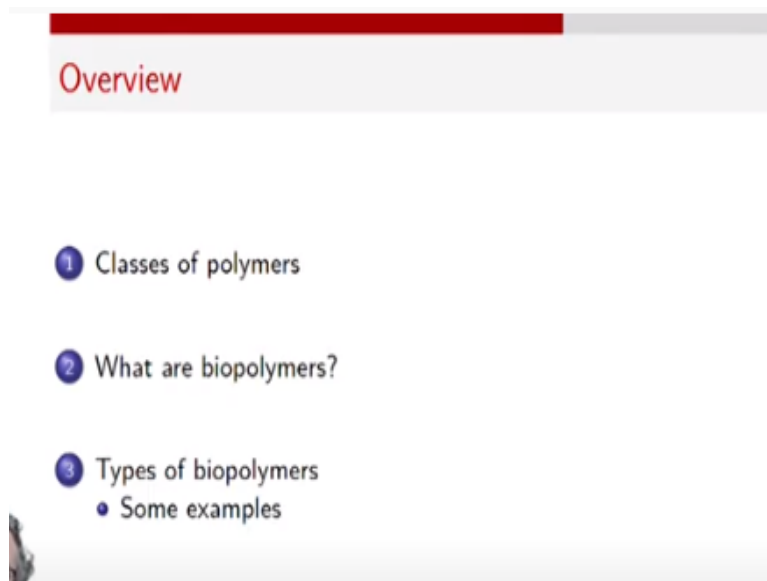


Polymers: Concepts, Properties, Uses and Sustainability
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Lecture - 04
Biopolymers

Hello, welcome to this lecture on polymers, where we are learning concepts and properties of these polymers, their applications and sustainability aspects. In this lecture, we will focus on biopolymers.

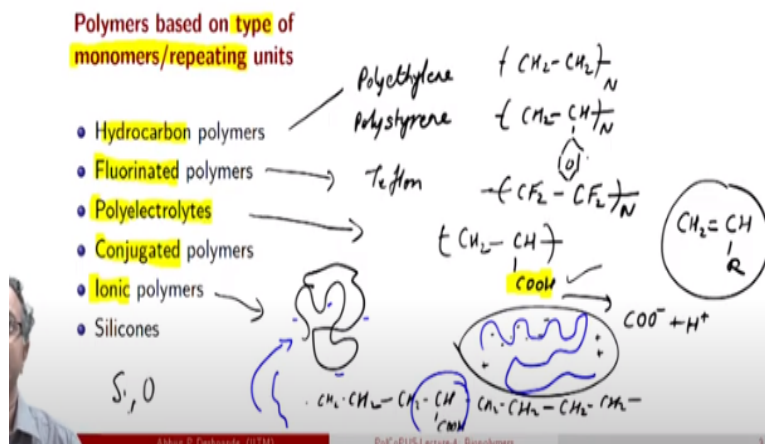
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We will do this by first looking at various ways in which we talk about classification of polymers. And then we will define biopolymers and then take a few examples of these biopolymers, especially with their applications in mind.

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Different types of polymers



So let us begin in terms of how we look at different types of polymers. So we could specify the type based on what is the nature of monomer or the repeating unit in the polymer. So for example, we could call something hydrocarbon polymer. And of course, immediately in your mind, polyethylene will spring as an example, because it is just carbon and hydrogen.

So many of the polymers indeed are hydrocarbons. Even polystyrene for example, is where you have a benzyl radical. And so these are examples of hydrocarbon polymers, carbon and hydrogen forming the backbone and if there are branches and other molecular architectural details, they also will be containing carbons and hydrogen. As the name suggests, we could also have fluorinated polymers.

