Polymers: Concepts, Properties, Uses and Sustainability
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Lecture - 07
Macromolecular Nature

Hello and welcome to this seventh lecture on this course on polymers. And in this week, we are getting introduced to macromolecules and several terminology associated with macromolecules and some basic concepts related to macromolecules.

And in this lecture, which will be the last one for this week, we will ponder over some of the issues that are related to the macromolecular nature, why this nature of macromolecules is a very important consideration when we think of polymers, plastics FRP and their sustainable use.

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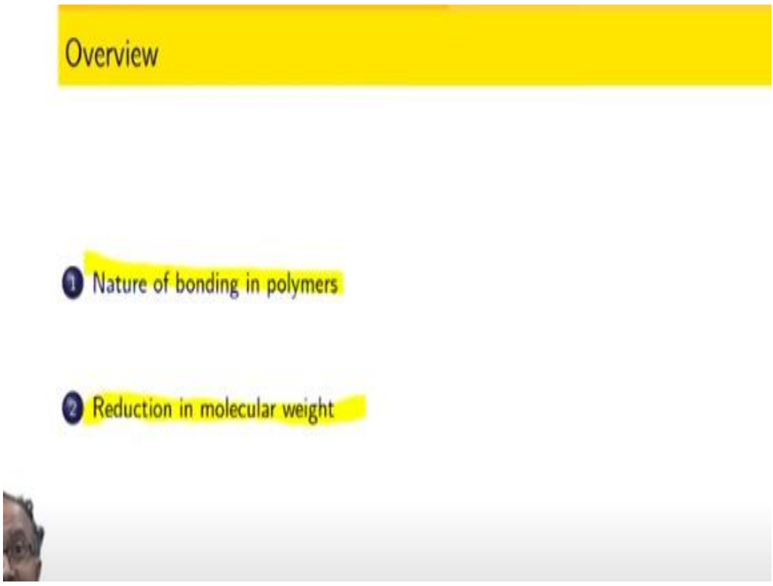

Overview

1. Nature of bonding in polymers
2. Reduction in molecular weight

So we will do this by specifically looking at and thinking about what is the nature of bonding in polymers, what do we mean by the types of bonds which are present in polymers as compared to some of the other materials that we know of. And other thing we will do is in terms of thinking of reduction in molar mass. We thought of polymerization, we learnt about crosslinking. And all of these are exercises and building up of macromolecules. Now is it possible to dismantle the macromolecules? And so with these two questions, we will try to ponder over what is so special and specific to these macromolecules. And only when we think about all these issues, we can come up with effective strategies in terms of sustainability of macromolecular materials.

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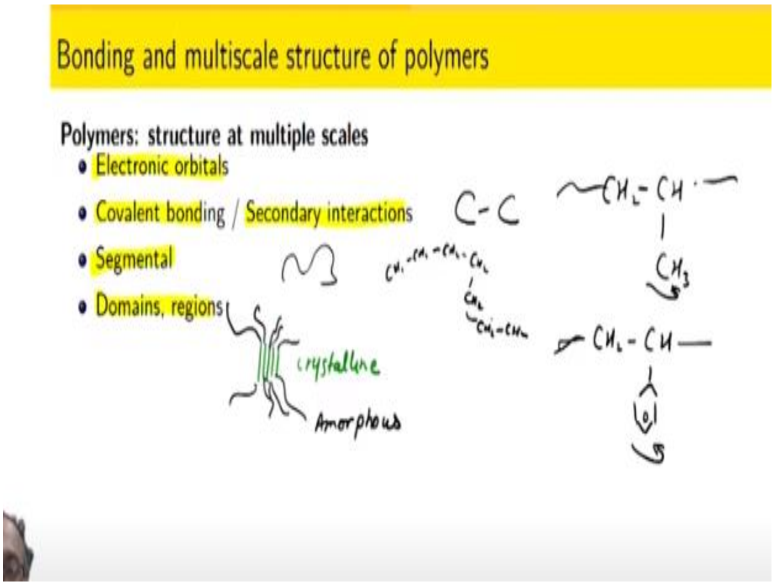

Bonding and multiscale structure of polymers

Polymers: structure at multiple scales

- Electronic orbitals
- Covalent bonding / Secondary interactions
- Segmental
- Domains, regions

So let us begin by first thinking about the macromolecule material. In terms of its behavior, in terms of itself response, it is a material which has multiple scales. And generally, when we think of a material, which is let us say a metallic or ceramic material, then we have multiscales there also in terms of atomic scale, then there is a crystal grain scale and then there is a bulk scale. In this case, we also have something called a segment. So we start with electronic orbitals or sub atomic description of materials. And then, in case of polymers, we have covalent bond, this is where the polymerization builds up. Covalent bond formation is the linkage which makes a macromolecule. Of course, there are secondary interactions also.

