An Introduction to Materials: Nature and Properties
(Part 1: Structure of Materials)
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Lecture- 31
Structure of Polymers (Contd.)

So, today, we will begin with new lecture, lecture 31 which is a continuation of last lecture, in which we started talking about structure of polymers, just as a brief recap of this last lecture.

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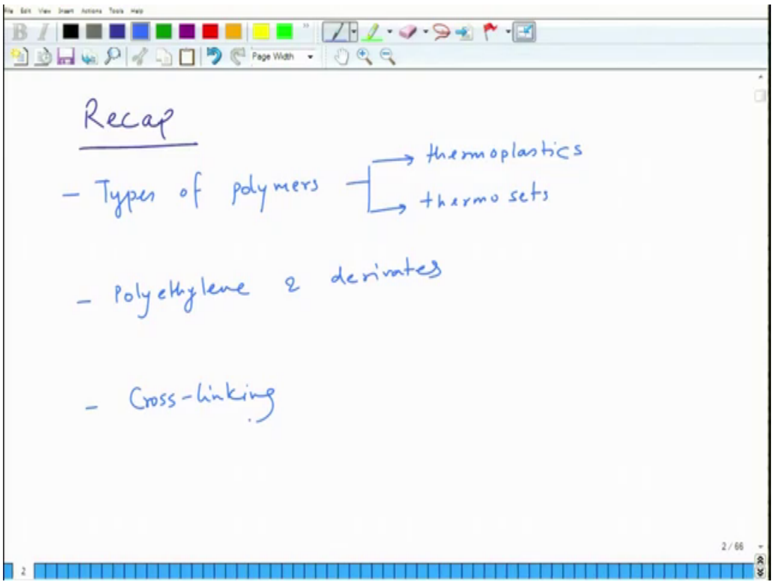

Recap

- Types of polymers → thermoplastics
  → thermo sets
- Polyethylene & derivates
- Cross-linking

So, we talked about various types of polymers and then we look at, there are two major categories one is thermoplastics and second is thermo sets, thermoplastics typically tend to soften with temperature and they are more softer in ductile. They can be formed easily and they have a little cost linking, between polymer chains, on the other hand in thermo sets. They are hard and brittle, they do not soften with temperature and with increasing temperature, they do decompose.

So, they have different applications, depending upon what you require and then we looked at, example of polyethylene and derivatives, where one could see that, one could make, convert polyethylene into various other kinds of useful polymers by replacing hydrogen with other functional groups, such as chlorine, or fluorine, or methyl, or cyanide, and of course, and then, we were looking at the polymers from the perspective of their cross linking. So, generally you have.

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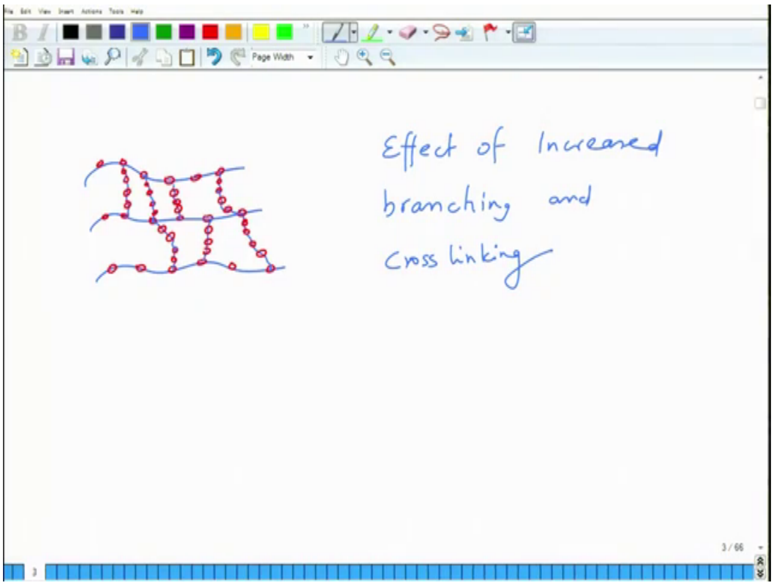

Effect of Increased branching and cross linking

So, your thermo plastics would be something like that. So, there is very little cross linking between the. So, these are mer units, these are running polymer chains. So, they basically make linear thermoplastics ok, linear polymer chains which are, which could be entangled to some extent, but they have a little branching or, cross linking as the ha. Let us say, if you increase the branching, so branching may increase like this. So, branching could be of same functional group or different functional groups depending upon what things are.

