Polymers: Concepts, Properties, Uses and Sustainability

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Week 9
Interaction of Polymers with Other Materials

Lecture-63
Biopolymers Applications

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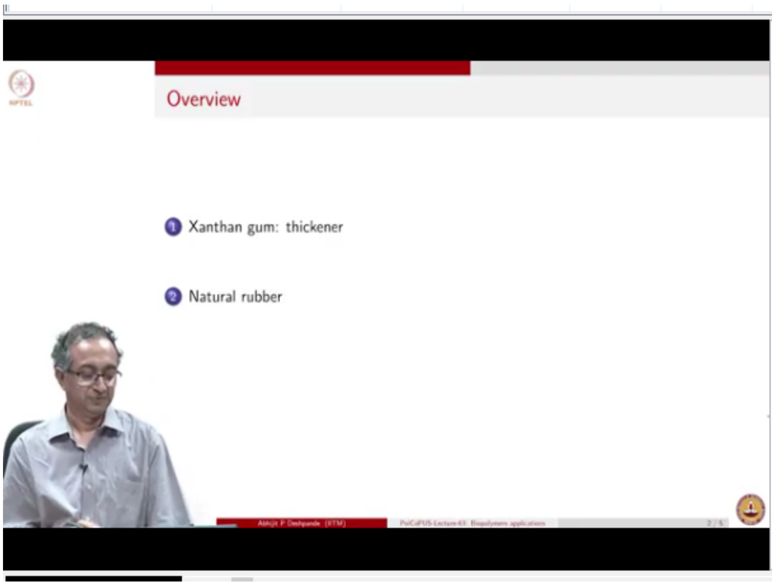

Overview

1. Xanthan gum: thickener
2. Natural rubber

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So, in this particular lecture we will focus on 2 biopolymers, the xanthan gum and polyisoprene and in next lecture on conformations and structure of biopolymers we will look at casein and pectin in much more detail, just to remind you that these biopolymers are used quite extensively in various applications and so it is important for us to recognize and understand concepts related to these biopolymers and how they are relevant in terms of being model system for us to design new sets of materials from a sustainability point of view.

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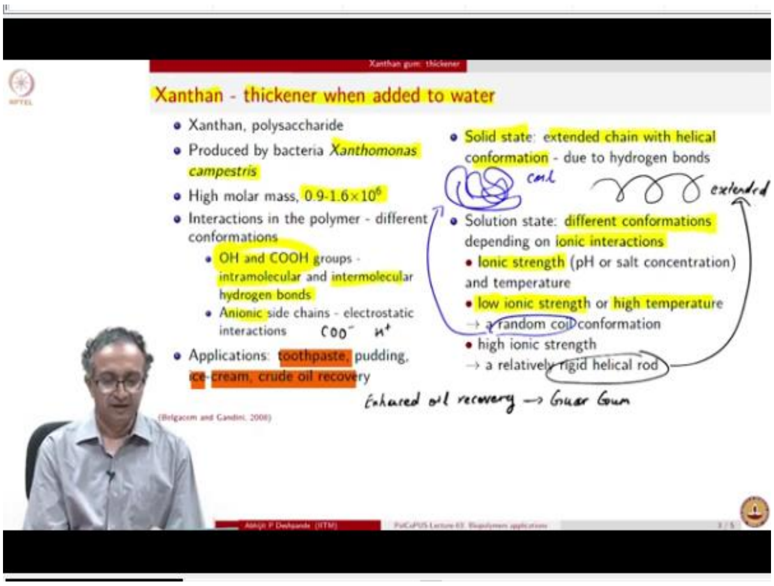

Xanthan gum: thickener

Xanthan - thickener when added to water

- Xanthan, polysaccharide
- Produced by bacteria *Xanthomonas campestris*
- High molar mass, $0.9\text{-}1.6 \times 10^6$
- Interactions in the polymer - different conformations
  - OH and COOH groups - intramolecular and intermolecular hydrogen bonds
  - Anionic side chains - electrostatic interactions COO^- H^+
- Applications: toothpaste, pudding, ice-cream, crude oil recovery

