Polymers: Concepts, Properties, Uses and Sustainability
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Week 9
Polymer Processing and Recycling Techniques

Lecture-65
Dissolution and Recovery

Hello, welcome to the course on polymers where we are looking at concepts, properties, uses and also sustainability. So, this particular lecture the focus is on sustainability and let me tell you why. In this week now we are going to start looking at polymer processing and recycling techniques. So, polymers are used so commonly because their processing is also easy, why do I say their processing is easy? One we can have very fast processing times, injection molding for example in 2 seconds you can make a part. Also you can make very complex shapes and all of this can be done at temperature and pressures which are not extremely high. So, therefore there is a general ease of processing associated with polymeric materials we can make large volumes rather easily and given that our emphasis on sustainability also while we are looking at polymer processing we will see whether many of these polymer processing techniques how useful they are for recycling as well.

And in this particular lecture we will look at one aspect of processing where we can process the waste plastic by dissolution and recover the polymer itself.

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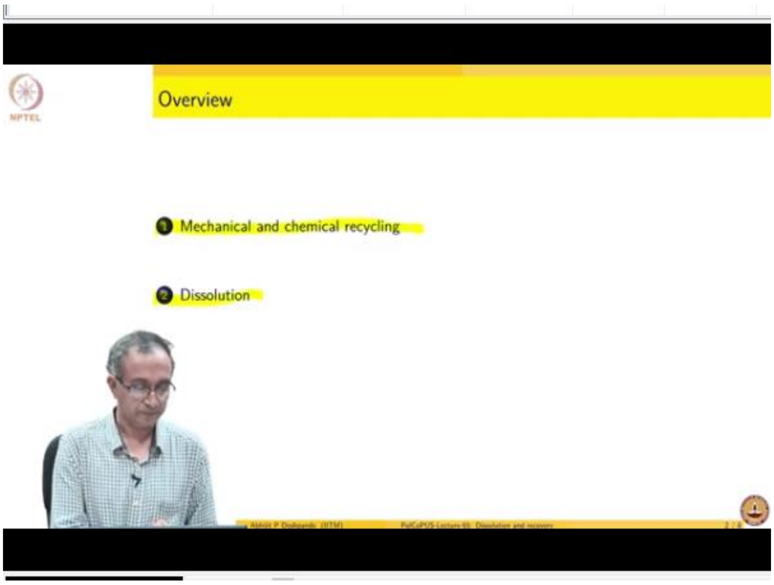

Overview

1. Mechanical and chemical recycling
2. Dissolution

And so why is this important? We will look at by first focusing on the different types of mechanical and chemical recycling processes that are generally available and then we will finally look at the dissolution as a phenomenon itself.

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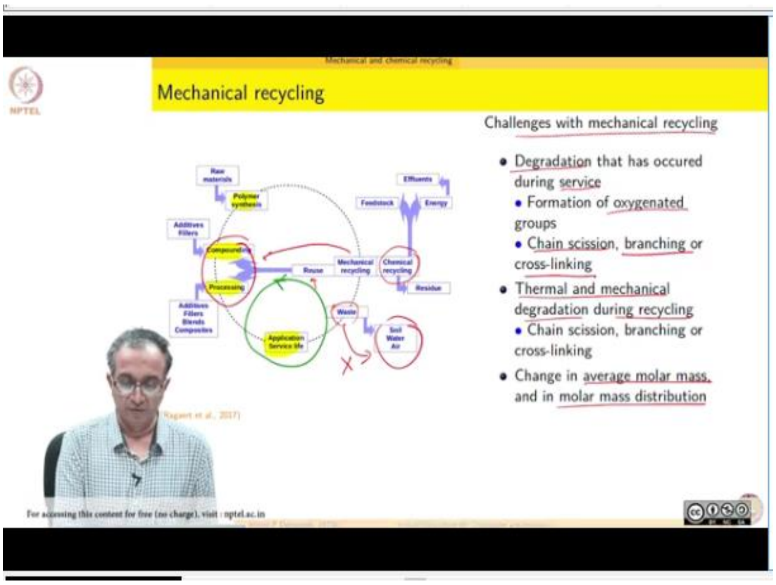

Mechanical and chemical recycling

Mechanical recycling

(Ragaert et al., 2017)

Challenges with mechanical recycling

- Degradation that has occured during service
  - Formation of oxygenated groups
  - Chain scission, branching or cross-linking
- Thermal and mechanical degradation during recycling
  - Chain scission, branching or cross-linking
- Change in average molar mass, and in molar mass distribution

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So, let us first look at the overall idea of how polymers are integrated into the overall cycle associated with its production and its use? And this we have seen earlier also that synthesis of polymers happens polymerizations and then they are led to mixing and modification and for a given application we need to make a formulation and compounding is done generally and then the fabrication and processing happens. And this particular week we are going to focus lot more on these processing operations. Once processing is done and service life is over then the material becomes a waste material and of course one of the things that can happen is it can immediately go to a waste disposal site where it can interact with soil water and air and it is our endeavor now to try to minimize this as making polymers improve their sustainability.