We saw example of xanthan gum and how there are several interactions possible between macromolecules of xanthan gum or within one macromolecule of xanthan gum itself. And what is important about multiscale properties in case of polymers is there is segment, which is a set of macromolecular bonds. Or a set of monomers or repeating units, because the macromolecule itself is completely immobile because it is entangled or crosslinked, but a segment can still move. And because of this segmental motion, polymers have a very unique behavior compared to other materials. Then of course, we have domains and regions. It could be if there are mixture of two polymers then there could be domain of one in another.

If it is a semi crystalline polymer, then you could have crystalline regions and amorphous regions and so on. So these are some aspects of multiple scales. When we say scales, we are meaning length scale. And electronic orbital, can you think of what is the dimension we are thinking of? What is the dimension of an individual atom and subatomic features. So you can go look up and see what is the length scale. Then we have the covalent bonds, so carbon-carbon bond. So what is the length scale associated with carbon-carbon bond. Then we talk about a segment. And when we say segment, we have learned to indicate it using a line like this. What I mean in case of polyethylene will be basically some CH_2- CH_2- CH_2 going along like this. And this is called a segment of a polymer. And instead of drawing all the details, if it is a polyester, then it will have COO, and the benzyl rings if it is a PET and so on. So we indicate it using a segment. So that is another scale. What is the length scale do you think? Because a segment may have let us say 10, 20 repeating units. So what is the length scale? And then domains where if it is a crystalline and amorphous domain then you may have some set of segments aligned like this.

And because these segments are combined with something else, of course, the macromolecule may continue and there may be amorphous region. And so you may have crystalline region and amorphous region. So then there are domains of amorphous and crystalline nature in a macromolecule. So these are different length scale. And I am sure you can look up and try to find out what is the length associated with each of these.

And another important feature that you should remember when we discuss multiple scales, you can also talk in terms of multiple timescales. So for example, what are the timescales associated with electrons or subatomic particle that electrons are when they change their energy states or when they change their the probability distribution in terms of an orbital, what are the timescales associated with it? So what we will see is they are extremely fast processes. So the length scale is very small and timescales are very fast or very less amount of time. So for example, for a bond level interaction, so if there is a propylene with this CH_3 or we talk in terms of polystyrene in terms of this benzyl group. So what if we talk in terms of rotation of this side groups. So bond rotation. What is the length scale associated with that? That is the length scale of the bond. And what is the timescale associated with it? It will be much greater than the electronic timescales. Now next level of scale, which is the segment, which is multiple bonds put together. What is the length scale associated with? It will be much larger than a side group. What is the timescale associated with it? It will be longer than associated with a bond rotation.

So all of these can be quantified and in fact, quantification of each of these timescales and length scale has enabled us to understand the viscoelastic nature of polymers. And the reason polymers are viscoelastic is multiplicity of timescales and length scale in their response. So this is something in future lectures we will discuss much more on.

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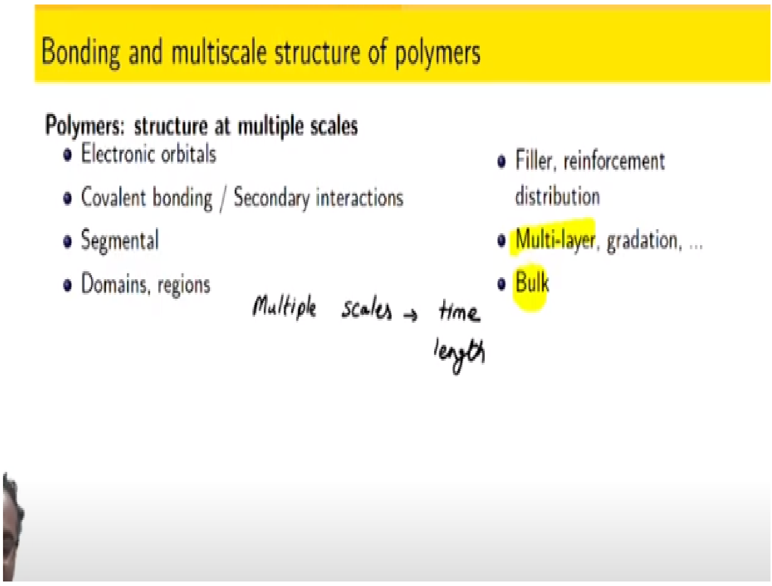

