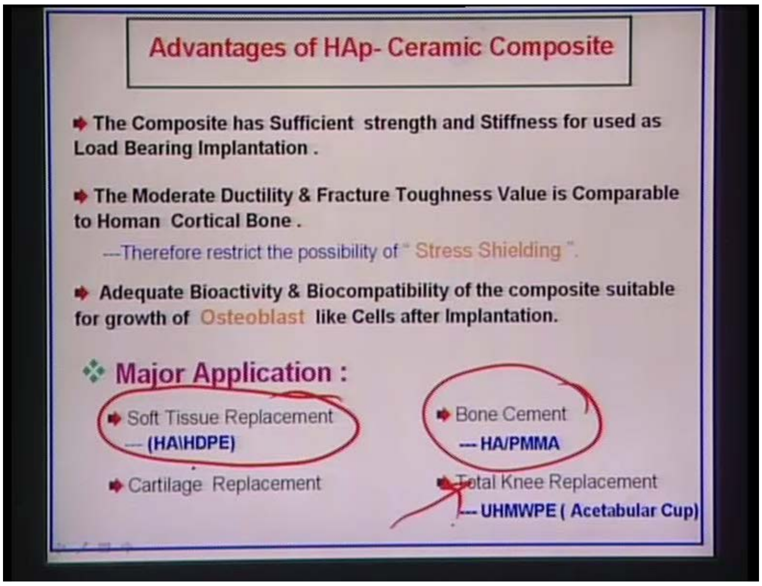

Advantages of HAp- Ceramic Composite

- **The Composite has Sufficient strength and Stiffness for used as Load Bearing Implantation .**
- **The Moderate Ductility & Fracture Toughness Value is Comparable to Homan Cortical Bone .**
  ---Therefore restrict the possibility of " Stress Shielding ".
- **Adequate Bioactivity & Biocompatibility of the composite suitable for growth of Osteoblast like Cells after Implantation.**

❖ Major Application :

- Soft Tissue Replacement
  --- **(HA\HDPE)**
- Bone Cement
  --- **HA/PMMA**
- Cartilage Replacement
- Total Knee Replacement
  --- **UHMWPE (Acetabular Cup)**

So, these are the advantages of the HAP ceramic composites, or HAP based ceramics composites, like, you know, you can have this soft tissue replacement like high density polyethylene hydroxyapatite; in the bone cement application also, people have developed polymethyl methacrylate, as well as combination of hydroxyapatite; total knee replacement in acetabular cup, or trimolecular polyethylene also, you have these polymer based materials.

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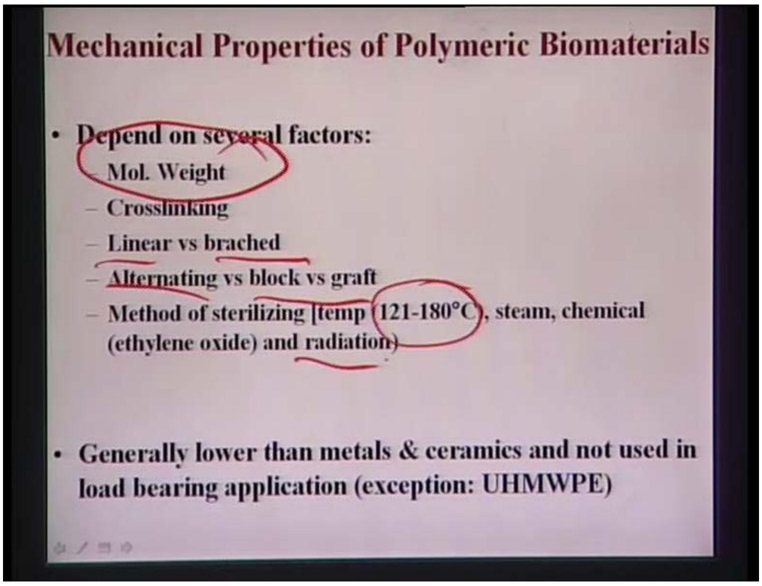

Mechanical Properties of Polymeric Biomaterials

- Depend on several factors:
  - Mol. Weight
  - Crosslinking
  - Linear vs brached
  - Alternating vs block vs graft
  - Method of sterilizing [temp (121-180°C), steam, chemical (ethylene oxide) and radiation]
- Generally lower than metals & ceramics and not used in load bearing application (exception: UHMWPE)

So, mechanical properties of the polymer, that depends on several factors; as I said already, molecular weight. The second one is the crosslinking; that is, crosslinking, in case of the rubbers, or crosslink polymers; then, depends on whether it is a linear polymers, or branched polymers; depends on whether it is a alternative versus block versus graft polymers; alternating polymer means, like, you know, this mer units are alternatively arranged in the back bone chains; block polymer means, you have a block of a mer units, then, you have a block b mer units, then, you have a block of c mer units; then, then a, b, c can be repeated in that sequence; graft copolymer means, you have a major back bone chain and where that another copolymer, or another mer unit, is grafted to the main back bone chain; so, that is called graft copolymer; then, method of sterilization; like, polymers, you can sterilize either at the steam autocline unit, like 180-121 degree Celsius, or by chemical treatment by ethylene oxide, or by gamma radiation.

