

Friction and Wear of Materials: Principles and case Studies
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Lecture –14
Fabrication of Engineering Polymers

So welcome back in this lecture I will cover a different class of materials and that is polymers. Now polymers they are essentially made up of carbon, hydrogen, oxygen, nitrogen and it is an extremely versatile material because it is used not only for household applications but also various engineering applications. So I will first briefly introduce what are polymers and then we will go through the different classes of polymers.

As we will see how to make polymeric materials, how to develop the how to use the different manufacturing technology to a process and fabricate polymeric materials.

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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.

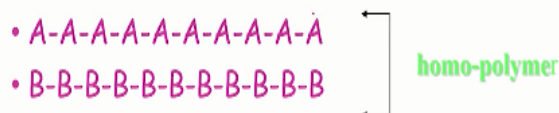
So what is polymer? the formal definition of polymer is that it is a large molecule or macromolecule composed of repeating structural units and these repeating structural units are called monomer. Okay so all these individual unit is called Monomer. And when these monomers they are clubbed up together or they are brought together they form a macromolecule that chain which is called as a polymer.

So the way the polymers are synthesized so one of the terms is very important its called degree of polymerization so degree of polymerization is nothing but number of monomer units which are attached to make the macromolecules structure and what is the polymerization process? this polymerization is a specific process which combines small molecules known as monomers into a covalently bonded chain.

So across the chain this monomer units are joined together by covalent bonding and during the polymerization process some chemical groups maybe lost from each monomers. So that is also important to know and monomer is a monomer is also known as a repeat unit because this is essentially repeated in linearly to make that a full polymer.

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Some mer's ?



- chains with identical bonding linkages to each monomer unit



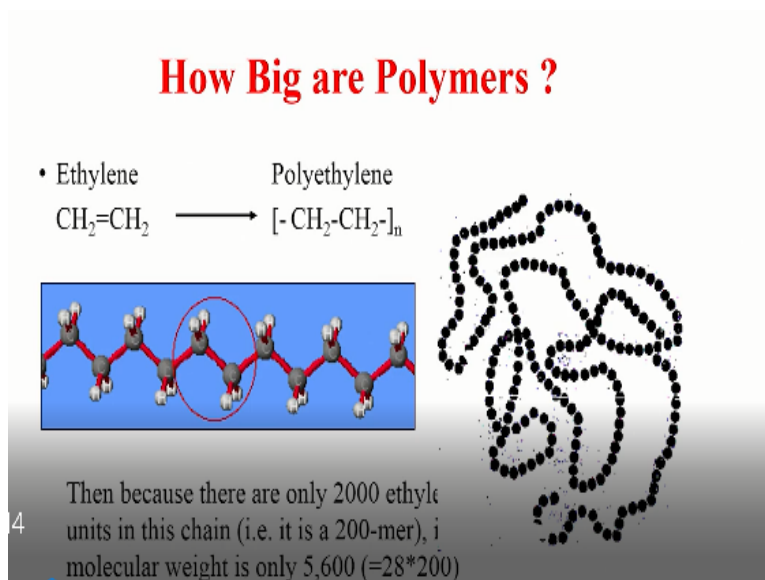
- chains with two or more linkages usually implying two or more different types of monomer units.

So what are the different classes of polymers? so here what you see that this AAAA this is called this BBBBBB this is called homo polymer. So here mer unit is A or the mer unit is B essentially the homo polymers are those polymers with identical bonding linkages to each monomer unit. What is copolymer when two different type of mer units are joined are polymerized together to form a large chain structure where two different mer units are covalently bonded to each other.

Then we call co polymer in most of the cases for engineering applications it is often the co polymers which have received more attention than homo polymers. Okay so these are the two

broad classification of polymers I repeat this is these two major classes of polymers are homo polymer and co polymer.

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Now few minutes back I mentioned that polymers are essentially large macro molecule or structure the question is therefore how large are those polymers? so just to give you an idea this is one of the large macromolecules structure you can see so it almost appears to you like a snake like morphology like snake if it is squeezed and if they are hiding somewhere in the forest they also have similar kind of structural configuration.

So this is a typical polymer chain they can squeeze they can unfold they can fold everything they can do simply because of the fact this polymeric chains are made of a lighter atoms like carbon hydrogen, oxygen and nitrogen those kind of items and for example here you can see there is a 2000 ethylene units and it is a 200 mer and therefore molecular weight is only 5600.

