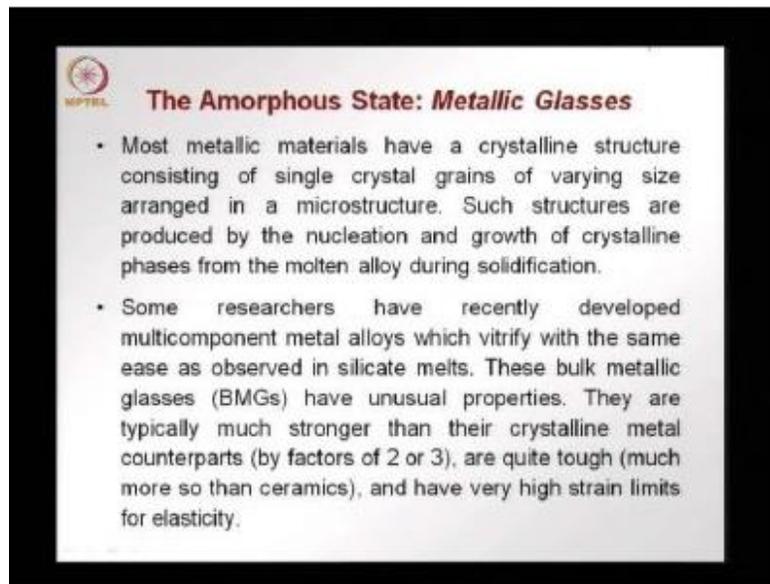


Modern Construction Materials
Prof. Ravindra Gettu
Department of Civil Engineering
Indian Institute of Technology, Madras

Module - 2
Lecture - 3
Structure of Solids

This is the third part of the lecture on structure of solids. Until now we have looked at crystalline structures, how crystals are formed and we looked at the defects that can occur in crystal structures. We looked at point defects, line defects, surface defects, volume defects and then we started looking at amorphous structures which are materials that do not have any order in their microstructure. That is they are not crystalline, they could be glassy or amorphous.

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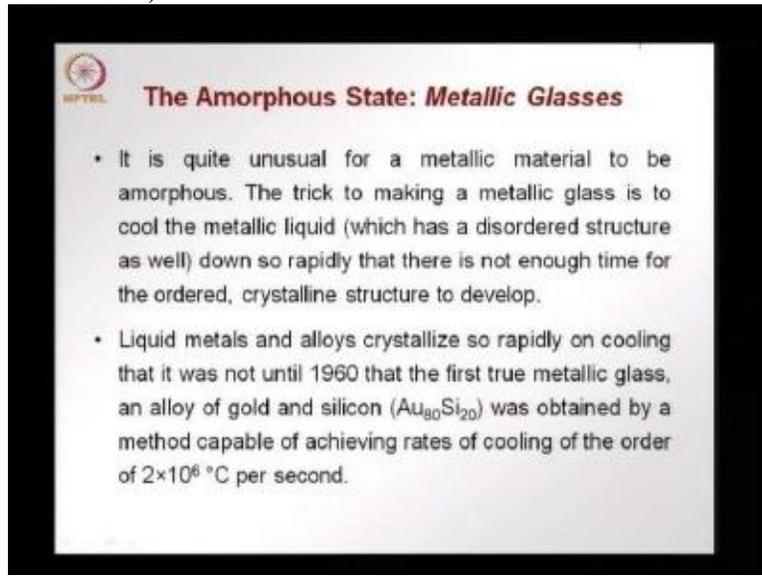


We will continue with amorphous structures. Now one interesting type of amorphous state is in metallic glasses. As we know, Metals generally have a crystalline structure, because of the metallic bond they form crystalline symmetric structure. We can have single crystal grains that can have varying sizes and these grains together make up the microstructure. The crystal structure is formed by nucleation growth of the crystalline phase from a molten material or molten alloy during the process of solidification. However, some researchers have developed multi component metal alloy which vitrify, means they

become amorphous with the same ease.

These bulk metallic glasses called BMG's have very unusual properties which make them interesting for engineering. They are typically much stronger than the same material in crystalline form by a factor of two or three that is two or three times as strong. They are also tougher, that is the work to fracture is increased or rather the ability to resist cracking is increased more than in ceramics and they are also more elastic or have a highest strain limit in the elastic range.

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It is however, not easy to make a metal into a glass, the trick or the technique is to make a metallic glass by cooling the melt for the metallic liquid very fast, so that the disordered structure is maintained and there is not enough time for nucleation and an orderly structure or a crystalline structure to develop. It was not until the 1960's that true or proper metallic glass was formed. It was done as an alloy of gold and silicon, this was obtained by very rapid cooling in the order of 2 million oC per second.

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 **The Amorphous State: *Metallic Glasses***

- More recently, new alloys have been developed that form glasses at much lower cooling rates, around 1-100 degrees per second. While still fairly rapid, it is slow enough to cast bulk ingots of these metallic alloys, and solidify them to form glasses.

Amorphous Zirconium



Crystalline Zirconium



A wedge of an amorphous Zr-Ti-Cu-Ni-Al alloy.

More recently, new alloys have been developed that become glasses at much lower cooling rates that is not so fast; only in the range of one to hundred degrees per second. Though this is still very rapid, it is slow enough to make pieces or bulk ingots. This is a piece of one metallic glass here. (refer slide)

We see the difference in structure between crystalline zirconium and amorphous zirconium on the left. You will see a more ordered structure in the zirconium. This is now a zirconium glass or an amorphous zirconium. On the right, you see a metal glass which is an alloy of zirconium-titanium-copper-nickel-aluminum. One thing that is common in the newly developed metal glass is that we have many different types of atoms together in the alloy. This makes the nucleation get delay, because to have an orderly structure with different types and sizes of atoms, it requires slower cooling. So, when you cool the material fast enough and alloy with many different types of atoms together has a higher chance of forming metallic glasses having magnetic properties. (Refer Slide Time: 04:56)

 **The Amorphous State: *Metallic Glasses***

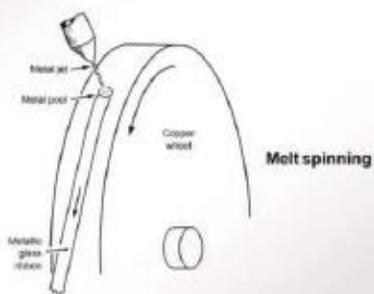
- Metallic glasses having magnetic properties are typically iron-rich amorphous solids with compositions such as $\text{Fe}_{0.8}\text{B}_{0.2}$ (iron-boron) and $\text{Fe}_{0.8}\text{B}_{0.1}\text{Si}_{0.1}$ (iron-boron-silicon).
- They are readily formed as long metallic glass ribbons by techniques such as melt spinning, where a jet of molten metal is propelled against the moving surface of a cold, rotating copper cylinder.