(Belgacem and Gandini, 2008)

- Solid state: extended chain with helical conformation - due to hydrogen bonds

coil

extended

- Solution state: different conformations depending on ionic interactions
  - Ionic strength (pH or salt concentration) and temperature
  - low ionic strength or high temperature → a random coil conformation
  - high ionic strength → a relatively rigid helical rod

Enhaced oil recovery → Guar Gum

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So, let us look at the xanthan gum as an example. So, again it comes from a microorganism but when you add this in water it acts as a viscosity modifier or a thickener and therefore it is used quite commonly, it is made by a bacteria as I mentioned already it has a fairly high molecular weight molar mass is quite high and very important chemistry or physical chemistry of this compound is related to the presence of hydroxyl and carboxylic acid groups which lead to very significant interactions mainly hydrogen bonding in this polymer.

So, whenever we put this polymer in water because of interactions which are between xanthan gum and water, xanthan gum and xanthan gum molecules we have a very rich behavior that arises. So, we have mainly a backbone and there is also anions present on this. We will soon see that we have COO^- and of course a counter ion which may be proton in this xanthan gum case.

And its applications are various applications related to from toothpaste, foodstuffs like pudding and ice cream and very important in crude oil recovery, we have a phrase called enhanced oil recovery; if you are interested you can read more about it in fact many of the gums are used in enhanced oil recovery. Another important example of a gum which is very common which is a biopolymer is guar gum. Just try searching about guar gum and where does it originates from and who is the largest producer and supplier of guar gum and you will be surprised that it is a vegetable which we are quite familiar with in different parts of India. Now going further this xanthan gum depending on which state it is in it can have a different molecular structure. So, generally as we have seen we have been drawing a macromolecule like this. So, generally in a solution state quite often it will be what is called a coil state, but for xanthan gum in solid state what we have is an extended chain with a helical conformation because of hydrogen bonds. Because these hydroxyl and carboxylic acid groups are there,

there is extensive hydrogen bonding possible in these materials and in the end what you end up getting is some helical structure like this. And then it is an extended chain as opposed to a coil. So, therefore this is called the extended chain. So, now going ahead and looking at the property which is important from the point of view of application the solution state of xanthan and interestingly here depending on whatever the conditions of the solution different conformation states can be seen.

So, the conformations change depending on what are the ionic interactions? How do we modify ionic interactions? Can you think of we have ions like COO^- , H^+ , Na^+, K^+ , Ca^{2+} , SO_4^{2-}. All these are ionic species and they of course interact with each other. So, how is it possible to modify interactions between these. So, there are 2 ways to do it generally, one is by changing concentration of ions themselves. And the concentration of ions can be changed by changing pH or by adding more salt or having less salt. So, what is called the ionic strength? So, one way to modify the interactions between ions is to change their concentrations or to change ionic strength of the medium. The other is of course temperature, because interaction with respect to the thermal energy which is present will determine how strong is the interaction?

Because thermal energy is always present which causes the molecules to undergo different conformations, it allows bonds to occupy different energy states. So, thermal energy is always propelling molecules or bonds to change from one state to the other and if interaction energy is strong then thermal energy in interaction energy ratio is what is important in terms of determining whether the molecules and bonds will occupy one state or the other. So, flipping back and forth between different states is very crucially related to the interaction energy on one side and thermal energy. So, temperature will always play a key role in terms of determining how strong the interactions are? So, in case of a low ionic strength or high temperature you can see the ratio right. So, whenever high temperature is there the ratio is less. So, let us say ionic interaction is in numerator thermal energy is in the denominator. So, you can see that how these both of these mean the same thing.

