

An Introduction to Materials: Nature and Properties (Part 1: Structure of Materials)

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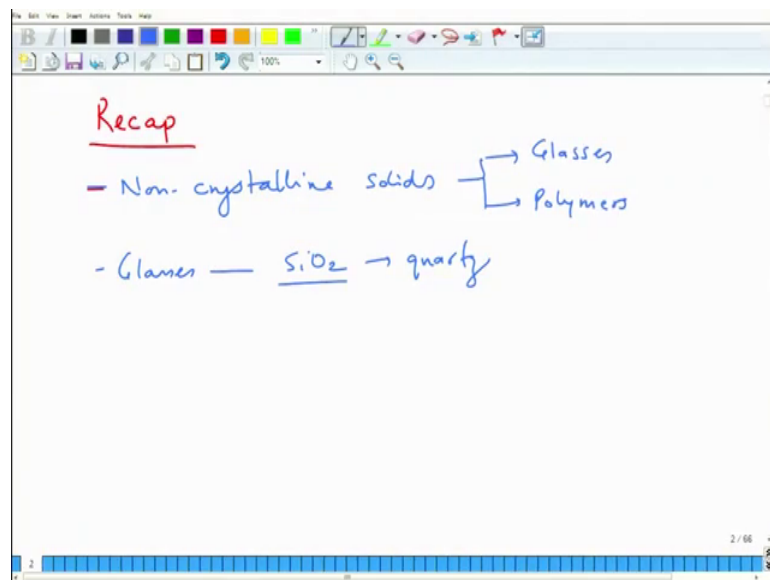
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Lecture - 29

Non-crystalline Solids Glasses Polymers

So, today again we begin with another lecture; which is a continuation of the previous lecture in which we talked about non crystalline solid structures mainly glasses. So, we will just finish that part in this lecture and we will start a new topic on polymers structure of polymers. So, let me just give you a brief recap on what we talked about?

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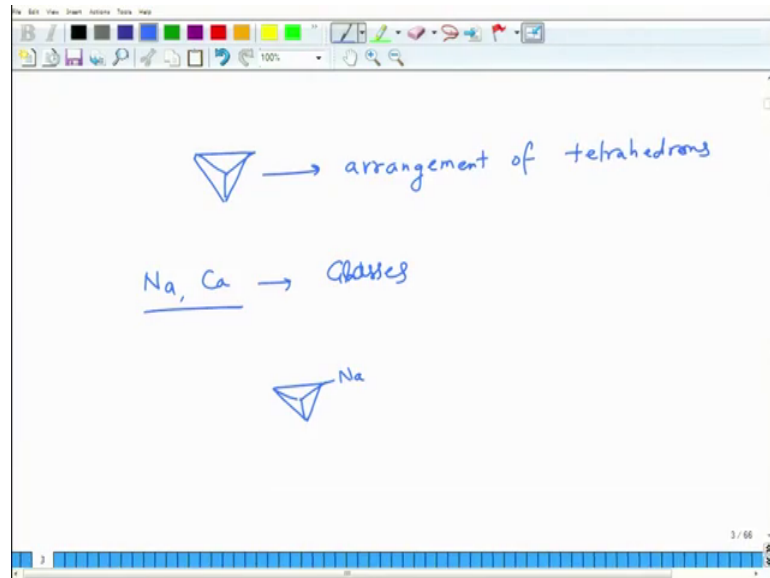


So, we introduced the topic of structure in non crystalline solids. And here mainly 2 categories we are going to talk about: one is the glasses and second is the polymer because many of these materials; glasses do not have any long range periodicity and polymers again most of the polymers do not have a long range periodicity; they have short range ordering possibly.

So, these materials so, we started with glasses, glasses are mainly based on SiO₂ units and it is the and the silicon is basically tetrahedrally coordinated. So, depends upon the sharing of oxygen atoms between tetrahedras; what kind of structures silicon oxide can give raise to? So, there are plenty of structure that we looked at in the last lecture

dependable the coordination of oxygen atom it can make a completely 3D crystalline structure as well which is in the form of quartz, if all the tetrahedras were beautifully arranged in a hexagonal fashion now ah.

