Physico - Chemical, Mechanical and Electrical Properties of Polymers

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Lecture – 35

Physical / Chemical Crosslinking

Hello, we have had 4 weeks of discussion of macromolecular systems, their introduction, which is largely focused on the macromolecular nature and structure. And this week and next couple of weeks are going to be focused on properties. And we will look at mechanical, electrical and physical, chemical properties of systems. One of the main ways in which properties can be changed is by changing the macromolecular nature itself.

And molar mass as we have seen is a very important criterion for determining the overall performance of macromolecules. We also saw that the molecular architecture plays a very important role. And crosslinking is one of the ways in which a fair number of polymeric products are made appropriate for a given application. And so, for example, any sealant application any gasket application, if you see it is a material, which is going to be crosslink material.

Similarly, for electrical insulation, polyethylene we think of as a grocery bag material. But for high voltage electrical insulation, it is crosslinked polyethylene, which has the right amount of hydrophobicity,because of only CH_2 CH_2 CH_2 everywhere, but crosslinking gives it the required stability for long term electrical performance also as a very good insulator, which does not fail easily. So, crosslink polyethylene, for example, becomes a product, which is in a completely different domain, a very important application.

So, in general, crosslinking is induced in a material to improve its performance and improve its stability. But the flip side of it is also, recycling or reshaping of these is not possible because of the crosslinks. As we will see, crosslinks basically imply the molecular weight of the overall sample is infinite, the whole big tire, for example, is one giant macromolecule. And but without the crosslinks, a tire cannot really function.

And so therefore, these materials have very superior properties at the same time they challenge. They are challenging in terms of their overall sustainability. So, in this lecture, I want to highlight the sustainability aspect by also looking at how is crosslinking done in biological part? So, with bio macromolecules, what is the type of crosslinking that is there? So, we look at crosslinking and engineering materials first, and then close the lecture by looking at biomacromolecules.

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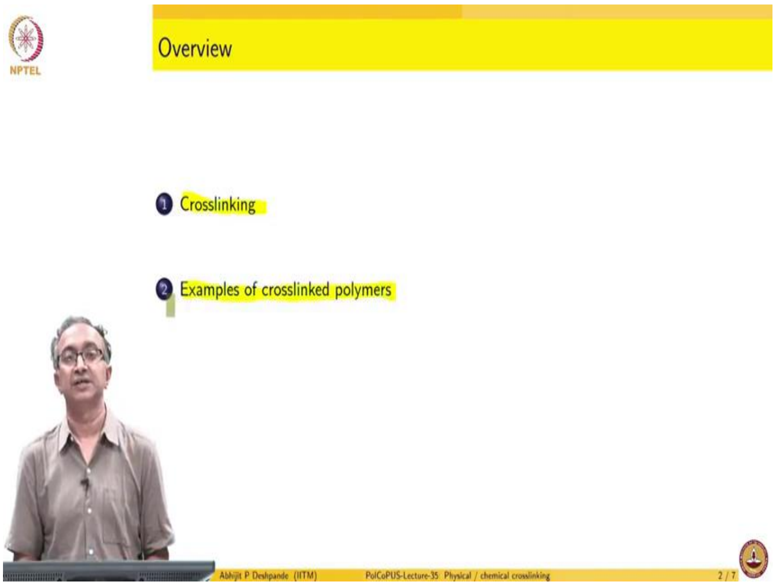

Overview

1. Crosslinking
2. Examples of crosslinked polymers

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So, we will look at what is meant by crosslinking and some examples, where we look at both synthetic applications as well as bio-macromolecular systems.

