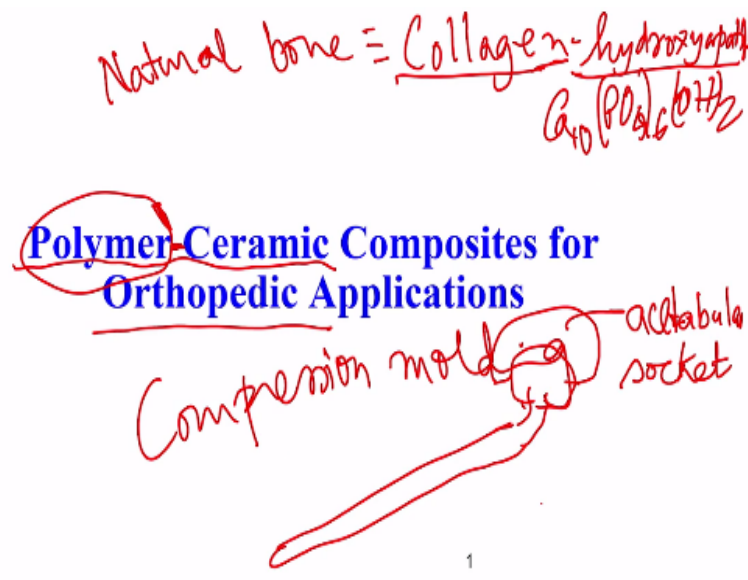


**Friction and Wear of Materials: Principles and Case Studies**  
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**Department of Materials Research Center**  
**Indian Institute of Science – Bangalore**

**Lecture – 15**  
**Polymer Ceramic Composites for Orthopedic Applications**

Welcome back to this particular lecture on polymer ceramic composites for orthopedic applications

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In the last lecture you have learnt how to make the polymeric materials like using conventional manufacturing techniques like compression molding or injection molding. So what I am going to discuss in this particular lecture on the friction and wear of polymer ceramic composites for orthopaedic applications. Now why polymer ceramic if you recall from your class 10 or 12 biology natural bone is nothing but collagen

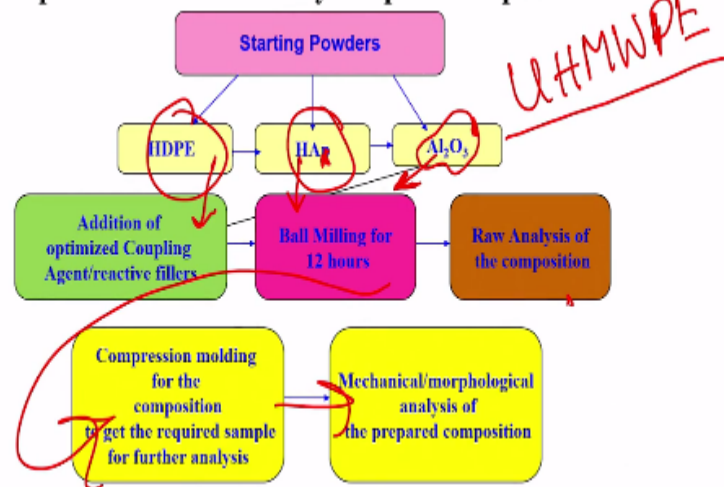
That is a polymer materials as well as hydroxyapatite as a composite, so this hydroxyapatite is nothing but  $Ca_{10}P_4O_{26}(OH)_2$ . So it is the hydrated calcium phosphate compounds and collagen is a kind of a protein and there are different variants of collagen like type 1 to type 10 and so on. But the further discussion collagen is beyond the scope of this lecture. However, it is important for you to remember that natural bone is nothing but a polymer ceramic composite.

So therefore significant interest was there in the community to mimic the natural bone composition and properties and that is why these polymer ceramic composites are being used for certain application for a load bearing orthopedic applications. So orthopedic applications means it is for a bone analog materials and also for biomedical applications. Now if you remember and that in the last lecture I have mentioned you have a femoral stem

And this femoral stem it will go to that acetabular and humeral head. Humeral head is essentially is that acetabular socket. So what I am going to show you in the next 20 or 25 minutes or so is that how could they will up these materials which is made up of the polymer and ceramic composites for the acetabular socket applications.