So, branching does not need, does not mean cross linking branching, just means there are side branches and these side branches often, make it difficult for the polymer chains to move around as a result their strength increases. Now, there could be cases in which you have cross linking. So, this cross linking can happen like this ok. So, these can, if these turn into cross links like these ok, the cross linking basically means that chains become even more rigid and this cross linking is typically done by other functional groups, such as sulfur in case of vulcanization of rubber.

And this cross linking leads to substantial increase in the strength of the material, because then, polymer chain becomes, polymer chains become even more rigid and then finally, you can have a network structure, just like you saw in case of silicon, you can have quartz kind of form in very rarely in polymers, but you can, there is a possibility, you can have a network like structure. So, these are different types of poly polymer that we did that we discussed.

So, essentially here, we talked about affect off, you can say, increased branching and cross linking ok. So, as degree of cross linking or branching increases that strength or hardness of polymers, typically increases. Now, now, we going to look at some, properties of polymers, which make them, describe an idea which is so, that we can describe them in different manners. So, this is called as the position of side groups.

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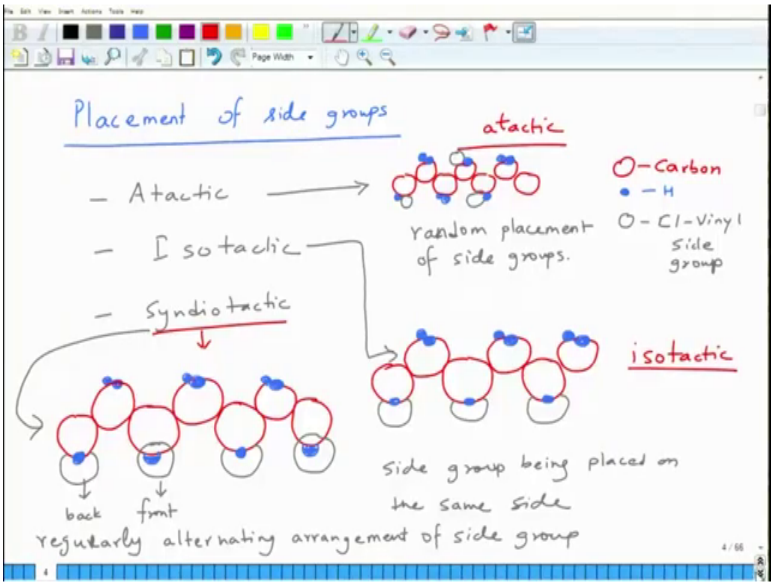

Placement of side groups

- Atactic
- Isotactic
- Syndiotactic

So, we can say basically, depending upon the placement of side groups, polymers can be characterized in three categories; one is a tactic, second is iso tactic and third is syndio tactic. These definitions are used to describe the position of functional groups, on the side the polymers. So, a tactic one would be for example, you have the case of, in this case PVC, you have these as functional units.

So, these are the main atoms, this is let us say the, carbon atom and then we add hydrogen and some of the rackem ok. So, let us say, we have one hydrogen here and another hydrogen on the front and in this case 1 hydrogen on the front and we add one pvc go ok. So, this is basically hydrogen and this is flowing ok. So, when I decide group, you can say ok. Now, it is a placement of these vinayl slider is random. So, for example, here you have it here and in the other thing, you have again, in this case let us say the 1 hydrogen are here and it becomes let us say in this case here and lets say in the other case, it is now, here and hydrogen comes here and other 2 hydrogen goes there and there.

So, if the placement is random vinyl group is placed randomly on the mer unit, it does not matter whether in the front or in the back alternating just randomly. So, this random placement gives rise to. So, basically we can say random placement of, of sign crews. This makes what we call as a, a tactic, structure ok, if you have isotactics that cases you have these as the carbon atoms ok, and on the back of every carbon atom, you had as if you had 1, like this on the back, you had 1 chlorine on the front, you had hydrogen and in this case 1 hydrogen will come like that another hydrogen will come like this all right. So, if. So, on the, this arrangement is basically, side group being on, on the same side.