They are typically high and rich amorphous solids with compositions such as iron-boron and iron-boron-silicon, and these are formed into long metallic glass ribbons by a technique called melt spinning, where a jet stream of molten glass is propelled. It is shot against a moving surface say cold rotating copper cylinder. So, when this jet hits the cold cylinder it cools down immediately.

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 **The Amorphous State: *Metallic Glasses***

- A solid film of metallic glass is spun off as a continuous ribbon at a speed that can exceed a kilometre per minute.



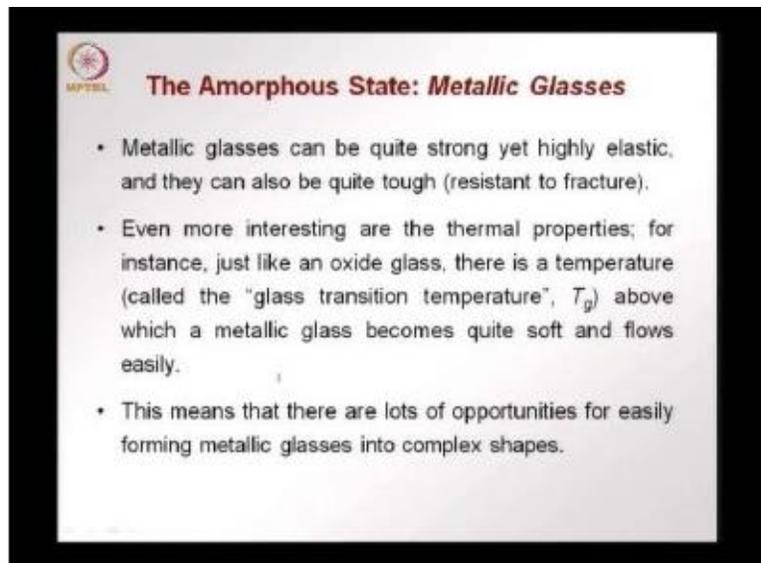
Melt spinning

Higgins

You can see in this diagram, this copper wheel that is spinning is kept very cold and then you have the jet of metal impinging against this copper wheel.

So, this is spinning at a fast rate and when this hits it cools down and forms metal glass ribbon. So, here in this case, the solid film of metal glass is spun off as a continuous ribbon. So, this is the ribbon which is coming at a speed that can exceed kilometer per minute because of the fast spinning of this copper wheel.

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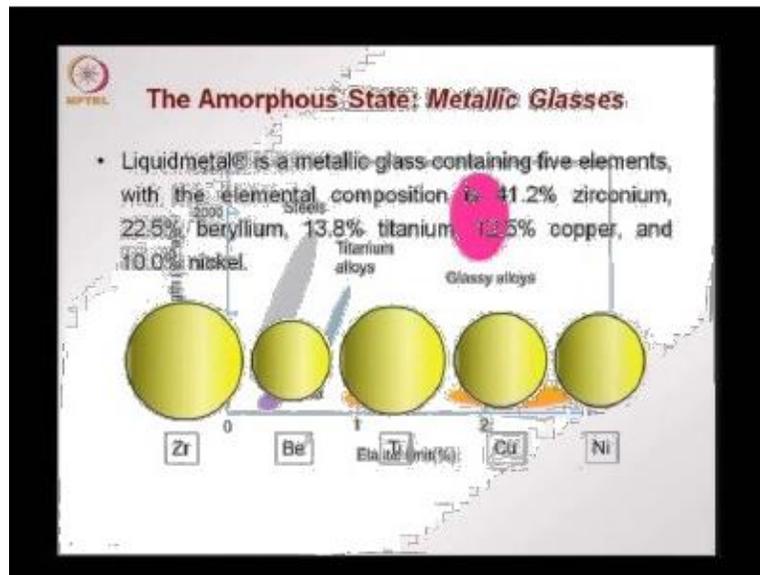


The slide features a logo in the top left corner consisting of a red circle with a white star and the text 'MPTEL' below it. The title 'The Amorphous State: *Metallic Glasses*' is centered at the top in a dark red font. Below the title, there are three bullet points describing the properties of metallic glasses.

- Metallic glasses can be quite strong yet highly elastic, and they can also be quite tough (resistant to fracture).
- Even more interesting are the thermal properties; for instance, just like an oxide glass, there is a temperature (called the "glass transition temperature", T_g) above which a metallic glass becomes quite soft and flows easily.
- This means that there are lots of opportunities for easily forming metallic glasses into complex shapes.

Metallic glasses can be very strong as I said initially, yet they can be highly elastic. Generally we find that strong materials are more brittle and have low elongation, but metallic glasses are interesting because they can be strong, elastic and tough; that means, they can resist fracture and cracking as well. Also more interesting are the thermal properties. For example, just like an oxide glass in the metal glass, there is a glass transition temperature above which a metallic glass become soft, like what we see in other amorphous materials polymers and so on. So, above the glass transition temperature T_g the metal glass becomes soft and flows easily. We can take this material to temperatures higher than the glass transition temperature and mould it into different shapes. So, there are a lot of opportunities for making metallic glasses into complex shapes.