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- Segmental
- Domains, regions
- Filler, reinforcement distribution
- Multi-layer, gradation, ...
- Bulk

Multiple scales → time
length

So going on further in terms of what are the multiple timescales and length scale if we make polymer with mixture with a filler or a reinforcing fiber then that introduces another level of scale. The domains and regions can be micron size or nanometer size. The filler and reinforcement can also be nanometer and micron size. And sometimes the length of the fiber can be continuous. Which means the whole sample itself has continuously running fibers. In fact, in aerospace the composites which are used, polymer composites, in that the fibers is always continuous, because we want maximum reinforcement with continuous fibers. So in that case the length of the fiber is as long as meters. Because the whole wing of an aircraft can have continuous carbon fibers.

And of course, from an engineering point of view we can have multiple layers. Food packaging is an example where we may want barrier to water, we want barrier to carbon dioxide, we may want barrier to UV light, we may want barrier to oxygen. So we can think of various species which should not reach the food item, we need multiple layers of protective packaging.

And so we use multiple multi-layer packaging. From a sustainability point of view, this is a challenge because now we are talking about scales in which 20, 30 micron film is actually a combination of 5, 6 films which are 2, 3 microns each, each material is different. That is why that is another scale of polymers that we have to worry about. And finally, the bulk. When we are designing a product, when we are designing a particular application, in the end we worry about the bulk properties of the material. In the end, the overall multi-layer film, what diffusion does it allow of oxygen or what kind of domains and regions does it have, so that diffusion coefficient is a given value and so on. So in end we are worried and targeting a bulk properties.

But underlying that bulk property is the structure at these multiple length scales and associated with all of these multiple length scale is the response of basic entities from electrons to fillers, where the timescales also are different. So this is an important concept as far as polymer physics is concerned is multiple scales and which include time as well as length. And this is something which we will come back again and again when we discuss dynamic mechanical properties of polymers, rheology of polymers, dielectric response of polymers. So all of these features, the fact that there is multiple timescales and length scales of response in the material will become very important.

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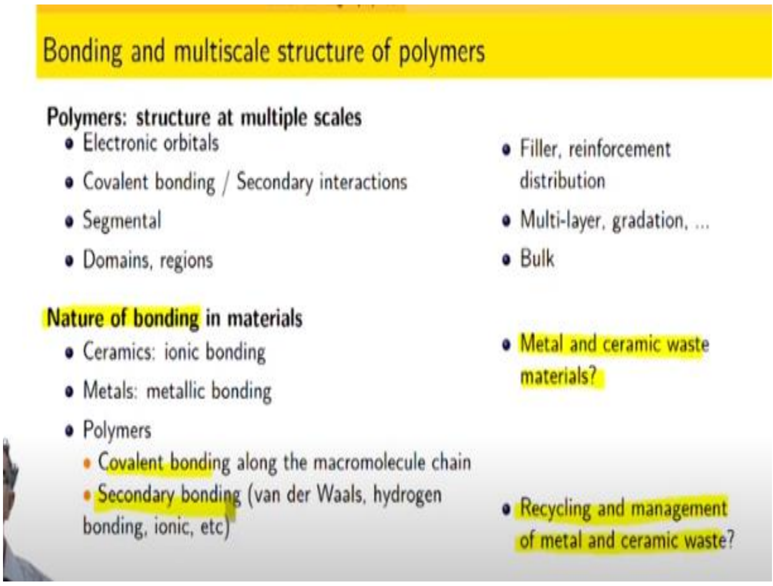

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Nature of bonding in materials

- Ceramics: ionic bonding
- Metals: metallic bonding
- Polymers
  - Covalent bonding along the macromolecule chain
  - Secondary bonding (van der Waals, hydrogen bonding, ionic, etc)
- Metal and ceramic waste materials?
- Recycling and management of metal and ceramic waste?

So let us ponder more about the macromolecular nature, what is the nature of bonding, which builds a macromolecule and as we said it is covalent bonding. How does this contrast with some other materials? For example in ceramics, it is ionic bonding. In case of metals, it is metallic bonding. So you can go and look up what is the energy associated with each of these bonds.

So this gives you an idea also of breaking of the bond, how much energy is required? So does it mean that if metallic bond and ceramic bonds are stronger, they will require more energy to break? Then why is it more difficult to break down a macromolecule? Why is it so difficult to degrade a macromolecule? Something for us to think about. In addition to the primary bonding polymers, it is extremely important to look at secondary bonding. Example of cellulose is a very common. It is a natural polymer. It is available in nature. It is part of biogeochemical cycle. So we never worry about it and it as a waste material. But at the same time, if you look at the degradation of cellulose, it is not as fast as many others and lignin for example is even slower. Why is that the case?

