Biomaterials for Bone Tissue Engineering Applications Professor Bikramjit Basu Materials Research Centre Indian Institute of Science Bangalore Module 6 Lecture No 30

So n this module we will discuss the fundamentals of polymers and polymers processing.



So briefly I will start what is meant by polymer. So since that polymers as a subject I have not introduced formally in any of the earlier module, so it is important and instructive first to define the polymers, their basic characteristics because that will define how one can process this polymers in lab scale as well as in the industry.

(Refer Slide Time: 0:45)



So this is a kind of a more text book type of a definition. Polymers is a large molecule, its called macro molecular structure composed of repeating structural units of monomer. And what is degree of polymerization? That is the number of monomer units in a polymer chain. So essentially what is the total number of monomer units is there in a polymer chain that is the degree of polymerization.

And what is polymerization? It is a process of combining many small molecules or monomers, into a covalently bonded cabin. During the polymerization process some chemical groups may be lost in each monomer. And this is that monomer is called a repeat unit.

(Refer Slide Time: 1:32)



So a a a and b b b this is the photopolymer, essentially means that the repeating unit is same or identical. Organic radicle. And chains with identical bonding linkages to each monomer unit and then chains with two or more linkages like ab aa bb ,this is kind of called co polymer. So essentially here copolymer essentially means a and b their chemical formula, their chemistry is different however their linked together along this backbone chain to make this polymeric material so that it is called co polymer.

(Refer Slide Time: 2:05)



Now how big is the polymer ? So you have that ethylene and you have polyethylene. Ethylene is ch2ch2 and polyethylene is ch2ch2n and this n can be very large unit let is say 2000 units, n can be 2000 or n can be 200 mar or more so that gives you that what is polyethylene. And for example in case of ethylene there is one mar unit, actually their weight is 28. So if it is 200 mar unit then molecular weight is around 5600.

What is the other things that what I have noticed here I have mentioned here that typically that polymer has a large macro molecular structure. What I sketched here, this macro molecular structure it is present in a very coiled form, so it is not a very straight line, so this is the very coiled for and this coiled form actually they have the flexibility, they have elastic property so they can be either stretched or they can be either or or they can be squeezed together, so all those elastic flexibility properties is very important.

(Refer Slide Time: 3:23)



Now as far as the molecular weight is concerned, they are three type of molecular weights, out of that two are mentioned here. One is the number averages molecular weight, mn. One is the weight average molecular weight, mw, and third one is that viscosity average molecular weight, m eta. So I said that mn, then mw, and m eta, eta is that viscosity molecular weight. Now as the name suggest number average molecular weight means weight of all the molecules divided by the number of polymer molecules.

Weight average molecular weight means that is the bigger molecule contains more of the total muscles of polymer sample than smaller molecules. And one can also distribute one can also make for example this is the frequencer number and this is the molecular weight here. Typical molecular weight distribution is this one. So then in this molecular weight distribution you can essentially define where is mn, or mw in this kind of molecular weight distribution for a polymer.





Now this is a very standard classification of the polymers, again in most of the text books you would find it. So there is three basic classification, one is called amore thermoplastic, thermosets and elastomers. Thermoplastic means this is softened on heating and stiffened on cooling. Thermoset means an infusible or insoluble mass on heating and elastomers means a polymer with the property of elasticity. So what it means is that when you heat the materials heat the polymers it softens and then it stiffen and then when you cool it, it becomes very stiff.

So these materials thermoplastic materials you can give it a different shape. Thermosets means an infusible and insoluble mass on heating. That means you cannot do any further working on the thermosets. Like you cannot shape it in different manner. Elastomers means a polymer with the property of elasticity. That means you can stretch it to a larger extent and once you stretch it then you can, it will it will exhibit what we call rubber like elasticity. Like rubber you can stretch it very long extent without failure then similar kind elastic properties you can essentially get with elastomers. Now thermoplastic, it can be classified based on that their chain arrangement. It can be classified further, one is called amorphous and another is called crystalline. Now this crystalline and amorphous must be distinguished from the way these two terms are defined in metallic bio materials. In case of metals essentially the word crystals are reserved for the any material which shows both long range ordering and short range ordering.