So, this means it is a isotactic arrangement of molecules or cycles and in some cases you can have alternating arrangements. So, instead of having in this fashion, you may have. So, for instance, in this case, the first one may go there with hydrogen atom being here. The second one may have hydrogen atom sitting on the back and this atom will coming on the. So, this is hydrogen atom and this atom will come on the front ok. So, this is back, this is front. Similarly, in the next one, it will get into the back and here it will come into the, this will come into the front and if you, I, if I make another one ye, just for the sake of clarity.

So, this hydrogen atom will go on the back and this will come on to the front and other two will go in the similar fashion one hydrogen atoms, second hydrogen atom, one hydrogen atom second hydrogen atom ok. So, this alternating, you can say regularly, regularly alternating arrangement of side groups, this makes what we call as a syndio tactic structure. This is, this is isotactic, sorry, what am I writing, just once. Second, this is a tactic, this is iso tactic and this is syndio tactic ok. These are three, um. So, you can have PVC, you can have, if you have benzene ring on the side, if you have the tile growth that can happen in any of the cases. So, you can also make things like copolymers. Now, copolymers, only you attach to polymers.

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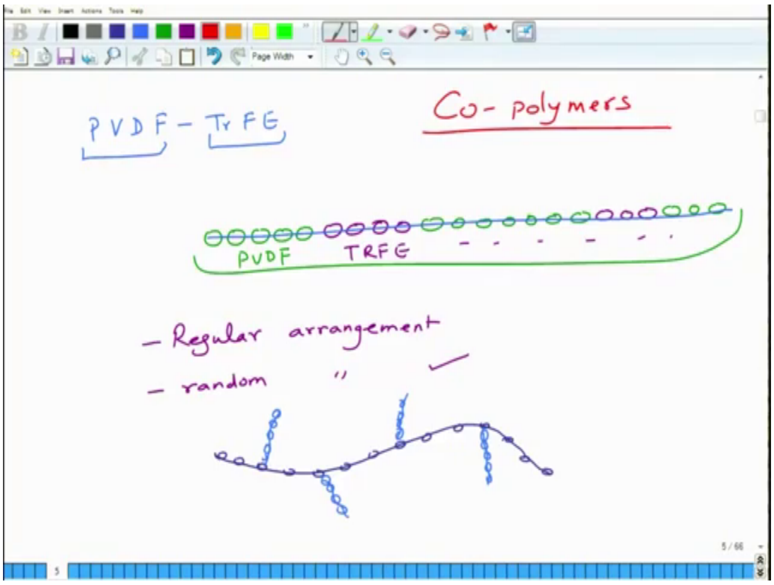

So, for example, we have cases of PVDF TRFE right PVDF is polyvinylidene fluoride and TRFE is trifluor, fluoro ethylene. Now, this, basically these two copolymers can arrange themselves in, in a fashion. So, that they are present in such a manner. So, that there are repeating units of. So, for example, you can have unit of PVDF then, you can happy with a unit of TRFE and there may not be any.

So, it can do itself in this fashion, there is a very straight chain normally, you will not have such straight chains. So, this sort of behavior, where you have this PVDF, you can have TRFE and so on and so forth. This will make a co polymeric structure of two materials. So, copolymers they can be copolymers also can be arranged in such a fashion. So, that you have a regular placement of copolymers or you can have random plate placement of molecules.

So, it could be both regular, arrangement, which is very unlikely and you can have a random and this is what is more common and this leads to loss of crystallinity in polymers, because; so, this is one way of doing it, another way of doing it could be, you have a, you have one polymer chain like this ok. This is one polymer chain and other polymer can attach itself as branches, this is also one possibility ok. So, they can attach along the length in this fashion.

So, you can have along the length. So, they can help repeating units, which will not be exactly repeating, because they are randomly placed in many cases or you can have the sideways arrangement of polymers. So, these are basically you can say copolymers all right. Now, typically as you have seen, molecular weight is effect, we described last time.