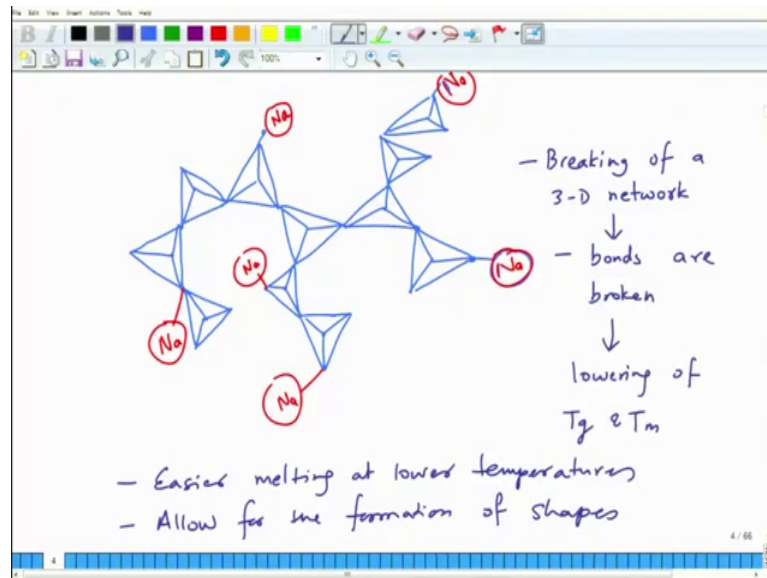
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So, you have basically this kind of arrangement, this is that silicon that silicon silicate tetrahedral. So, these are all corner of tetrahedron at the centre of the tetrahedron you have silicon ions sitting. So, it is essentially the arrangement of tetrahedras tetrahedrons which governs basically; how what kind of structure will be formed?

So, we add impurities like sodium and calcium to glasses because they can break this network and. So, for example, you might have situations like this in which you have a tetrahedral and since it has 4 corners which need to be satisfied, silicon disk for example, sodium or potassium can sodium or potassium or calcium can attach themselves these corners satisfying some of the bonds, as a result you do not you have no longer this condition of having to satisfy 4 corners.

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So, as a result that structures that you might form may look like something like that for example, you have a you know you no longer need 4 corner sharing as a result you might have things like these ok. So, and in one of them you can have let us say a sodium linker so, the sodium linker can possibly go here as well. So, you can see that you can satisfy some of these so, some of these corners using sodium linkers. So, you do not necessarily have to go through can remain so, you no longer need.

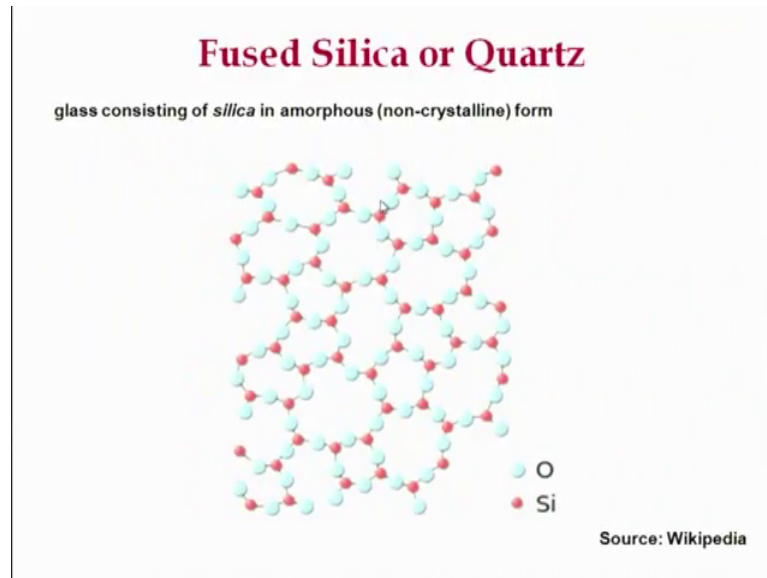
So, they may remain arbitrarily coordinated in the 3D space, they do not have to follow a hexagonal pattern. So, you might have so, this might have correlation in some other direction like this, this might have correlation in some other direction in this fashion, again you might have a sodium atom here and so, on and so, forth.