That means if certain bonding or certain atomic arrangement is extended in the similar repeatable, reproducible manner within a few inter atomic distance at the same time similar kind if repeating, reproducible arrangement can also be extended to much longer length scale then you call it as a crystalline material. Whereas the amorphous material means within very few inter atomic distances that repeating or reproducible arrangements of atoms are actually conserved. So therefore there is a very clear distinction between that amorphous and crystalline material. But in the context of polymers these two terms are differently defined.

For example crystalline means that is the part of polymeric structure where all the chains are arranged in a particular repeated and particular pattern. But wherever the pattern is lost in terms of this chain arrangement we call that particular region is amorphous region.

(Refer Slide Time: 7:35)



So a ya, now let me explain this term little bit more clearly with this help of this schematic diagram. Now if you refer to this particular chain arrangement of any hypothetical polymer, now this particular arrangement of chain if you see this is very repeated arrangement, so we call this as a big c that is the crystalline region. But similarly just in the neighborhood if you see this kind of a region we call it as a big a, it is called amorphous region.

So this region is called amorphous region because there is no repeated, regular arrangements of the chain and this region we call as a crystalline region that is very repeated arrangements of the chains in that small local region. So so there are some polymers that may be completely amorphous like there is no local arrangement of these polymers. No repeated arrangements of the chains but most are a combination of both crystalline and polymer and those polymers are called semi crystalline polymers.

So semi crystalline essentially means that polymers with some fraction is that crystalline fraction and some fraction is the amorphous fraction. So when crystalline to amorphous transition takes place then that is called typically glass transition temperature and this that point at which polymer hardens into a amorphous solids. Amorphous solids means once it becomes amorphous you cannot do much. And this terms is used because the amorphous solid has properties is similar to glass. So normally a given temperature again is defined with respect to certain glasses, like certain inorganic glasses also we call it as glass transition temperature.

Popular example is that mica based dental glass ceramic which are used for the dental restorations. We call when this crystalline goes to amorphous we call it as glass transition temperature. In the context of the polymer glass transition temperature means that the point at which the polymer hardens into a amorphous solid. And this once it goes to the transition to amorphous solid at that point transition temperature which is called as a glass transition temperature.

And once it goes to amorphous state the chains have little orientation throughout the bulk of the polymer. Or in other words chains will have extremely random arrangements in the bulk of the polymer and therefore you cannot do much on these kind of polymeric materials in terms of further working.

(Refer Slide Time: 10:10)



So little bit more classification, little bit more discussion on the thermoplastics. So with some examples so polyvinyl chloride, polystyrene, polymethyl methacrylate, polystyrene these are all thermoplastic. So ps, pmma. So pmma is more used as a bone cement. So therefore bone cement which is traditionally used as a, used more clinically so this material is thermoplastic polymer. Thermosets which soften when heated and can be molded but harden permanently and then they will decompose when reheated. Example are epoxy, phenolic, and polyester resins and so on.

(Refer Slide Time: 10:49)



So this is that polyethylene. I mean polyethylene has several variety, one is called low density polyethylene, ldp, another is called hdp, high density polyethylene, and third one is called uhmwp that is ultra high molecular weight polyethylene. So all this distinction between low density, high density and ultra high molecular weight polyethylene essentially is based on the molecular weight.

So if you go from ldp to hdp molecular weight increases. If you go from hdp to hmwp molecular weight further increases. So in that ultra high molecular weight polyethylene has a larger applications like in acetabular socket, in artificial hips and knee joints and so on. So there ultra high molecular weight polyethylene is used.

(Refer Slide Time: 11:36)



Poly methyl methacrylate this is that mar unit so poly ethylene methacrylate you have certain methyl groups. So this is two methyl groups is there. And then you have that other functional group is also attached to that and it is used as a bone cement. The other applications of poly ethylene methacrylate is intra ocular lenses and hard contact lenses. So there also again poly ethylene methacrylate is used.



Now polymer structure here two terms are important, configuration and confirmation. Configuration refers to the order that is determined by chemical bonds. Confirmation actually refers to the order that arises form the rotation of the molecules about the single bonds. So these two terms are distinctly different or fundamentally different. So often people tend to use these two terms interchangeably, that is not right.