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### Preparation of chemically coupled composites



Now so far that it is one of the materials which is widely used in the acetabular socket application is ultra-high molecular weight polyethylene Now ultra-molecular polyethylene has a higher molecular weight so higher the molecular weight the mode is the viscosity and mode is the viscosity means more difficult would be these polymaths to process Okay so if you want to add some new materials or if you want to add some new phases like ceramic phase

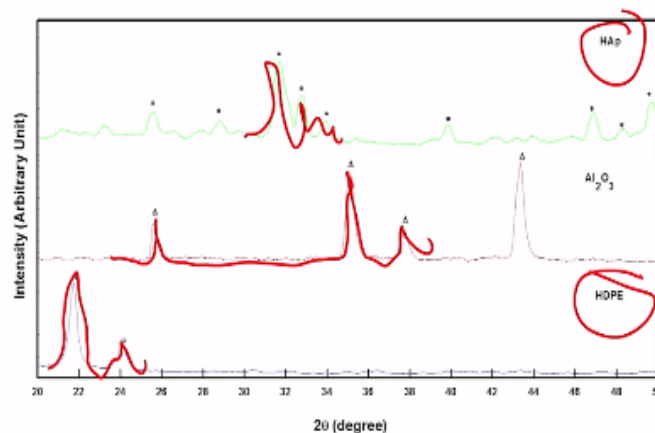
Like hydroxyapatite or alumina, you cannot do it with ultra-molecular polyethylene. So therefore what we do we use it high density polyethylene we add hydroxyapatite as I said in the last slide. That hydroxyapatite is the inorganic component of the natural bone so if you put this

hydroxyapatite to any polymeric matrix it makes certain bone like properties. It provides certain bone like properties to these material and alumina.

So what do you do we add some coupling agent why coupling agent is required because high density polyethylene is a polymeric phase by the polymeric matrix? Hydroxyapatite is a ceramic phase alumina is a ceramic phase. Now to ensure very uniform and homogenous distribution of the hydroxyapatite alumina into high density polyethylene matrix you need to add coupling agent or reactive fillers.

After that you do ball milling after ball milling you do compression molding, so directly after ball milling you do compression molding, then you do mechanical and try biological properties  
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### *XRD :Starting powder*

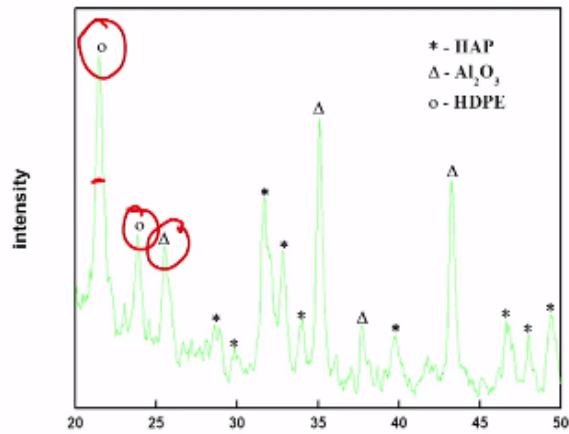


*Note: Semicrystalline HDPE powder*

Okay so what are the different and this is the starting powder so high density polyethylene as you see this peak is little broad so therefore is a semi crystalline polymers. It is not a fully crystalline like the case for many other polymers. Now we have alumina is also crystalline peak and hydroxyapatite is a very characteristic 3 weeks which are placed around 30 degree of both values.

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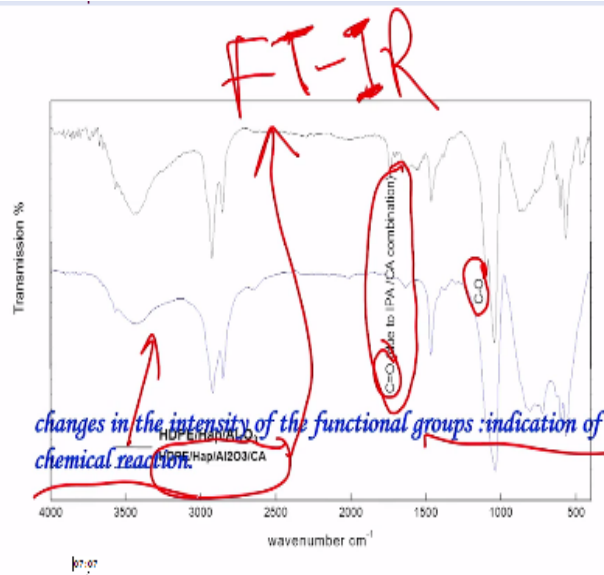
*XRD pattern of compression molded HDPE-HA-Al<sub>2</sub>O<sub>3</sub>*



Note: Semicrystalline HDPE Matrix

So when you add these two phases like 20% hydroxyapatite and 20% the alumina you get a very clear semi crystalline peak but this peak which is little bit decreased. Now in the compression molded samples and you have a hydroxyapatite and you have alumina phase as well.