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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.

What is the molecular weight of the polymer that is one is a number average molecular weight and there is a weight average molecular weight? So number average molecular weight is essentially the total weight of the polymer molecules in a sample divided by the total number of polymer molecules in a sample. So that is why it is called number average and weight average molecular weight means.

It is essentially this M_w is based on the fact the bigger molecule contents more of the total mass of the polymer than the smaller molecules. So therefore there is a need to define a different type of molecular weight and that is why it is used at weight average.

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Molecular weight and dispersion

Synthetic polymers always show a distribution in molecular weights.

number average :

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

weight average:

$$M_w = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

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

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The polydispersity index is given by M_w/M_n

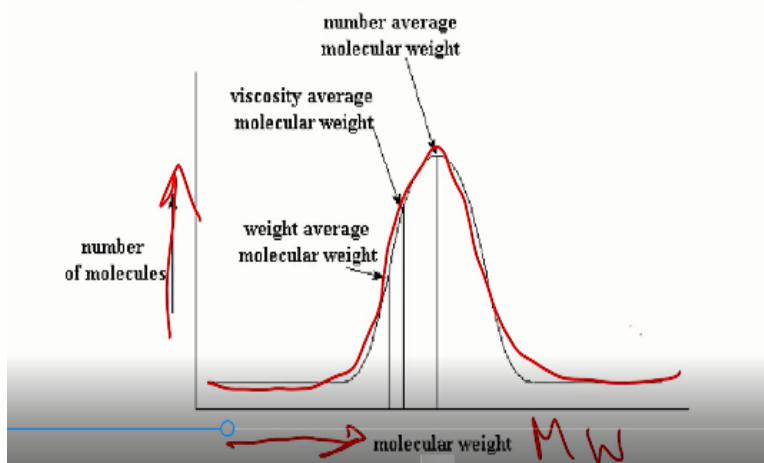
This is the formal definitions or mathematical expression to define what is M_n and what is M_w what do you see? M_n is nothing but $\sum n_i m_i / \sum n_i$ so where n_i is the total number of in n_i is essentially number fractions of the molecules of mass M_i . What is the weight average molecular weight? Weight average molecular weight is essentially $\sum w_i M_i / \sum w_i$ now what is w_i .

That is the weight fraction of molecules with molecular mass the weight fraction of the molecules of the molecular mass M_i . So these you can write down as $\sum n_i M_i$ because w_i is nothing but $n_i M_i$ right. So you have w_i is a weight fraction it is nothing but $n_i M_i$ if you do this further simplifications you $M_w = \sum n_i m_i^2 / \sum n_i m_i$. So this is fairly easy to understand one of the major parameters often in this in the in the polymer science.

Or in the polymer engineering that the people use to distinguish two different classes of polymers is the poly dispersity index. So poly dispersity index is known as PDI so they do not many times attend polymers they do not mention M_n or M_w values but they mention about the PDI and PDI is typically defined as M_w/M_n that means the ratio of the weight average molecular weight to number average molecular weight it is what PDI essentially meant.

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Graphical Representation of molecular weight distribution



So this is an important plot what you see here this number of molecules which are plotted and along the y axis the molecular weight it is plotted on the x axis and what you see here that in this

particular graph your mean of the graph is essentially your number average molecular weight. So that is M_n and M_w is your weight average molecular weight that is here and there or viscosity average molecular weight that is M_n .

So it is very clear that M_n is typically $>M_w$ okay so this is how the molecular weight distribution graph that looks like for a hypothetical polymer.