And I do not know if you can think of an example, which is used quite often in kitchens, which is a fluorinated polymer. I do not know if you can think of nonstick immediately. So nonstick pans have a Teflon coating which all of you are familiar with. And Teflon is nothing but very similar in terms of molecular formula to polyethylene, but instead of hydrogen we have fluorine. So this is an example of fluorinated polymer. There are several applications of these fluorinated polymers, in terms of their physical and chemical stability. So they are used as coating sometimes, like in case of kitchen. They are used as tubings. Whenever there is a possibility of corrosion and then if we need very stable material then some of these fluorinated polymers are used as tubing materials.

Polyelectrolyte is an example where we have an electrolyte attached to a polymer chain. And by electrolyte we mean something which can serve ionic conduction in its solution or melt or solid medium. And sodium chloride solution for example is the

most common example of electrolyte that you can think of. In lead acid battery we use sulfuric acid which is again an electrolyte.

So a polymer which can have ions and this is one example. Again you can see that many of these are very similar in that all of these are broadly made from monomers which are of this kind. So this monomer is very versatile. By changing R we can achieve, so if we change R one example we can get polystyrene. If we can change R to a carboxylic acid group, we get what is called polyacrylic acid.

And this particular polymer, if I visualize it, what you will have is the polymer chain will have let us say a coil like structure. And then periodically along the chain, there are all these negative ions. And where do these negative ions come from? They come from this COOH group. Basically, this COOH group can dissociate and therefore, it can lead to. So basically, whenever we put this ion, this particular species what we will have is water molecules which are surrounding and then negative ions, which are there on the polymer chain. And then there will be positive ions which are in the counter ions, which is nothing but proton. So this is an example of a polyelectrolyte.

Conjugated polymer are very important from the point of view of conductivity, electrical conductivity. So many of the conducting polymers are conjugated. I do not know if you remember what is meant by conjugation. You can search for it. In fact, if it is alternate single and double bond conjugation, it is called conjugation. Maybe you remember that. You can search for it. And in fact, you will also come to know that in benzene for example, there is conjugation and that leads to delocalization of electron. And delocalization of electron implies conductivity may be possible. So that is why conjugated polymers are conducting polymers also. Sometimes when instead of every repeating unit having an ionic group if there are few ionic groups on the chain then it is called an ionic polymer. So for example, you may have an ionic polymer and few ions may be there.

So what you have is many of the repeating units have no ionic group, but some repeating unit have ionic group. So for example, you could combine polyethylene and acrylic acid and make an ionic polymer. So you can have CH_2-CH_2 which is what is polyethylene and then if this is combined with $\text{CH}_2-\text{CH}-\text{COOH}$ and let us say what you do is you put a lot more units of polyethylene.

And so what you will have is very small number of ionic groups on a polymer chain. So then it will look pretty much like this, where the polymer chain has few number of ionic groups. So these are called ionic polymers. And silicones are polymers, where

silicon and oxygen as opposed to carbon, hydrogen or fluorine some of the examples that we have seen. So we have also a very important rubbers and many other applications where silicones are used. And so this is one way of classifying polymers and thinking about different types of polymers.

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Different types of polymers

Polymers based on type of monomers/repeating units

- Hydrocarbon polymers
- Fluorinated polymers
- Polyelectrolytes
- Conjugated polymers
- Ionic polymers
- Silicones

Common families of polymers

- Polyolefins
- Polyamides → $\sim \text{CONH} \sim$
- Polyimides
- Polyacrylates → PMMA $\left(\text{CH}_2 - \overset{\text{CH}_3}{\underset{\text{COOCH}_3}{\text{C}}} \right)_n$
- Polyesters → $\sim \text{OH} + \text{COOH} \sim$
- Polythiophenes

There is another way quite often we refer to a family of polymers and this is based on whatever is the repeating unit or monomer in the polymer. For example, polyester clearly implies an ester bond and we know that ester is formed based on a reaction between hydroxyl group and a carboxylic acid group. Similarly, we also have polyamide. Nylons are all examples of polyamide. And so here, what you will see is a repeating unit like this.