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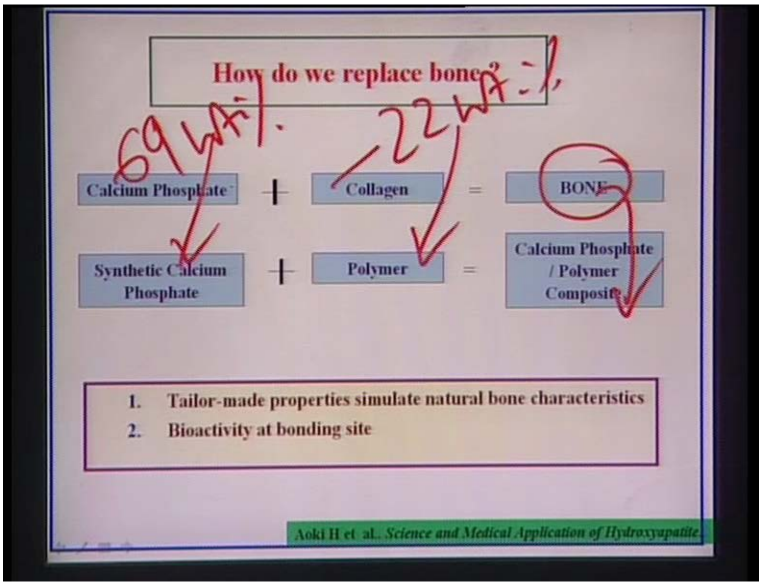

How do we replace bone?

69 wt%.

22 wt%

Calcium Phosphate + Collagen = BONE

Synthetic Calcium Phosphate + Polymer = Calcium Phosphate / Polymer Composite

1. Tailor-made properties simulate natural bone characteristics
2. Bioactivity at bonding site

Aoki H et al., *Science and Medical Application of Hydroxyapatite*

Now, this polymer ceramic composite, what is the motivational? Why this ceramic composite has been developed in different research laboratories? Now, you know that, natural bone is a polymer ceramic composite, that I think, I have mentioned at several point of time, during this course. So, similarly, people try to, since collagen is a polymeric based material, or polymeric based natural polymer, so, people try to mimic the bone composition, by adding synthetic calcium phosphate to some polymeric, suitable polymeric base, or suitable polymeric matrix. So, therefore, the natural bone can be mimicked, as close as to the calcium phosphate polymer composite. And remember, in the natural bone, you have 69 weight percent of calcium phosphate materials; you have around 22 weight percent of collagen. And therefore, if you want to make that similar kind of composition here, if you load the 69 versus 22, then, I think that, these polymer composites will be quite challenging and this will be quite closely mimicking the natural bone properties; but the point is that, how you can load this 22 weight percent of polymer in (( )) 69 or 75 percent ceramic base or ceramic matrix.

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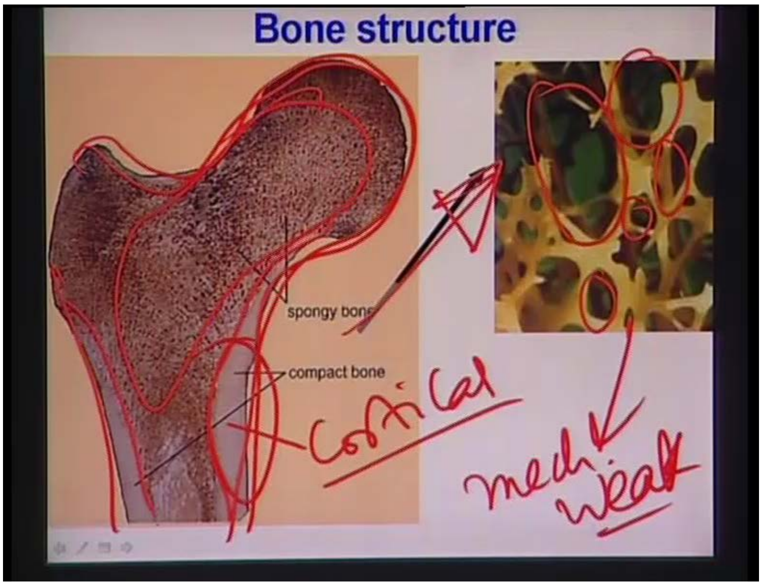

Bone structure

So, that requires kind of care, quite careful processing technique, or optimization of the processing parameter. Just to remind you that, these typical compact bone, that has a cortical shell, cortical outer shell and then, internal…So, this is your cortical shell and this cortical bone has a much larger, or better mechanical properties, compared to that is the spongy bone structure. So, spongy bone means, that is, porous bone structure; other synonyms of spongy bone is the cancellous bone or trabecular bone. So, spongy bone, trabecular bone, cancellous bone, all be are the same meaning. So, this is the typical ultra structure, or finite details of the spongy bone. You can see, this is largely porous structure and because of this large porosity in this spongy bone, these are essentially, mechanically very weak; that means, it has a much inferior combination of elastic modulus and strength properties, in comparison to what you have in the cortical bone. So, that is also biologically quite intelligent way of manipulating structure, in a sense that, if your structure has a very stronger outer shell, then, that structure will be protective also; that inner coat, that trabecular bone is protected by the very fact that, these trabecular bone is always contained in a very hard shell and this hard shell is essentially, the cortical bone. So, that is what, that is also very intelligent way, that the nature has developed this kind of bone structure and that is also one of the reason that, why these bone structure people try to mimic very closely.