So, small molecule, a weight will mean smaller chains and longer higher molecular weight will mean basically larger chains longer chains and it turns out that as you increase the molecular weight, it is, it becomes more and more difficult for the chains to, basically what to arrange themselves? So, they entangle, they are, they are entangled more, when the chains are longer.

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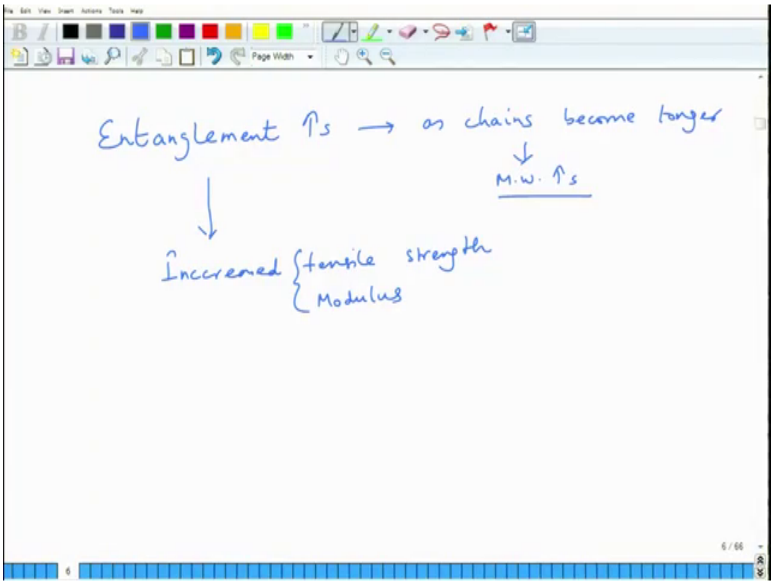

So, basically you can say the entanglement increases as change become longer and what is this? This to do with molecular weight, this is to do with increase in the molecular weight. So, basically and this leads to increased. For example, tensile strength, higher molecular weight for example, higher molecular weight polyethylene will be more stronger as compared to lower molecular weight polyethylene, you have two forms; a value in the market HDPE and LDPE low density polyethylene and high density polyethylene.

So, so basically both tensile strength as well as in some cases modulus as well, they tend to increase with increasing into entanglement, which could be as a result of chains becoming longer, which could be as a result of increasing molecular weight or degree of polymerization. So, now, let us look at other kind of polymers, some of them this category is called as elastomers right.

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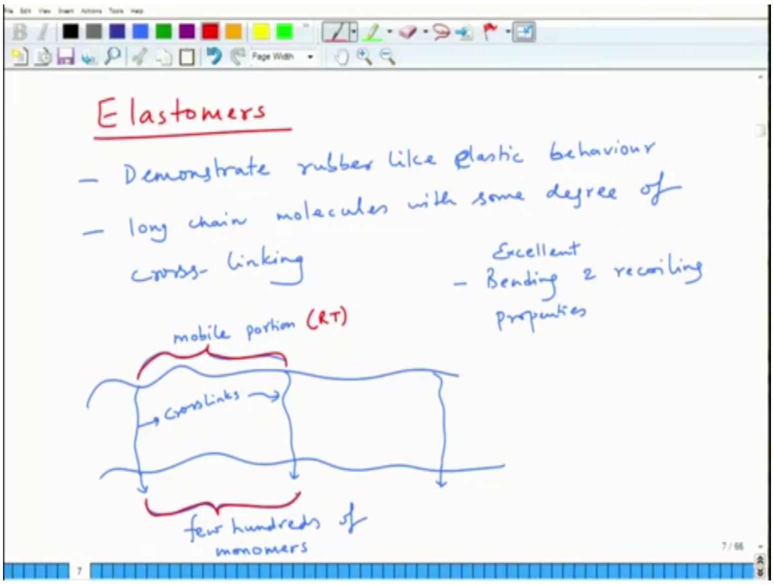
Elastomers

- Demonstrate rubber like elastic behaviour
- long chain molecules with some degree of cross-linking
- Excellent Bending & recoiling properties

Elastomer the properties of elastomer are, they demonstrate robot like; plastic behavior, elastic behavior, rubber like elasticity. They have and basically, they have long chain molecules, with some degree of cross linking and. So, you can have this kind of structure and these are cross linked ok.