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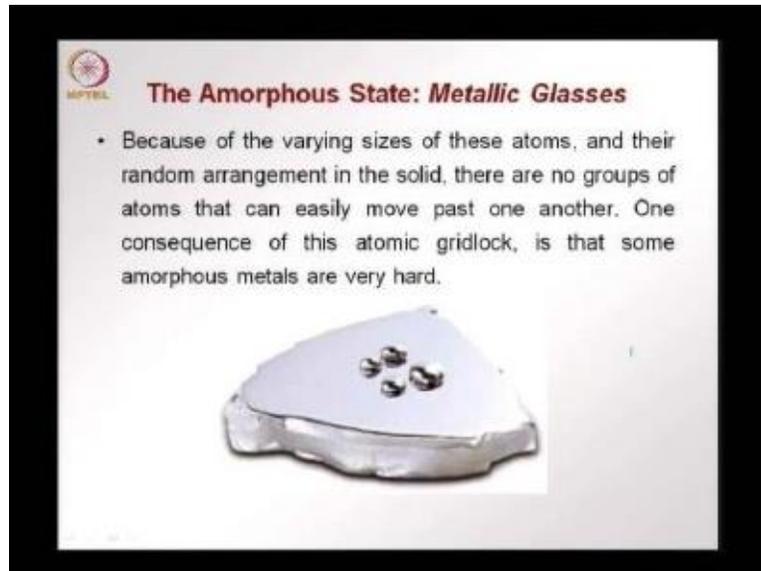
Here you see how the metallic glasses or glassy alloys are placed in the space of strength and elastic limit. On the x axis you have the elastic limit at failure, on the y-axis you have strengths and you see that polymers can be very elastic; that means, they have a very high elongation, but the strength is not very high. Metals on the other hand can have high-strength, but their elastic limit is limited. On the other hand we have these metallic glasses which now have both high strength and high elongation, which makes it very interesting in terms of properties that we need in civil engineering. Obviously, there are other materials which are in the other end of the spectrum like glass and brittle materials, which have neither high elastic limit nor very high-strength.

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One type is called liquid metal. It is a patented product with a mixture of zirconium, beryllium, titanium, copper and nickel and here just to give you an idea, we put the different relative sizes of the atoms of this mixture and you see that the sizes of the atoms are quite different. So, for nucleation to occur, an orderly structure to occur with all these different types of sizes of atoms there is slow cooling that is required to get a

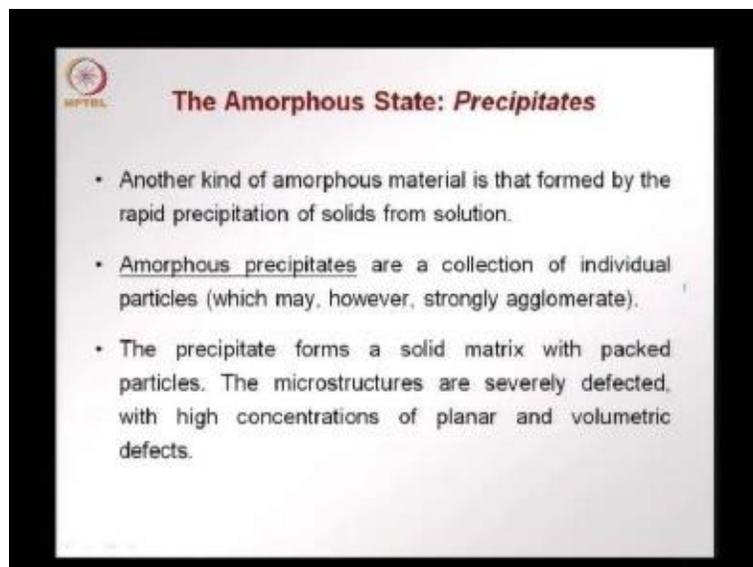
crystalline structure. So, when the cooling is fast this type of material can form metallic glass relatively easily.

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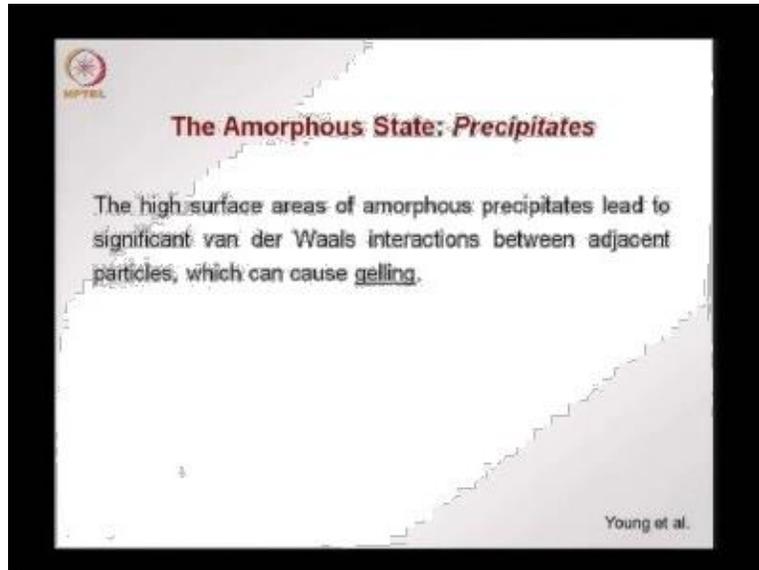
So, as I said because of the varying sizes of these atoms and their random arrangement in the solid, it is very difficult for groups of atoms to move past one and other. Because of this we have what is called atomic gridlock, and this imparts a lot of hardness in the amorphous material. Slipping or sliding of the atoms against each other along planes is very difficult. This is something that we discussed already when we looked at alloys or point defects.

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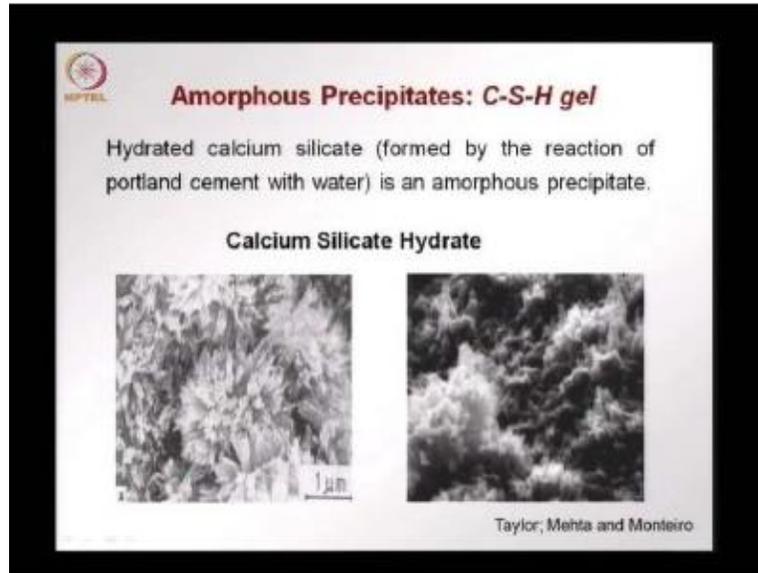


Another kind of amorphous material is that which is caused by precipitation of solids. Precipitation is often to a disorderly structure. Amorphous precipitates generally are a collection of individual particles, which can be strongly stuck together, but still they do not have orderly or a crystalline structure. The precipitate then forms a solid matrix with packed particles. These structures are generally severely defected; that is they do not have very dense packing; they have high concentrations of planar and volumetric defects. Defects such as grain boundaries and pores can occur very easily in such precipitates.