So, then there are options related to mechanical recycling which immediately will let us use the polymers once more maybe with additional mixing, compounding and modification of additives and so on and other way also is to reuse the material as we have discussed earlier. However, there are other options related to what is called chemical recycling. Why are we looking at chemical recycling as a way of improving the soil state of waste handling in case of polymeric materials?

Is because there are challenges associated with mechanical recycling, even though mechanical recycling seems to be easiest in terms of implementation because we have all the processing techniques which are in place and then we can just collect the plastic and then recycle them back and reprocess them and again continue to do this as many times as we want. But then there are issues because degradation in the polymer may have happened during the service life and why is this so? Because there is always oxidation possible, though macromolecules are stable with time and with temperature and with availability of oxygen, availability of free radicals, availability of acidic groups and so variety of conditions under which small amount of oxidation can happen and when we are now trying to reprocess this can also lead to further oxidation and therefore the properties can vary significantly. Similarly some breakage of chains can be there or branching and cross linking. So, formation of new bonds in macromolecules can be there. Secondly when we are processing itself these processes can again happen where macromolecules can break, macromolecules can branch and so on. In general what this leads to is change in molar mass as well as molar mass distribution.

And so when we are trying to do this again and again ideally what we would like is if we once make the polymer and if we can just do this cycle again and again that we use the service life, then mechanically recycle, do compounding processing, use it again and so this will be an ideal thing. But unfortunately at each recycle there is a degradation in property and so therefore chemical recycling is also an effective way of trying to reduce the amount of waste that gets to the soil water and air. So, therefore our emphasis since is to reduce amount of waste which comes to soil water and air chemical recycling becomes an important option.

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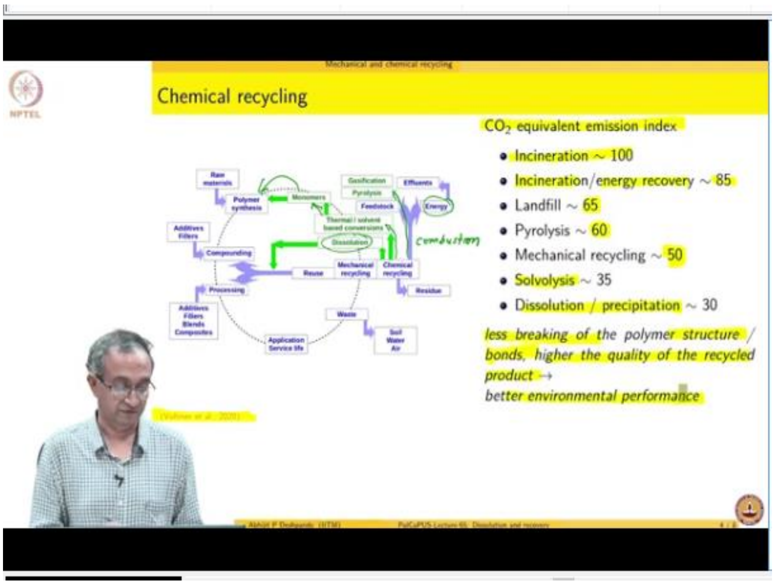

Mechanical and chemical recycling

Chemical recycling

CO_2 equivalent emission index

- Incineration ~ 100
- Incineration/energy recovery ~ 85
- Landfill ~ 65
- Pyrolysis ~ 60
- Mechanical recycling ~ 50
- Solvolysis ~ 35
- Dissolution / precipitation ~ 30

less breaking of the polymer structure / bonds, higher the quality of the recycled product →
better environmental performance

Now what are the different chemical recycling methods which are available? So, you could use combustion and one way to deal with waste is just to burn it without even worrying about the operation as such. But that is actually just not other than reducing the amount of waste it is not doing anything. So, generally what you can do is while combusting it you can try to recover the energy. So, therefore energy production using combustion is also possible. The other thing that can be done is using some solvents we can try to recover the monomers and these monomers can be again fed back to the polymerization and then it can become a part of cycle. Alternately we can also have these rather than doing combustion we can do pyrolysis or gasification reactions rather than converting the macromolecules all the way to CO_2 and water which are the usual combustion product.