So, this can have relation with another this thing you can have a sodium here and so, it does not need a basically a 3D network to continue the to make the structure. The angles are arbitrary as well; you have a random sort of network with branches all over the you can have something like that. You have 1 sodium here let us say and so, on and so, forth we can have a sort of breaking of a tetrahedral bonds, as a result you do not necessarily have to have 4 fold coordination with 4 tetrahedras. And this basically allows so, what does it result in it results in breaking of a 3-D network.

As a result it result as a result it leads to in so, basically the bonds are broken and this results in lowering of T_g and T_m . So, these basically they introduce weaker bonds in the

network. So, easier melting at lower temperature allows for the formation of shapes at lower temperatures. So, there are variety of these glass modifiers which are put into a system, I will show you some compositions in the in the next few slides. Now the next thing the silica can also make a random network where hexagonal network will be maintained, but it will not be ordered it will not be hexagonally ordered.

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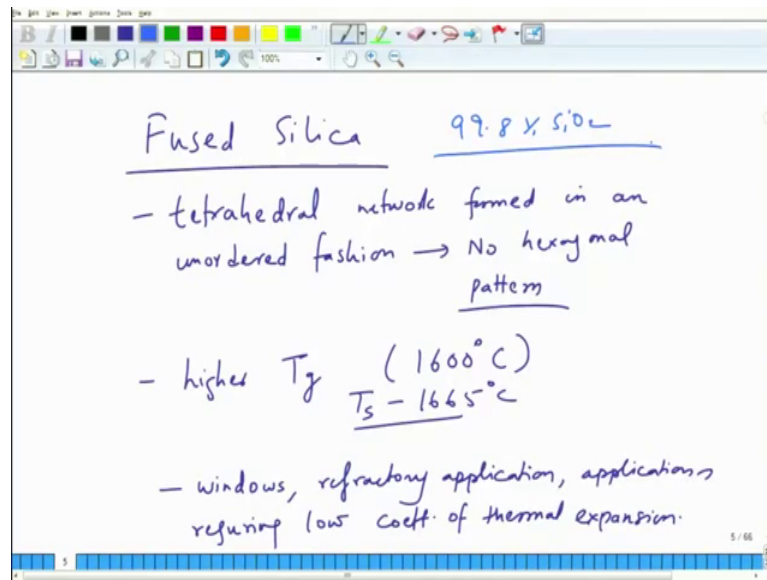


For example you can have a pattern you can have a situation like this in which you have a few silica or quad structure in which there are no impurities it is 99.8, 99.9 percent pure silica. So, basically it is a glass which consists of silica only, but in amorphous and or non crystalline form.

So, here you can see that you have each oxygen atom ah. So, these are the silicon atoms the these ones and these are oxygen atoms. So, each oxygen atoms are shared by 2 tetrahedras on the sides and then 1 on the one and there will be 1 on the top as well right. So, they make a hexagon they make a network in 3 dimensions, but it is not a hexagonal network and this ah. So, they do satisfy the requirement of each oxygen being coordinated between 2 tetrahedras, they do satisfy that requirement; however, that requirement does not take place does not get fulfilled in an ordered fashion. As a result you form a structure which is which does not look like a hexagonal network of tetrahedras and hence this form of silicon silicate glass is called as fused silica or quartz basically fused quartz ok.

So, it does not have a crystalline structure it is used for lot of applications because it is cheaper for application which requires high temperature softening. So, this has relatively higher temperature of softening as compared to your sodium or potassium or calcium substituted trusses. So, wherever you so, these are used as for instance ah.