So confirmation is much more used to describe for example protein structure. So confirmation essentially refers to that arises from the rotation of the molecules around the single bonds.





Crystallinepolymers, amorphous polymers this is already discussed a few minutes ago. This is the classic example of crystalline polymers simply because here all these chains are perfectly parallel to each other. This is the classic example of amorphous polymer simply because that here chains are oriented in a very random manner so there is no no regular arrangement of the chains.

(Refer Slide Time: 13:10)



Now this mechanical properties why I briefly introduced because this mechanical properties has a larger relevance how you make this polymers. Like this is a classical example of semi crystalline polymer. In the tensile stress response you have initial tensile response, then followed by followed by deformation at a constant stress and then followed by fracture of the materials. And you can see each time the polymer undergoes large elongation and then it fractures.

Now this is the case for semi crystalline polymer, it shows typically many of the polymers, classical thermoplastic polymers they behave. Now if you have the polystyrene in contrast what you see it is a very linear and then it undergoes fracture. So what is the difference between these two although their elastic modulus is roughly similar but polystyrene has high strength. But polystyrene has nil or negligible deformation.

What would be the relevance of that? Like when you do this processing for polystyrene you cannot deform this polystyrene to any reasonable extent. Like you cannot give the polystyrene a particular shape of a mold or any particular shape of any material to the polystyrene materials. So therefore polystyrene it simply goes, it goes to fracture but it can bear higher load than many semi crystalline polymers. So that is the fundamental difference between polystyrene and this is called p. So here it is simply because that how the fundamental difference that ps versus p is there.



(Refer Slide Time: 14:46)

This is little bit more details about what I have shown you in the last slide. That is the thermoplastic polymer. So the your non linear elastic deformation starts from here. And this is

the classical example of visco elastic deformation and then it goes to fracture. So you have the yield strength here and you have the necking part here. Now this linear part will give you the slope will give you the elastic modulus of the materials.



(Refer Slide Time: 15:12)

Now in the context of polymers apart from elastic response that other things that is very important that is viscous elastic. And also inelastic behavior, so this is that this is one, this is the truly elastic response. Like you load and you unload. Now whenever it is total elastic then your strain increases and then it goes back.

So tais the application of strength and then tris the reversal or removal of the strain. In case of viscose elastic solid then it will go up, then it will keep in increasing. The when you release the string it will not drop it immediately so this dropped part is crossed, that means it will not behave like this but instead they will undergo this strain, the strain will be released in a very sustained manner and it will take infinite time.

So that is the characteristics of the viscose elastic response which is other way not observed in a typical elastic metal or elastic plastic metal. And completely viscose fluid they will behave like this, it will go straight and then it will reach the steady state and it will retain there even if there is no strain. So remember if you have to correspond this to this, and you have to correspond this

to this, so here your load your strain is load is removed or strain should go down to 0 but it doesn't go down immediately and neither in this case of the viscose fluid.



Ok. So and then these these particular things I'd like to explain, like particularly this region that why polymers can exhibit or can sustain deformation at a constant stress? And then what is the things that are changing in case of polymers during this time of application? So what you see here in the mechanical, this is that classical dog bone type of geometry. So in the classical dog bone type of geometry you apply the tensile force from both the directions.

Now what you see this small short chains, this is shown in the white this short chains here, the way I'm sketching. Now this short chains will try to align along the tensile stress axis and once you start doing that you see that you just observe the way it is changing, at the central region this short chains is now aligned with each other in a parallel manner. So although the length is increasing the short chains are elongated in a along the stress direction.

Now this constant deformation or large deformation at constant stress essentially allows this short chain to align along this tensile stresses much more flexible manner. So that at the level where maximum stress point is reached all the chains are oriented along the tensile stress axis in a seamless manner. And that is how this thing takes place.

So this is called necking and crystallization. Again crystallization in context of polymer, I repeat, crystallization essentially means that certain specific arrangements of the polymeric chains in q localized region and therefore that localized region will have certain ordered arrangements of polymeric chains and that is what is called crystallization.