So, these are cross links and. So, these segments between the cross links are the segments, which are called, which are basically mobile segments, mobile portions. They can move around, they can flex themselves and these cross links points are the anchor points. So, they move around these anchor, anchoring points. So, these are the points at which it is crossed links. So, they gets anchored, but between them.

So, this distance between the two anchoring points is fairly large. It could be of the order of few hundreds of monomers. So, it provides sufficient spacing between the two anchoring point for the chains to be flexible and these elastomers have this natural tendency for bending and recoiling. So, they have excellent bending and recoiling properties. The segments that you see here, these, these segments here, they can flex and move at room temperature. So, these are mobile portions at room temperature. So, they provide enough flexibility to the, elastomers. So, for example, let us see the first the case of what we call is nylon, nylon.

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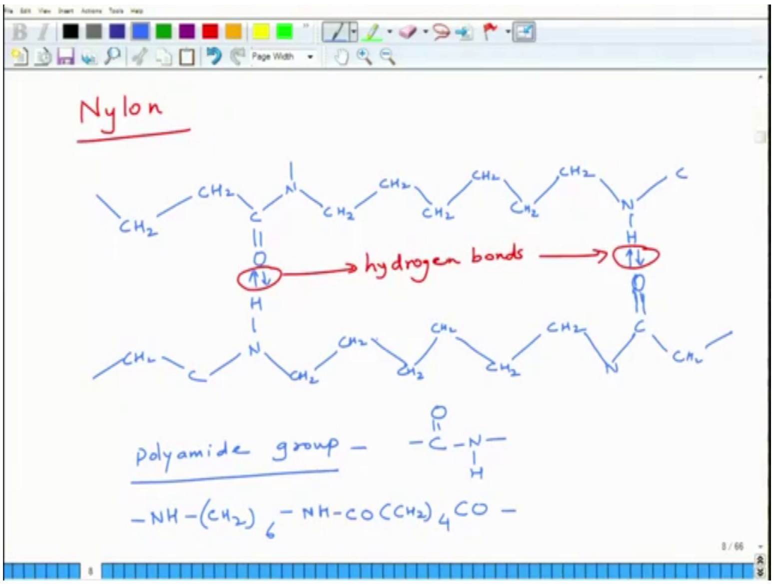

What happens is that you have make nylon structure. So, you have CH 2 group goes like this, CH 2 group, and then you have carbon, and then you have nitrogen, and again you have CH 2. You have CH 2 again; you have CH 2, again a CH 2, again a CH 2. So, you have three of these CH 2s, and then they could connect it to N and then they have C ok, on the bottom side, another chain you will have CH 2 and then again C and this will be into N and here you have CH 2, CH 2, CH 2, CH 2, CH 2 and then, think you will have here, instead of N you will have; so, this will be CH 2 and so, hang on just once second.

So, we have CH 2, C N, CH 2, CH 2, CH 2, CH 2, CH 2, CH 2 and then we will have N, and then we will have C. So, then we will have CH 2 again. So, we got missed out somewhere and the C and N here, they will get connected to NH and O. This O will make double bond with carbon, this carbon will make double bond with O, and they will be hydrogen bonded with the image group on this side. So, these are you can say. So, basically you have, you have (Refer Time: 22:01) group here, which is C O N H these. So, you can have, you have 1 here, 1 there, the CO NH groups are connected to each other through hydrogen bonds.

And these hydrogen bonds which, which are present between the chains, they are more stronger as compared to secondary wonder balls bond and in this case the monomer you can see, monomer will become N H CH 2 6 repeating units 1 2 3 4 5 6 and then NH again and CO CH 2 4 CO. So, this will be the repeating units in this structure. So, this is a very long pretty tough big monomer and. So, this whole functional you, these chains, which are made up of these monomers, they are connected to each other through hydrogen bonds and these segments are fairly large, as a result they allow flexibility of this nylon, nylon is a very well known flexible material. So, another example that you have, you know about it is, wood right.