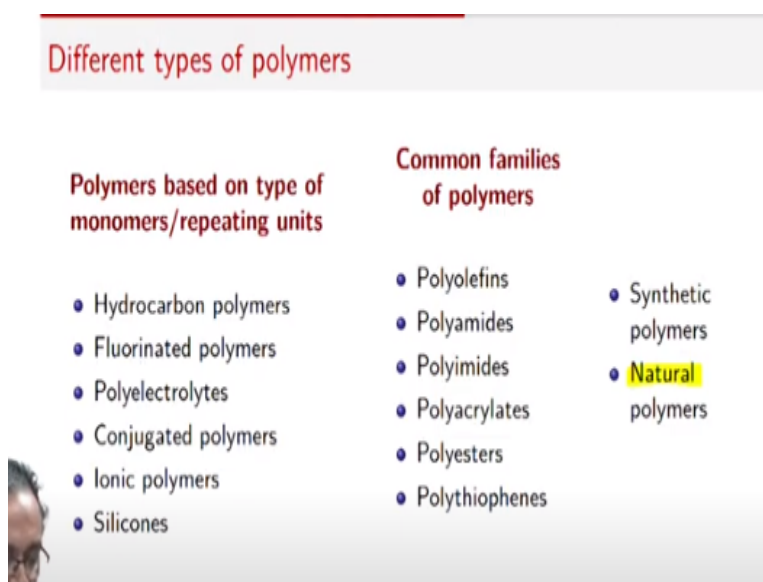
So this is called the amide linkage. What you will have is CONH. So this is how the amide linkage. So there are monomers which are attached with an amine functionality and there are monomers which have an acidic functionality and when these two react, we get what is called an amide linkage. Polyolefins of course, are a very large class of materials. It is also very important because very large volumes of polyolefins are used. Polyethylene and polypropylene, two most important polyolefins in fact, are bulk of the plastics that we use, very high amounts of polyethylene and polypropylene is used. And so all of these are based on olefins.

Another important class of polymers which are quite widely used are polyacrylates. So in this case the acrylic group, if you remember on the previous slide, we looked at acrylic acid, polyacrylic acid. So which is nothing but CH_2CH and COOH . So instead of hydrogen being here, if there are various other groups that can be substituted, then

we get an acrylic family of polymers. So an important example of polyacrylate is poly(methyl methacrylate), PMMA. It is quite commonly used and in fact perspex windows, which is non-breakable plastic, but optically very excellent properties so that we can use them as glass materials. So they are used PMMA. So as, if you remember from last slide so this is the acrylic group, but instead of that, if we have so this becomes methacrylic. And just to remind you and instead of hydrogen which was there on the polyacrylic group, if we have a methyl group. So we remove this hydrogen and then we add so methyl methacrylate. So acrylates are a very important class of materials.

Polythiophenes are materials which are very important class of conducting polymers, conjugated polymers. So this is some examples of common families of polymers.

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We also can distinguish polymers based on what their origin is. And various polymers are called natural polymers because they are made by biological in the biological world from species such as bacteria to plants, to animals, and so they are called natural polymers. And then we also have synthetic polymers, which are quite often based on petroleum based raw materials.

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So let us look at now examples of natural polymers, which are called biopolymers. So just to pause here and ask some questions and note some important features of these natural polymers. So one thing which we have highlighted earlier also that nature does use polymer, or macromolecules, proteins, DNA and there are several other examples, whether it is cellulose or starch. So nature does use polymers quite extensively.

Biopolymers - natural polymers

- Nature uses polymers (macromolecules)
 - Macromolecules in nature perform many functions: mechanical, packaging, coating, ...
 - Based on diversity of functions in nature, there are varieties of macromolecules
 - Macromolecules in nature do not accumulate like waste plastics do
- 1 Why can't we use polymers which nature also uses?
 - 2 Why can't we design polymers which are similar to natural polymers?
 - 3 Why can't we modify natural polymers so that they are suitable for engineering applications?