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Polymer Processing

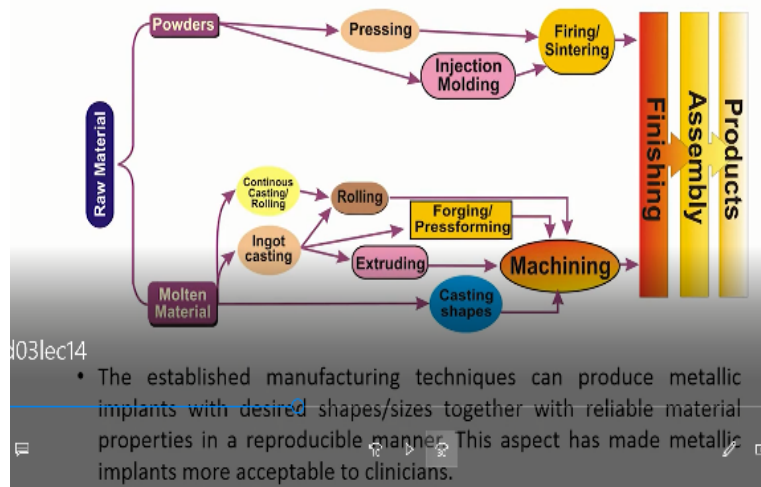
- Various methods used to form polymers into appropriate shapes
 - Polymers are very viscous, additives help in processing
- Compression Molding-for thermosets
- Powder Injection Molding
- Extrusion
- Transfer Molding

Now before I show you that how the friction and various distance of different polymers or polymer based composites they are different from that of the mathematics composites and other classes of materials I thought it would be important for you to know what are the different ways you can make this polymer in the laboratory or in the industry. So these are the different techniques that I have mentioned here.

One is a compression molding for thermosets, powder injection molding, extrusion and transfer molding. So what we can do I what I can do is next few minutes or so I can go through some of the individual techniques for you to show that how different processing techniques are being applied here.

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Sequence of processing steps



This is one of the very useful slide it does not give it not only gives the idea of the manufacturing of polymers but also it keeps a broad idea that how different techniques manufacturing techniques can be used for metals, ceramics and polymers. Now if you follow this kind of trade so you have a raw material so it is a molten material. So molten material based techniques are mostly used for the metals.

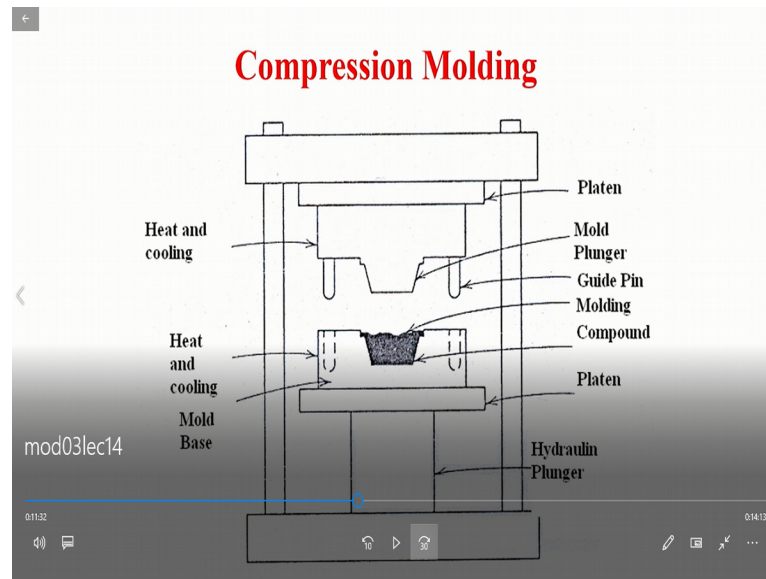
So it goes to castings and different shapes it can go to conventional custody it can go to the continuous casting rolling after it is rolled then it goes through machining or if it goes to inward casting then inward casting then it can be extruded it can be forced it can be rolled and then after the extrusion again it will go to machining. After machining all this finishing operation is to be done then assembly then products.

Now from the powder based techniques like you know what like metal powders or ceramic powders are polymeric powders you can do injection molding and from injection molding you can do firing or centering and then or you can do pressing or you can do firing and intering after that you can do finishing. So these are the two different classes of routes I I have mentioned and another one is a route 2.

So route one essentially is the molten material based route and route two essentially based on powders so depending on what is the starting material you are manufacturing techniques can be

quite different one of the reason that metals are very popular because all these techniques like you know welding, casting, rolling and machining they are very much reproducible and they are very widely used in the metallurgical industry.

