

**Simple Concepts Related to Single Macromolecules**  
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**Lecture - 11**  
**Application based terms**

Hello, let us continue our discussions on polymers and in this lecture, we will finish some of our definitions related to types of polymers and how they are referred to especially from an application point of view. So, application based terms with a specific emphasis on how polymers are used, we do this in.

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Overview

- 1 Types of Polymers
- 2 Thermoplastics, thermosets, rubbers
- 3 Polymers for electronics, fuel cells and batteries, sensors and actuators
- 4 Solutions, dispersions and gels
- 5 Polymers in composites

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And to do that we will just look at what are the different types of terms which are used and many of these terms you are familiar with. We will also just spend small amount of time on polymers for energy and robotics and applications which are more advanced. And then also things like paints, where polymers are used and an important application of polymers is in composite materials, where polymers are incorporated with an another material.

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Types of Polymers

### Types based on applications

- Large-scale applications
  - Thermoplastics, plastics
- Crosslinked polymers, thermosets, elastomers, rubbers
- With solvents: solutions, dispersions, emulsions
- Gels, hydrogels - crosslinked polymers
- Polymers in composites

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So, generally the way to look at how different polymers are applied in engineering or scientific applications, one of the key things, why plastics are everywhere are dependent on these usage as large scale applications. And here one of the key terms which are used and which we are familiar with is the term plastic and plastic implies the ability of the material to retain permanent deformation when subjected to loads as opposed to elastic.

So, when we look at mechanical properties of polymers, we will look at how many of the polymers show this deformation, a key term which is used is also thermoplastic - in which case, materials can melt and reform. So, this is one way of classifying the materials where it is based on plastic materials. The other large scale application materials are cross linked polymers. And they belong to 2 large classes, thermo sets, where the degree of cross linking is very high and elastomers and rubbers where degree of cross linking is very low.

And based on degree of cross linking the way I mentioned high and low, I hope you can see why rubbers are flexible and softer materials while thermosets, you can expect them to be harder and more rigid materials. Many of the polymeric systems are used with a solvent if it is with water, then you can have a gel or a hydrogel kind of material. We can also have them in the form of solutions and dispersions, and emulsions.

All of these have a specific definition. Solution implies it is a molecular mixture between a polymer and a solvent. While dispersion and emulsion implies it is a 2 phase or even multiphase

mixture, where both the polymer and the solvent phases retain their phase identities and of course, usage in composites.

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Thermoplastics, thermosets, rubbers

### Plastics and rubbers

- Thermoplastics: melt upon heating
  - Polyvinyl chloride (PVC), Nylon, Poly (ether ether ketone) (PEEK), ...
- Set upon polymerization reactions - crosslinking / formation of three dimensional network
  - Prepolymer, resin
  - Hardener, curing agent, crosslinker
  - Epoxy / Hexamethylene diamine, Polyester / benzoyl peroxide, Urea-formaldehyde

**GATE 2016**

Match the elastomers listed below to the appropriate curing agent:

Elastomer	Curing Agent
P. Silicone rubber	1. Zinc oxide + ethylene thioana
Q. Natural rubber	2. Diamine
R. Chloroprene rubber	3. Sulfur
S. Acrylam elastomer	4. Decanyl peroxide

(A) P-4, Q-3, R-1, S-2  
(C) P-4, Q-1, R-3, S-2

(B) P-3, Q-4, R-1, S-2  
(D) P-2, Q-3, R-4, S-1

- Lightly crosslinked polymer
  - Latex
  - Chloroprene, Ethylene propylene diene monomer (EPDM) rubber
  - Rubber, elastomer

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So let us first look at the two broad terms which are related to plastics and rubbers. So generally when we use in common terms, both thermoplastic and thermoset just get referred to as a generic term plastics. The thermoplastics are the one which can melt upon heating. So whenever we talk of recycling, it is only these thermoplastics when we are talking about it is another class of materials called thermo sets, which actually set when you finish the polymerization.

So, when we are fabricating thermosets, we have to carry out reactions and then make the shape of the material. And once we set the material then we cannot melt it again. So, recycling of thermosets is a challenge because there is a formation of 3 dimensional network in case of the thermoset resin. So, this is also referred to as a resin when it is in the liquid form before it has become set and become the final solid polymer. We also refer to it as a prepolymer.

These imply basically that the molar mass of macromolecules is small and only when polymerization reactions happen, the molar mass builds up eventually leading to a 3-dimensional network. And to get this 3-dimensional network, we need a crosslinker which is also referred to as a curing agent. We essentially say that you know, we take the prepolymer or resin and then we cure it so that it becomes solid.