And these polymers are macromolecules in nature, perform very important functions and variety of functions. So it is they are very diverse and they can perform a mechanical role. They can perform a barrier role, what we need for let us say for a packaging material. They can also have a protective coating. So various functions. They can provide conductivity, they can provide optical performance. So basically whatever we need from an application point of view, all those roles are performed by macromolecules in natural conditions also. And so based on the diversity of the requirements, we also have variety of macromolecules. In fact, cellulose itself can be made in various different forms, depending on the species that requires it. Similarly, starch also.

So that is why for example, in kitchen when sometimes when we use cornstarch is different properties compared to some other starch. Because each plant and each species has a specific requirement, and therefore, these biopolymers exist in variety of forms. And the key thing about these polymers in nature is that they do not accumulate as waste plastics.

So within the natural cycles, what are called the biogeochemical cycles, the generation and consumption of these chemicals, these macromolecules is already built in. So therefore, there is no accumulation of these waste plastics. So this is a key indicator. Given the requirement of waste utilization and waste handling of plastics the way we use, and mainly these synthetic plastics, the question that we can ask is, given all these similarities with macromolecules of the natural polymer, can we not pose some questions to ourselves? Why cannot we use polymers which nature itself

uses? We need polymeric materials, we could borrow them from nature. Why cannot we design polymers, which are similar to natural polymers? So that is another strategy. The natural polymer may not be able to exactly do the job that we are looking for. So can we design polymer, which has some of these advantages that we talked about in the way in the natural world macromolecules are taken care.

Macromolecules are taken care in the sense that they are produced in a variety of different forms, they perform various different functions. And once their function is over, they become part of a cycle so that they are consumed, they are degraded and they therefore do not accumulate like plastic waste. And one more approach which we could take, can we modify the natural polymer so that they become suitable for the engineering applications that we want?

So therefore, this is a very a useful set of pointers for us to think of new set of polymers that might help us take care of some of the issues related to sustainability of polymers. In this case, the raw materials that are required for polymers may also be part of the natural cycles. And since they are based on the physics and chemistry of natural systems, they are likely to become part of the biogeochemical cycles.

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Related terms

- **Biobased polymers** - polymers made from **natural resources**, as opposed to petroleum based resources
- **Polyactides** - derived from corn sugar
- **Polyhydroxybutyrate** - fermented by **micro-organisms**
- **Polyols** - polymers from **sugar-alcohol** ; from **glycerin** and **ethylene glycol**
- **Natural fibers** - jute, coir, **sisal**, banana, ... → *fibers → mechanically strong composite with polymer*
- **Biocompatible polymers** - polymers compatible with living tissue (**health** application - human body)
- **Biodegradable polymers**

Can polymers be renewable
PolCap05 Lecture 5: Biodegradable Polymers

So just to pause and look at related terms to these biopolymers. So some polymers are called biobased polymers, in which case the raw materials come from natural world. So an important example of this is polylactic acid. And we will look at in little more detail renewable sources for polymers in lecture 8 also. So polylactic acid, which is considered to be a very good candidate material for packaging. It is a biodegradable polymer and it is made from corn sugar. We also have a hydroxybutyrate,

polyhydroxybutyrate, which is made by microorganisms. And this is also another example of a biobased polymer or polyols which are based on sugar alcohol. And so these are examples of polymers which are made from renewable resources or biobased resources and therefore they are called biobased polymers.

Another important use of natural polymers, which is already used quite a bit is in terms of natural fibers. We can extract fibers from variety of plant species whether it is coconut we get coir fiber, from jute we can get fiber, from sisal. These are some other examples from banana, pineapple, so many plants are there from which we can extract fibers. And then these fibers, which are mechanically very strong, they can be used along with polymers as composite materials. So we can make a composite of polymer and these natural fiber and they are used. So many quite often about a decade or 15 years ago, many automotive companies or many other transport based companies started saying that they are using green composite in their vehicles. What that implied was using a polymer, which was a synthetic polymer along with a natural fiber, so that at least part of the material that they are using comes from natural polymers and which can be again part of the overall cycles that are there in natural system.