There are nature of secondary bonding in these materials. In case of cellulose, it is hydrogen bonding in case of lignin it is hydrophobic interactions. Because of very strong hydrogen bonding it is difficult for water to get in cellulose. In case of lignin again because of hydrophobic interactions, water is difficult. And many of the biological processes, degradation processes require presence of water. And so you can see that within nature itself, a specific set of secondary interactions have been introduced to manipulate the degradation characteristics of a polymer. So in case of polymers there is specific types of secondary interactions such as Van der Waals, hydrogen bonding, ionic interactions, all of these are very important.

In fact, a fruit peel becoming hard or soft depends on what is the nature of macromolecule and what is the crosslinking that it has. And crosslinking in this case is ionic crosslinking. So therefore, in nature there are examples of macromolecular bonding being manipulated in such a way that polymerization is also achieved and depolymerization or degradation is also achieved but at a rate which is required from the point of view of a natural function.

So now when we think in terms of all these materials with their different types of bondings, we can ponder in terms of why is it that we do not hear as much about metal and ceramic waste materials as we hear in terms of plastic waste materials? How difficult or how easy or how challenging or how manageable is recycling of metal and ceramic waste in comparison to polymer waste?

And has these questions got to do something with what is the nature of bonding in these materials? For example, you will hear a phrase that a metal waste can be recycled infinite times. Why is it not possible with a polymer waste? If I take PET bottle how many times can I recycle? If I recycle it can I make again PET bottle? Why is it not possible? What is in the nature of primary and secondary bonds in case of polymers that prevents me from recycling PET infinite number of times? And therefore, in terms of material science, there are a lot of challenging questions associated with all of these materials. For example, ceramic waste again is something which we are dealing with more and more. Construction waste for example, which is cementitious materials.

And so it is challenging to find out how to use these materials. Fly ash which is a byproduct from a coal thermal power plant. Again what to do with that fly ash and how to utilize it is again a challenging problem. So therefore, waste utilization and recycling are present for multiple types of metals. But in case of polymers, because of their macromolecular nature, covalently bonded macromolecules and the stability of these macromolecules. At the same time, the stability is not so strong that when I recycle, it continues. So that is why PET bottle when I post the question, I cannot keep on recycling. Macromolecule is stable. But when I start recycling, it starts breaking down just a bit. And so the bottle that I made the first time the second time, I may not get exactly the same properties and so on.

So the presence of covalent bonding, its stability on one hand, but at the same time, its instability on the other hand, is a very crucial set of factors, which lead to challenges in terms of waste management and overall sustainability of polymeric materials.

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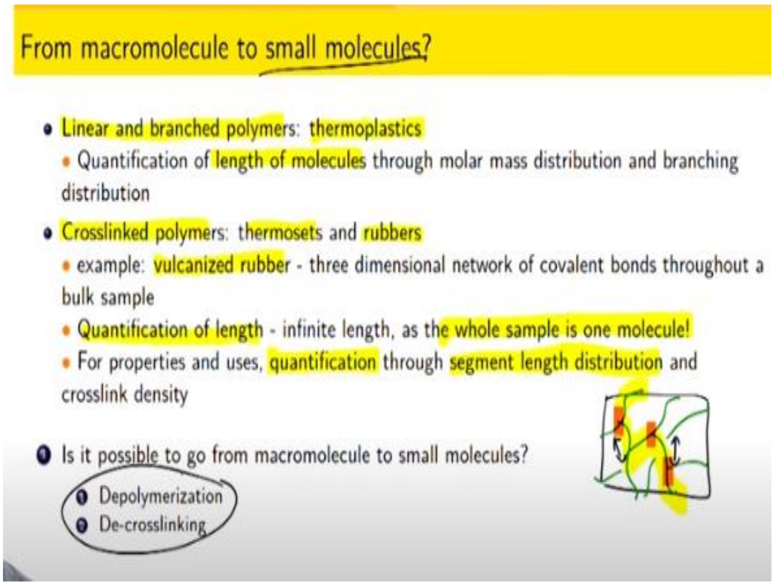

From macromolecule to small molecules?