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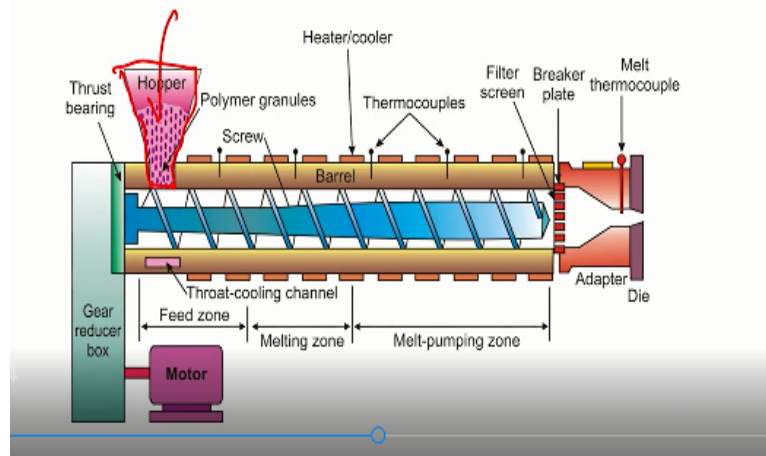
Now coming back to them different polymer processing techniques for example here I am showing you compression molding. Now compression molding is used very widely in the polymer industry so it is a really simple techniques the heart of the compression molding technique is that how you design the mold. Because the designing of the mold is dictated by the fact that what would be your final shape and size of that polymeric products.

So you have a male and have a female of this particular design designing of the mold then one cavity you can pull it you can fill it with the polymer powders and then this particular top punch it can be lowered and then it can be pressed and this is there is some pencil heater which is also attached to this pattern. So through these pencil heater you can heat this is lower punch lower part of the mold

And as result by the application of heat and pressure this particular these polymers can be shaped into particular product.

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Extrusion process for polymers



Another polymeric processing techniques which is also quietly used is called extrusion of the polymers. Now in this particular sketch what you see here that you have a hopper here right? so this hopper or feeder essentially gives the input right? so this is your polymer powders are more than powders it is a polymer beads or polymer granules which are taken into the extrusion chamber

And then what you see here you have screws and this screws threads have differential geometry. So the moment this polymer granules are fed into the extraction chamber and then screws that we will push this polyamory things to this particular area and this is the Die orifice and then extruded rods can be taken out from this end. Soo this is your extruded rod of polymer so depending on what is the diameter of this die orifice.

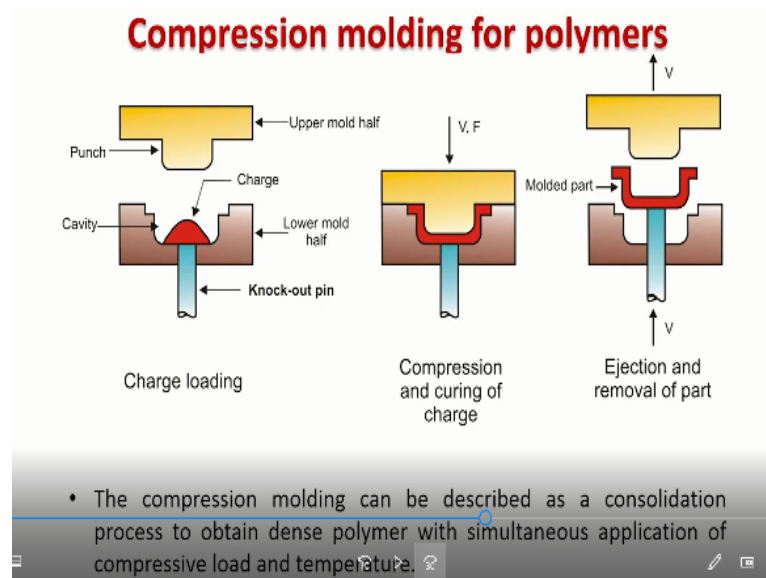
Extruded rod has a specific diameter now what happens in this reaction chamber? so there is a feed zone. Feed zone is essentially where there is a hopper or heater essentially feeds the polymeric dynamics into the reaction chamber because of the continuous screw action and friction in there screw and polymeric granule interface that will locally heat you can also have the specific heating station along the length of this reaction chamber.

You can also insert certain thermocouple just to monitor the temperature of the polymeric feed or polymeric melt as it goes through the reaction chamber finally the melt temperature also is

monitored by melt thermocouple all these temperature monitoring is very important because polymers viscosity is directly dependent on the temperature. So therefore there should be very close monitoring of the polymeric temperature of the melt.

So after the feed and there is something on melt zone and then third one is called melt pumping zone. After the melt zone these polymers getting post to melt and pumping zone and then it will finally it will go through the die and then you can get the extruded rod of the polymer.