So, therefore, the crosslinker is called a curing agent. And naturally it is also a hardener, because it takes the material from a liquid prepolymer resin prepolymer to solid thermoset. And prominent examples of these thermosets are epoxy. You can look up the applications of epoxy, it is a fantastic adhesive for bonding, dissimilar materials, there is not many, there are not many adhesives, which are as good as epoxy.

One of the things you always can prod yourself in terms of thinking is when I say that epoxy is good adhesive, the question is why. Why is it a good adhesive? So, the answer to that may lie in looking at the molecular structure, and what are the interactions that epoxy can have with the surfaces with which it is going to bind. For example, epoxy is an adhesive for cellulosic cardboard those kinds of substances, it can bond metals also. So it can bond metals to FRP. Metals to polymer composites.

That is why it is used in automotive applications also quite a lot these days. So, you can go and look at the structure of epoxy and then try to think in terms of what are the interactions which make it a good adhesive material. Polyester is a very commonly used material with FRP thermoset polyester fiber reinforced plastic. Generally glass fiber is used in a variety of applications such as in sporting goods or in boat making and things skis and bats and stumps - variety of materials when they are made quite often.

It may be a thermoset polyester with glass fiber as reinforcement. And urea formaldehyde is also a prominent example. Now, just to highlight the fact that you know the curing and the hardening is done with a substance - crosslinker. We can think of which crosslinker is good for which material. So, this is for example, an exam question where we are asked to guess and know which rubber or which elastomer is cured with which curing agent. And so, of course, most of you may be quickly able to spot that natural rubber is cured with sulfur and so, Q 3.

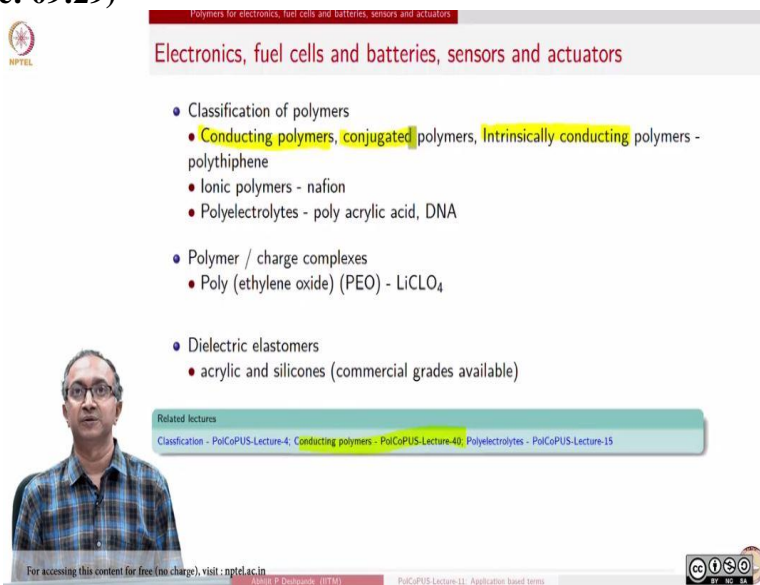
So, actually you can see that now, these are the 2 options from which you have to think. So, in terms of looking at this; what you can try to figure out is look at what are the bonds in acrylate. What is the functional group in acrylate? When we say that silicone rubber is getting polymerized is there a functional group or is does it happen through an activated mechanism? If

it does happen through activated mechanism, then you need an activator - generator, which is either a free radical or any other activated species.

So, thinking like that you can then try to do and know what curing agent is used for what rubber. So, just think about this and at the end of the lecture, we will come back and look at the answer. In terms of cross linking the difference between thermoset and rubber as I mentioned is degree of cross linking. And elastomers are materials which are lightly cross linked. And the material before cross linking is also referred to as latex.

So, latex is collected from a rubber tree and then it is vulcanized - crosslinked to get the final rubber part. And there are several examples, natural rubber is of course obtained from trees, but we have several formulations of synthetic rubbers and they are predominant in applications which include from tire to vibration isolation to variety of sealant applications. And so, we refer to it as both rubber and elastomer. Elastomer implying that you can stretch it to a very significant degree.