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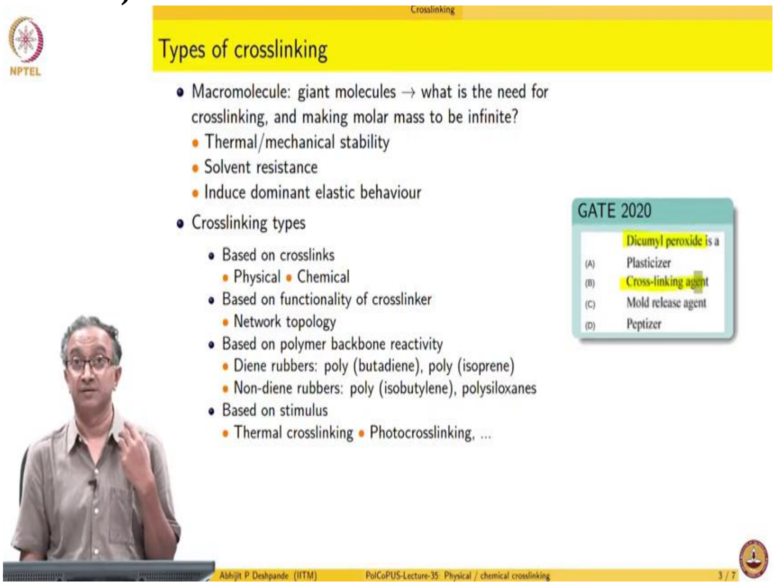

Crosslinking

Types of crosslinking

- Macromolecule: giant molecules → what is the need for crosslinking, and making molar mass to be infinite?
  - Thermal/mechanical stability
  - Solvent resistance
  - Induce dominant elastic behaviour
- Crosslinking types
  - Based on crosslinks
    - Physical
    - Chemical
  - Based on functionality of crosslinker
    - Network topology
  - Based on polymer backbone reactivity
    - Diene rubbers: poly (butadiene), poly (isoprene)
    - Non-diene rubbers: poly (isobutylene), polysiloxanes
  - Based on stimulus
    - Thermal crosslinking
    - Photocrosslinking, ...

GATE 2020

Dicumyl peroxide is a
(A) Plasticizer
(B) Cross-linking agent
(C) Mold release agent
(D) Peptizer

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So that crosslinking is, one could pose a question as to you know, macromolecule is already a very giant molecule, we have repeating units, which is 10^4, or even a higher number of repeating units, what is the need for even more increase in the molecular weight, because as I mentioned, once you have crosslinking, basically, one macromolecule is joined with all the others and basically, so you have an infinite molecular weight.

And so, I can start from one end of the macromolecule. And I can travel basically all the way. And so, it is like a maze, where one end of the sample is connected with another end of the sample by just traveling along macromolecular chains. And so, of course crosslinking is done, because stability is much higher, whether it is thermal stability, whether it is mechanical stability, the resistance to solvent or whatever other physico-chemical environment that the material sees.

Important from the point of view of let us say acid solutions being it is being exposed to or oil it is being exposed to so quite often the materials with crosslinks end up showing better performance. Now can you imagine why you would solvent resistance of such a crosslinked polymer would be better, when compared to if let us say these macromolecules were just randomly organized as in case of either a branch or a linear polymer.

What does these crosslinks which are chemical crosslinks, what do these crosslinks do in terms of both mechanical stability as well as solvent resistance? And these covalent bonds are of course, permanent bonds as supposed to the interaction points here, which are based on physical interactions and entanglements. So, what is it that is related to crosslinking that makes it so, rewarding in terms of performance?

The other thing that you can also consider is because of these crosslinks, the elasticity behaviour is generally ensured. So, if you think in terms of stress strain curve, as we have seen in the 32nd lecture, that for a heavily crosslinked polymer, we basically have a brittle failure, but you have an elastic behaviour when we look at sigma stress as a function of strain. So, if you want perfect elastic behaviour, then crosslinking induces that.

So, because we have crosslink points, which are permanent, the macromolecular orientation and other phenomena associated with yield and plasticity are not present at all. So, sample will extend just based on energy, because the macromolecules will get displaced with respect to each other, but beyond a certain point the chains will break and then it will be a failure of the sample.