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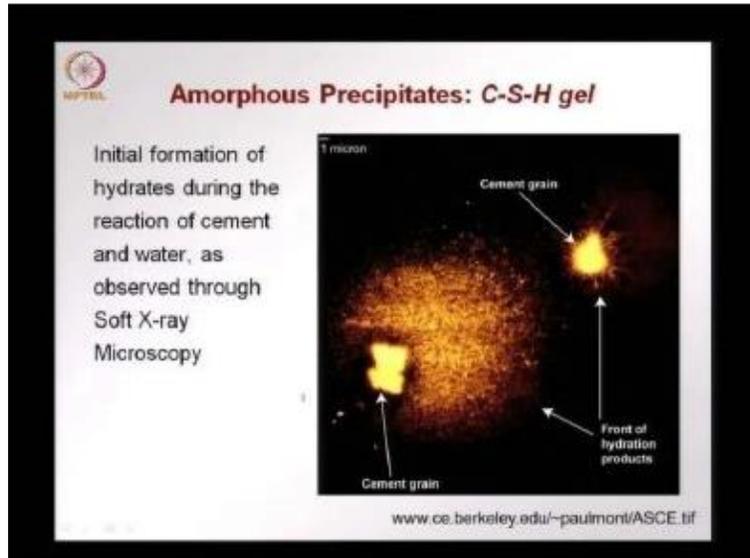


Because of the defected nature, these precipitates have high surface areas and because of this there is a lot of van der Waals interaction between the adjacent particles which gives rise to gelling. A gel you would remember is a material which has liquid between solid particles. Because these materials have a lot of surface and volumetric defects, you can have a lot of gels being formed due to precipitates.

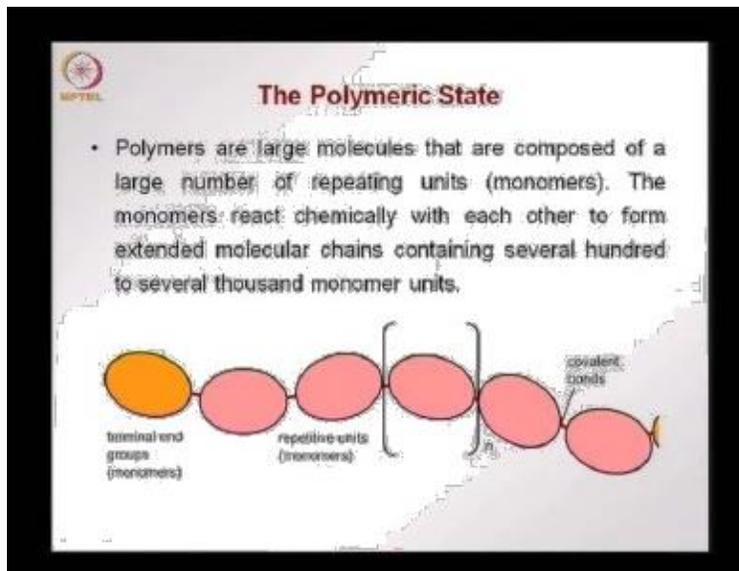


One important gel in the area of civil engineering materials is the calcium silicate hydrate which is formed as an amorphous precipitate due to the reaction of Portland cement and water and this is the glue that binds the hydrated cement paste and therefore concrete together. The pictures at the bottom are taken from Taylor, Mehta and Monteiro, where you see the gel structure of the calcium silicate hydrate. You see the sponge structure here, with lot of particles put together, lot of clumps of calcium silicate hydrated gel. Within these layers you have a lot of water, called the gel water and there is a lot of porosity outside also. Though this structure is much defected and porous it gives the strength required to make concrete very useful material.