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The slide content is as follows:

- Polymers for electronics, fuel cells and batteries, sensors and actuators
- Electronics, fuel cells and batteries, sensors and actuators
- Classification of polymers
  - Conducting polymers, conjugated polymers, Intrinsicly conducting polymers - polythiophene
  - Ionic polymers - nafion
  - Polyelectrolytes - poly acrylic acid, DNA
- Polymer / charge complexes
  - Poly (ethylene oxide) (PEO) - LiClO<sub>4</sub>
- Dielectric elastomers
  - acrylic and silicones (commercial grades available)
- Related lectures
  - Classification - PoCoPUS-Lecture-4, Conducting polymers - PoCoPUS-Lecture-40, Polyelectrolytes - PoCoPUS-Lecture-15

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Dr. P. Dhanasekar (BITM) PoCoPUS Lecture 11: Application based terms

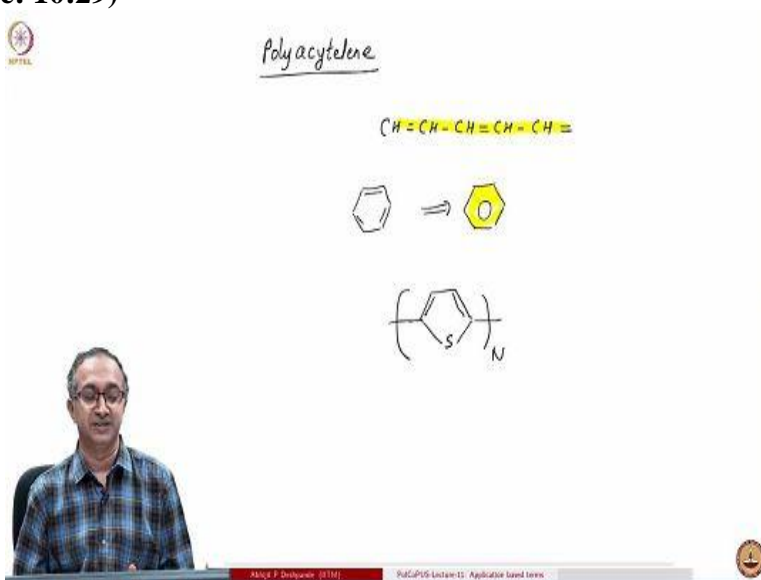
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As far as polymers for electronics or electro chemical cells or batteries is concerned we use polymers which have a certain electrical property. So, classification of polymers and those kinds of applications are based on different terms. Naturally, many of these applications are of more recent origin while the applications of thermoplastics and thermosets have been around with us

for a significant amount of time. So, generally we use in electronics, we use polymers which are conducting and they are also called intrinsically conducting polymers.

And so, in a lecture later on we are going to look at much more closely as to how electronic conductivity can come in polymer. Just to make you think about how conductivity can come in a polymer the aspect of conjugation you can think of. You can try to anticipate why or how does a polymer become conductive.

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So, for example, if you look at a polymer called polyacetylene, what you will see is it is a polymer which has alternate single and double bond. And you might also recall that benzene, the single and double bond instead of drawing like this, we know that the electrons are delocalized and therefore, we indicate that delocalization figuratively by drawing indicating delocalization. So, same delocalization can happen along this chain because of alternating double and single bond.

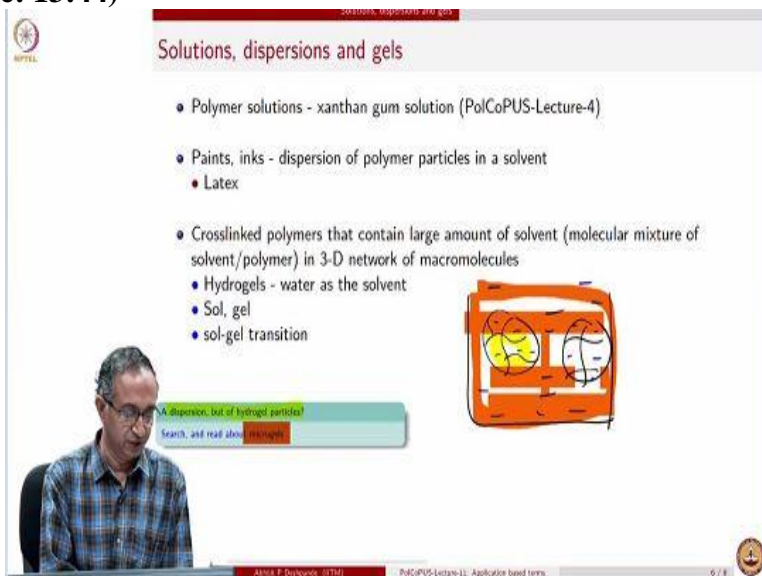
So, this is the origin and the conjugation is important in making polymer conducting polymer. You can also think the important polymer which is used as conducting polymer is thiophene. Thio implying sulfur and it has a structure of this kind. Now, you can draw a chain of polythiophene and again think in terms of how conjugation is there, and therefore, how delocalization of electrons can take place and how a polymer chain can become conducting.