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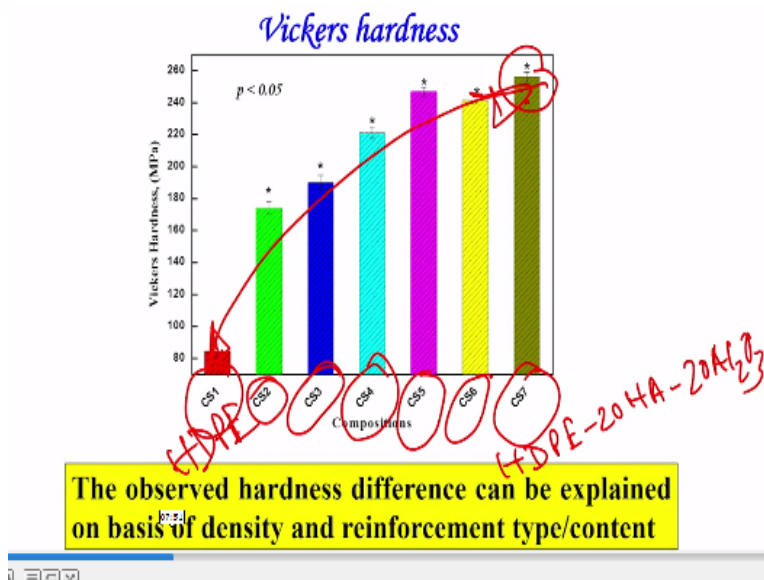
In the matrix now how these phases they are distributed in the polymeric matrix so essentially what you see these phases are these are like alumina and these are the bright particles and little bit grey particles are hydroxyapatite. Now these chemical composition of these two phases can be confirmed by using that eds composition analysis of the alumina and hydroxyapatite peak and then you have a polyethylene.

That is that polyethylene is this chunk of this polymer which are dispersed in the matrix. Now in terms of the micro FTIR analysis of this material FTIR stands for Fourier transform infrared spectroscopy. This essentially this Fourier transform infrared spectroscopy technique which is used to characterize the surface bonding. Now in this particular case we have used that is ASTP and ASTP happened alumina.

So this is the one for STP happened alumina with the coupling agent so because of this coupling agent, you will see that there is C double bond OPS and there is also it is a shoulder band at around thousand centimetre inverse that is sincerely C single bond or that is also forms and changes in the intensity of these functional groups from the materials with coupling agent and without coupling agent.

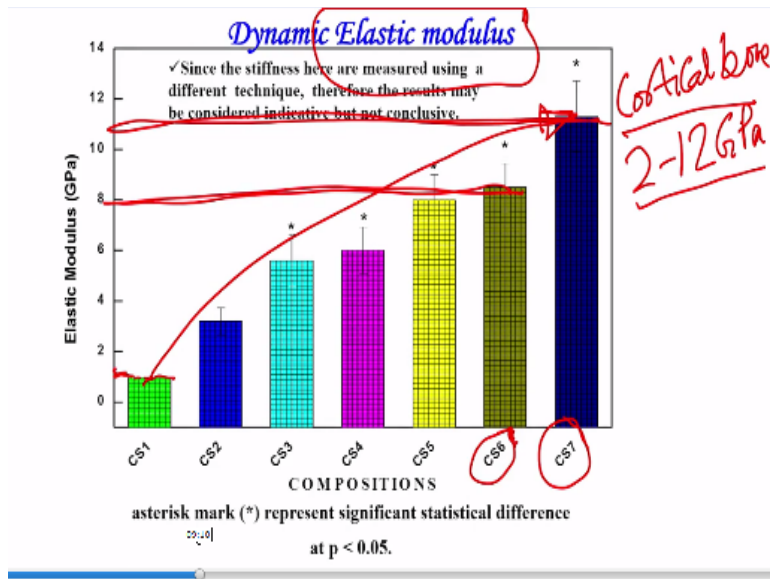
This indicates that is heart and chemical reactivity which is signature of certain chemical reactivity due to this addition of the coupling agent.

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Now in terms of the hardness of this materials if you see this hardness of the material cities increased almost like 3 times from the baseline materials like CS1 is the pure HDP and CS7 is a HDP 20% HAP and 20% alumina other materials which on the line between HDP and HDP 20% HAP and 20% alumina like CS2 HDP is 20% HAP CS3 is 20% alumina CS4 is HDP 40% HAP and CS4 IS 40% happened alumina and CS7 is 20% HAP and 20% alumina.

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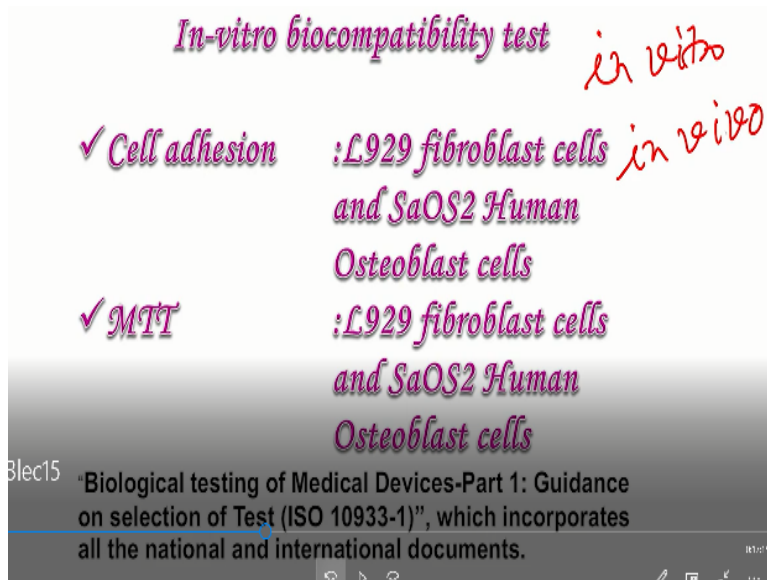


So there is also another properties which are important for tribal logical applications which I have mentioned earlier is that elastic modulus because this that is if there is a difference in the elastic modulus suddenly the different magnitude of the 809 contracts process that will be developed at the tribal logical surfaces.