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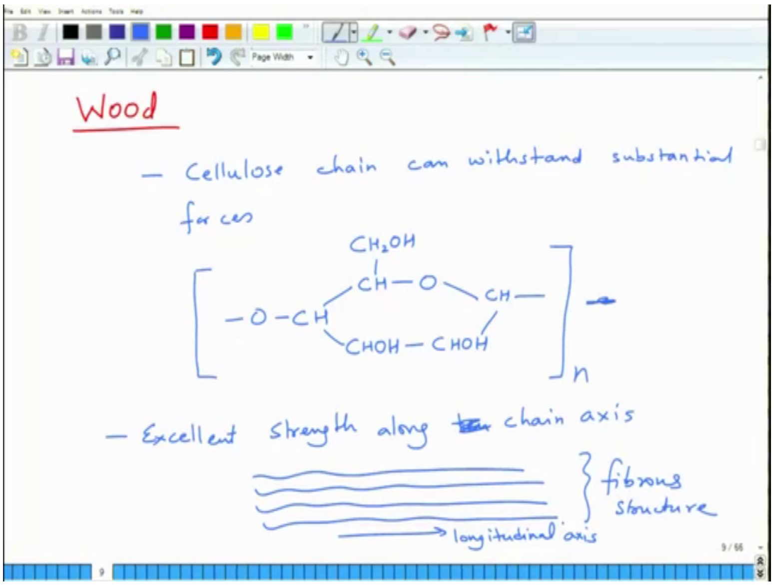

Wood

- Cellulose chain can withstand substantial forces

- Excellent strength along ~~the~~ chain axis

} fibrous structure

longitudinal axis

What is also flexed, fairly flexible? Lot of trees can bend easily right; they do not break when the wind blows. They can flex in either direction and this is possible through arrangement of. So, basically cellulose chains are can withstand substantial forces. So, what you have here is basically these cellulose groups and the, I am just going to draw the monomer. So, you have O CH, which is connected to CH O. So, then corrected 2 CH. So, these are the monomers. So, N.

So, this will make our basically cellulose structure and this will provide very excellent strength along chain axis, which is basically longitudinal direction. So, chains are aligned in this fashion and the wooden wood structure, these are cellulose chains, there is very little of cross linking between them, they are basically it is a fibrous structure, fibrous structure their chains are aligned without much entanglement and in the longitudinal direction. So, this is the three, longitudinal axis and they have excellent strength along this axis and then we have this thing called as natural rubber.

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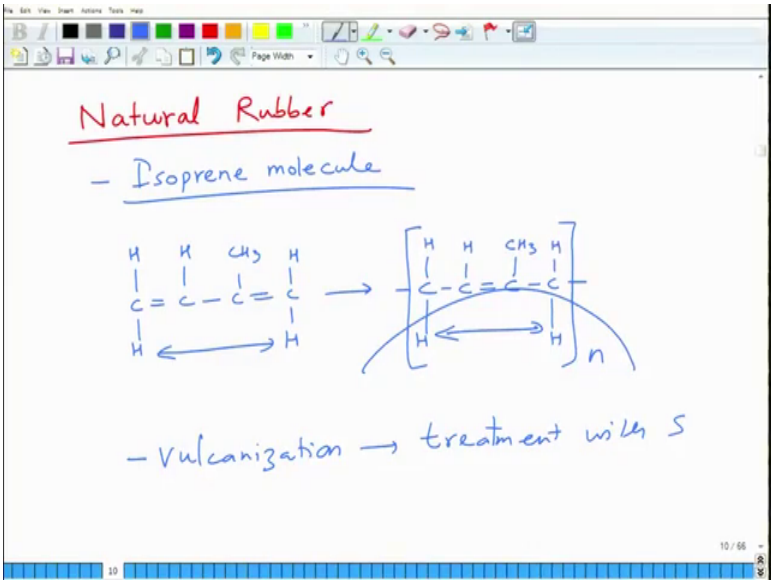

Natural Rubber

- Isoprene molecule

- Vulcanization → treatment with S

And this natural rubber is basically, it is isoprene molecule ok. So, it is called as Iso prene molecule and here, what you have here is CH double bond, C H C C H 3 double bond C H H and this basically converts into. So, you have H H H Ch 3 H H. So, you can see, you earlier had two double bonds, which get broken, you have only one double bond as a result, you have this monomer and this can be attached. Now, these are. So, you can see there is, there is a bit of spacing there. So, this is spacious, this side is, is precious, this size is not a spacious.