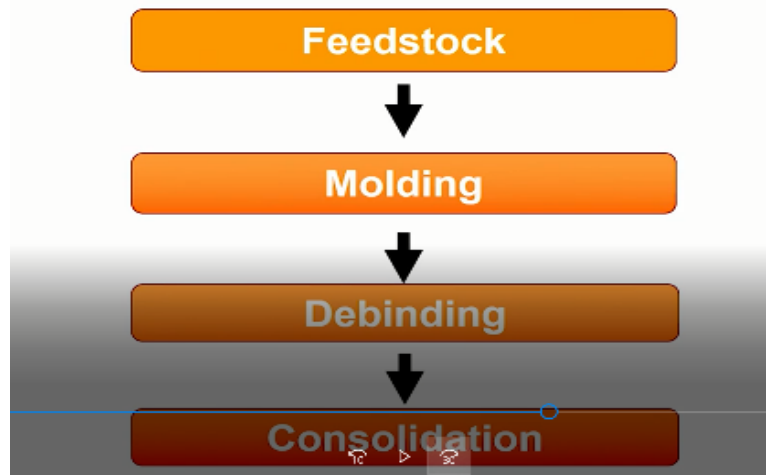
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This is another way that this is that another very simplistic description of the compression molding which I have shown you just two slides back. So you have this polymeric charge polymeric powders then you place these upper mold in close contact with the lower mold. Then you take it out then you get the molded part ejection and removal of the part.

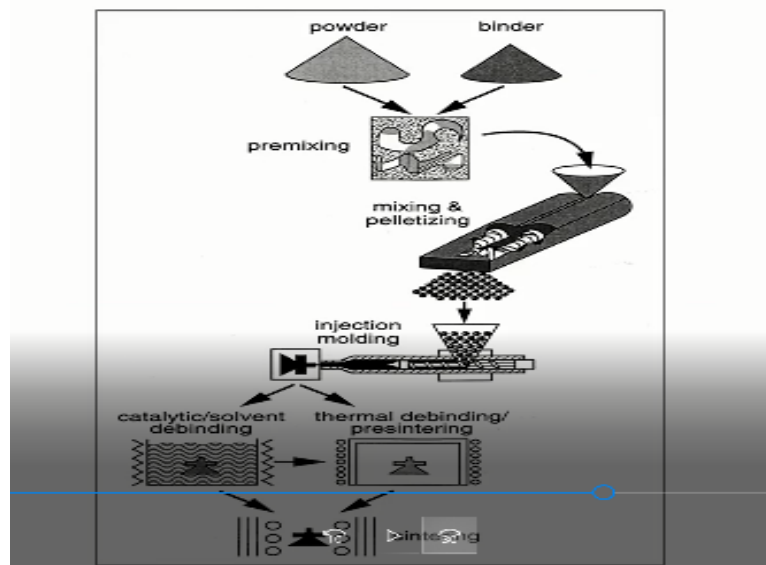
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Major Steps in PIM



Now powder injection molding that is also another technique which is commercially used now injection molding is not really used for polymers it also used for ceramic or solvent based materials so this is the generic description you have the Feed stock then you have the molding operations then you have the De binding and you have the consolidation. So De binding essentially is to remove the binders from this feedstock after the molding is over and consolidation is finally something to consolidate the material into a very dense structure or dense shape.

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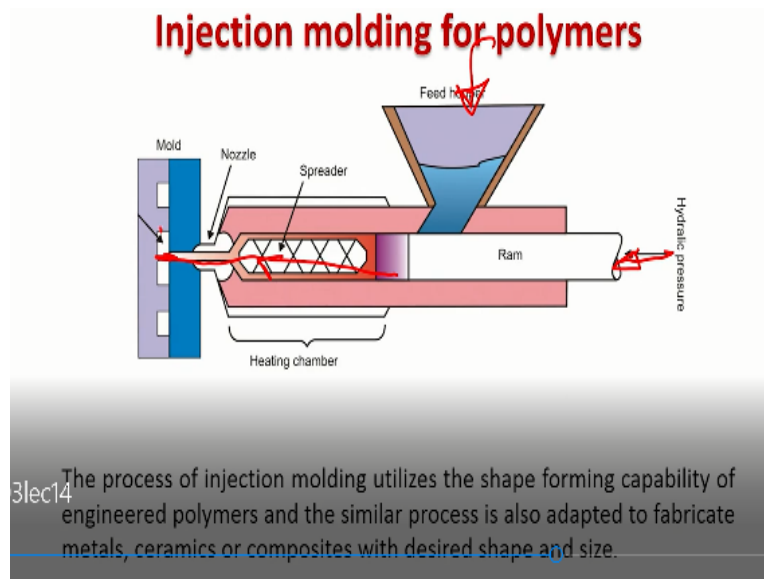