Therefore, elastic modulus determination is very important, now if you notice elastic model as of the pure HDPI is summer and one gigapascals. If you go to the CSF and like whether HDP have 20% HAP and 20% alumina with a coupling agent and CS6 is the HDP 20% or 20% alumina without coupling agent. Here you are getting almost like 8 gigapascals with coupling agent you are getting almost like 11 gigapascals.

So this more is the stiffness particularly in this window of < 20 or 30 gigapascals it is important why I am saying that? Because cortical bone or natural bone typically they have an elastic modulus I am saying that cortical bone that is a natural bone structure. So it has elastic model as of two to 12 gigapascals so these materials HDP 20% HAP 20% alumina can well replace the cortical bone in these physiological system or it will have a cortical bone replacement property.

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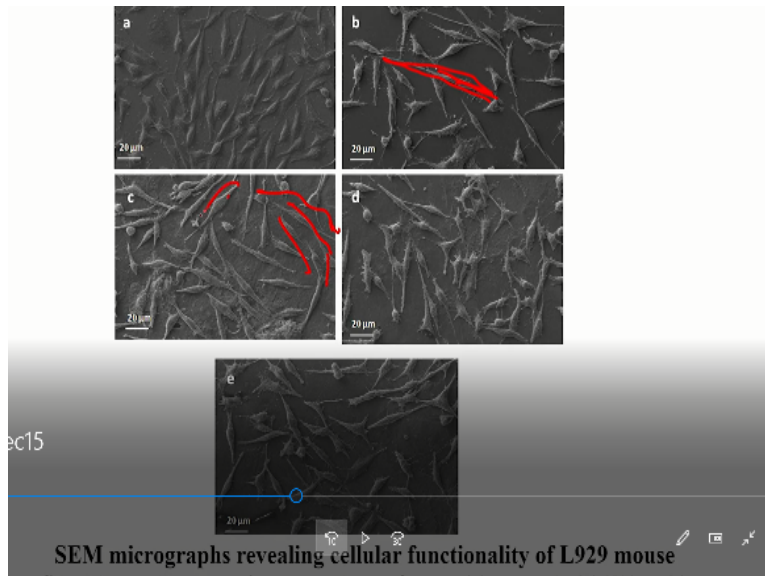


So as part of the study we have also done the cell adhesion and cell proliferation study because cell adhesion and cell proliferation is very important at the end of the day. These materials had to be used for orthopedic applications. So therefore the application specific or target application specific cells like L929 which is like fibroblasts cells fibroblast meaning it is a connective tissue cells sarcoma osteosarcoma this is like human osteoblast cells.

So these are the cells which are used for this particular In-vitro study. In-Vitro means they experiments which are conducted in that glass ware. So any experiment which is conducted in the glassware in the laboratory scale they are known as the In-vitro test. In vivo means experiments which are conducted in the whole organism like any experiments which are conducted in that live animal like you know putting some materials in the animal.

Those are the experiments which are called as an In-vivo so this is In-vitro typically when one writes In-vitro that should be always italics and when one writes In-vivo that should also italics meaning of In-vivo is that animal experiments meaning or In-vitro is the experiments which are conducting in the glass value.

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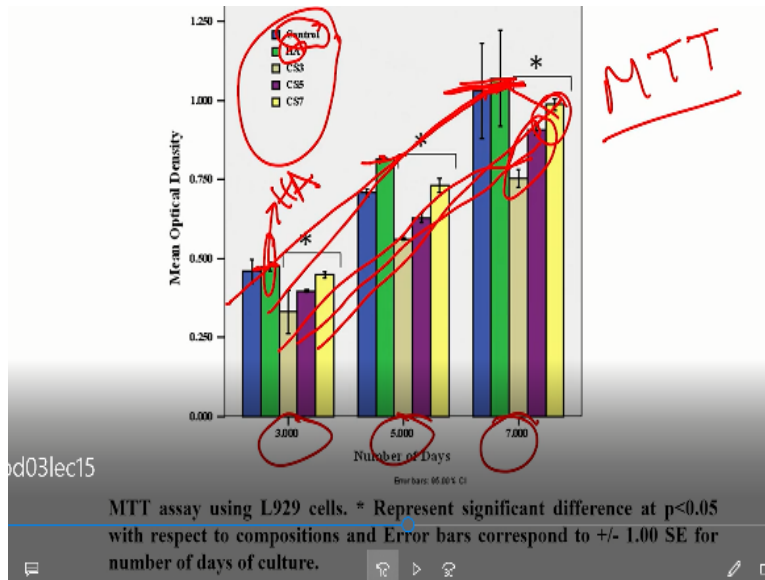


So if you look at these images what do you see that this is the cells which are adhered on the material substrates and these cell proliferation or if you now quantify that how many number of cells per unit area of the surfaces you will see that most of the surfaces they actually exhibit comparable cell adhesion behaviour. So none of the materials you can exclude here on the basis of their ability to support the cell adhesion and cell growth.