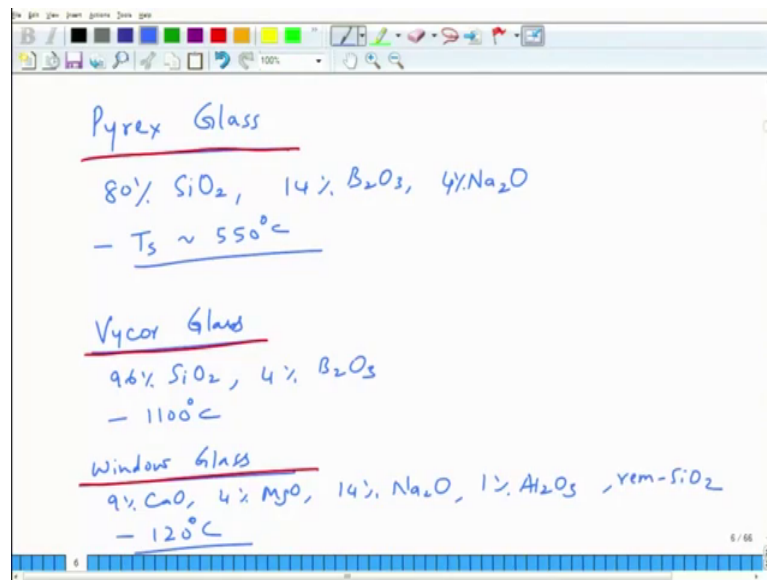
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So, this fused silica is basically is you can say it is a tetrahedral network formed in an unordered fashion. So, there is no hexagonal pattern there, but the requirements of coordination's are fulfilled and these are. So, they have relatively higher T_g so, there is often at higher temperatures as a result they are used in ah.

So, higher softening temperature is about 1600 degree centigrade. So, to be precise at 1665 is the softening temperature T_s. So, as a result these can be used for applications which require high temperature ah. So, they are transparent as a result they are like glasses, but they can withstand very high temperatures. So, for example, windows refractory applications and since applications which require low coefficient thermal expansion because they have higher softening temperature, their coefficient thermal expansion is lower. So, application requiring lower coefficient of thermal expansion. So, this is the 3D network of the tetrahedras not arranged in an ordered fashion, but in a disordered, but in an unordered fashion.

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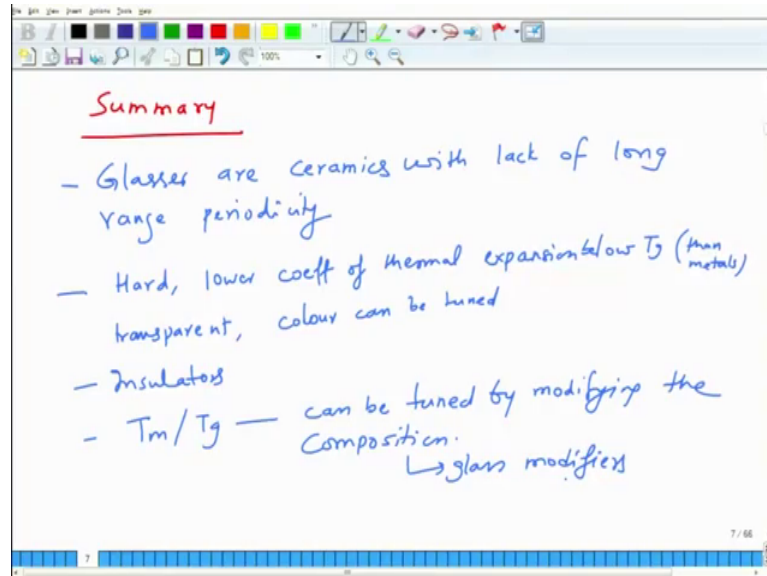


So, there are typical glass compositions which I will now list. So, there are some glass compositions first one is Pyrex glass, which is a very well known name that you might have heard of Pyrex glass, this contains 80 percent silicon oxide and it contains 14 percent of boron oxide and it contains 4 percent of Na₂O and this has a softening temperature of around 550 degree centigrade. So, this is something which is used in laboratories quite extensively where you require the material to withstand it is form until about 400, 500 degree centigrade. So, Pyrex glass is something that we use in our laboratories, chemists and material scientists use it quite extensively ah. Then we have Vycor glass this Vycor glass as it contains 96 percent silica and 4 percent boron oxide, this softens at about 1100 degree centigrade.

So, higher than Pyrex glasses. So, any temperature where you require even higher temperature stability you use this boron substituted silica silicate glass and then typical window glass that we have window glass is basically 9 percent calcium 4 percent magnesium and 14 percent Na₂O, 1 percent alumina and remaining silicon oxide this has a softening temperature of about 120 degree centigrade. So, it is useful for only low temperature applications all right ah, but it is it is can it can be formed in shape into the into shapes very easily at lower temperatures as a result it is very popular glass and then of course, you have fused silica which I showed you earlier which is 99.9.

So, fused silica is essentially 99.8 percent SiO_2 ok, these are the crystal non crystalline structures that we have so, basically you can say that glasses are.