The other sets of polymers which are used in applications of electro chemical cells are in fuel cells, which are sulfonated polymers such as Nafion and we will take a closer look at Nafion in a future lecture. Polyelectrolytes are used in variety of applications also. They are macromolecules with ions. There is other class of materials where polymer and charge complexes are there. So, in this case macromolecule itself does not contain the ion, but polymer and charges are mixed together that is why they are called complexes.

And finally, an important applications for soft robotics where we can use materials which are elastomeric, but at the same time they can respond to electric fields. So, dielectric elastomers are important class of materials in fact, commercially available acrylics and materials which are silicones can give you very good performance in terms of electromechanical response, when we say electromechanical, it implies that subjecting material to electric field will give us mechanical response or subjecting material to a load can give us electrical response.

So, dielectric elastomers are important examples of electromechanically active materials. And so, we will spend time on poly electrolytes in just a couple of lectures down and of course, some of these classification we also looked at and so, continuing further.

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The screenshot shows a presentation slide with the following content:

- Polymer solutions - xanthan gum solution (PolCoPUS-Lecture-4)
- Paints, inks - dispersion of polymer particles in a solvent
  - Latex
- Crosslinked polymers that contain large amount of solvent (molecular mixture of solvent/polymer) in 3-D network of macromolecules
  - Hydrogels - water as the solvent
  - Sol, gel
  - sol-gel transition

There is a diagram on the right side of the slide showing a 3-D network of macromolecules (represented by orange lines) with yellow circles representing solvent molecules. A green box at the bottom left contains the text: "A dispersion, but of hydrogel particles? Search, and read about hydrogels".

Let us look at now the solutions and flowing applications of polymers. When we say thermoplastics, thermosets and rubbers we are implying solid polymer use, but polymers are used in their different liquid like forms also. So, solutions of course, an example we looked at

again in the fourth lecture was Xanthan gum solution which is used in petroleum and recovery and also food applications. An important application of polymer is in the dispersion form where polymers are retained as particles.

And then there is a solvent or dispersing medium. And this is also referred to as latex, because the latex that we get from rubber tree is also a dispersion of isoprene pre-polymer in an aqueous medium. And an important class of materials which are soft, they are solid like but at the same time they contain large amount of solvents. So, we have a cross link polymer just like rubber, but rubber is a dry material in the sense that it does not contain solvent.

But if a crosslinked polymer network is swollen with large amount of solvent then we call it a gel material because it is soft, solid-like at the same time. It appears like a jelly the way we see it in our food applications. And so, hydrogels are crosslinked polymers that can have large amount of water. And in this case, one important characteristic that is usually used is to distinguish between the materials with starting out where it is sol and then material finally, when cross linking is done called gel.

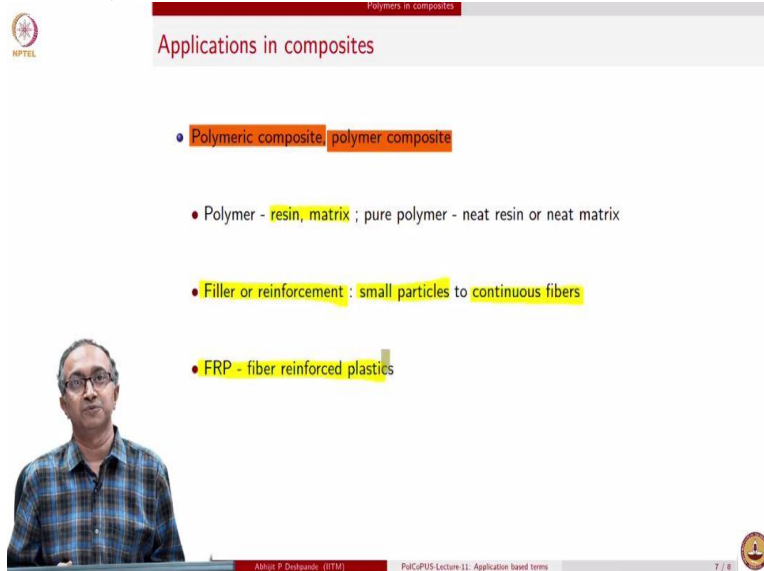
So, there is a sol to gel transition, which is very important in these gel like materials. And the final application may be in the gel form, but while we are manipulating the material, it may be in the sol form. So, all the manipulation has to get done before the gelation reaction happens. So sol-gel transition is an important transition in these kinds of materials. An interesting question that you can think of that it is a dispersion, but it is mixture of hydrogel particles.