So also interestingly certain features you can see like there is a large cellular filopodia extension like human beings you have hands and legs cells also have filopodia lamellipodia through which cells can expand on a particular physical surfaces and that is what you can see it here also like you know different filopodia extension which is present for the L929 fibroblasts cells.

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So this is more quantitative information on the cell viability and this is one of the day one of the assay biological acid that is used is called MTT assay. Now MTT assay is used to quantify what is the cell numbers and how the cell numbers they increase with the number of days like 3 days to 7 days. Now if you see for any given material cell numbers increase with increasing time and culture.

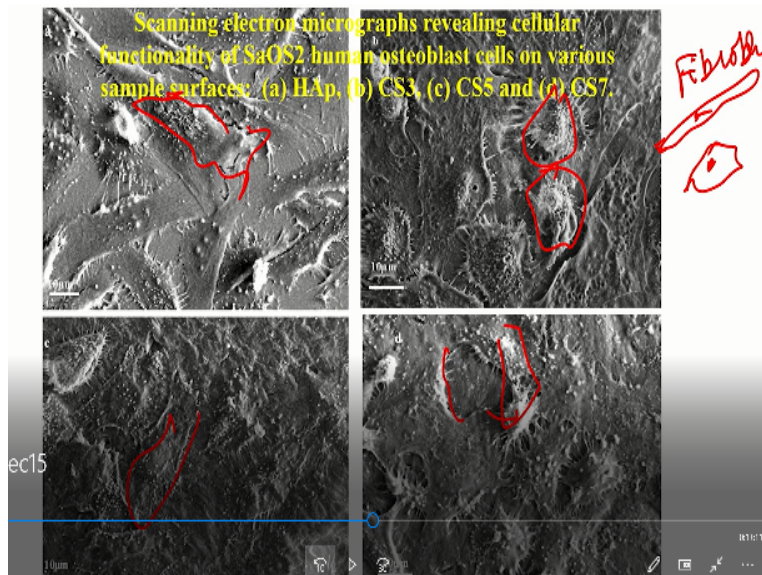
If you look at the blue bars or if you look at the green bars in all these cases the slope may be different but the cell numbers constantly increase with time and that is a very good information that how cell numbers they increased with time. Okay so that is very important that means cells are able to multiply or cells are able to divide when they are adhering to that material substrate. So essentially all these materials whatever we have used here.

We are used to control one is that typical control like PC culture polystyrene like full is expected to support the cells another one is hydroxyapatite that is the green one this is the hydroxyapatite why hydroxyapatite because hydroxyapatite alone should be able to support the growth of the fiberglass cells. If you look at very carefully what do you see that in most of the cases like these 3 days 5 days or 7 days.

Hydroxyapatite can support the maximum growth of the cells even much better than high density polyethylene 20% and 20% aluminium the reason behind hydroxyapatite is the most bioactive

material and high density polyethylene is more bio inert material. So if any material which is bioactive that should include simple support both cell adhesion and cell growth rather than the bio inert material.

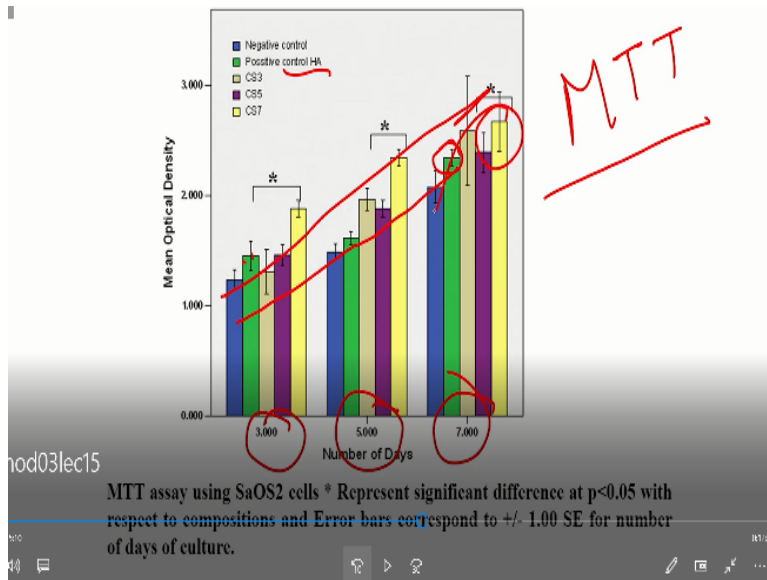
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This is also the case for the scanning electron microscopic images you will see that these are the human osteoblast cells like SaOS2 sarcoma osteosarcoma cells now you can see very clear features of the osteoblast which is much more different because fibro blast is much more spindle shaped. If you see the fibroblasts morphology this is the fibroblasts morphology and osteoblast morphology it is more like more flattened shape.