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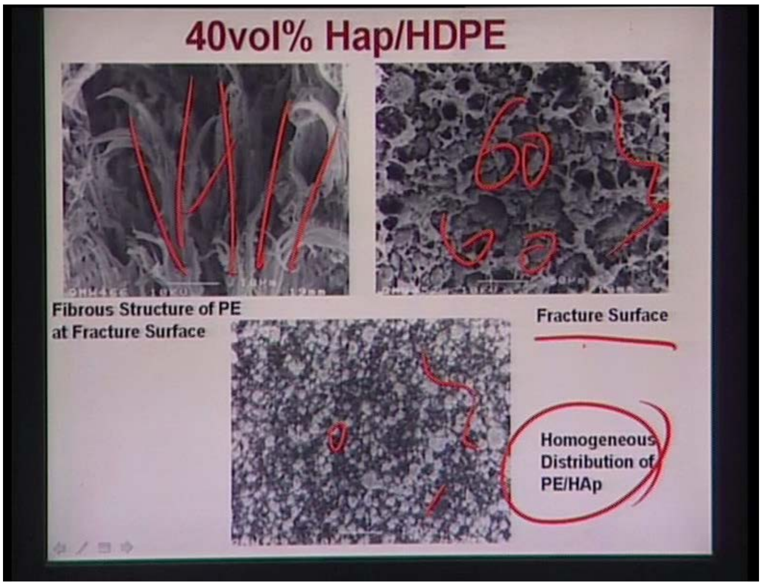

40vol% Hap/HDPE

Fibrous Structure of PE at Fracture Surface

Fracture Surface

Homogeneous Distribution of PE/HAp

Now, this is some, you know, results that is taken from literature, that essentially shows you that, you have these 40 volume percent hydroxyapatite in 60 volume percent high density polyethylene. This is the, typically a high density polyethylene polymeric fibers and you have these large amount of hydroxyapatite particles, which are dispersed homogeneously in the matrix. This shows that adhesion of the osteoblast like cells, on this polymer ceramic composites.

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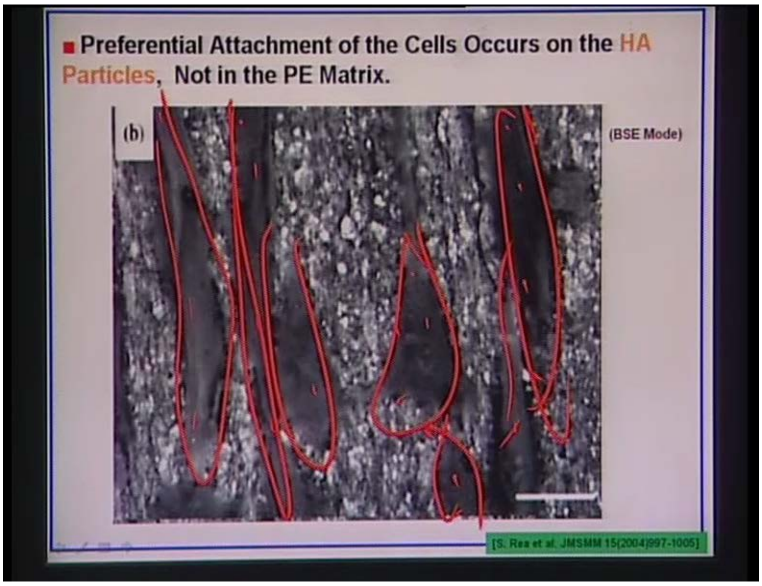

- Preferential Attachment of the Cells Occurs on the HA Particles, Not in the PE Matrix.

[S. Rea et al. JMSMM 15(2004)997-1005]

Now, what you see in these areas, the cells are adhering and they have expanded, and the rest of the area is not covered by cell; what it means? It means, wherever there are the hydroxyapatite particles are agglomerated, only those particles are attracting the osteoblast cells; not the high density polyethylene matrix as such; because, high density polyethylene matrix, is essentially bio-inert; it is not bioactive like hydroxyapatite.

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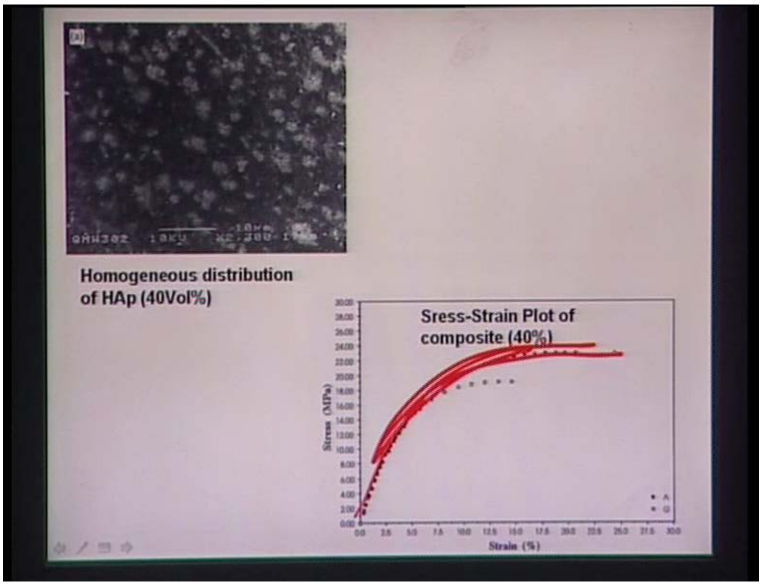

Homogeneous distribution of HAp (40Vol%)

Sress-Strain Plot of composite (40%)

So, this is typically stress-strain plot of the 40 percent composite, that is that, 40 percent hydroxyapatite loaded composite; you can see, depending on the processing conditions, it has some linear and some non-linear properties, that it shows in this particular stress-strain curve.