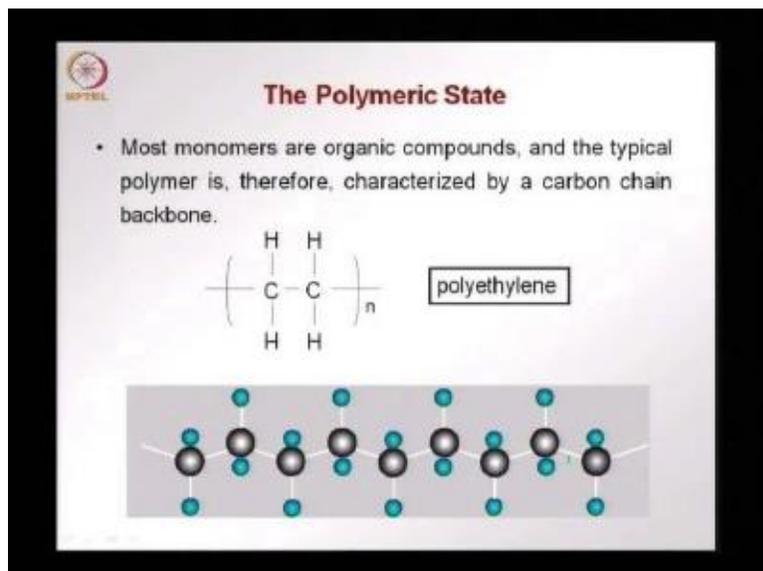
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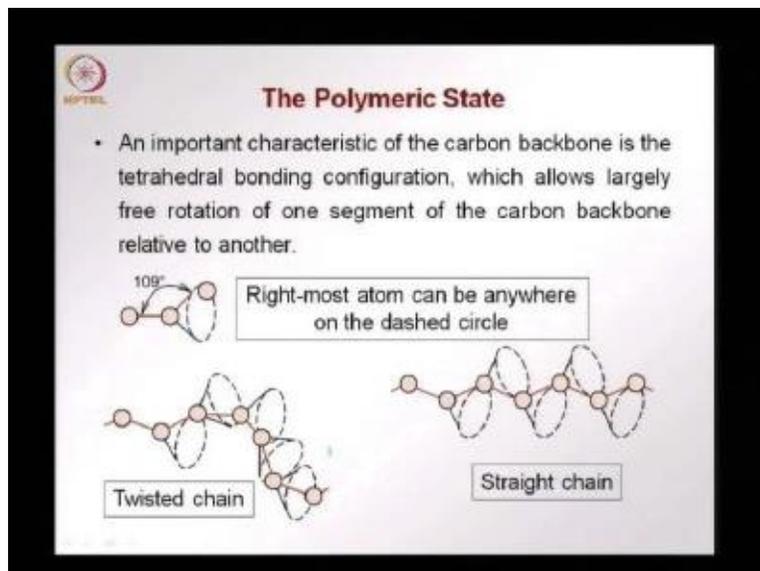
This is a very interesting picture from soft x-ray microscopy from Berkeley from the paulmont group, where you see the initial hydrates forming when you have a cement grain in water. So, these dark yellow one's are the cement grains and this is in water and you see the gel forming. This light brown structure that you find is the amorphous precipitates forming, as the cement now reacts with water.
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Now, we go on to a different type of materials, the polymers. Polymers are large molecules, chain molecules which are made out of several repeating units called monomers. So, each of this is the monomer and together when they join together we call them polymer. The monomers react chemically with each other, we saw before that there is covalent bond which develop between the particles and form these molecular chains which can have several hundred to several thousand monomer units. So, it is a repeating unit of this type which keeps recurring through the polymer chain. So, this is very different from the structure that we have discussed before.
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Most of the monomers involved are organic compounds and the typical polymer is therefore characterized by a carbon chain backbone; that backbone is the central structure of the polymer; which is made up of carbon atoms. What we see here in this diagram is how polyethylene looks. So, these are the hydrogen atoms, this is carbon and we have hydrogen on the other side. So, this forms a chain and you remember when we discussed about covalent bonds that long strong chains can form due to covalent bonding and the other thing is that the covalent bond was directional. So, there is certain directionality in how these monomers are bonded together.
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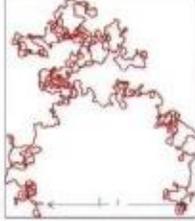


And this gives rise to a very interesting characteristic of polymers. One of the important aspects of the carbon backbone is that there is a tetrahedral bonding configuration; that you see here and this allows for free rotation of one segment of the carbon backbone relative to another. So, if you see this diagram you find that the rightmost atom, this atom can be anywhere on this dash circle for this angle to be maintained (refer the slide for better understanding). So, if this is rotated on this circle by maintaining the 109° angle, you find that there is a lot of movement or strain obtained without breaking any bond. So, this leads to either change like this, which can be relatively straight, maintaining this angle or the same chain can be twisted into this and in this process we're not breaking any bond. So, there is a lot of flexibility that is obtained because of this type of formation of the polymer chains.

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 **The Polymeric State**

- Single chains are capable of rotation and bending in three dimensions.
- Entanglement of chains prevents crystallisation and causes high viscosity in the liquid state.

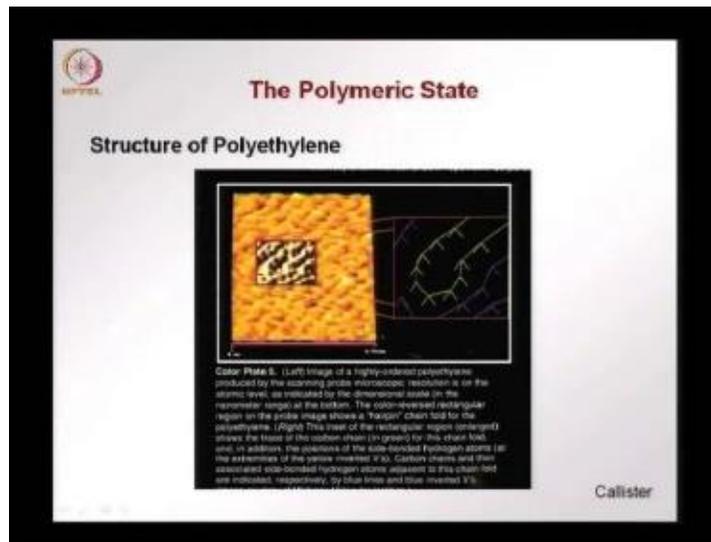


Callister

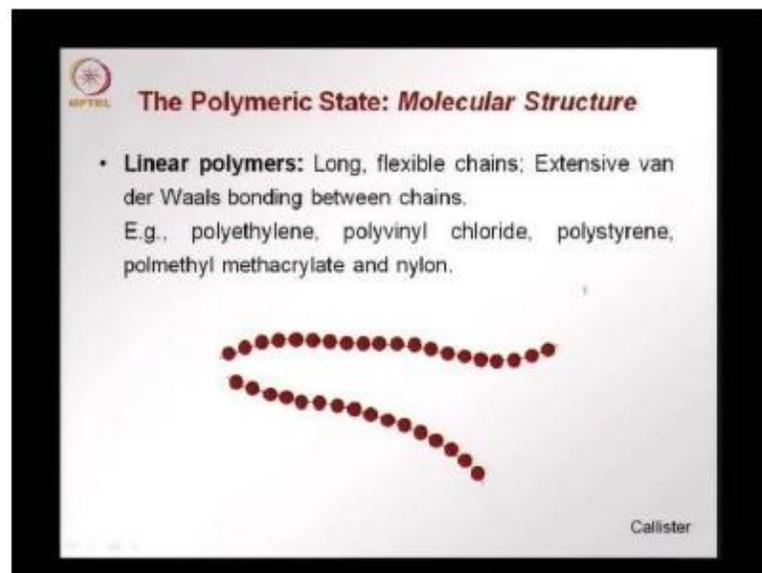
Consequently the single chains of polymers which are very long or capable of very large rotation and bending in three dimensions can undergo lot of displacements, lot of strains without braking also this long chains now get entangle. They get caught among themselves and this entanglement prevents crystallization of the polymer, reduces the possibility of all these chains getting aligned in an orderly manner, because they get entangle very easily. You can see in this picture how there is the polymer chain, which is entangled by itself and you can imagine how difficult it will be for all these chains to be aligned in orderly structure and this also gives rise to very high viscosity. Because as these chains get entangle it is very difficult for the liquid to move easily, these chains

get entangle among themselves and with neighboring chains. So, that the material does not flow very easily. So, two of the very important consequences of the covalent bond within the polymer plate is that; it gives rise to lot of ability for the chains to rotate and bend and this prevents crystallization. The level of crystallization in polymer is reduced, they become more amorphous and very importantly they become highly viscous as the polymer chains are formed and are made to flow.