One other phrase which is used is biocompatible polymers. These are very different notation though 'bio' is common to all of this. Biocompatibility usually implies compatibility with human beings. So the application here is in health or biomedical and within the human body. So several class of synthetic polymers are also biocompatible. So many materials which are used in medical implants need not be just natural polymers or biobased polymers. They can be synthetic polymers also. There, the requirement is that the tissue in our body has to be compatible with whatever are the foreign materials that we are implanting. An important set of polymers that we are looking for to avoid the overall complication associated with waste accumulation is biodegradable polymer. And so here also again biodegradability does not imply that it is a natural polymer.

Many synthetic polymers can also be made to be biodegradable. In fact, you will be surprised to know that there are some natural polymers which are not as easy to biodegrade. And so that is a, so within the natural world also there are few polymers, select polymers, which the time required for their degradation is much longer than many other polymers. And of course, this is part of the natural design, where some

functional requirements are always the key determinant of what a polymer property will look like.

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Related terms

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 - Polyols - polymers from sugar-alcohol ; from glycerin and ethylene glycol
- Natural fibers - jute, coir, sisal, banana, ...
- Biocompatible polymers - polymers compatible with living tissue (health application - human body)
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Can polymers be renewable
PaCoPUS-Lecture 8 Renewable resources for polymers

Biodegradation, Biodegradable polymers 1/2
PaCoPUS-Lecture 35 PaCoPUS-Lecture 87

We will also look at the aspects of biodegradation in the lectures to come. And we will specifically look at the phenomena of biodegradation and the biodegradable polymers in lectures down the line.

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Biopolymers - natural polymers - biomacromolecules

- Based on type of macromolecule
 - Proteins - casein ✓ Adhesive
 - Polynucleotides ✓
 - Polysaccharides - pectin ✓ Gelling agent
- Based on origin
 - Plant - polyisoprene ✓ Tyre, Vibration mount
 - Animal - gelatin ✓
 - Microorganisms - xanthan gum ✓ Thickener

Applications of biopolymers
Biopolymers are widely used, but not in as high volumes as commodity plastics

So let us continue with our journey related to biopolymers. And these are also called by the way 'biomacromolecules'. So given that they are present in biological world, and they are macromolecules. So these are few examples again of how do we talk about different types of bio macromolecules or biopolymers. So we could classify them based on the type of macromolecule. And this we have already seen in one of

the introductory lecture, where proteins or DNA, RNA, which are examples of polynucleotides or polysaccharides. So this is three different important sets of biomacromolecules which are present in the biological world. We could also classify them on the basis of which part of biological world do they come from. Do they come from a plant? Do they come from an animal? Or do they come from a microorganism? And so here what I have done is given just a couple of examples of these biopolymers. So casein is a protein which comes from milk. And pectin, which is there in variety of fruits and vegetables. This is from the rubber tree polyisoprene or natural rubber. And xanthan gum is made by a bacteria. Of course, we have examples like gelatin which comes from animal and during the course later on, we will have a chance to look at many of these polymers. One important thing that you can notice is of course, these polymers are used. So it is not that synthetic polymers are only used. Lot of natural fibers are used as I pointed out earlier.

Many of these biopolymers are also used quite commonly for variety of application. So many of these biopolymers are used extensively and for example, adhesive application, casein is used quite a lot. Pectin is used extensively as a gelling agent in foods. So therefore, pectin also gets used quite a bit. Of course, natural rubber is also quite commonly used in variety of applications, whether it is tyre or vibration mount, and so on. Even in shoes or many other footwear applications, we use natural rubber at times. Also in terms of modifying viscosity, thickener, so that thickener is an application where we add a small amount of a material, and that changes the viscosity. In this case, let us say if xanthan gum the way it is used is we use it along with water, and then it increases the viscosity by orders of magnitude. And that is why it is called a thickener. So you can see that very wide ranging applications of these biopolymers are present.