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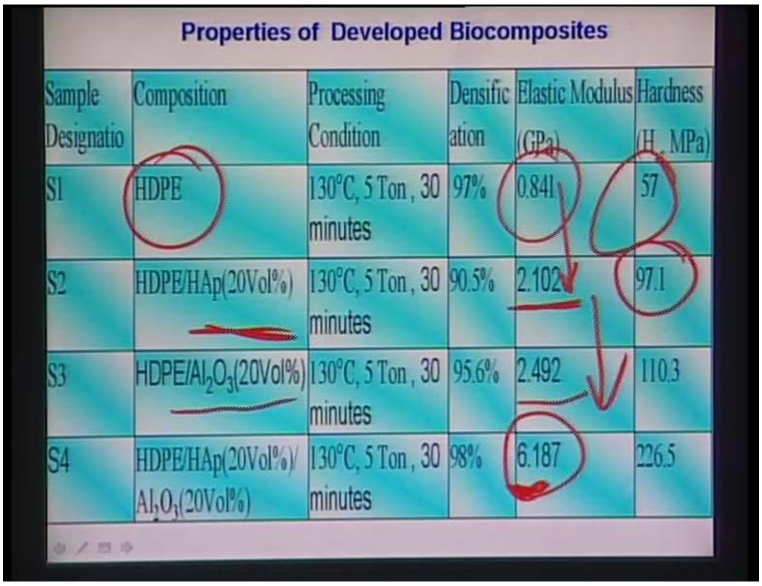

Properties of Developed Biocomposites

Sample Designatio	Composition	Processing Condition	Densific ation	Elastic Modulus (GPa)	Hardness (H, MPa)
S1	HDPE	130°C, 5 Ton, 30 minutes	97%	0.841	57
S2	HDPE/HAp(20Vol%)	130°C, 5 Ton, 30 minutes	90.5%	2.102	97.1
S3	HDPE/Al_2O_3(20Vol%)	130°C, 5 Ton, 30 minutes	95.6%	2.492	110.3
S4	HDPE/HAp(20Vol%)/ Al_2O_3(20Vol%)	130°C, 5 Ton, 30 minutes	98%	6.187	226.5

Now, we have developed several composite materials in our laboratory and this shows summary of that, what was the initial developmental stage of this high density polyethylene ceramic composite. So, you start with the pure high density polyethylene, without any ceramic fillers; you have a elastic modulus, which is close to 0.8 gigapascal. So, this elastic modulus is what has been reported in the text book also; and, it has a hardness of 57 megapascal, which is measured by Vickers' indentation technique. Now, when you add this 20 volume percent hydroxyapatite in this materials, then, elastic modulus goes to 2.1 gigapascal, that is quite good and it has a hardness property also, 97.1 megapascal. If you add 20 volume percent alumina, alumina is relatively stiffer phase, compared to hydroxyapatite, and therefore, addition of 20 percent alumina, actually increases much more, than when you add that similar volume fraction of hydroxyapatite. And there, that high density polyethylene and alumina composite have 2.5 gigapascal elastic modulus. Now, when you add their combination of both 20 percent alumina and 20 percent hydroxyapatite, then, you are getting almost like 8 times that of the elastic modulus of high density polyethylene; and there, the elastic modulus is 8 times, that is around 6.2 gigapascal.

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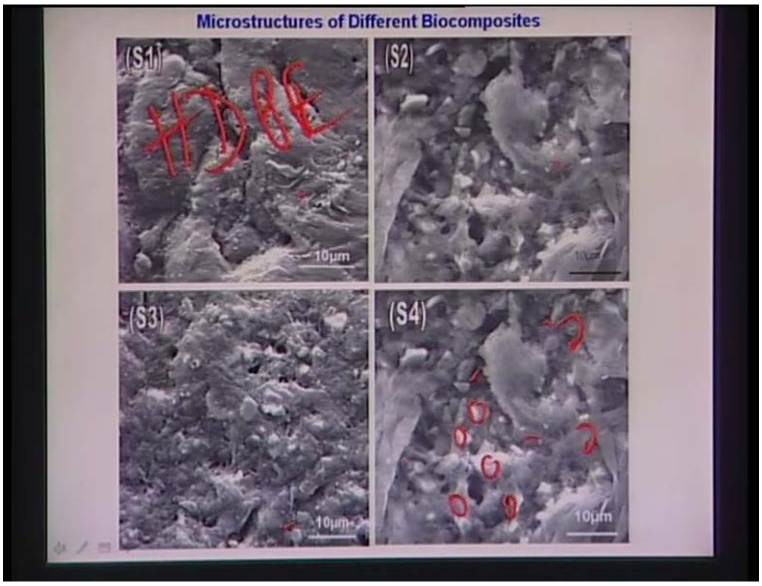

Microstructures of Different Biocomposites

Now, this is the microstructure of the different composites. So, S, S 1 means, this is pure HDPE. Now, when you are adding this ceramic fillers, this ceramic fillers like alumina, or hydroxyapatite, they are kind of distributed homogeneously, after this materials are compression molded. And, these compression molding, if you see, their condition is 130 degrees Celsius in a 5 ton (( )) and for 30 minutes. Now, this is the beauty of the material science. Now, one end, you can see that, you can make the polymeric materials at 130 degree Celsius; other end, you can see, for hydroxyapatite ceramic itself, it requires 1200, or 1300 degree Celsius. So, it is a scale of 10 difference. So, what you can, where you can process the materials at 130 degree Celsius, but pure hydroxyapatite, you can see, (( )) to require 1200 degrees or higher temperature. So, that means, almost like ten times difference in the temperature that you require, to make the different kind of materials for biomedical applications.