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Now, in summary you can say that glasses are ceramics with lack of long range periodic struct periodicity yeah they contain same attributes as of ceramics, they are hard, they have ah. So, they are they are hard harder than metals, they have lower coefficient thermal expansion provided you use them below the softening temperature.

Then metals below T_g or T_s than metals, they are transparent and color can be tuned by putting impurities and there of course, insulators thermal and electrical insulators and. And then they have their melting point T_m or T_g melting point of glass transition temperatures they have different definitions in the glass sense, but it can be tuned by modifying the composition and as a result by.

So, basically the elements that you have add are called as glass modifiers such as sodium, calcium, boron these kind of materials these kind of elements. You can see that typically the elements that you are putting have variance lower than that of silicon ok.

Student: sir what is the use of this glass transition temperature?

Ah glass transition temperature you need to know because this will determine at what temperature the glass will softened. So, it is basically a indicator of softening of class. So, wherever it is also it is useful from the perspective of forming shapes what kind of

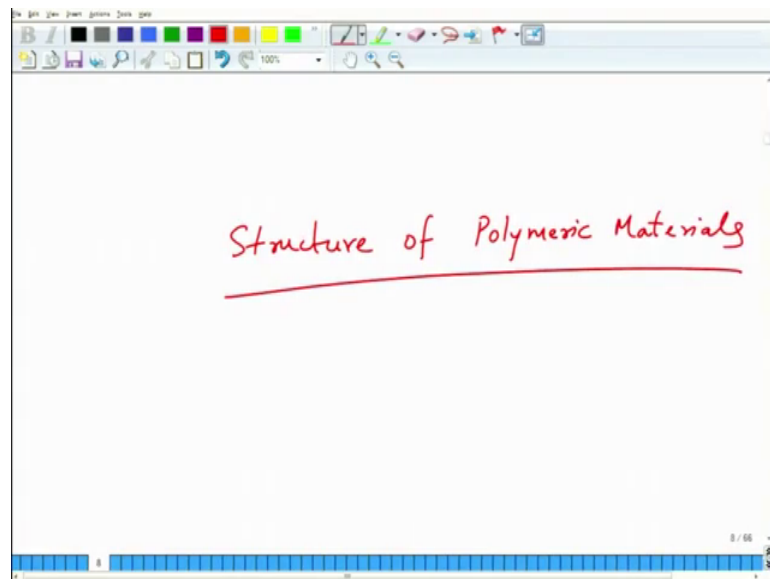
temperatures you need to use, it is useful in the perspective of determining the surface temperature of glass, suppose you want to use glass as a window and if glass has a transition temperature of 50 degree centigrade then it is no use in this country because the temperature reaches in this country surface temperature can reach as high as 60, 70 degree centigrade during summers.

So, depending upon the type of application for example, if you have a furnace or a vacuum chamber wherever you have some high temperature phenomena going on and you want to put a window there that window cannot be a low temperature glass, it can be it has to be a high temperature softening high glass transition.

Student: (Refer Time: 16:39) softening temperature?

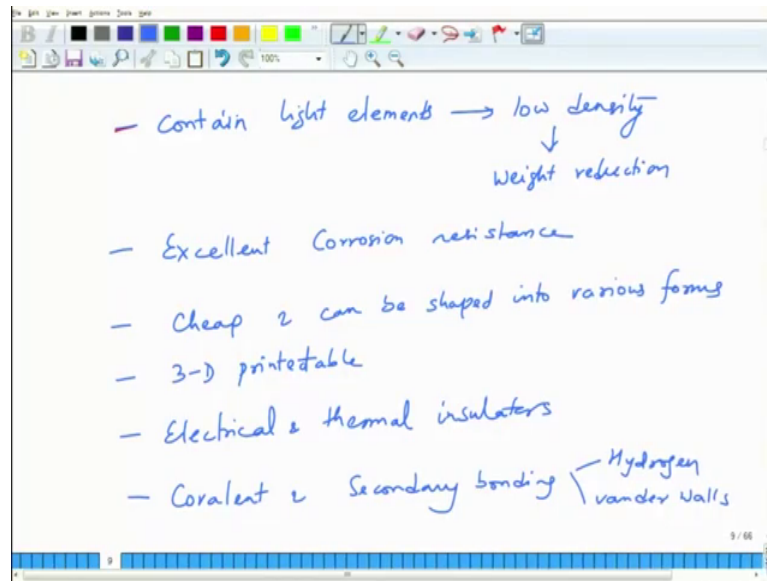
Sort of yeah glass transition temperature is indicator of softening temperature, then move to next class of materials structures which are basically you can say structure of polymeric materials.