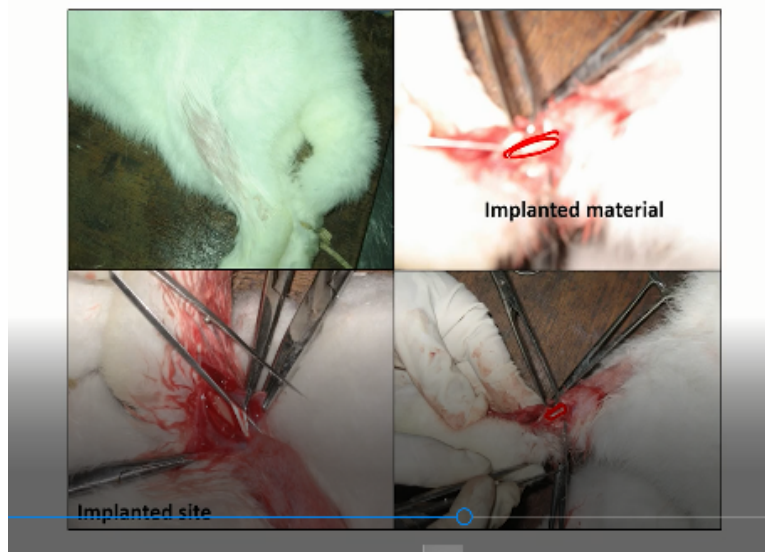
And exactly if you see that this shape is also very different here and you can see that is more these kind of shell shaped. So essentially the general observation of the osteoblast and fibroblast that entire cell surface is kind of powered with these kind of features of the of fibroblasts and osteoblast cells and they kind of form a very good network of the cells on the surfaces.

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Now like fibroblast cells, we have also missed that the cell numbers using MTT as say and again we have taken the cell count at 3 days 5 days and 7 days we have used a different kind of control one is a positive control hydroxyapatite and also these hydroxyapatite compared to hydroxyapatite these osteoblast cells their STP happened alumina the either they support comparable or even more cell growth on these particular materials.

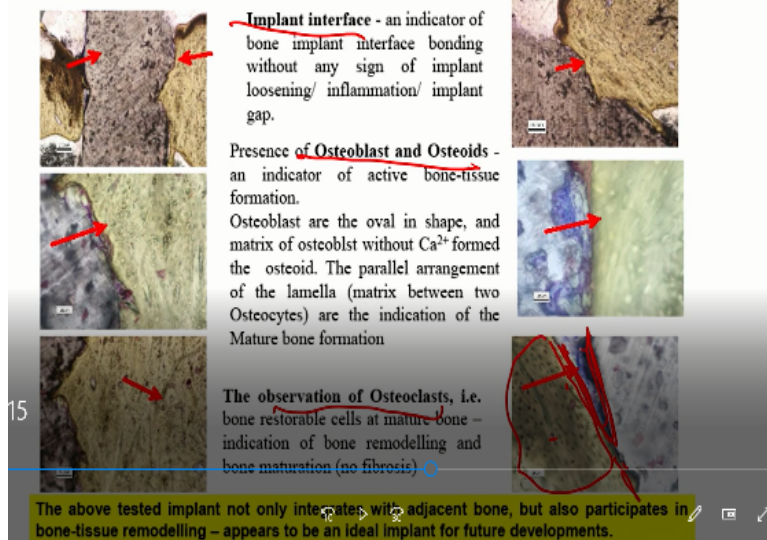
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Okay so we have also done In-vivo experiments this is that mouse experience mass model experiments where you can put these long implanted material here in the femur of this mouse and then we can do histological experiments.

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## Histological analysis : Bone/HDPE-20HA-20Alumina interface

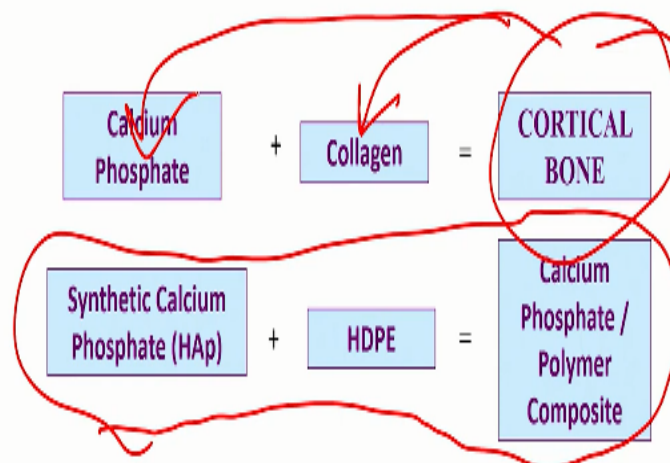


Am I trying to show these are the experiments which are conducted at All India Industrial medical sciences and then after that these experiments are for Osteoblast and Osteoid and implant surfaces and you can very clearly see that how these osteoblast cells they are active at the bone material interface? So this is your natural bone and this is your natural bone and this is your hydroxyapatite happened alumina composite.