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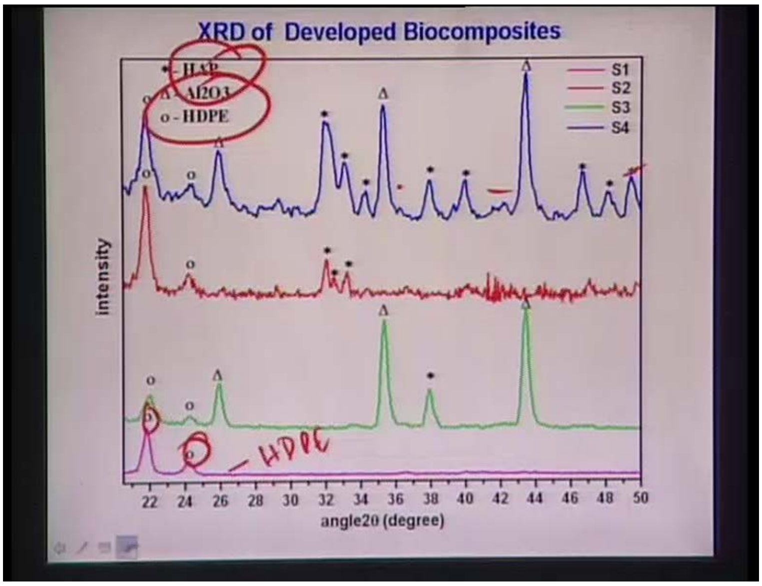

XRD of Developed Biocomposites

This is the XRD plot of this developed biocomposite and these biocomposites are processed by compression molding. So, this is your semi-crystalline high density polyethylene. So, these two characteristic peaks, essentially indicates that, this high density polyethylene is semi-crystalline, because if it would have been amorphous, it would not give such a characteristic peak; and, if it, if it is very much crystalline, then also, it gives a much sharper peak; but these peak has certain breadth; so, that means, that shows that, this material has some kind of semi-crystallinity property; all the other ceramic fillers like alumina and hydroxyapatite, they are also present in this biocomposite materials.

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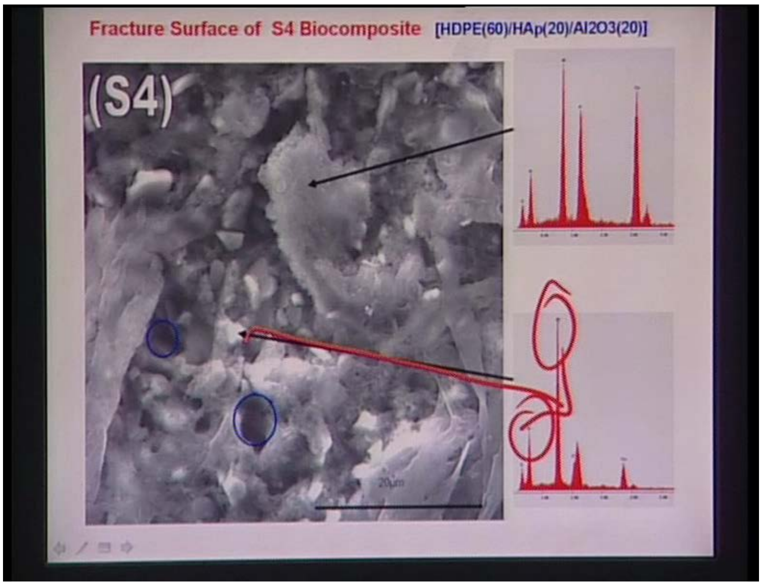

Fracture Surface of S4 Biocomposite [HDPE(60)/HAp(20)/Al2O3(20)]

Now, this shows that, you know that, there are Eder spectra, if you take, you can see aluminum peak and oxygen peak. So, they, essentially, that shows that, this is alumina; whereas, the other positions, if you take, you can get also hydroxyapatite phase also.

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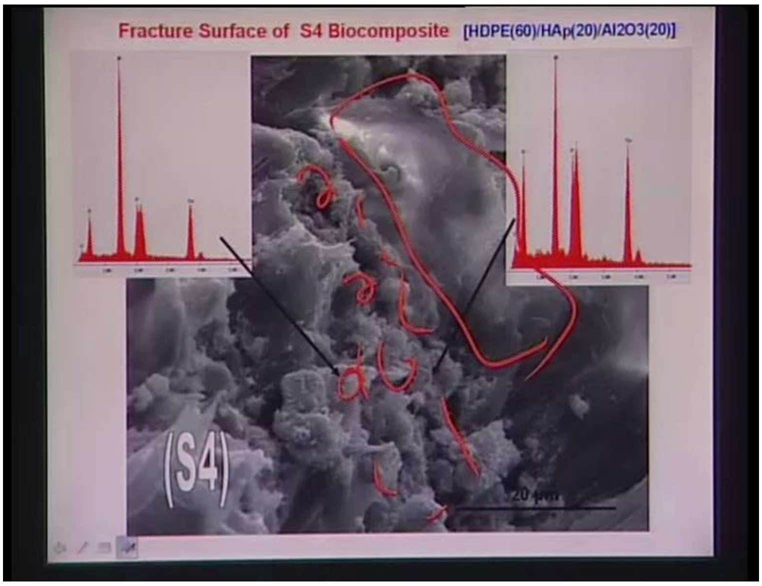

Fracture Surface of S4 Biocomposite [HDPE(60)/HAp(20)/Al2O3(20)]

Interestingly, you can see, this is like a typical polymeric kind of behavior; like, you know, polymers are getting deformed in the fracture surface and in this polymeric chain, this, different ceramic fillers are also adhering; and that, you can see from the Eder spectra.