So, we have basically induce more elasticity in the sample if we introduce a class called crosslink point, the same thing is true in the rubbery state also, because these crosslinks, if we have a rubber material, which is lightly crosslinked system, polymer chains are dangling between crosslinking points. And so, one crosslink point and another crosslink point and when we stretch, the segment can stretch itself.

And that is again the origin of rubber elasticity and any of the polymeric material and it is rubbery state. So, therefore, crosslinking is very important from the point of view of stability and inducing elasticity in the material. And there are several ways in which we can do crosslinking, we can distinguish crosslinking based on whether it is based on physical interactions, hydrogen bonding can be an important source of crosslinking if hydrogen bonding between macromolecules is possible.

In fact, cellulose has a very extensive hydrogen bonding network between different macromolecules of cellulose. Chemical crosslink is what is used in many of the synthetic polymeric application. So, whether it is thermoset materials or whether it is rubbery materials, we could have the crosslinking type depending on the functionality and in this case, depends on the functionality as we have discussed earlier is how many times a molecule can react and if crosslinker can react 4 times then it will attach to macromolecules.

And so, therefore, this will lead to a different topology or structure of the network compared to a trifunctional. So, depending on the functionality, we will get different types of networks and therefore, different type of crosslinked polymer in terms of the backbone itself, what is the mechanism by which crosslinker and the backbones of the macromolecule interact? So, what is the nature of these linkages crosslink which are being formed?

So, for example, in case of diene rubbers, we have the double bonds associated with the backbone itself and these double bonds can be used for vulcanization in case of non-diene rubbers such are not present, but then free radical has to be found using peroxides or other initiators and crosslinkers So, that crosslinking can happen. So, depending on the mechanism of crosslinking reaction we can distinguish the crosslinking type.

We could also distinguish crosslinking based on what is the stimulus for crosslinking. So, for example, is acidic environment there or is temperature high temperature is required before radicals can be generated or in the presence of UV light or other photo of light based radiation can we have enhanced crosslinking or crosslinking can be initiated based on these. So, therefore, these are various ways in which crosslinking is induced into the materials.
And just to look at this question, clearly since I am discussing it on this slide, dicumyl peroxide is a crosslinking agent, but you can think of which of these classification does it belong to? Is it a physical or chemical crosslink that dicumyl peroxide will form? Is it a tri functional, tetra functional di functional what kind of crosslinker is it? What is the backbone requirement if dicumyl peroxide is being used as a crosslinker and then what is the stimulus required?

Does dicumyl peroxide perform when UV radiation is there, or does it perform when pH is right, or does it perform when temperature is high? So, all these aspects can then distinguish as to dicumyl is a crosslinking agent and how effective it is for crosslinking different types of polymers.

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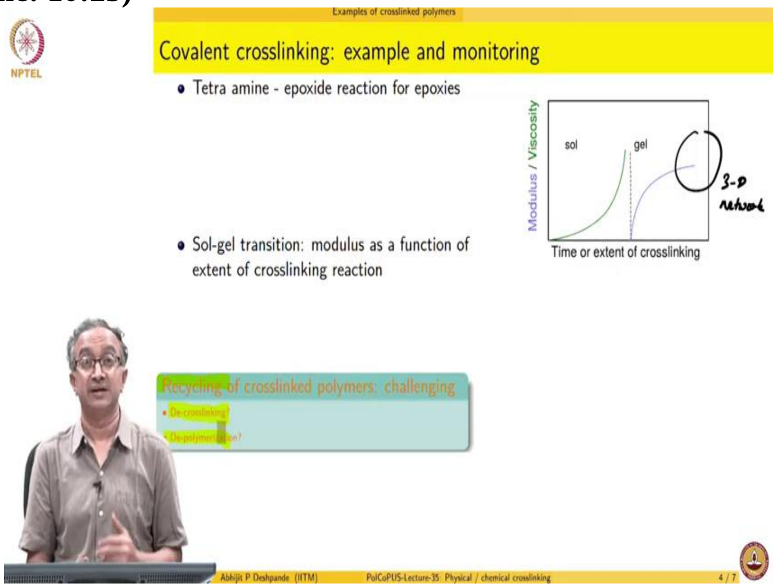

Examples of crosslinked polymers

Covalent crosslinking: example and monitoring

- Tetra amine - epoxide reaction for epoxies
- Sol-gel transition: modulus as a function of extent of crosslinking reaction

Recycling of crosslinked polymers: challenging

- De-crosslinking?
- De-polymerization?