(Refer Slide Time: 18:53)

So this is much more description of this crystallization. So you see that this chains are orientated here. So this is called crystal part and this is called amorphous part of the chain. Now as you are increasing this as you are increasing this things in this direction now these chains are slowly getting aligned but not completely. So once this completeness of this chain alignment along this

tensile stress axis is done, then polymers cannot be deformed any further and then it will undergo fracture.

So essentially during the tensile deformation or even when the polymer undergoes processing at a specific temperature, this mechanical properties will actually determine how and to what extent that polymers can be deformed during a specific processing approach. Or during a specific deforming route.



(Refer Slide Time: 19:49)

Final deformation, final fracture of the polymer takes place in a manner which is quite different from that of the way that metals or ceramics are fractured. Now simply because in the polymers you have the macro molecular structure you have chain like arrangements. So all these chains are kind of oriented in this direction, so what will happen in car if the excessive deformation?

(Refer Slide Time: 20:15)







Craze formation in Polymers



Craze followed by a crack CD Crack



If I go back to this original discussion so in case of excessive deformation at a constant stress, I'm now talking to the point from onwards, so this arrow onwards. What is happening to the polymer up to this point onwards so if I mark this point like a, b, c, d up to b c part I have explained through this particular slides. This is the part of the bc part and now I'm explaining this is also the part of the bc part of that particular stress strength curve.

And then I'm explaining the cd part which is the last part of this deformation that is that when polymers have already experienced extensive deformation then its going towards the fracture. Now how this fracture part takes place in case of polymers like this is they call craze formation like there is localized void formation which will where the polymeric chains are disentangled or that will not be connected to each other and this region is essentially nucleus, that is called micro voids.

So nucleation of micro void first form and there is some fibrillar bridges. Fibrillar means this microvoids are still connected to each other by some small fibrillar structure or some small fiber structure. Now why is this micro voids increase in size because of the application of the stress and remember the stress is applied in these direction ok? Now once these micro voids are are increased in size then they will club up together they will collage together, and then they will form a small this crack like feature.

And this cracks will progress in a direction perpendicular to the stress direction and this will lead to compete failure. See doted dot dotted direction essentially shows that how this crack will essentially or how the crack is expected to increase in length and size in a direction perpendicular to the tensile stress direction.

(Refer Slide Time: 22:16)



So there are three processing approacies that I'd like to cover in next 5 or 10 minutes or so. That is the compression molding, injection molding and extrusion.



Now compression molding is essentially fairly simple. Now in the compression molding you have this polymeric powders here. You just put it in the mold cavity, you have the negative plunger here on the top. You just apply pressure here. So this will be compressed now in the mold. Ultimately it will take the shape of the mold cavity.

So that is how the compression molding is conducted and the temperature requirement in compression molding and polymer processing is fairly small. Fairly fairly low compared to that of the metals and ceramics.



(Refer Slide Time: 23:02)

So in case if the metals, let is take example of metals. For example steal. Steel is typically molten 1600 degree Celsius. Ceramics typically they are sintered as high as that greater than 1200 degree Celsius or 1000 degree Celsius. Whereas polymer this most of the processing is done less than 250 degree Celsius. Now you can imagine the temperature requirements or the heat requirement in case of polymer processing is fairly small or fairly low compared to that of the steel and ceramic.





So what are these other techniques called powder injection molding? So this is extends the safe forming capability of engineered plastics to other high performance metals like metal ceramics and composites. So essentially powder injection molding can be universally used not only to engineered plastic but also to metals and ceramics.

(Refer Slide Time: 23:53)



So what is how this technique is done ? So you have the powder and you have the binder. So this powder and binder will be mixed in the first mixing stage and then it will be fed into the mixing and palletization. This small small palette of this spherical shaped palette of different size and

shape, that will be fed to the injection molding chamber. Then it will go to the injection molding chamber then it will get the shape of the mold.

Now this you have to do the binder removal simply by heating the binder at a temperature where binder will evaporate or you can do sintering in case of the that powder metallizing technique like metals or ceramics. So this is a generic description. Now variation from the generic description is applicable for individual classes or materials. Be it metals, ceramics or polymers.