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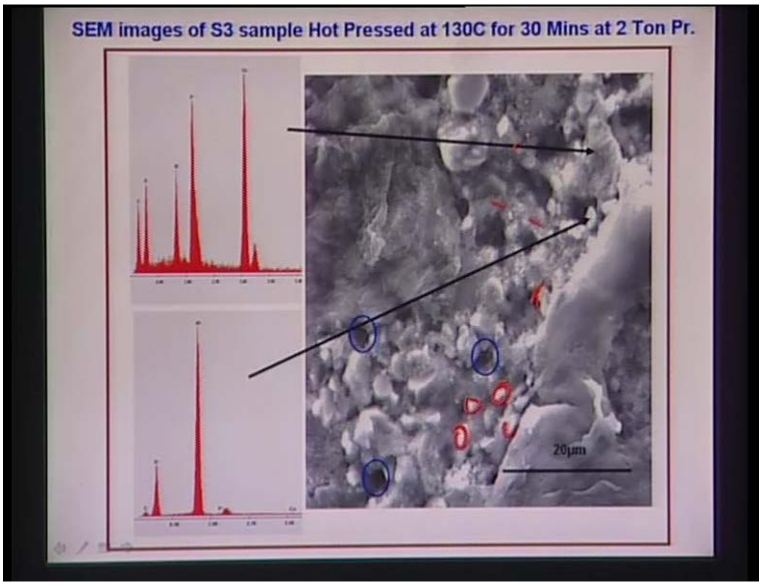

SEM images of S3 sample Hot Pressed at 130C for 30 Mins at 2 Ton Pr.

Like, these are like ceramic fillers; like, you can see, these are like ceramic fillers, either alumina, or hydroxyapatite; these shows you typical Vickers' indent on that, taken on the polymer ceramic composites.

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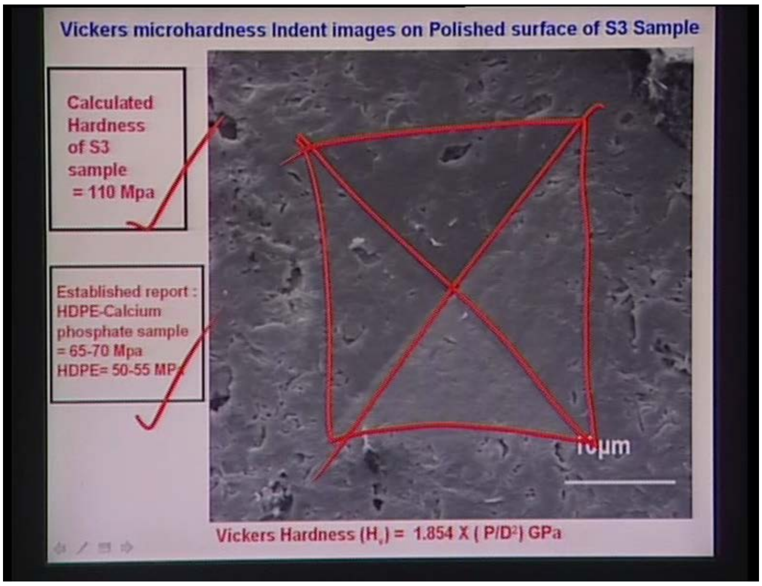

Vickers microhardness Indent images on Polished surface of S3 Sample

Calculated Hardness of S3 sample = 110 Mpa

Established report : HDPE-Calcium phosphate sample = 65-70 Mpa HDPE= 50-55 MPa

Vickers Hardness (H_v) = 1.854 X (P/D^2) GPa

Now, from this diagonal length, you can calculate, what is the hardness of this materials and these hardness is typically taken, is calculated as 110 Mpa; whereas, pure HDPE is (( )) here is 50 to 55. So, twice the hardness properties you can achieve, just because, you are adding the ceramic fillers to high density polyethylene polymers.

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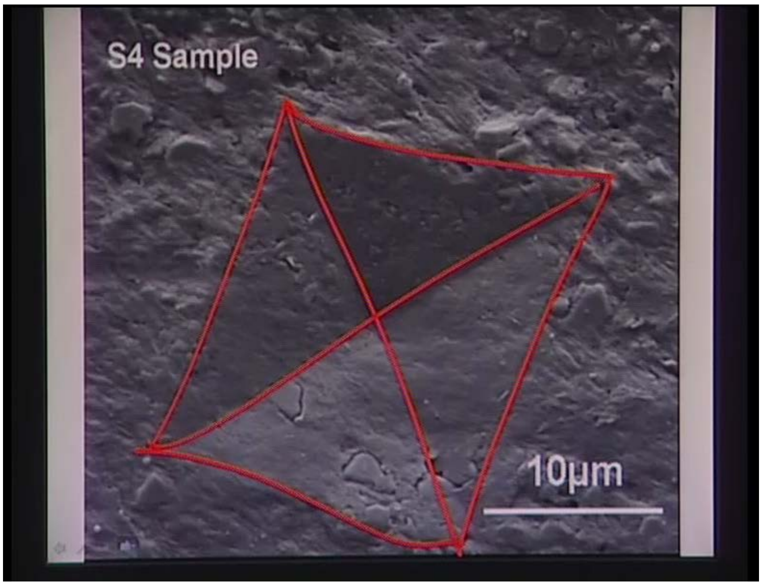

This is the material, which is like 20 volume percent HAP and 20 volume percent alumina. Again, you can see the Vickers indent and then, from that diagonal, you can calculate that, what is the hardness of this materials. So, one of the other driving forces for developing that high density polyethylene HAP alumina composite, is to improve the wear resistance properties of this materials.