So in this particular case we observed that high density polythene have conducted alumina all are biocompatible in both In-vitro and In-vivo experiments. So what I am going to do is that in the next few minutes.

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## WHY POLYMER CERAMIC COMPOSITES ??



I am going to show you that how does this friction and wear properties of these materials that they vary against a different making materials that is that alumina, steel and zirconia ball. So I reiterate my earlier statement that the major motivation for developing high density polyethylene aluminium composite is to mimic the natural bone or cortical bone properties in terms of the phase assemblage like you it has a calcium phosphate and it has collagen. In case of cortical bone but here we have high density polyethylene happened alumina.

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## HDPE-HAp composites (HAPEX™)

### ❖ Salient Features of HA/HDPE Composite

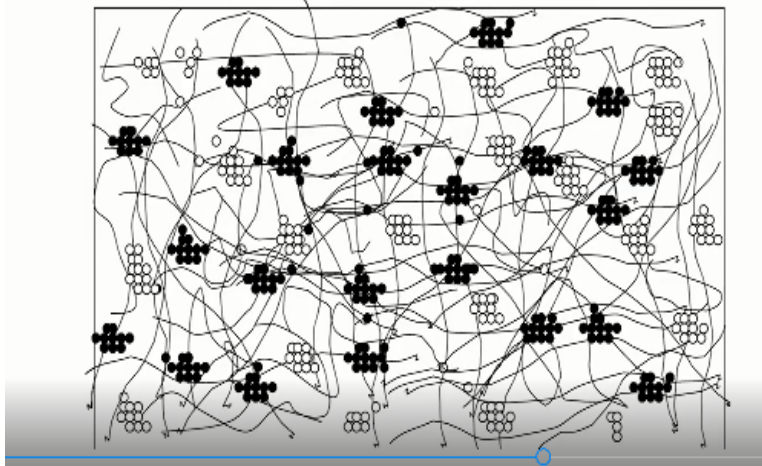
COMPOSITE	FILER VOL (%)	TENSILE STRENGTH (MPa)	YOUNG's MODULUS (GPA)
<b>HUMAN BONE</b>	<b>0</b>	<b>60-160</b>	<b>3-80</b>
<b>HAPEX</b>	<b>10</b>	<b>17.30</b>	<b>0.98</b>
<b>HAPEX</b>	<b>20</b>	<b>17.77</b>	<b>1.60</b>
<b>HAPEX</b>	<b>40</b>	<b>20.67</b>	<b>4.29</b>

And the salient features of these particular materials which were developed by Bill Bonfield in Cambridge so that time actually when he was working at Queen Mary University in London I think Serena Best was also involved in this particular developmental work so high density polyethylene and hydroxyapatite they were developed for medially or orbital implants and their strength properties were around 17 megapascal pascal and elastic model as is 0.98 close to 1 or 16 gigapascals.

We have developed with significant alumina and hydroxyapatite that these particular material can be developed with a much more higher modelers and strength properties.

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## Schematic of Physical Cross Linking Concept



So what is the rationale or what is the physical principle which can be used for  $x$  which can be used to explain that enhancement in the physical properties like you have the alumina particles and you have the hydroxyapatite particles which are shown here by different fields circle or open circle and you have the high density polyethylene chains which are running around a particular materials what do you see that this chain can slide first each other.

And that can lead to viscoelastic properties in the traditional polymer matrix composites but which is not the case in this particular case because the very fact that alumina particles and hydroxyapatite particles they are they entangled this polymer chain that polymer chain cannot be moved just very easily. So if there is more resistance to the sliding of the polymer chain that would essentially increase more strength.

And hardness and elastic modellers of the hybrid polymer, polymer ceramic hybrid composites and that is simply the case for high density polyethylene hydroxyapatite and alumina.