(Refer Slide Time: 24:41)



This is more clear description of this injection molding. So here is the feed hopper, here you can either feed powders or palette. Now once you feed that powders or palette in this injection molding, then there is a ramp here, so ramp will push the powder palettes to go to the heating chamber. Now heating chamber has the capability of heating material to somewhere in the 200-250 degree Celsius depending on what polymers you are using.

Then it will allow this liquefied and little bit viscous polymer to get into the mold. Now this mold cavity once it goes, then it will take shape of the mold cavity and this is the mold that is there. So essentially hydraulic pressure will push continuously the polymer the viscous polymer to take an exit from the mold through the nozzle to get into the mold cavity.

(Refer Slide Time: 25:47)



So this is little bit more process description. So in the torpedo section as I said the polymer is heated up to 200-250 degree Celsius and it is somewhat equivalent to the dye casting of metals but in dye casting the temperature requirement is more. Now to prevent premature solidification molten material is forced at 35-40 mega Pascal. So this is the stress this is the stress that this with with this hydraulic pressure is acting through the ramp.



(Refer Slide Time: 26:18)

Let me show you one of the example that from our own research that high density polythene hydroxyapatite alumina based material that when we are developing through injection molding. Now this is that,this blue ones, this is that how this torque is generated Ok? And then red one is the temperature. As you can see the temperature is close to 180 degree Celsius, little less than 200 degree Celsius.

This is the barrel temperature or process temperature. Now the torque is important because this torque essentially will allow the polymers to undergo some of the deformation. Another important thing is the sheer rate, now you see that once you load, so this composition is high density polyethylene and you have some ceramic fillers and this is that x percent aha, and y percent alumina let is say. Now x 5, 10, 15, similarly y can be 5, 10, 15 and these 2, h and alumina can be added there in 1:1 ratio. Like if it is, x is 5 y is also 5.

Now what you see that 10 percent volume loading means 10 percent of hydroxyapatite alumina when it is loaded, then sheer rate decreases. Now when you add this 10 percent alumina and 10 percent h, then the sheer rate is further reduced. Now then if the sheer rate is reduces so less then beyond certain low sheer rate, you cannot simply process this material. So therefore this sheer rate estimation or sheer rate determination is important

So that you can define what is the processibility of a specific polymer loaded with ceramic filler combination. The other thing is that what is the volume flow rate. Volume flow rate is also important like what is the bulk material size that you can essentially eventually fabricate through this injection molding technique and this volume flow rate again as you see it decreases like in sheer rate. Whereas viscosity increases with sheer, viscosity increases in a different direction.

Now as you know for the polymer that higher the viscosity more difficult is the processability. So therefore the viscosity needs to be as low as possible and that is how beyond this 30 percent and 40 percent onwards that you cannot use this polymer process this polymer by injection molding.



So last process that is the extrusion. Even in this extrusion process you through this powder or palette, you throw this one and then it will go to the barrel, and in barrel has three different zones. Feed zone, melting zone and melt pumping zone. And once it push it then again you have a dye here. In the dye this polymeric materials will take the shape of the dye and each point then you have to take that to the thermocouple, what is the temperature.

This monitoring of temperature is important as you can see at various places in that barrels this thermocouples are placed just to see that how this temperature is carried over three different regions, feed zone, melting zone and melt pumping zone. Melting zone where polymer undergoes incipient infusion or melting and melt pumping zone where melt is pushed through the adaptor and to get into the dye orifice.

(Refer Slide Time: 28:38)

(Refer Slide Time: 29:27) Schematic illustration of a typical extrude Barrel heater/cooler Filter Breaker Melt Thrust Hopper Barrel screen plate thermocouple bearing Throat liner Thermocouples Barrel Screw Adapter Throat-cooling channel Die Feed zone Melting zone Melt-pumping zone Gear reducer box

So this is that more clear picture. This is also again in text book that what is this, how this polymers is going. So you can see this hopper and then each place with a thread in this extrusion region, melting and extrusion this polymer will go and take the shape of the mold.



(Refer Slide Time: 29:45)

And these are compression molding so I think I will stop here. This is the end of this polymer processing and little bit about the properties