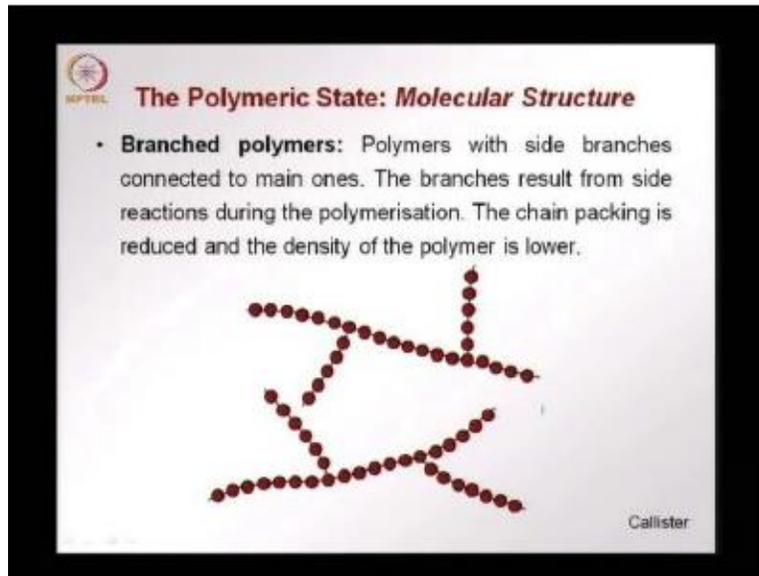
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This is an image taken from scanning probe microscopy from Callister, where you can see the chains entangled; these are different chains of polyethylene which are here. Even though the chains are very large you see some sort of an orderly structure. (Refer Slide Time: 18:56)



There are different types of molecular structures which occur. The simplest structure is a linear polymer, where you have long flexible chains with extensive van der Waals bonds between the chains. If you remember we said that, within a polymer chain you have covalent bonds. But these chains bond with each other with a weak van der Waals bonds. So, this happens in many polymers that we come across, such as polythene or polyethylene, PVC- polyvinyl chloride, polystyrene, polymethyl methacrylate and nylon. So, these are linear polymers.
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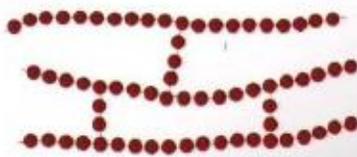


You can have polymers with side chains also, these are called branched polymers, where we have these branches occurring from the main chain. So, there are side reactions which cause these branches during polymerization and you can imagine that it will be now more difficult for such structures to be ordered and become crystalline. So, that is why we see higher degree of crystallinity, orderliness in linear polymers than other type of polymers like branch polymers. In branch polymers it will become more difficult for an orderly structure to form, because of this branches which will get in the way of the polymers being aligned and packed.

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 **The Polymeric State: *Molecular Structure***

- **Cross-linked polymers:** Adjacent linear chains are joined to one another by covalent bonds. This cross-linking is achieved by additive atoms or molecules that are covalently bonded to the chains.
E.g., rubbery elastic materials.



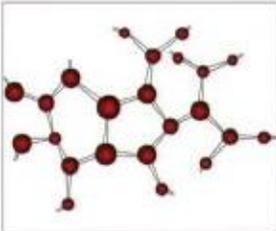
Callister

We also have crossed linked polymers, where we have covalent bonds between different chains. Instead of the covalent bonds only occurring along the chain, now we have covalent bonds which are linking different chains together. So adjacent linear chains are joined through covalent bonds and this is called cross-linking, which is achieved by additive atoms or molecules that covalently bond with a chain, and one example of this is rubbery elastic materials, which have a lot of elasticity and can undergo a lot of strains.

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 **The Polymeric State: *Molecular Structure***

- **Network polymers:** Trifunctional *mer* units, having three active covalent bonds, form three-dimensional networks.
E.g., epoxies.



Callister

We have network polymers; polymer that linkup together to form a three-dimensional network and here because of the covalent bonds you can have a very strong material. So, here we have tri functional mer units with active covalent bonds, you see that each has three active bonds and you get a three-dimensional networks such as in an epoxy and all of us have huge plastic which are hard and strong in many applications such as in epoxies.

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The Polymeric State

Major Classes of Polymers

(a) **Thermoplasts** (will melt under high temperatures)

- Polymers derived from single monomers are homopolymers.
- When different monomers are used in the synthesis of a polymer, it is called a copolymer.

homopolymer

Statistical copolymer

Block- copolymer

Two major classes of polymer can be made depending on how they function under high-temperature, first is called the thermoplasts. Thermoplast polymers are homo polymers where we have the same type of monomers in the chain. They could be a mix called a copolymer, this is called a statistical copolymer where we have a random mix of two polymers or we have a block polymer where some part of the chain is of one polymer another part of the chain is of another polymer. So, whenever we have different monomers used in synthesis of a polymer it is called a copolymer and both of these can be thermoplasts. Thermoplasts means that the polymer will melt at the high temperature and when you cool the material it will go back to a solid state. So, that is what is called a thermoplast.

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The Polymeric State

- The crystalline state may exist in polymeric materials.
- Polymer crystallinity is the packing of molecular chains to give an ordered atomic array.