Now this is a schematic representation a process description of the De binding and what you see here is that you have a powder it can be ceramic powder a polymer powder into the binder. First

it is premixed the premixed the pre-mix powder with binder is charged into the mixing and pelletizer it then it forms a pellet of different size. Then it is fed into the injection molding chamber and then depending on the mold shape and size.

You finally get this particular product which can be further which can further undergo de binding either by thermal de binding or presintering or by sintering.

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So this is that essentially the lower part of the earlier slides so you have a feed hopper where you can put the polymer granules or small pellets then the ram will be forced from one end to push the polymeric charge material to get into the mold.

Now if you have a mold cavity depending on how many cavities that you have with particular shape these polymeric melt can be pushed into individual cavity by displacing these things in these particular directions and then you can allow the melt to cool down and then you can get the polymeric parts or injection molded parts at the end of the processing.

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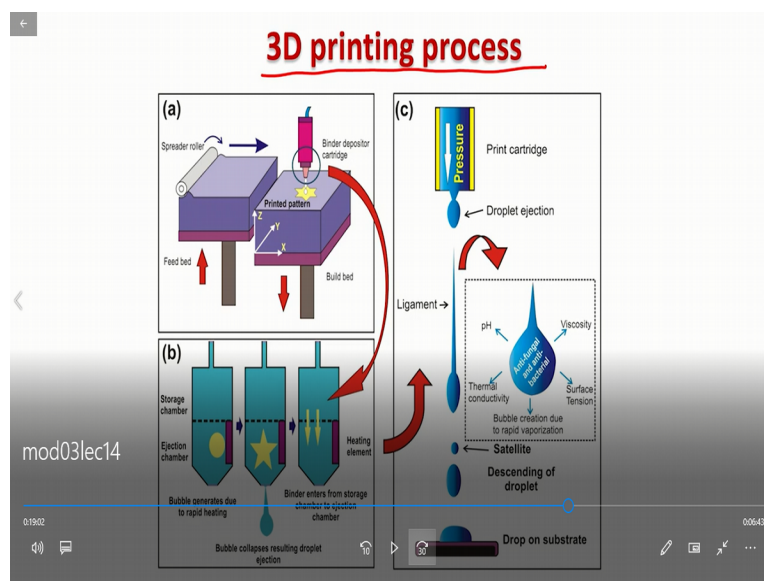
Advanced Manufacturing Of Polymers

- In the context of orthopedic applications, selective laser sintering (SLS) and electron beam melting (EBM) methods can be adapted to produce patient-specific metallic implants with high architectural complexity.
- The conventional processing approaches can only produce porous ceramics with uncontrolled pore size, shape and volume distribution. The additive manufacturing techniques are capable of producing patient-specific scaffolds with close control over pore architecture in 3D space.
- Microwave sintering results in uniform heating of entire volume of powder compact via oscillation of free electrons and ions via application of microwaves (frequency of ~2.5- 85 GHz).
- The patient-specific scaffolds/implants with precise control on the porous architecture (size, shape and interconnectivity) can be manufactured using an additive manufacturing technique.

Now these are called what is called conventional manufacturing techniques of the polymers. But there are certain advance manufacturing of manufacturing is also investigated in the lab scale and some of them have also been used currently in the industrial scale production of the polymers particularly for many of the biomedical applications like orthopaedic applications it is the selective laser sintering which is important or electron beam melting is important and microbes sintering is also another thing.

That is used for the uniform heating for the ceramic based materials.

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So one of the techniques advanced manufacturing techniques which has particularly received wider attention is 3D printing now 3D printing is also used for polymeric based materials so this particular slide provides you in a very schematic DE presentation about how 3D inkjet powder printing works. Or what is a working principle of this particular additive manufacturing technique. What is additive manufacturing?