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So, let us look at the covalent crosslinking and one example of it and so, here for example, we can look at an epoxide and an amine reaction and so, this is the epoxide linkage and this can react with amine, so, I have not drawn here the other parts of the chain segment, but basically you can have this amine attached to several there are tetra amines and tri amines and vary the group also can be Hexa group C_6 or it can be different groups there can be branching also.

So, all of these possibilities are there, but basically reaction is between the epoxide group and amine for epoxide and when this reaction happens, what you have is basically the one more bond is formed where NH and so, this hydrogen from the amine group basically forms the hydroxyl group. So, this is the reaction. So, from epoxide we go to this epoxy molecule, but what you can notice is there is NH still remaining.

So, now, another epoxide can come here. So, you can draw another epoxide, and this can react with this NH and so, if I have a tetra amine 4 such reactions are possible. And so that is how the crosslinking happens and the molecular network keeps on building. So, if I look at different stages of what is happening during a crosslinking reaction, initially at low time basically I will have only these fragments, which are much smaller molecules.

So, in a sample, I will mostly have these small molecules, if I go to slightly later stage now, what is happening is there is some amount of crosslinking but there is some amount of small molecules also present when we go to a critical point called the gel point, what happens is all throughout the sample now, there is a percolating network and there are of course, smaller molecules also present.

So, as crosslinking happens, you would expect viscosity to increase because molar masses increasing and we will discuss this when we look at the rheological response of polymeric system. But, we have already discussed the mechanical properties of the polymer in the 32 lecture for example, we looked at stress strain response and generally we will not look at stress strain response for a liquid material because they can keep on deforming infinitely, we know that liquids cannot withstand any stress.

But, if this 3-dimensional network is formed, then it can withstand and so, that is the point at which in fact modulus starts to be non zero. And so, we can measure the modulus even though there are some smaller fragments present in the sample, since there is a percolating network and as I mentioned, from one point of the sample, you can go basically to the other end of the sample traveling along the macromolecules.

And so, that is called the gelation point. So, this transition is called sol to gel from a solution liquid like system to a gel solid like system. And this gel point is also very important from a practical point of view, because all the shaping has to be done before this gel point is reached, because once the gel is formed, it acquires a solid like feature. So, if you were to do this in a beaker, and if I were to just take the sample initially and do a stirring, what I will get is a liquid like response.
Where it will stir like a liquid, but at this point, when I stir, it will rotate like a solid, it will become one blob. And even though it is a soft solid because there are many small molecules still present some of the prepolymer is still there, some of the hardener is still there are small molecules, but the gel fraction is spanning the whole sample and so therefore, it will rotate like a big solid blob inside the beaker and there will be slipped between the overall blob and the surface of the beaker.

So, therefore, this is one way to also monitor crosslinking reactions, we can measure either the viscosity or the modulus and try to monitor what is the weight extent of crosslinking is there in the sample. And so, the sol gel transition is a very important indicator of when to do what kind of processing when we are dealing either with thermoset materials or with crosslink rubber materials.

And because of this crosslink once formed, and once we get a 3 dimensional network, we have seen that recycling is a challenging aspect, because we have to first think in terms of decrosslinking so that we get rid of the 3 dimensional networks because tire for example, is one giant molecule. So, recycling of tires, for example, therefore, is quite challenging, we cannot really melt it, because it is not macromolecular in terms of linear and branched it is one giant macromolecule connected from one end to the other.