So, if you have let us say the 3-dimensional network of hydrogel, in which each and every hydrogel particle has lots of solvent, and now, this hydrogel particle is dispersed in water. So, each and every particle has retained its identity in terms of the crosslink network, and there is water in this medium also and of course, all of this is like a dispersion in a medium. So, in this kind of a complicated material system where hydrogel particles are dispersed in a water medium, what we can do is, these particles can encapsulated a drug and the overall dispersion can be used as a drug.



So, therefore, in addition to whatever we have discussed, there are very interesting possibilities of combination of macromolecules in various forms for different types of applications. So, you can read about these micro gels. It is a very fascinating new area of work.

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The slide is titled "Applications in composites" and lists the following points:

- Polymeric composite, polymer composite
- Polymer - resin, matrix ; pure polymer - neat resin or neat matrix
- Filler or reinforcement : small particles to continuous fibers
- FRP - fiber reinforced plastics

At the bottom of the slide, there is a footer with the text "Abhishek Chakrabarti (IITM) Pol/GPUS Lecture 11: Application based terms 7 / 8".

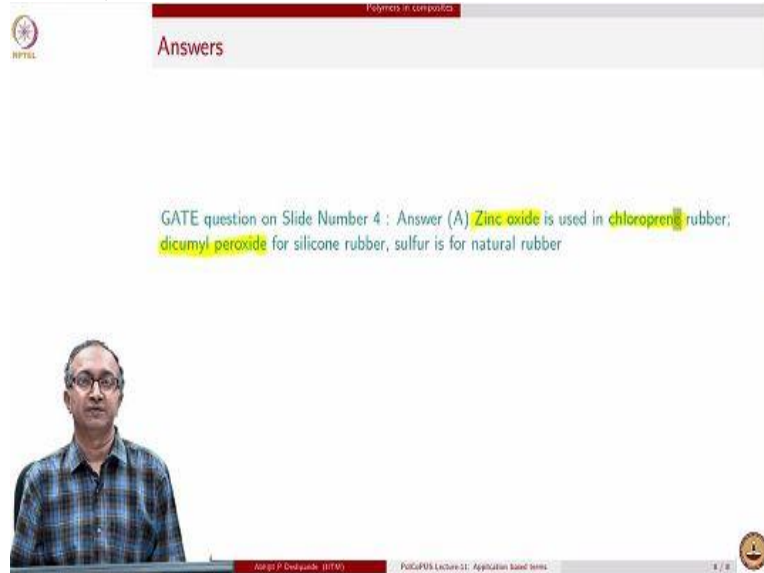
Now, we will close this lecture by looking at the terms associated with polymer usage in composites. So, these are called polymer composites, or polymeric composites. And polymer is referred to as resin or matrix. It is also sometimes called neat. So, neat resin or neat matrix implies that when the reinforcement or filler has not been added, while composite is when polymer is mixed with fiber or filler, and notice that I am using the word reinforcement as well as a filler.

And there is a small distinction between them reinforcement when we say we want a property to be enhanced, while filler more often than not can be to just reduce costs. So, that filler is low cost compared to the polymer which is being added. So, generally, these both of these terms are used. And sometimes we need to be careful when somebody saying filler, they may actually imply that it is also for enhancement of properties. And so, both fillers and reinforcements can be from very small particle to larger particles.

And in fact, reinforcement will be best when it is a continuous fiber it is a very long fiber. And in fact, in case of aerospace when an aircraft wing is made, the wing which is meters of length, continuous fiber can be running through the whole wing itself. And that is when the maximum

mechanical property advantage that we can get is obtained. And another term which is used to describe these materials is also fiber reinforced plastic, again implying that plastics which could be thermosets or thermoplastic and in that continuous fiber or other fibers are incorporated to reinforce them and improve their mechanical properties.

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The screenshot shows a presentation slide with a red header bar containing the text "Polymers in composites". Below the header, the word "Answers" is written in red. The main content of the slide is a text block that reads: "GATE question on Slide Number 4 : Answer (A) Zinc oxide is used in chloroprene rubber, dicumyl peroxide for silicone rubber, sulfur is for natural rubber". The text "Zinc oxide is used in chloroprene rubber" is highlighted in yellow. In the bottom left corner, there is a video inset showing a man with glasses and a plaid shirt. The bottom of the slide features a red footer bar with the text "Atul P. Deshpande (IITM)" and "PolGAP03 Lecture 01: Application based tests". A small circular logo is visible in the bottom right corner of the slide.

Now, just thinking back about the question related to the curing of elastomers for silicone, we use an activated peroxide material. Zinc oxide is used for chloroprene. And so therefore, you can now go back and try to justify as to why an amine material can be used for acrylics and then you will have the complete answer for that question. Thank you.