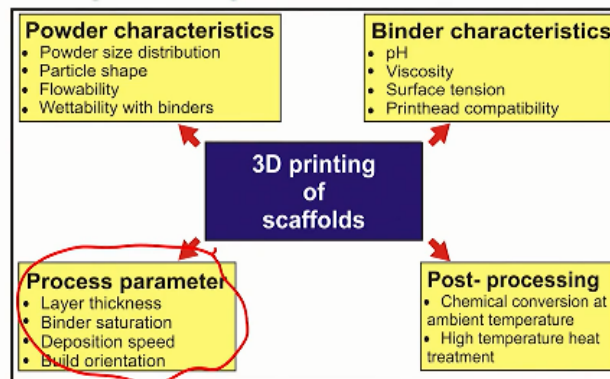
This is a special class of manufacturing which involves layer by layer assembly of a particular product depending on what is the input design. So if you look at this particular slide if you look at this panel A here so this is a binder deposit or cartridge here and this is your essentially build bed. Build bed is the bed where the product is kind of built up and this is the feed bed. So feed from feed bed the powders are displaced.

And it has been sent to the build bed and each layer by layer this build bed this particular product is being built now when these by now if you look at this particular thing that how it looks you will see that this is the binder deposited cartridge and they are the heating element is there so in this heating element it increases the temperature of the binder then there is a bubble formation there is a bubble burst.

And this binder will be ejected from this surface and these binder ejection then it comes and then it is essentially it will be falling on this particular powder bed and this powder bed this binder will interact will penetrate into the powder bed and that will be physical chemical introduction. So some of the important parameters of the binder which are important like pH that is managed logarithm of the hydrogen concentration of those have binder solution, thermal conductivity, the viscosity, surface tension and so on.

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Important parameters for 3DPP



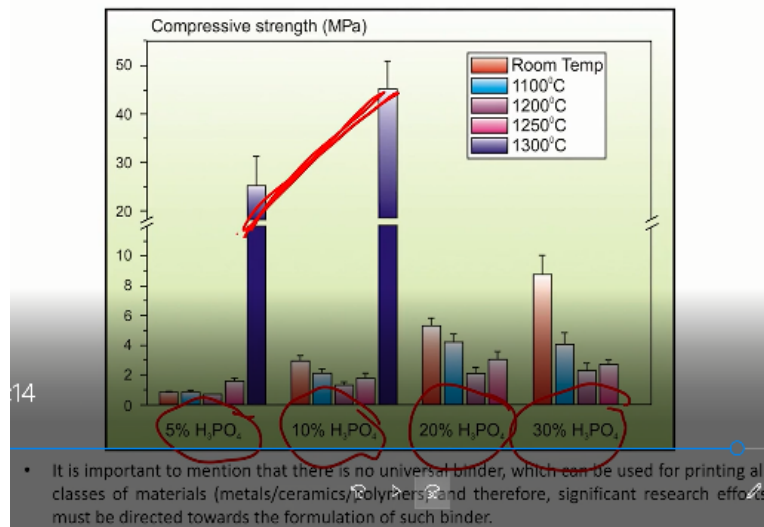
- 3D powder printing process involves the creation and slicing of a virtual computer model, usually followed by the layer-by-layer fabrication process.
- Phenomenologically, 3D powder printing process involves the creation and slicing of a virtual computer model, usually followed by the layer-by-layer fabrication.

What are the important parameters? for 3D powder printing one is the process parameters like what is the layer thickness in each case of this layer and therefore what is the binder's saturation the position, speed, field orientation. Field orientation means suppose this is the one of the orientation of the build. The build orientation can be -45° $+45^\circ$ also so they are maybe different type of build orientation and what is the binder characteristics?

I have already mentioned what is a powder characteristics what is the powered size distribution particle safe, flowability, weight ability with binders and what is the post processing like chemical conversion at ambient temperature and high temperature heat treatment is equally important.