So, if you could decrosslink it, then we could reprocess it. And of course, if we have to get it into raw materials and then make it part of the overall cycle, then we need to also depolymerize it. So, in case of recycling of thermoset and crosslink proper polymers there are additional challenges when we compare them with other linear and branched polymers.

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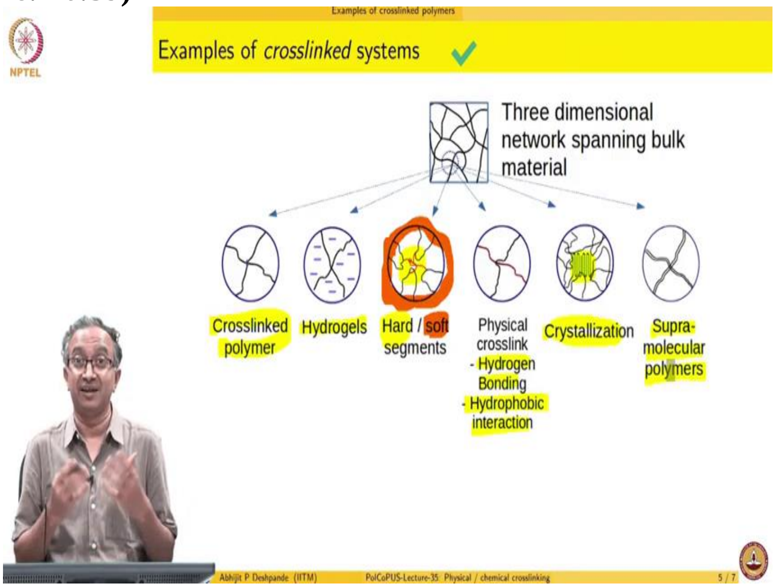

Examples of crosslinked polymers

Examples of *crosslinked* systems ✓

Three dimensional network spanning bulk material

Crosslinked polymer

Hydrogels

Hard / soft segments

Physical crosslink
- Hydrogen Bonding
- Hydrophobic interaction

Crystallization

Supra-molecular polymers

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So, the question that can be asked is can we not have a set of crosslinks which are may be more amenable to manipulation and decrosslinking may be something which is achievable. And so, there are several examples of crosslink systems which are there. And from an engineering point of view, of course, what we have used are covalant systems, where like we saw in case of epoxy, there is a specific covalent bond formed by the crosslinker.

And that is why crosslinker also called hardeners, because they basically induce from a pre polymer liquid like material to a final thermoset gel solid like polymer, it is hardens the material. And the other applications of covalent crosslinks are also in there in super absorbent polymers and various other applications of drug delivery, where the solvent is present along with the crosslinked polymer network.

So, these are what are challenging from the recycling point of view, but can we not think of crosslinks as physical crosslinks, in which case de-crosslinking as a process may be easier to achieve. This point, I would like you to just think about it as to why cellulose is so stable, because cellulose does not have chemical crosslinks. So, though I am trying to point out that you know, chemical crosslinks are the ones which are more difficult to de-crosslink.

Sometimes even secondary crosslinks, such as found by hydrogen bonding networks in cellulose can also be difficult. We will also see another example of chitin as a polymer. So many of these systems, physical crosslinks can also be challenging, but in general, we will find physical crosslinks to be easier to de-crosslink because for example, crosslinks can be found by just hard segments in a sea of soft segments.

So, the black chains here are basically soft, and they are distributed in this hard. So this hard point wherever for example, polyethylene, polypropylene, so whenever red polypropylene chains are there, they are surrounded by black polyethylene flexible chains, and the red part of polypropylene chains will try to act as a crosslink point keeping together fixed the polyethylene chains which are more flexible.

You could also have as I mentioned, hydrogen bonding or maybe hydrophobic interactions as the specific sticking points between different macromolecules and inducing physical crosslinks, crystals could also form a crosslink. So, if you have flexible chains in the rubbery state, but there are crystalline portions, then what happens is we know that each and every lamella will have chains coming sticking out of it.