So, if this is the case when its low ionic strength and high temperature we have a random coil state and if we have low temperature or high ionic strength then we have a rigid helical rod. Now one of the things that you may want to consider is whether this is just qualitative or can we actually get quantitative estimates of how much extended a chain is and how coil like a chain is? What is the size of the polymer chain when it is in coil state or what is the size of the polymer when it is an extended chain? The answer is yes, we can get quantitative estimates.

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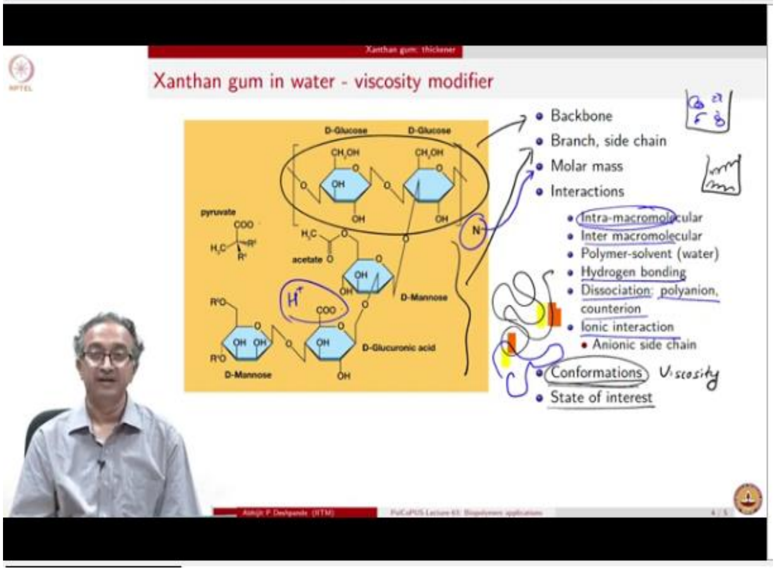

Xanthan gum: thickener

Xanthan gum in water - viscosity modifier

- Backbone
- Branch, side chain
- Molar mass
- Interactions
  - Intra-macromolecular
  - Inter macromolecular
  - Polymer-solvent (water)
  - Hydrogen bonding
  - Dissociation: polyanion, counterion
  - Ionic interaction
    - Anionic side chain
- Conformations Viscosity
- State of interest

So, let us continue looking at this xanthan gum as a molecule just look at this diagram for the details okay, look at the complexity of a biopolymer. What are the features that you can observe? Since the first lecture we have talked about variety of concepts, we have talked about backbone, we have talked about side group, we have talked about branching, we have talked about polyelectrolyte, we have talked about interactions between macromolecules. We have talked about degree of polymerization; can you spot all of these things in this picture? And if you can then you have got lot of graph of these aspects related to polymers, you can just pause here and maybe try to identify all the things that you can in this graph. Let us continue, these are all the features that are there in this and this is the beauty of a natural polymer, variety of contents are there which allow lot of interactions to take place and therefore this polymer to exhibit one type of property or the other.

So, of course the backbone itself is there, you can see that there is a side branch, the molar mass of course depends on the degree of polymerization the interactions. So, here very importantly we have intra macromolecular and inter macromolecule and just the way we have been drawing a polymer macromolecule you can notice that one part of polymer molecule can interact with another part. So, therefore intramolecular interactions are possible, same macromolecule interacting with another and of course next to this we can have another macromolecule and therefore we also can have intermolecular interactions. So, in this case all the interactions that are possible that we have talked about for example hydrogen bonding or ionic interactions, they are all possible between 2 xanthan gum molecules or within 1 xanthan gum macromolecule. The other important thing that we have spoken about is dissociation to lead to a poly anion where polymer chain itself has negative group and there is of course the counter ion. The counter ion is not drawn in this picture, but I am sure those of you who have been following the lecture will immediately spot that this is the COOH group which leads to this polymer chain being poly electrolytic or ionic.