- Linear and branched polymers: thermoplastics
  - Quantification of length of molecules through molar mass distribution and branching distribution
- Crosslinked polymers: thermosets and rubbers
  - example: vulcanized rubber - three dimensional network of covalent bonds throughout a bulk sample
  - Quantification of length - infinite length, as the whole sample is one molecule!
  - For properties and uses, quantification through segment length distribution and crosslink density
- Is it possible to go from macromolecule to small molecules?
  - Depolymerization
  - De-crosslinking

So let us continue our thought processes and pose the question, yes, if it is difficult to deal with macromolecular waste, how do we manage to convert these macromolecules to small molecules and then maybe handling the waste maybe easier, degradation of small molecular waste maybe easier. Not always the case, because if small molecules end up being toxic, then it will be difficult. But this is a thought question which we can ask. So in this case, for example, in macromolecules, if we have linear and branched polymers, which are generally called thermoplastic, and we usually will quantify them by molar mass distribution, we need to ask the question as to can we reduce the molar mass.

If it is a crosslinked polymer, which we are generally specifying as thermo sets because when you heat it, once it crosslinks, it becomes solid. Then you would not be able to melt. Thermoplastics you can melt them after heating. So rubbers and thermosets, example is of course, vulcanized rubber or even epoxy adhesive is an example of this crosslink thermoset. So in this case, how do we quantify the length of the macromolecule. In fact, the length of the macromolecules is infinite. If you look at a bulk sample of rubber or thermoset in this, if I draw the macromolecules, they are all connected with each other. That is why it is called a crosslinked network.

So if I get a big sample, for example, some which is a crosslink sample, from this and if I start and travel on the macromolecule, I will be able to reach the other end. So therefore, basically, one end of the sample is connected with another end through a maze of macromolecules and therefore, the molecular weight in this case is infinite. The whole sample is just one molecule. What are we talking in terms of molecular weight or molar mass.

So of course, quantification is done using segment length distribution. So instead of quantifying we look at the number of crosslinking points which are there per unit volume and count them or we look at the length between two crosslink points. So what is the length between crosslink points and that is how we quantify. So now the question is when we think in terms of getting to smaller molecules, can we de-crosslink?

Can we remove the crosslinks and then can we break down the segments? So therefore, the question is, if we have to think in terms of sustainable use of polymers, just the way we talked about polymerization and building of molar mass, can we talk in terms of de-polymerization and de-crosslinking.

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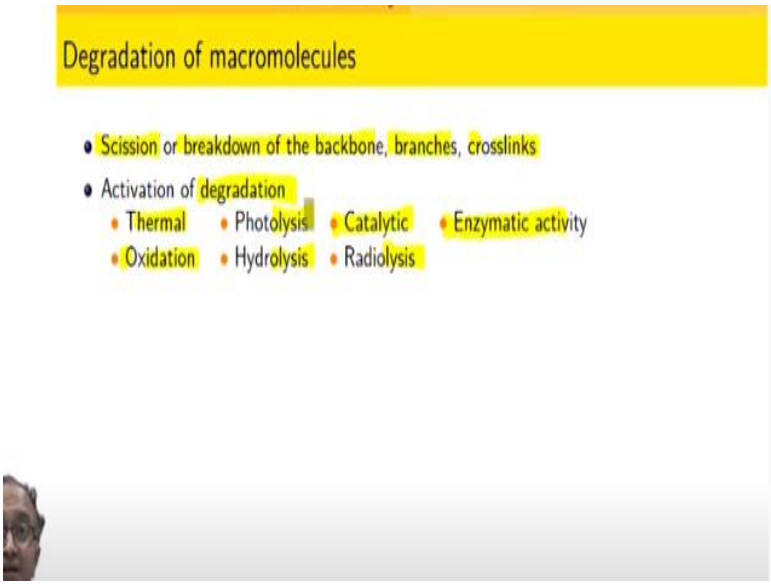

Degradation of macromolecules

- Scission or breakdown of the backbone, branches, crosslinks
- Activation of degradation
  - Thermal
  - Photolysis
  - Catalytic
  - Enzymatic activity
  - Oxidation
  - Hydrolysis
  - Radiolysis

But the overall questions that this the thought process poses are based on what happens to macromolecules in terms of de-polymerization or de-crosslinking or degradation. And degradation of macromolecules in general, by reduction of molecular weight is scission and breakdown of backbone or removal of branches and crosslinks. Just to point out here for a given application, it may be some time that crosslinking is the degradation. For example, a polymer may be a thermoplastic polymer which can be molten and reprocessed. But if it is subjected to either light or other condition in which a crosslinking reaction can happen, then we will say that from the point of view, the macromolecules are building, the molar mass is building. But from an application point of view, the polymer is becoming less usable because it is becoming crosslinked.

So such features are possible, but these are finer aspects. But in general, whenever there is a macromolecular buildup, we think that it is a requirement and whenever there is a macromolecular breakdown, we think that is not good. And so degradation in general will imply reduction in molar mass from that point of view. And how does degradation happen?