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Influence of post-processing, binder concentration

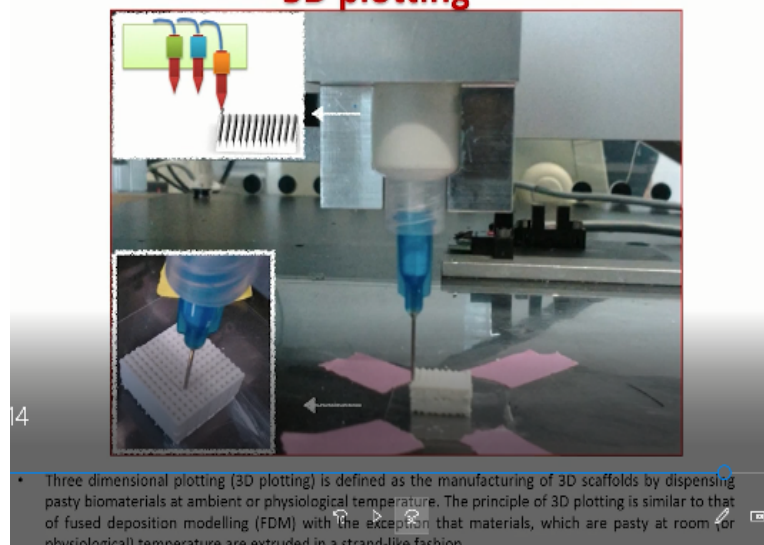


Okay so what are the just to show you that what is the importance of the different binders? what are the materials which is being printed using different phosphoric acid concentration like 5% to 30% phosphoric acid concentration? You can see that that particular competition the strength increases and then however after the debinding and however if you increase a higher concentration of phosphoric acid strength again drops down.

So therefore what these results indicate that 10% phosphoric acid binder concentration is the most suitable for the post processing.

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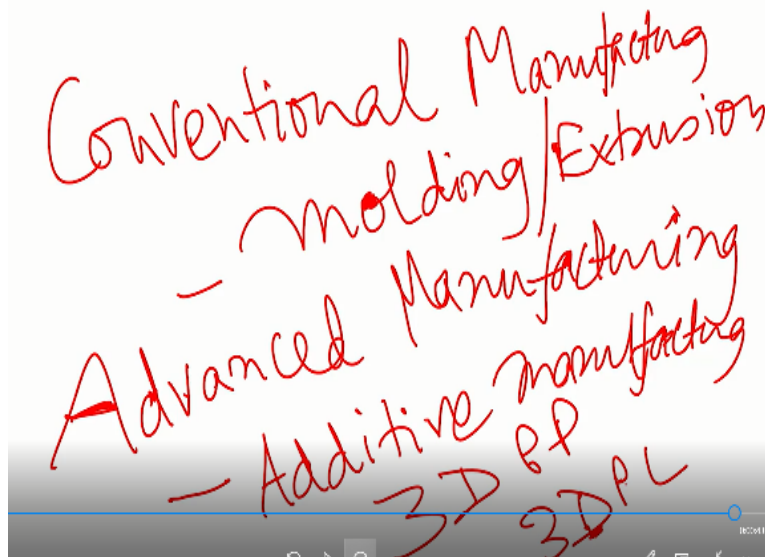
3D plotting



This is also another technique which is currently used for 3D plotting of the polymeric materials like alginate and so on. So again like 3D printing it also develops these total structure by layer by layer deposition however here these starting material cannot be powder starting material can be a paste and that is why it is known as a manufacturer of 3D scaffolds by dispensing pasty biomaterials at ambient or physiological temperature.

So essentially it is very similar to fused deposition modelling but here these materials should be pasty and it is extruded in a stand-alone process. So I think that the most of the manufacturing techniques that I have shown that are quite useful not only for conventional manufacturing but also for advanced manufacturing.

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So summarize what we have learned from this particular lecture is a conventional manufacturing and advanced manufacturing and conventional manufacturing is mostly based on molding of polymers. So it can be either injection molding compression molding or it can be by extrusion okay and one of their biggest advantage of the polymers processing with that of the with respect to the metals is that polymers have a very low processing temperature.

Most of the polymers they can be molded or extruded as low as 250 or 280 degrees Celsius which is not the case for ceramics or which is not certainly for the case of metals. In case of ceramics it requires very high processing temperature more than 1200 or 1400 degrees Celsius and in

case of metals like steels normally steel melting takes place at 1600 degrees Celsius. So therefore these two polymers that way it is advantageous.

Because it does not require very high temperature advanced manufacturing we have mostly learnt about the additive manufacturing technique. An additive manufacturing in name actually is a more generic name and some of the things that we launched is 3D powder printing or 3D plotting 3DPL. So these are the two layer by layer fabrication technique which can be adopted very easily for polymers as well thank you.