And so what is of interest from a practical point of view is what are the conformations that a polymer molecule takes and what is the state of interest? So in this case it is the solution state which is of importance and we would like to know whether it is taking an extended conformation or it is taking a coil like conformation. In terms of application it might help for you to think of why should viscosity be determined based on what type of conformation a polymer takes.

Just to think of this further you could think of a beaker in which you have coil like objects and how easy or difficult will be to stir this, as opposed to another beaker in which you have extended chains of xanthan gum. So, if you want to stir one versus the other clearly if viscosity is different, then the amount of energy required to stirring will be different. So, will it be different is something for you to think of.

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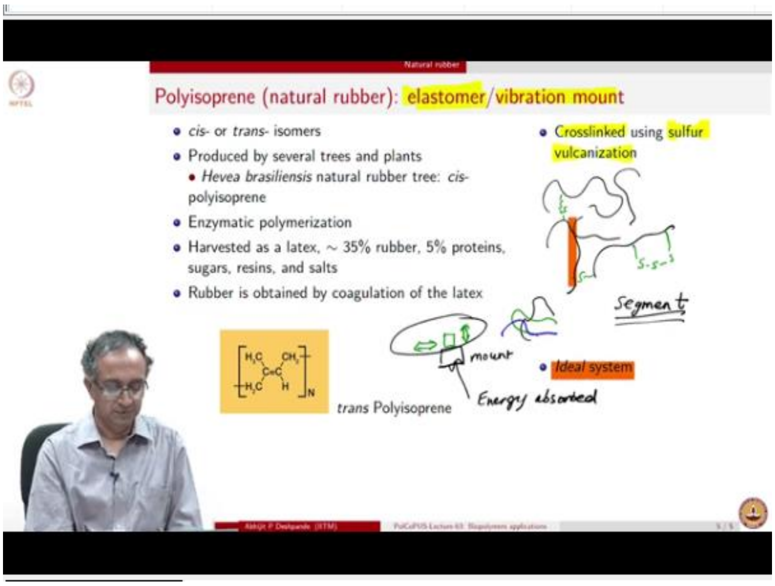

Natural rubber

Polyisoprene (natural rubber): elastomer/vibration mount

- *cis*- or *trans*- isomers
- Produced by several trees and plants
  - *Hevea brasiliensis* natural rubber tree: *cis*-polyisoprene
- Enzymatic polymerization
- Harvested as a latex, ~ 35% rubber, 5% proteins, sugars, resins, and salts
- Rubber is obtained by coagulation of the latex

- Crosslinked using sulfur vulcanization
- *Ideal system*

Let us continue our journey and look at another example of a natural polymer. In this case this is from a tree several trees are producers of gums and natural rubber and most common that we use is a natural rubber tree and this is an example of a cis-polyisoprene. So, cis and trans isomers are possible. The application of natural rubber is elastomeric something which stretches and when you release it, it comes back. So, that is an elastic rubber band kind of an application, quite importantly in vibration mounts natural rubber is still the most preferred material to be used and in this case it is a damping application, an instrument or an equipment when it is running it vibrates and that vibration will be passed on to the floor and from the floor to the other and in fact the reverse way also. If something else is vibrating it will come to the instrument and it might affect its functionality. So, generally this instrument or equipment is mounted on the floor and there is a what is called a vibration isolation device which is used, because you do not want vibration from one equipment to carry to the other or vibration of a floor being carried to the equipment or equipment carrying its vibration to floor. So, that the people around there will feel the vibration. So, vibration isolation is a very important application, it is there in vehicles also when we travel. So, this is a very important engineering application and natural rubber mounts are extremely important in this vibration isolation application, what natural rubber is able to do is to absorb all the mechanical energy and therefore it does not transmit the vibrations.