So, basically different chains of flexible chains are bonded together through this crystalline portion. So crystalline portion can also act as a crosslinking point and the way we can decrosslink this is just to melt it. So, the once if the crystal is molten either by increasing the temperature or by adding a small molecule which will change the crystallization condition. So, crystals can be taken away. And in that case then deeper decrosslinking can happen easily.

There is also an interesting possibility, which has been discussed a lot in research literature in the last 10, 15 years is related to supramolecular polymer. The concept here is to get away from covalent bonding even in macromolecular formation because I talked about in the previous slide about de-crosslinking and de-polymerization. So, both are challenging aspects from a sustainability point of view.

Now, can we not assemble a polymer, and which is called a supramolecular polymer? So, here the monomers are also attached to each other through physical interactions. And of course, many of these materials are nowhere near the applications that we have, for example, from an epoxy material, or even polyester material. But this is an interesting possibility that we can assemble and disassemble as we want. And so some of these materials can probably give partial answers to overall sustainability challenges which we are facing.

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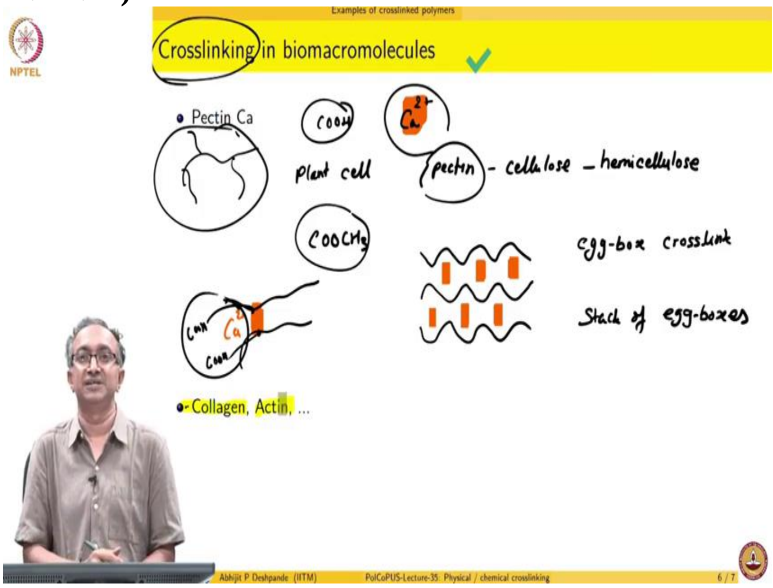

Examples of crosslinked polymers

Crosslinking in biomacromolecules

- Pectin Ca
- Collagen, Actin, ...

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So, just to again highlight as to how is crosslinking done in natural world, and in bio macromolecules, we will just take a close look at pectin calcium system. And as we have seen earlier, pectin is a fairly complicated molecule with different types of hydrophilic, hydrophobic domains and branches being present. But one of the key things that is there on the pectin molecule is the carboxylic acid group. And this can be crosslinked using a calcium ion.

And so, the importance of calcium in overall biology is well known and one of the functions that calcium also does is crosslinked with pectin. Now, why is this important? Because, in plant cell wall, for example, we have distribution of pectin, cellulose and hemicellulose. And it is the pectin with it crosslink with calcium which determines how the cell wall behaves. In fact, when fruit ripens, we know that its skin becomes soft.

And part of the processes which happened to change the mechanical response of the skin is what happens to pectin. If let us say instead of carboxylic acid groups, we have this group then it can be crosslinked using calcium. So, the way the calcium crosslinks are present in pectin and the nature of amount of crosslinking which is present is very important determinant of what the plant cell wall property will be and this is not all of it, how calcium crosslinks pectin is also extremely interesting.

So, we can have basically one pectin chain and another pectin chain being crosslinked by this calcium. So, calcium can I just draw it using this right the highlight, so, basically, we have this calcium interacting with 2 COOH which groups from two different chains. So, there is a COOH group here and there is a COOH group here and this is the crosslink which is formed.