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So, we will start with a new topic Structure of Polymeric Materials, a polymers of course, are very important as we know they are used in variety of applications. So, they basically contain elements which are light elements which are carbon, hydrogen, nitrogen, some cases oxygen as well.

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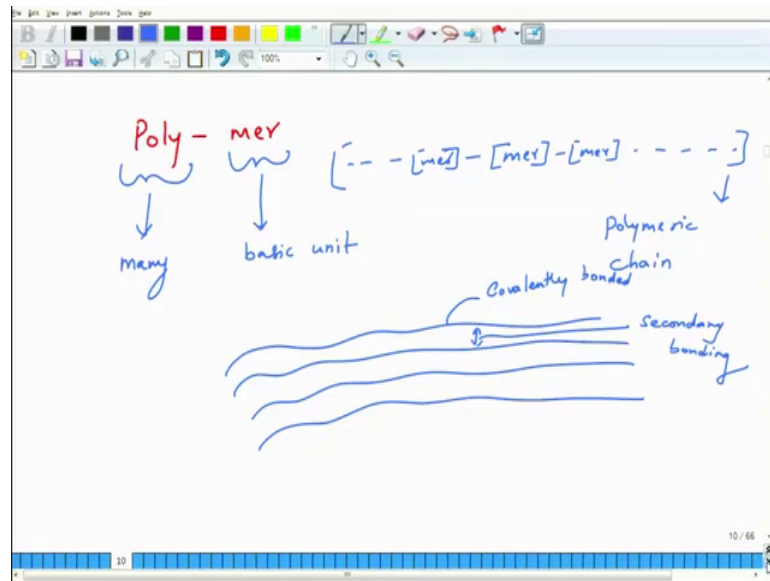


So, they so, polymers as we know they are basically contain light elements which means they have low density. So, they can be used for weight reduction so, which allows you to have weight reduction ok. Then they have excellent corrosion resistance for example, Hf, Hf cannot be stored in glass bottles it can only be stored in plastic bottles.

So, they have excellent corrosion resistant and they are cheap, because they can be formed at lower temperatures the processing is easier and can be shaped into various forms. In fact, 3D printing nowadays which is a very important manufacturing method which has the revolutionized manufacturing polymers can be 3D printed very easily. So, 3D printing is something so, basically they have 3D printability and they have lot of other attributes such as they are electrical and thermal insulators and the bonding they have is basically they are mix of covalent and secondary bonding right, secondary bonding could be your hydrogen or Vander walls type.

So, these are certain attribute of polymers and which are which and there is an interest in studying polymeric structures what kind of structures they have. So, polymers basically predominantly these are all non crystalline materials.

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So, if you look at the name Poly-mer, Poly means many and mer means basically a basic unit which is which gets repeated. So, basically these are they contain various units of mers. So, one moderator is attached to another mer, is attached to another mer and this process goes on for thousands of units and they make a basically chain this is basically a polymeric chain which is typically covalently bounded within the chain, but if you have many such chains 1 chain, second chain, third chain. So, the chains are covalently bonded, but between chains you have secondary bonding. So, this secondary bonding between the chains allowed to be flexible there is a flexible in the structure of polymers. So, basically there are now depending upon how they how do is change our arranged in space and the polymers could be a linear polymer.

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Linear Polymer (Chain type)
- arrangement of monomers in ~~the~~ a chain in a curvilinear fashion

Network Polymers
- Arrangement in a cross^{linked} network in 3-D

The whiteboard contains handwritten text and diagrams. The first section is titled 'Linear Polymer (Chain type)' and describes the arrangement of monomers in a chain as curvilinear, accompanied by a wavy line diagram. The second section is titled 'Network Polymers' and describes their arrangement as a cross-linked network in 3D, with a diagram showing a grid of interconnected lines.