There are one of several things. I talked about for example, temperature. So thermal is possible. Oxidation processes in the polymer. There can be some metallic components present or other catalytic components like acidic or basic medium, which can catalyze a set of reaction. We can have biologically based activity which can cause degradation. So there are several lysis which means breakdown of bonds, which are possible either in terms of radiation or light or water.

And so all of these are mechanisms by which degradation in a macromolecule can happen. And of course, this is very important from an application point of view.

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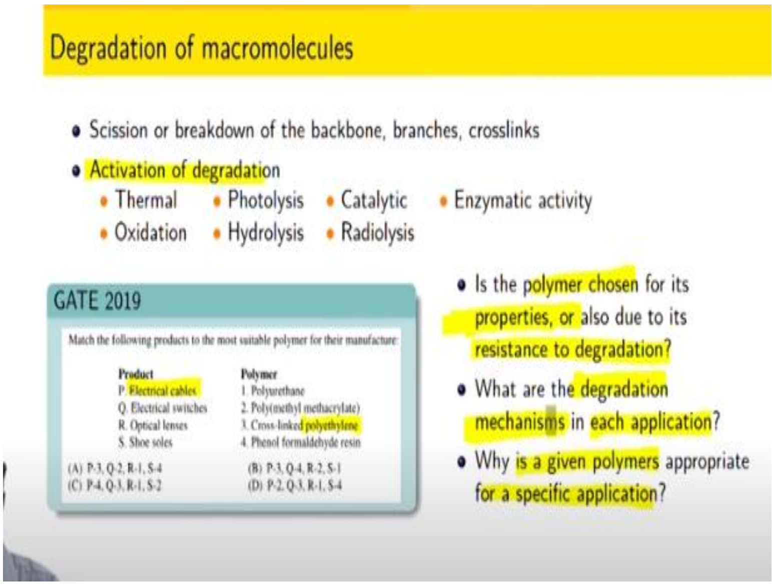

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GATE 2019

Match the following products to the most suitable polymer for their manufacture:

Product	Polymer
P. Electrical cables	1. Polyurethane
Q. Electrical switches	2. Poly(methyl methacrylate)
R. Optical lenses	3. Cross-linked polyethylene
S. Shoe soles	4. Phenol formaldehyde resin

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

- Is the polymer chosen for its properties, or also due to its resistance to degradation?
- What are the degradation mechanisms in each application?
- Why is a given polymers appropriate for a specific application?

Here we can ponder over this question, for example. That you know in this case, we are supposed to match a product to a polymer. And of course, all of these products are very familiar in our day-to-day life. Let us say for example, electrical cable. Now why would you choose a particular polymer for an electrical cable application? Your answer immediately will be that of course, it has the right insulating properties.

Is that all? Some of you may add that oh not only it has to insulate it has to be mechanically stable also. So again all of you are thinking in terms of properties alone. But is that the only reason we will use a product for a polymer for a given application? And the answer is, no there are other consideration also. So is the polymer chosen only for its properties or also its resistant to degradation during the application?

So continuing with this electrical cable application, we not only want a given set of properties today, this is an application in which insulation has to carry on otherwise it becomes unsafe. And so we would want the insulation to remain stable and therefore, degradation in properties not to happen. And if degradation should not happen, which means macromolecular nature should remain intact, which means, any of the degradation reactions that we talked about should not happen during service life. So degradation mechanisms that we talked about should not be present till the service life is present.

So for example, for a given application, we will have to think in terms of what are the degradation mechanisms possible and then choose an appropriate material. So if you look at many of these, the materials here, if you look at electrical cables, what I want to highlight is polyethylene is the only one with carbon and hydrogen alone. Otherwise, there is oxygen or other hetero atom, what is called a hetero atom.

And so would it be surprising that for electrical cables polyethylene is used and that too crosslinked? Anyway think about. So in each of these cases, the question to think about is why is a given polymer appropriate? So it is appropriate not just because of the properties that are chosen, but also because what is the degradation mechanisms that makes it appropriate till the service life is over.