So, the spacing allowed, allows the rubber molecules to flex. So, this can go in this fashion. It can bend, because there is a spacing on the. So, this is basically, rubber molecules flexibility the reason, because there is a lot of spacing on one side, there is, there are more functional groups on one side then on the other side as a result it becomes, it can flex. Now, there is a treatment, which is done to rubber, which is called as vulcanization, which is basically treatment with sulfur to make it stronger and, because sulfur makes covalent bonds with carbon. So, when you make, when you do the treatment with sulfur.

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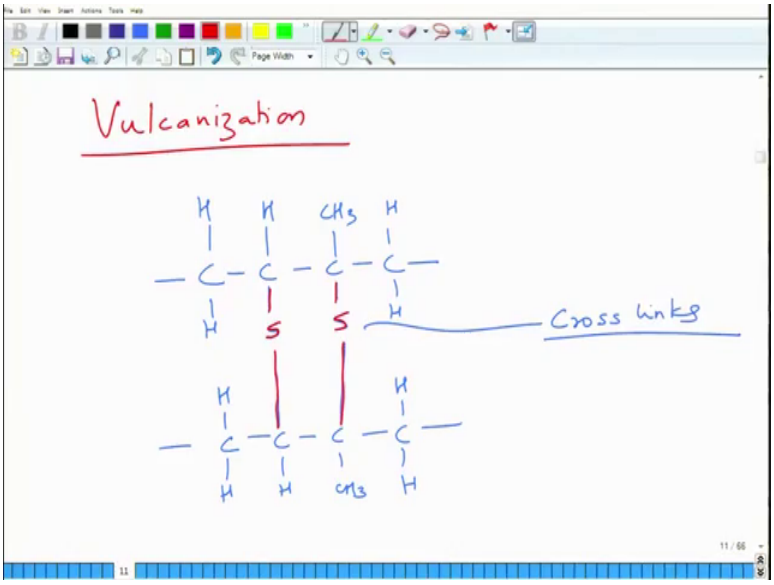

Then what happens is basically, you have these Ch H C H Ch 3 C H and you add a sulfur here. So, the between these, you will have sulfur and there will be another molecule here, and the sulfur basically, gets attached here. So, otherwise you will have weak bond of balls bond, but the sulfur will ensure too attached, how will, it will attach, it will.

So, this sulfur basically attaches itself in this fashion. So, it breaks the double bond again. So, this double bond goes off, what you will have here is basically sulfur attaching itself. So, this hydrogen can go here, this is how it attaches itself. So, it provides cross links. So, these are cross links. Now, the empty spaces are all filled with sulfur right. So, these are cross links if I draw them using different color, these are cross links. So, it becomes this now, becomes a solid mass and cross linking can convert a natural rubber into. So, cross linking, let me just write it again.

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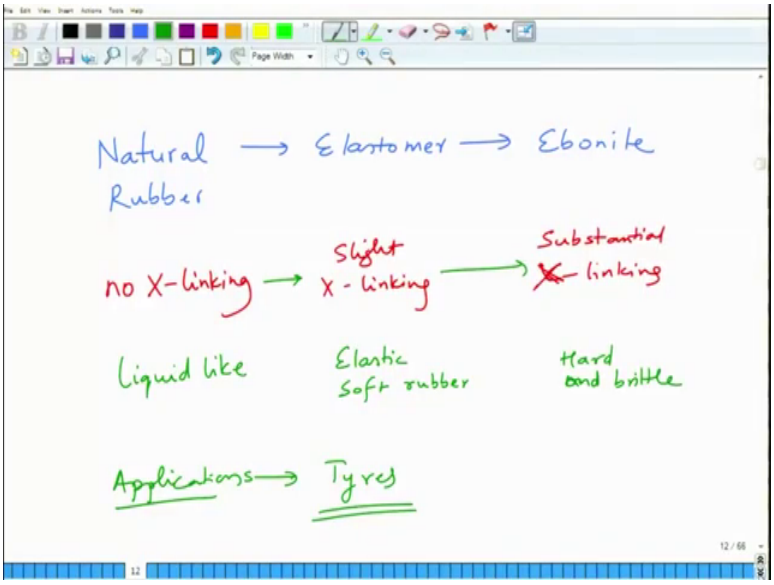