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## Mechanical Properties

*Compression Molding*

Sample Designation	Composition	Processing condition	Hardness (H <sub>v</sub> , MPa)	Elastic Modulus (GPa)
S1	HDPE	CM, 130°C, 0.5 h	56.5±0.3	0.8±0.03
S2	HDPE/HAp (20Vol%)	CM, 130°C, 0.5 h	129.5±1.1	2.4±0.45
S3	HDPE/Al <sub>2</sub> O <sub>3</sub> (20Vol%)	CM, 130°C, 0.5 h	131.1±5.6	2.7±0.45
S4	HDPE/HAp (20Vol%)/Al <sub>2</sub> O <sub>3</sub> (20Vol%)	CM, 130°C, 0.5 h	226±21.5	6.2±0.91
S5	HDPE/Al <sub>2</sub> O <sub>3</sub> (40Vol%)	CM, 130°C, 0.5 h	252±9.6	7.1±0.5
S6	HDPE/HAp (40Vol%)	CM, 130°C, 0.5 h	176±7.3	-

But what is more important for you to see here and realize that high density polyethylene alone has a hardness of <100 megapascals when you go to high density polyethylene 20% have 20% alumina the hardness goes almost like 4 times higher than their compared to baseline elasticity. In terms of elastic less which is more important for biomedical applications as well as for tribological applications it shows an increase from 0.8 giga pascal to 6.2 giga pascal.

So 0.8 versus 6.2 it is like 8 times higher elastic modular compared to HDPE. Now whereas 56.5 to 226.5 it is almost 4 times higher the hardness. So this increase in the hardness and increase in the elastic modelers is essentially are attributed to the fact that there is a concept called physical cross linking those who are from the polymer background they know that polymers can be cross linked by adding sulphur to polymer.

The process is known as vulcanisation so vulcanised rubber or highly crosslinked rubber is all is used for some of the engineering applications because the fact that it has a very high strength because they are chemically crosslinked. In contrast to chemical crosslinking here we are able to physically cross link this material by dispersing hydroxyapatite that is which is bioactive hydroxyapatite fillers and alumina which is a bio inert.

So these alumina is used to increase the elastic model as such and hydroxyapatite which is a bioactive which can increase the biocompatibility property or cell compatibility property why

high density poly high hydroxyapatite uses that bio compatibility because hydroxyapatite is the inorganic composition of natural bone. So because of the chemical complex similarity and structural similarity.

We that of the natural bone hydroxyapatite has every potential to increase the biocompatibility of any composites containing the same phase. So this physical crosslinking apparently explains well the fact that that with addition of the hydroxyapatite with the addition of alumina one can achieve much higher hardness and much higher elastic modulus properties. These particular materials if you see that they are processing conditions CM stands for compression molding.

So these are essentially compression molded materials so these compression molding materials these after this compression molding the simple 10 millimetre diameter pellets were used for all these property measurements as well as the micro structure evaluation and XRD and what is the temperature, temperature of this compression molding for all these materials is 130 degree Celsius 0.5 hours.

So 130 degree Celsius and 30 minutes is that typical compression molding conditions for all these HAP half alumina composites. Now if I remember number if I compared the processing conditions of the typical ceramic even if you take the example of the pure hydroxyapatite. So hydroxyapatite is a ceramic phase and if you take the ceramic powders of hydroxyapatite and if you want to consolidate the hydroxyapatite powders.

Then you need to sinter the hydroxyapatite powders at least at 1200 degrees Celsius for 2 hours or so to get the dense hydroxyapatite ceramic. So these compared to the ceramic the advantageous of the polymers that I have mentioned you before it can be processed at much lower temperature almost like an order of magnitude lower temperature than most of the ceramic based materials or steel based materials.

So that is the by far the largest advantage of using polymers because these polymers can be processed at definitely lower temperature while updating a reasonable properties. But these properties of the polymers can be enhanced through careful addition of the ceramic fillers. Now



these fillers are essentially used to increase the mechanical properties in the context of biomedical applications.

One has to carefully select these fillers like alumina or hydroxyapatite. Hydroxyapatite is anyway it is a double start materials because it has very good biocompatibility also a ceramic phase may give rise to very large mechanical properties like elastic modelers unless it is toxic each unless it is not toxic in nature some of the ceramic phase can cause toxicity and this potentially toxic ceramic phase must be provided.

In developing any polymer composites for biomedical applications so therefore random selection of the ceramic fillers to increase the hardness or elastic modelers thereby increasing the wear resistance property should not compromise with the bio compatibility properties in other words for biomedical applications if one needs to use polymer ceramic composites then one has to carefully choose the ceramic phase to disperse in the polymer which are also biocompatible in nature.

So in the next class, I will just ill describe the tribological properties of this polymer ceramic composites and I will also main mentioned the relevance of these tribological properties if you remember correctly in that total hip joint replacement these polymers ceramic composite based materials which forms acetabular liner that actually wraps very closely with that of the femoral head

And that is the contacting interface between femoral head and acetabular socket which experiences maximum wear. So therefore we need to understand that different wear mechanisms when these high density polyethylene hydrox and alumina they are slid or fitted against different materials of interest for femoral head and these materials of interest for femoral head can be either steel or alumina or Zirconia.

So depending on what is the materials of interest you use as femoral head the wear conditions can change as well as the wear rate can also vary significantly so that will be the subject of discussion in the next lecture thank you.