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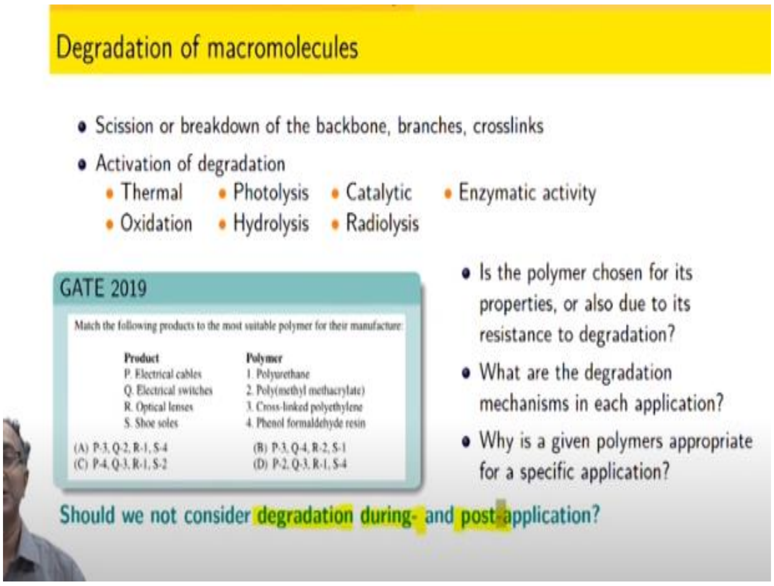

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Should we not consider degradation during- and post-application?

So given all this discussion of macromolecular buildup and its breakdown during service life, if we have to think of in terms of overall sustainability, should we not think of degradation during and post application also. So this is a thought in terms of utilization of polymeric materials on a long term sustainable basis.

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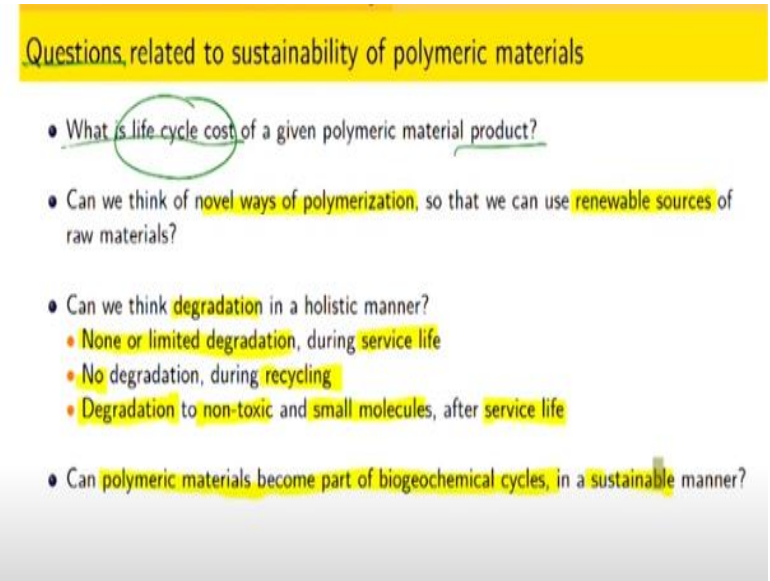

Questions related to sustainability of polymeric materials

- What is life cycle cost of a given polymeric material product?
- Can we think of novel ways of polymerization, so that we can use renewable sources of raw materials?
- Can we think degradation in a holistic manner?
  - None or limited degradation, during service life
  - No degradation, during recycling
  - Degradation to non-toxic and small molecules, after service life
- Can polymeric materials become part of biogeochemical cycles, in a sustainable manner?

And so the questions that I will leave you with, and again many of these are research challenges today. And as polymer scientists and engineers, it is these set of questions that we have to come up with effective answers for. This is what is being demanded from us from the point of view of sustainable use of these materials. So the questions that are related are the following.

What is the life cycle cost of a product? So we should not think of a product cost purely in terms of the usage and what is its cost for buying and selling? What were the raw materials that were utilized? When the product finishes its service life, how much cost it is going to be to use later on or recycle later on or dispose later on? So therefore, this is a concept of life cycle. And this is where polymers have to be compared with other materials of choice. And only when we look at life cycle cost as a whole, then we can talk about which material is better than the other and not really based on the product cost itself. The other question that we can think of is, can we not have newer processes of polymerization, which we can use renewable resources?

In which case the dependence on petrochemical resources can become less. Now degradation which we have thought about in this lecture, can we not think in more holistic manner? So we want degradation to a very limited scale or none at all if best possible case scenario during service life. And of course, if we want to recycle it infinite number of times, then there should be no degradation during recycling also. But as soon as we have decided now that it cannot be recycled or reused and now it has to be part of the overall biogeochemical cycles or part of the environmental systems, then can it degrade to non-toxic and small molecules? So after service life and reuse and recycling and all of those options are exhausted, when the material is disposed, can it not degrade? So you can see this is a very challenging proposition.