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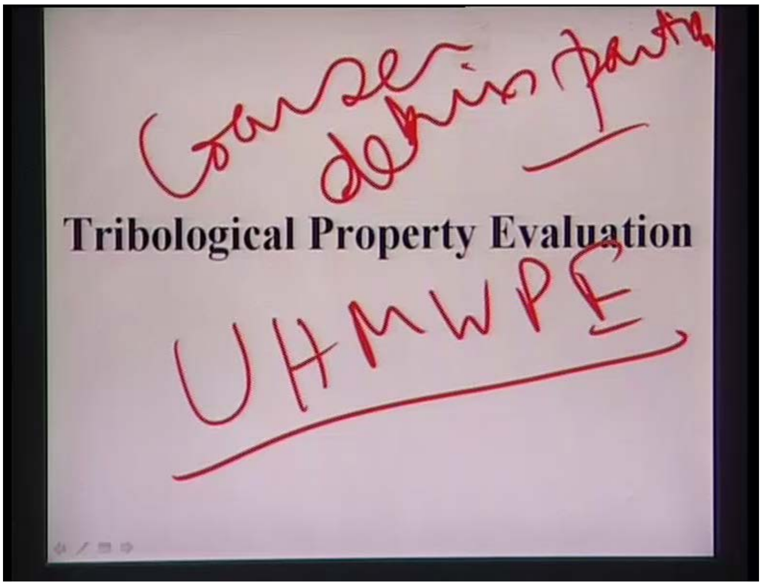

Cause debris parti

Tribological Property Evaluation

UHMWPE

Now, why wear resistance is important? One of the competing materials, which is ultra high molecular weight polyethylene based materials, now, what happens with this U H

M W P E that, these materials, they have very poor wear resistance, and then, they form coarser debris particles. Now, this coarser debris particle means, it is like, you know, the debris particles have sizes of, some microns size; so, very coarse debris particles. So, on the other hand, high density polyethylene itself, has a very good friction properties; like here, the friction coefficient is 0.1, or less than 0.1. So, we would like to see, whether the addition of hydroxyapatite, or alumina, will in anyway degrade the tribiological properties or not; if it does not degrade, then, it is better, because, it has a better combination of hardness, elastic modulus; and then, if it has a good tribiological properties, then, it will be beneficial for particular applications.

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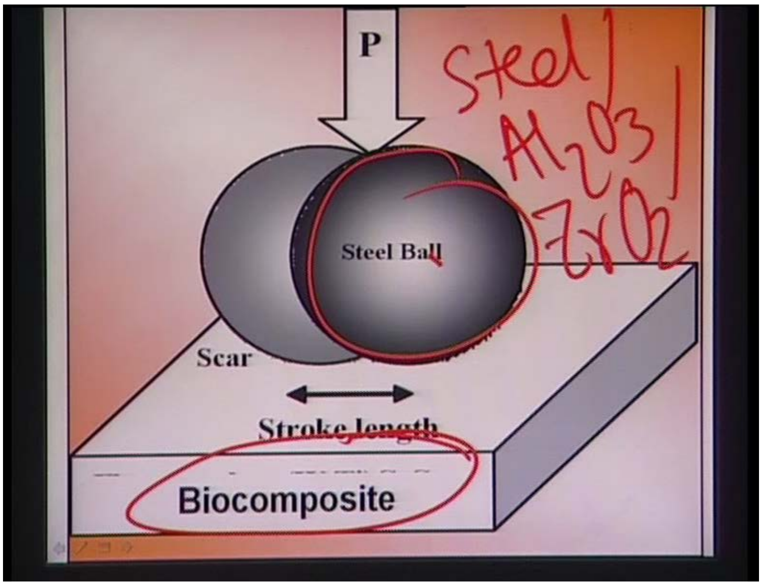

Now, we have used this ball and flat type of configuration, where we have used this high density polyethylene biocomposite as a flat, and steel ball, either steel, or we have used alumina, or we have used zirconia, these three are the mating materials. So, these three materials, these three balls we have used as the counter body materials.

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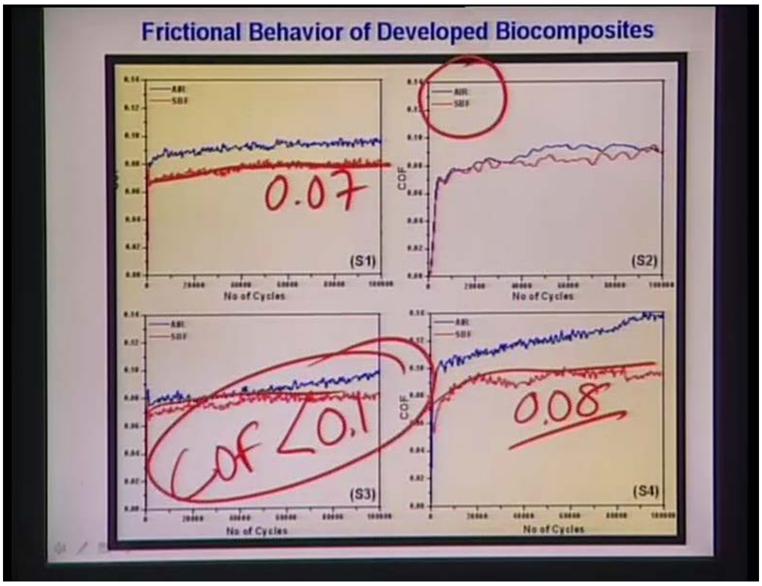

Frictional Behavior of Developed Biocomposites

So, these three counter bodies, that steel, aluminum, zirconia we have used and then, what you see here that, we have done that experiments both in air, as well as SBF, that is simulated body fluid environment, and you can see that, this is the pure high density polyethylene material, which is showing the frictional coefficient of 0.07. Now, in the S 3 and S 4, here also, the frictional coefficient is roughly 0.08. So, roughly, steady state coefficient of friction you can get, is less than 0.1, in all these materials. So, essentially, by adding 20 percent HAP and alumina, you are not increasing the coefficient of friction; you are almost like maintaining the similar coefficient of friction, like the way you are getting without any ceramic filler. So, that is good and these materials, therefore, have good potential.