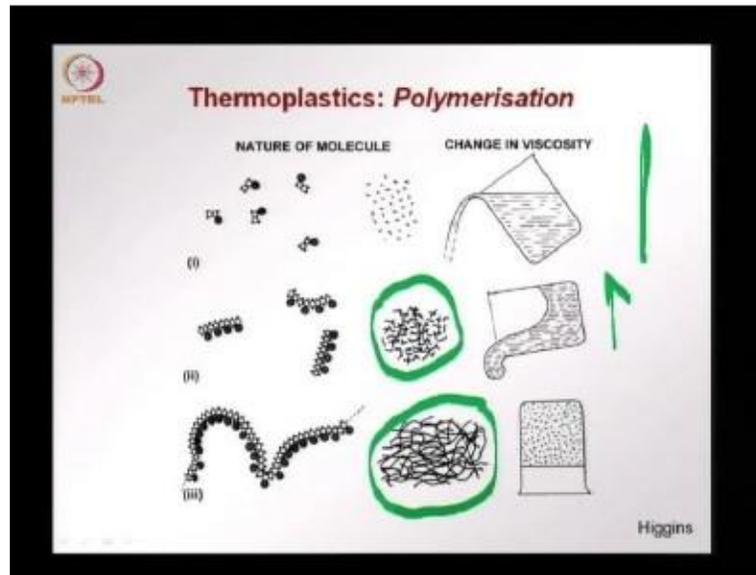
amorphous thermoplastics semicrystalline thermoplastics

Region of high crystallinity Amorphous region

Callister

These thermoplast polymers can occur in amorphous state, disordered, entangled chains or it could be crystal and to some extent, say this part this part is orderly. There are chains which are closely packed together and you see here that this is a crystalline part, the rest could be amorphous. So, that is why it is called semi-crystalline, that is partly crystalline. So, we find that the crystalline state may exist in polymer materials and as far as polymers are concerned, we say a polymer is crystalline when there is an orderly packing and when you have an array of the chains. So, in the same polymer you can have an amorphous region and you can also have a crystalline region and the proportions between these two will tell us what the degree of crystallinity of the polymer is.

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Thermoplasts also have a viscous behavior, when they are polymerizing. Initially when you have just the monomers, you have a lot of flow possible in the material, the viscosity is low. The monomers do not entangle they are all separate and the material can flow easily. As the monomers now start to linkup and form chains, the chains become longer, there is more and more stickiness or entanglement and you find now that the liquid material does not flow that easily or the viscosity is now higher. Now this increases as the polymer chains become longer and longer they reaches state, where they become totally entangled and even though the individual chains are flexible, the whole mass does not move because the chains get entangled and reaches a state that it will not even come out of a vessel that you are put in, because of the viscosity being very high.
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 **The Polymeric State**

Major Classes of Polymers

b) **Thermosets** (will not melt but decompose at high temperatures)



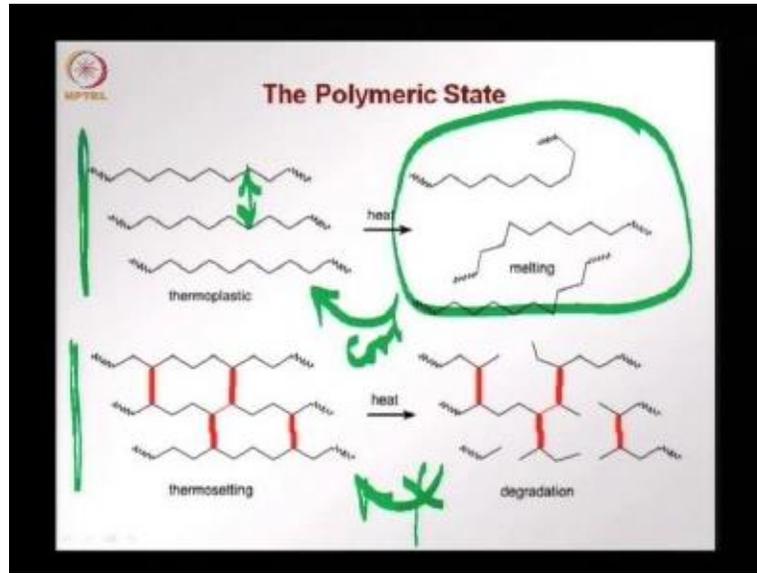
cross-linked polymer

- Thermosetting polymers are plastic in the primary stages of manufacture but once moulded ("set") they cannot be softened by "re-heating".
- Thermosetting is due to covalent bonds between the chains.

The other class of polymers a call thermosets; thermo sets are those which will not melt, but will only decompose at very high temperatures and these are generally cross-linked polymers. They are not the chain polymer that will look as that in the case of thermoplasts. The thermoset polymer is generally plastic in the primary stages, but once molded or set, once the cross-links have been formed, they cannot be softened again. You cannot make them into liquid again by reheating, like we could do in the case of a thermoplasts.

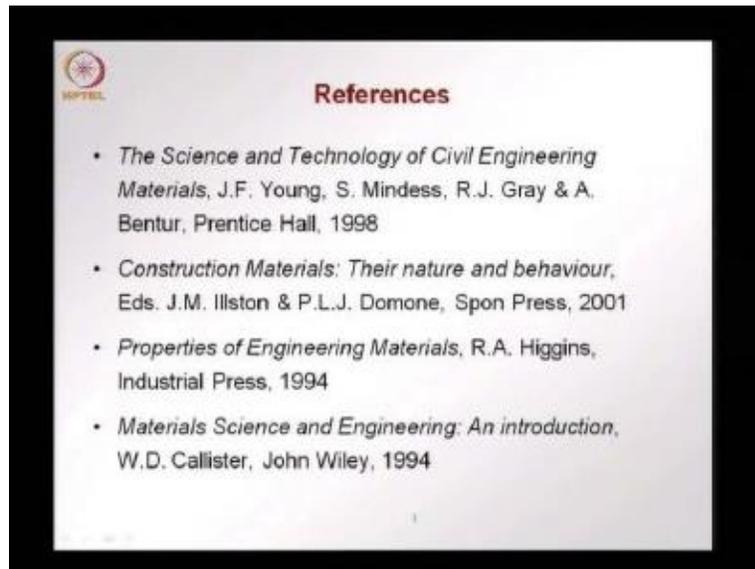
So, once they are set, they stay that way and they cannot be reheated to soften and to the remolded state. This is because of the covalent bonds between the chains. In the case of thermoplasts, we had only van der Waals bonds between the chains. So, these van der Waals bonds could be broken easily. The chains could move around and when the temperature is brought down again the van der Waals bonds are strong enough to keep them in place. Here between the chains we have covalent bond which are not so easy to break and when they are broken they do not form again.