So, it you can have a linear polymer which is also called as chain type structure. So, basically it requires that monomers monomer means 1 mer ok. Arrangement of monomers in a in a chain in a chain in a curvy linear fashion like this and then you have what we call as network polymers, this network polymers have arrangement of monomers in a arrangement in a in a across network in 3D. So, there is a cross crossing so, you have these. So, they are branched in 2D and they have also branched in other dimension. So, they basically a branched cross linked network in 3 dimensions you can say cross linked ok. So, let me now define polymers.

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Thermoplastics
- Soften with ^{increasing} Temperature followed by melting
- little cross linking
- Ductile
- Polyethylenes, polypropylenes, polycarbonates, polystyrenes

Thermosets
- large degree of cross linking between the chains (10-50%)
- high rigidity
- hard & brittle
- Donot Soften with heating
- Decompose at high T

The whiteboard compares thermoplastics and thermosets. Thermoplastics are described as softening with increasing temperature, having little cross-linking, and being ductile. Examples include polyethylenes, polypropylenes, polycarbonates, and polystyrenes. Thermosets are described as having a large degree of cross-linking (10-50%), high rigidity, being hard and brittle, and decomposing at high temperatures. A diagram shows wavy lines for thermoplastics with a red arrow pointing to them labeled 'very little X-linking', and a grid diagram for thermosets.

There are so, these polymers typically are characterized as the first category is known as thermoplastics and the second category is known as thermo sets ok. Thermoplastics have generally thermoplastic they can be softened so; they softened with temperature with increasing temperature with increasing temperature. So, they have a sort of melting light phenomena they melt at very high temperature. So, and followed by melting so, they can be formed in various shapes just like a liquid metal it is casted into solids they have very little cross linking between chains. So, if you have chains of polymers, there is very little cross linking.

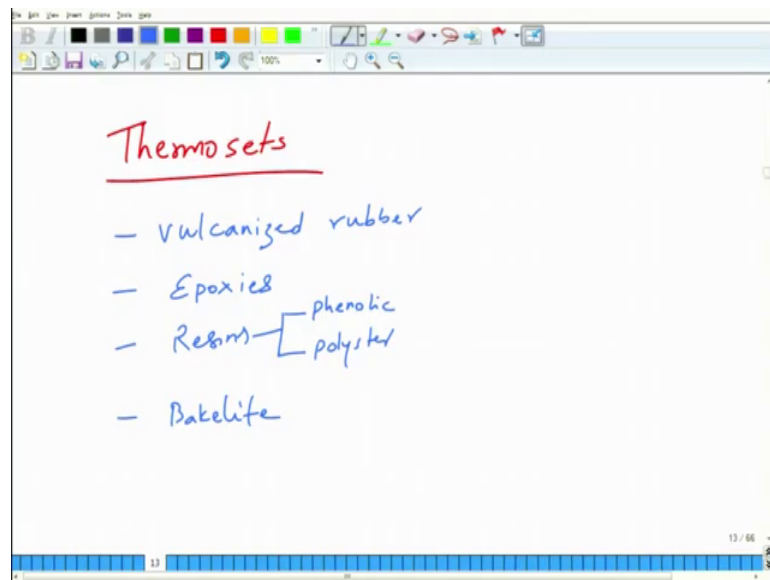
So, you can say very little cross linking, you can say cross linking and then they are typically ductile means they have high ductility, they have high they can withstand high strain ok. And the examples typical examples include polyethylene, polypropylene, polycarbonate, polyethylenes, polycarbonate, propylene, polycarbonates, polystyrenes. You will see typically the name is poly right like many ethylene molecules, many propylene molecules, many carbonates, many studies put together ok.

So, this is the category which is called as the thermoplastics thermo sets on the other hand they have a behavior, they have very large cross linking large degree of cross linking between the chains. So, the chains that you chains the chain that you see here they have cross linked, they are linked by some other branches. So, these branches so, as a result they are rigid.

So, higher rigidity because these cross links do not allow them to allow the chains to move as freely as in a so, it could be the cross linking could be 10 to 50 percent of the total number of mers ok, nearly 50 percent mers can be cross linked as high as 50 percent in a very heavily cross linked structure. So, they have higher rigidity, they are as a result hard and tend to be brittle and they do not soften with heating and they generally degrade at high temperatures they decompose at higher temperatures ok.