So, mechanical energy is nothing but vibrations, it absorbs all those vibrations and does not transmit the mechanical energy. Natural rubber is produced by trees using enzymes. So, proteins are used in catalysis. So, therefore we call it enzymatic polymerization. Generally we harvest this as a latex. So, this is a common term used in polymer science whenever we have a dispersion. So, if we have a dispersion of polymer or oligomer particles in a solvent. So, it is also called a latex. So, in fact paints are also examples of latex. So, it contains some amount of rubber and then of course other biological chemicals and then rubber has to be obtained by coagulation. So, in this case coagulation is a process where dispersion is broken. Broken is a common English parlance term. But more coagulation is the term which specifies that these particles which were there will start coagulating with each other and then form exclude the solvent and therefore you can form the solid natural rubber piece and so just looking at how does a natural rubber trees polyisoprene look like, here what I have shown is trans polyisoprene. So, I hope through your earlier chemistry knowledge you should be able to draw how does a cis-polyisoprene look like.

So, just to draw this if we have this H_2C-C and then of course if you remember from your this is the CH_3 group and then this is H. So, this is an example of cis-polyisoprene. So, as we have seen rubber is obtained by coagulation of the latex and in this stage natural rubber is not very useful, because it still will have more liquid like properties and when we want to use it as a vibration mount or when we want to use it as an elastomer we need solid like character where these latex particles should get joined with each other.

And this is done basically by cross linking the rubber, what is cross linking is basically using sulphur to vulcanize and this is something of course from school onwards you might have learnt about. So, if you have these rubber chains which are isolated, what you can do is incorporate sulfur and combine and there are various interesting ways in which sulfur can interact and so it can form a cyclic where it is not really cross linking 2 molecules.

It can form multiple S and then only it can form cross link and so variety of the chemistry of cross linking of rubber is also very diverse, but generally we use sulphur vulcanization. There are other many cross linking agents also using which cross linking can be done. A biopolymer example that we looked at in terms of xanthan gum we saw it was so rich in terms of the interactions.

They were hydrogen bonding interactions; they were ionic interactions and so everything was determined based on the strength and weaknesses of these interactions. In this biopolymer example the interactions are in fact not relevant at all. In fact this is an example of what we will call an ideal system. I do not know if you can remember which other context you have usually seen ideal in terms of a chemical in either thermodynamics or physical chemistry we talk of ideal gas. And what do we mean by ideal gas is a set of molecules where there are no interactions, we say that ideal gas is a molecules which can overlap with each other and so on. So, there are various ways in which we try to signify that interactions between molecules are not important when we have an ideal gas. So, similarly here when we have an ideal system interaction between macromolecules is not very important in terms of determining its properties.

So, this elastomeric properties as well as vibration mount properties how can we explain them using no interactions. So, in fact in this case the key is a segment of polymer. So, we have talked about for example a section of polymer chain between cross link points and this is a word which we have used earlier also defined it called a segment. So, what segments do is pretty much determining, how will this rubber component behave. When we stretch the rubber for a rubber band, elastic rubber band kind of application quite often we are doing this at a reasonably low rate and so in this case the segments also get stretched and when we release it the segment want to come back to coil like state. So, therefore interaction between segments is not important how a segment gets stretched and how it comes back is sufficient for us to explain the elastomeric behavior of a rubber.

When we are using it as a vibration mount then again in that case we have a vibration mount, let us say this is the mount and then we have another component which is let us say vibrating and this is basically vibrating either up and down or depending on the instrument. So, it is going basically this while the bottom is the rubber component which is the mount. So, now what happens is again the segments do not get stretched but the segments start doing all kinds of conformational changes. So, a segment which was in one instant like this may change its conformation and become like this, again may change its conformation and become something like this and so what you have is segment keeps on changing its conformation in this process it absorbs the mechanical energy and dissipates it in the form of heat. So, therefore whatever is the energy which is being transmitted by this vibrating part it is absorbed in this vibration mount?