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SEM Image of Worn Surface of S4 Biocomposite [HDPE(60)/HAp(20)/Al2O3(20)]

Fretted at AIR under 10N load for 1,00,000 cycles

Wear Rate $=5.7X10^{-6}$ mm3/Nm

Now, coming to the own surface of this materials, these materials have a wear rate, which is 5.7 into 10 to the minus 6 millimeter cube per Newton meter and this kind of wear rate, which is of the order of 10 to the power minus 6 millimeter cube per Newton meter, they have very good potential for the wear resistance applications, because many of the ceramic composites also, they have 10 to the power minus 6 or 10 to the power minus 7 millimeter cube per Newton meter wear resistance property.

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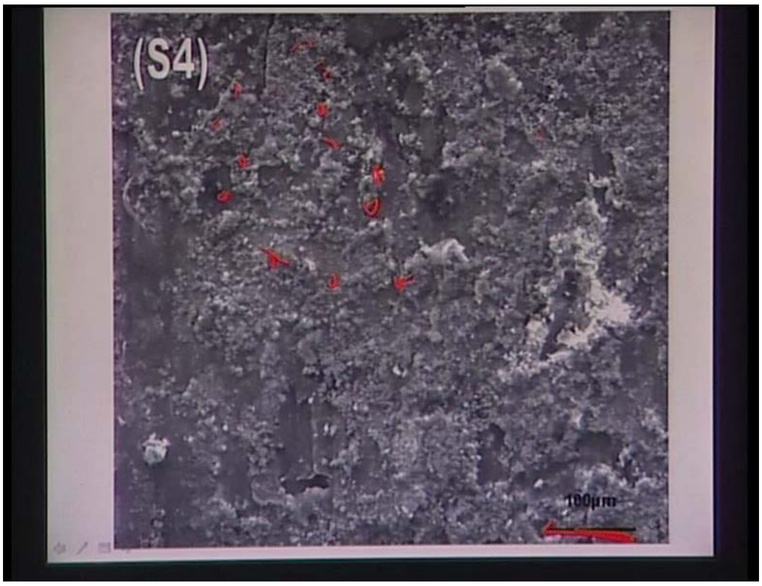

The other things, that you notice that, the wear debris particles here. So, this is your 100 micron bar and these wear debris particles are very fine, and often, they are in agglomerated conditions. Now, this wear debris particles is roughly 1 micron, or 2 micron, around that 1 to 5 micron meter maximum, that is the size. So, that is itself is a good indication that, this material has a very good wear resistance property; and, they do not form very coarser wear debris particles like the alkaline molecular polyethylene materials, they essentially produced during the wear experience.

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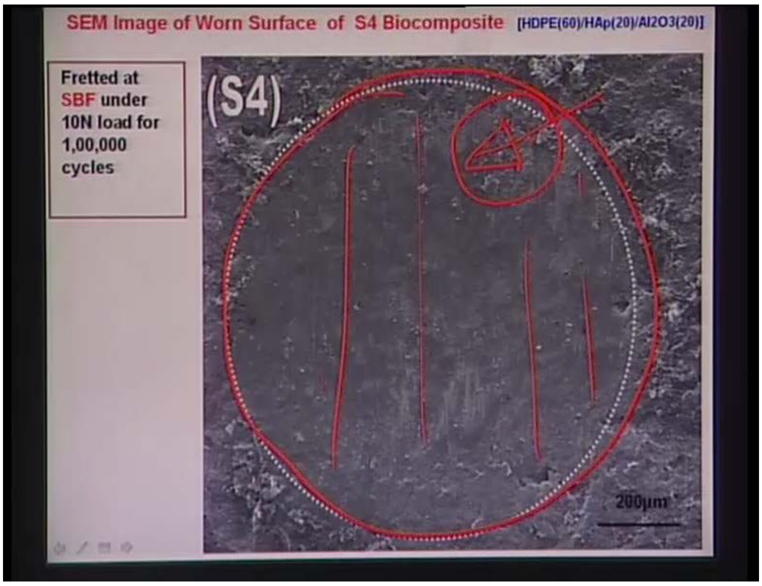

SEM Image of Worn Surface of S4 Biocomposite [HDPE(60)/HAp(20)/Al2O3(20)]

Fretted at SBF under 10N load for 1,00,000 cycles

Other things that you can notice that, in the SBF conditions, that this, this is your worn scar, and there is some mild, you know, that abrasive scratches you can find on this materials, because of the fretting action; however, that the amount of wear debris particles is much less, compared to what you have seen in the dry conditions, in just few slides back. So, therefore, if the wear debris particles the amount is less, so, that shows that, this materials will be quite a good replacement, against the traditional use of ultra high molecular polyethylene in the acetabular cup of the Total Hip-joint Replacement. I think, I will stop here and will continue in the next class.