But this is what is required if we have to continue to use many of these materials on such large scale. And so the overall question is can polymeric materials that we are using on these large scale can become part of biogeochemical cycles in a sustainable manner? This is the overall question I want you to leave with. Remember, these are all research questions and challenging questions.

They are scientifically important questions from a management point of view, from a systems point of view, from a social behavior point of view, they are important questions and from policy point of view, they are very important questions. So this will round up the first week of the lectures related to macromolecular nature. And next week onward, we will start looking at properties of a single macromolecule and continue our journey.

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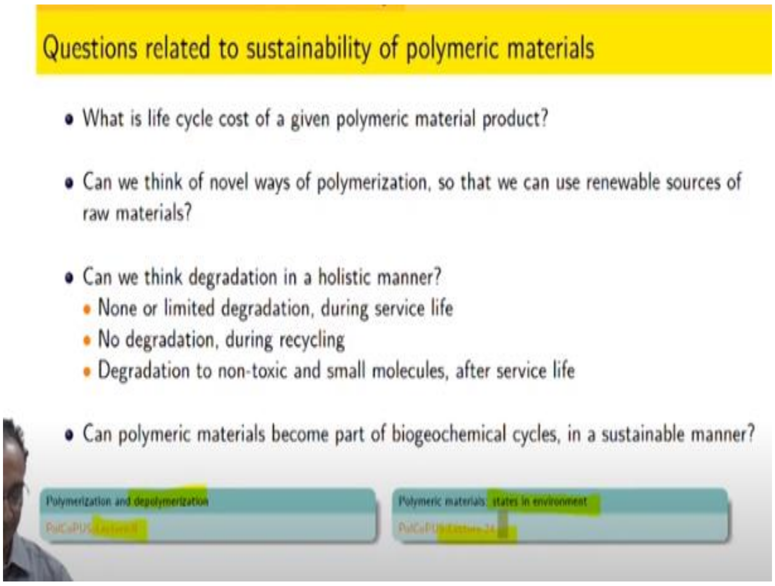

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Polymerization and de-polymerization and states in environment are some specific aspects that we will look at further lectures later on.

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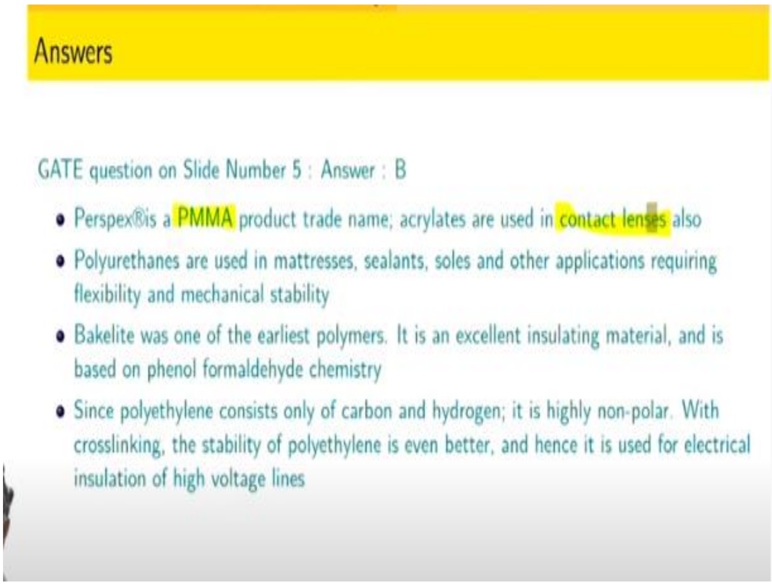

Answers

GATE question on Slide Number 5 : Answer : B

- Perspex®is a PMMA product trade name; acrylates are used in contact lenses also
- Polyurethanes are used in mattresses, sealants, soles and other applications requiring flexibility and mechanical stability
- Bakelite was one of the earliest polymers. It is an excellent insulating material, and is based on phenol formaldehyde chemistry
- Since polyethylene consists only of carbon and hydrogen; it is highly non-polar. With crosslinking, the stability of polyethylene is even better, and hence it is used for electrical insulation of high voltage lines

Just to provide you with some hints related to the answer for the question that was posed. Each and every polymer has unique properties, whether it is optical, mechanical or electrical. And so therefore, each application is specific to those properties. But more importantly, we also have to consider the degradation mechanism.

So if for example, if PMMA is used as a contact lens, we have to make sure that in the environment of the body, it should not degrade during the service life. So with this, I will leave you to ponder about the macromolecular nature and its sustainability, its application considering not just properties, but also the overall degradation mechanisms. Thank you.