So, energy gets absorbed and in all of this explanation I did not really use how are the rubber macromolecules interacting with each other? So, therefore this is an example where what segments are doing? Whether they are getting stretched and recovering or they are changing conformations and segmental motion basically can explain both elastomeric as well as a vibration mount applications of this. So, here therefore we have seen 2 beautiful examples of biopolymers, in one case xanthan gum where molecular interactions was everything that was important and rubber where molecular interactions could be neglected to explain the features of its application.

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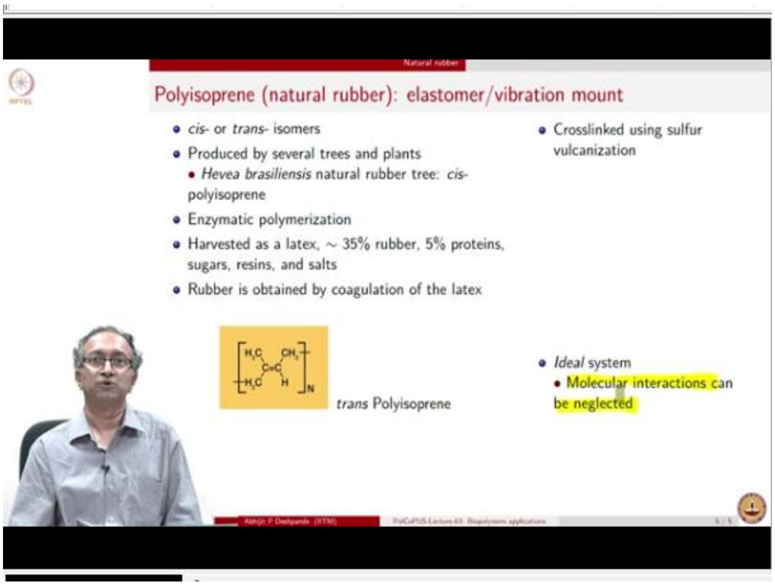

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trans Polyisoprene

- Crosslinked using sulfur vulcanization

- *Ideal* system
  - Molecular interactions can be neglected

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Just to remind you again when we say an ideal system what we mean is molecular interactions can be neglected and which is what we did in case of explaining elastomeric and vibration mount properties of rubber.

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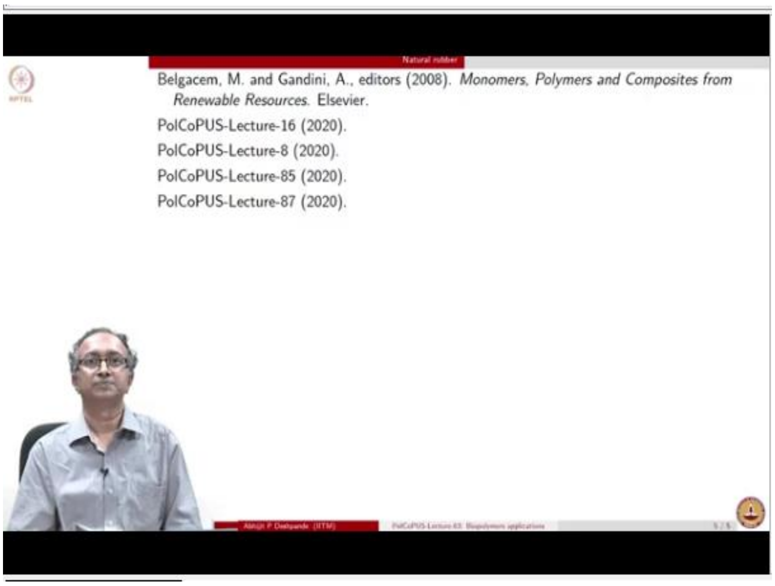

Natural rubber

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PolCoPUS-Lecture-16 (2020).

PolCoPUS-Lecture-8 (2020).

PolCoPUS-Lecture-85 (2020).

PolCoPUS-Lecture-87 (2020).

So, with this we come to close to this lecture on biopolymers, thank you.