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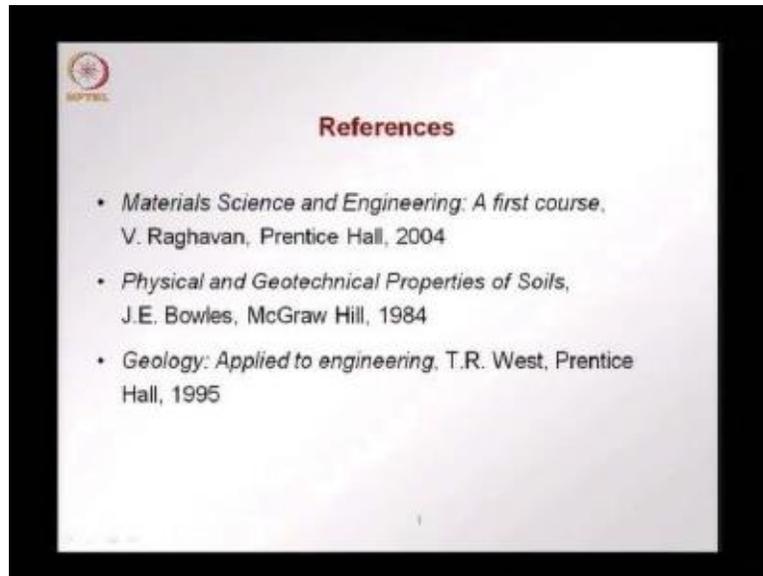
So, this is a comparison of what I have explained. In thermoplasts we have these chains, usually linear polymers and between the chains we have van der Waals bonds and with heat these van der Waals bonds are broken and the chains can move around easily. So, this is what happens when the thermoplast is melt , the chains are separated and when they are cooled again the Van der Waals bonds will keep them together. However, when we look at a thermoset you have the chains bonded to each other by covalent bonds and when the heat is applied, these covalent bonds do not break and join again when they cool, but we have the chains disintegrating. We have degradation of the chains so the chains breakup and when the cool back they do not join again or they do not go back to the same way. In the thermoplasts we can go back when we cool, but in this case they do not go back that is why it is called a thermoset.

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So, with this we have looked at different types of material, different states of materials we have in the last lecture, last part of this lecture we have looked at how polymers are formed. We looked previously at how amorphous materials occur and before that we looked at crystalline materials. These are the different references. Some of these concepts could be difficult to assimilate, you should go through these references.

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There is several of this which will give a good background on how the material structures are formed and what is very important for us to understand as civil engineer is,

how the bonds leads to certain types of structure and how these structures go on to influence the behavior of different materials and this is also interesting when you look at a new material that you have not been taught how it behaves or you have not come across before. Knowing what is the type of material, what is the family; the chemical family that it comes from, you can understand how it will behave. Because there are lot of materials which are being produced on a daily basis and to understand these materials or at least to predict what could happen in this materials, it is good to know what is the structure of the material, how the structure is being formed and we have given you some basics in this lecture on structure of solids.

Now in the lecture that follow, we will go on to see how movement occurs in the solids and other properties link to the structure and later on we will build up on this to take you want to look at different materials that we use in civil engineering.

Thank you

We will take some question on structure of solids from some of us here.

Yeah!

Sujatha: "Sir which type of polymer can elongate more, linear or cross-linked polymer..?" Generally the linear polymers do not have covalent bond between the chains, since we have only van der Waals bonds then they can elongate much more and you also know that when we have network polymers, with lot of covalent bonds like in

epoxies, they are very brittle, even though they are very strong and hard. Sir, “we know that the ionic bond is a strongest what about diamond crystals which are based covalent once, but we still have them strongest material as diamond..?”. See covalent bonds are also strong along the direction of the bonds and in the case of a silica and diamond. We have network which is formed entirely covalent bond and because of that you have a strong material. Generally covalent bonded materials are not very strong because we have the sheets and the chains which are linked only by Van der Waals bonds, but here in the case of diamond we have a network structure that is entirely linked with covalent bonds. I wanted to also tell you one interesting anecdote. I had students come to me after one of these lectures, and if you remember in this lecture that i talked about metallic glasses and the students brought me this mirror from a place called Aranmula in Kerala. So, if you're not familiar with India, Kerala is a one of a southern states and here we

have something that is very typical of a certain town called Aranmula in Kerala, where they make this mirrors and what you see in the middle is not glass, it is not a glass mirror, but it is a metal mirror and this is made after when alloy of copper with very high tin content and it is very well polished to become this mirror type surface. What I have understood that it is also very brittle material and it retain its shiny surface, but if you drop it, it can break very easily and we have one of our students from this place Aranmula and may be Sunitha can tell us a little bit about the village and anything else you know about this mirror.

Aranmula is a village in Pathanamthitta district. Pathanamthitta is a where Sabarimala is also situated. So, the main industry of this mirror manufacturing is around Parthasarathi temple, where you have Krishna and Arjuna. That is only temple in India which has Arjuna's idol and this mirror has a importance that in Kerala marriage ceremonies we have something called Ashtamangalyam, where when the marriage takes place, there are eight auspicious things that are kept on a on a plate and which is used to receive the bride and the bride group. So, this mirror belongs to one of the Ashtamangalya things. So, it is considered to be very auspicious and also it brings in luck if you have it at home. So, that is the myth behind the mirror. I do not know the much about the manufacturing because it is very kept very secretive. It is belonging to only one family and they have been passing on through generations this secret.

Good , thank you .

So, what we do know is that it is an alloy of copper with very high tin content and as Sunitha said, not much is known about the exact proportions and it is kept as a family secret, but also what we know is that, it can be polished, it can be made into a very reflective surface like what you see here, but it is also a very brittle material, because we have introduced in this material so much of tin that is basically unstable in terms of the lattice. Because you have put a lot more tin than it is stable for the lattice structure of copper and that is why it becomes very brittle and it is not able to create the shearing or the slip planes within the material. So, if it is dropped, it breaks very easily which is not typical of a metal, so going back to the question that the student asked me, this is not the metallic glass, but it is a reflective surface. Particularly in this case it is a copper tin alloy.

Thank you very much