Natural Rubber ⟶ Elastomer ⟶ Ebonite

no X-linking ⟶ Slight X-linking ⟶ Substantial X-linking

Liquid like

Elastic soft rubber

Hard and brittle

Applications ⟶ Tyres

So, cross linking can convert natural rubber into a elastomer. So, this is the clear degree of cross linking and then it can convert this to something called as ebonite, which is heavily cross linked. So, this is, no cross linking. This is slight cross linking and this is substantial cross linking and as a result, the, natural rubber has a liquid like behavior, it is liquid like, this is elastic soft basically, soft rubber and this is hard and brittle. So, the same material can we convert and we convert it from liquid like material to a solid, which is soft to hard and brittle, you already have an a bakelite, bakelite is very hard that is how bakelite is made. So, this is how the cross linking changes the materials properties in polymer.

So, for example, tires the tires that we see, applications are in tires right, tires need to be hard. So, they cannot use natural rubber, they have to be some degree of cross linking to make them tough of course, tires are composites, is something else interest, but the rubber that is used is cross linked. So, if you, this is how you basically, substantially. This is how, if you increase the degree of cross linking, you can make a rubber stronger, harder and more useful for many applications. So, let me summarize.

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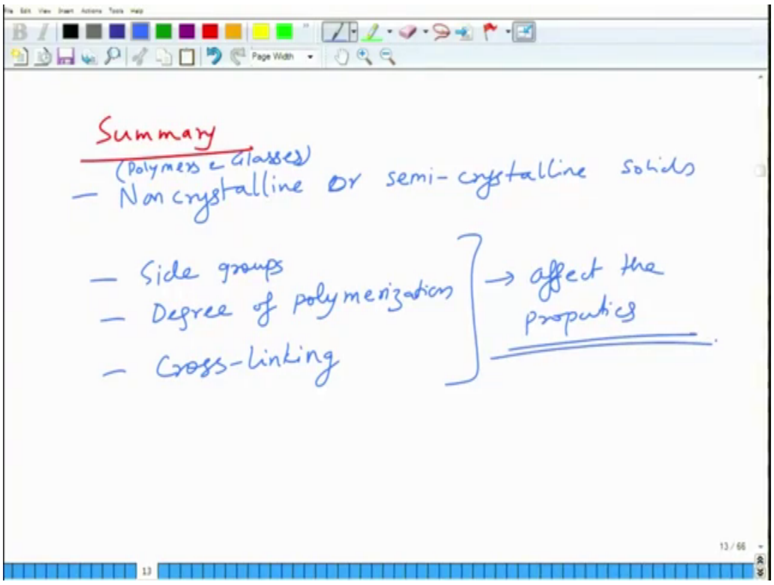

Summary

(Polymers & Glasses)

- Non crystalline or semi-crystalline solids

- Side groups
- Degree of polymerization
- Cross-linking

→ affect the properties

Basically, here that polymers are essentially non crystalline or you can say, semi crystalline solids. So, polymers and glasses, they are non crystalline or semi crystalline solids, polymers can be, linear chain polymers or they can be heavily cross linked polymers or they can be copolymers depending upon the degree of cross linking, the strength tensile, strength modulus hardness of polymers can be increased substantially and by changing the functional groups on polymeric chains, you can again modify.

Their properties make them stronger, increase change, a melting point change their glass transition temperature and then by controlling the degree of polymerization, which is the number of molecular weight of the polymer, it again achieve the same characteristics. So, they are fantastic materials. The key parameters in them are side groups degree of polymerization, cross linking right, least three group, least three can affect the properties and their behavior ok. So, will stop here, we have finished our polymers and glasses. Now, will now, move on to structural characterization using X-ray diffraction.