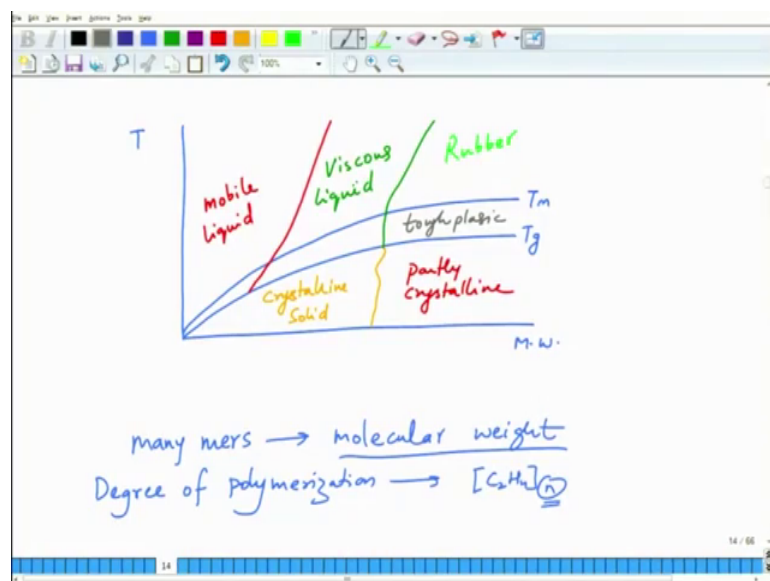
So, the examples of thermo sets let me give you some examples of thermo sets.

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The examples are for example, vulcanized rubber, many epoxies and resins for example, phenolic resin, polyester resins. If you are a metallurgist you might have used the resin to set the sample right, it is used for metallographic samples and that resin becomes very hard after curing and if you heat it up it just degrades, it does not melt ok. Similarly, any epoxy Bakelite, Bakelite another example of Bakelite was used in a lot of electrical applications it can withstand high temperature, but it decomposes at high temperature rather in melting it is not softened. So, these are some examples of so, ah.

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If I now so, polymers since polymers have many formula units many mers as a result they have a molecular weight right and there is a factor called as degree of polymerization. So, degree of polymerization basically is degree to which chains must attach to each other.

So, if you have higher molecular weight which means if you have, let us say C_2H_4 molecule this n is the degree of moly degree of polymerization. So, higher molecular will mean higher value of n so, higher the degree of polymerization higher the molecular weight of polymers will be. So, if I plot for example, as a temperature as a function of molecular weight of polymers, generally they have a behavior which is like this let us say this is T_g T_m melting point is slightly higher then ah.

So, we can basically divide this in various regions let us say this is a region up to which it remains mobile liquid at high temperatures, at lower temperature basically there are 2 regions loosely drawn these are 2 regions. In the first region it is basically a crystalline solid ok, in the second region it tends to become a partly crystalline because if chains become longer and longer and the molecular weight increases it is difficult for them to maintain the crystallinity because of cross linking and because of bending and flexibility of chains. So, it is partly crystalline the crystalline T tends to decrease as the molecular weight increases and at higher temperature it tends to convert into liquidy shape.

So, for lower molecular weights conversion from crystalline to mobile liquid happens at lower temperatures, at higher let us say range somewhere in this range it makes a viscous liquid and that makes sense because you if increase the molecular weight it becomes more and more difficult for change to move. As a result the viscosity of the liquid goes up even the melt form and then at very high this thing it tends to become a rubber shaped material and then in between somewhere it acts like here it acts like a tough plastic ok.

So, these are typically regimes of polymers as a function of molecular weight with respect to temperature. So, at lower molecular weights the crystalline solid or partly or it has certain crystallinity and it tends to convert into a liquid which could be mobile, which could be liquid with low viscosity or liquid with high viscosity depending upon the molecular weight. At very high molecular weights the polymer it is partly crystalline and it tends to have a wider region between the glass transition and melting point. Between these 2 regions it tends to be act like a tough plastic and before it becomes more

rubbery at higher temperatures. So, these are you can say viscosity related behaviors of polymers as a function of temperature and molecular weight.

So, we will stop here in this lecture and we will cover the remaining part in the next lecture.