So, this is one way of doing the crosslink, but what happens based on the COOH which are located on the pectin chain is an very interesting formation which is like this, where there is a pectin chain, and then there is calcium. And I do not know if you can think of what this reminds you of. This is called an egg-box crosslink. It is as if calcium is sitting in the slots formed by the pectin box.

And moreover, the fascinating aspect of macromolecular assembly is that we can have stacking of such egg boxes on top of each other. So, we can have we can have stack of egg boxes. So, look at how crosslinking variety is there are different types of crosslinks different amounts of crosslink by manipulating the chemistry of the macromolecule and the molecular architecture with hydrophobic, hydrophilic different groups to again ensure different types of interactions.

So, a bio macromolecular system such as pectin has all these varieties from basic monomer level all the way till crosslinking to do tunability of its properties. And so, this can serve as an inspiration for us to also think of polymeric products with such tunability. But as sustainable as these pectin chains are because once the fruit is done, the peel can easily get recycled and get become part of the overall cyclic processes.

So, can that be done with the polymeric materials that we have, and just to see these multiple heterogeneities and complex assemblies of bio macromolecules that we have, you could also just look at, you know, collagen and its crosslinking collagen is a basic component of tissues. And it is a very important structural component, it gives mechanical properties, barrier properties and it is it is basically what makes it possible for tissues to sustain themselves.

So, what kind of crosslinking is there in collagen or actin which is again part of cell wall and the cytoplasm and so, how crosslinking in these kind of systems also is very influential in determining the overall performance and quite often the elasticity is induced based on these crosslinking networks. So, generally network polymers and their crosslinking is very important area for us to look at.

Because, of the practical engineering applications as well as from the point of view of understanding biology. Now, can we merge the two in terms of getting the right amount of crosslinks for the engineering application where de-crosslinking can also be easily achieved?
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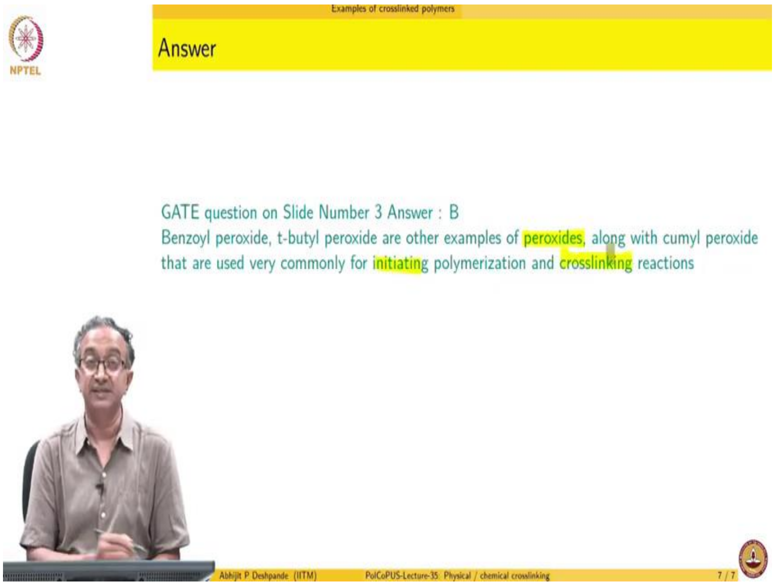

Examples of crosslinked polymers

Answer

GATE question on Slide Number 3 Answer : B

Benzoyl peroxide, t-butyl peroxide are other examples of peroxides, along with cumyl peroxide that are used very commonly for initiating polymerization and crosslinking reactions

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So, with this thought, we will close this lecture and the peroxides are actually very common materials for initiating and crosslinking reactions. So, they have basically 3 radical processes by which they do the initiation and crosslinking in the monomer or the macromolecules as the need. Thank you.