Let us say for a hydrocarbon product we can try breaking it down where we get maybe pyrolyzed fuel like product or fuel in terms of petrol like product or we could get gases which are again useful and which can be again used as fuel. So, therefore these are different ways in which you could chemically recycle, one other important way of chemical recycling is by dissolution.

So, can we not take the plastic waste material and devise a strategy of dissolution and then re-precipitation. So, that we can get the polymer back and then we can again compound it process it and reuse it as a product. Now the advantage of this dissolution is that the chemical changes, the chain session and all of those processes can be minimized. So, just to give you why this dissolution and recovery is a promising option. I am showing you some calculations done in the literature where they are looking at basically the impact of each of these recycling options which are available and it is measured in terms of a carbon dioxide equivalent emission index. So, how much carbon dioxide is emitted if you do any of these operations and incineration which is the worst where we are just burning without getting any other use from the waste is 100 let us say. Then what happens is if you at least try to do energy recovery along with incineration immediately the emission index comes down. So, it becomes a more favorable process from a climate change and from a sustainability point of view. If you do just a landfill and assuming that macromolecules are not going anywhere else, they are not interacting with water and soil, then maybe it has again certain value.

If you do pyrolysis by which you get a product which again can be reused as part of several other processes industrial as well as consumer processes, then it again becomes somewhat less of an impact and if you do mechanical recycling that is again very good relatively. Because again in terms of carbon dioxide emissions you are not again reproducing those macromolecules. And so but it has limited use because after 2, 3 use again you will generate waste and also mechanical recycling would involve removal of some of these additives and so on sorting and things like that. The other thing you could do is to use a solvent and break down polymer and then you can obtain the smaller fragments which again can be reacted. So, this also could be improvement.

But look at at least the estimation from the literature, dissolution and precipitation seems to be the best option and this is so because there is less breaking of the polymer structure bonds and because of that the recycle product promises to have a higher quality. Because whenever we are doing mechanical recycling or any other reactive processing the control on what exactly do we get at the end is little bit less. In the dissolution precipitation we are getting basically the same polymer that was used earlier. So, therefore it leads to possibly a better environmental performance.

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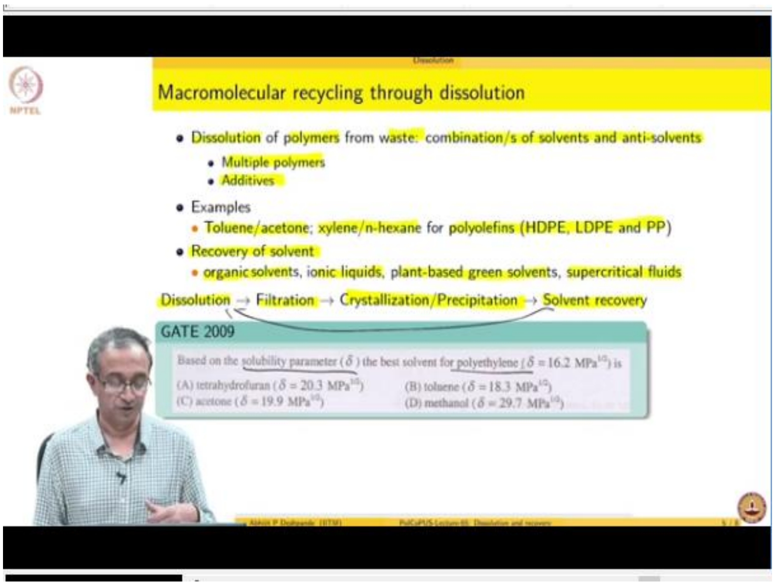

Macromolecular recycling through dissolution

- Dissolution of polymers from waste: combination/s of solvents and anti-solvents
  - Multiple polymers
  - Additives
- Examples
  - Toluene/acetone; xylene/n-hexane for polyolefins (HDPE, LDPE and PP)
- Recovery of solvent
  - organic solvents, ionic liquids, plant-based green solvents, supercritical fluids

Dissolution → Filtration → Crystallization/Precipitation → Solvent recovery

GATE 2009

Based on the solubility parameter (δ) the best solvent for polyethylene ($\delta = 16.2\ \mathrm{MPa}^{1/2}$) is

(A) tetrahydrofuran ($\delta = 20.3\ \mathrm{MPa}^{1/2}$)
(B) toluene ($\delta = 18.3\ \mathrm{MPa}^{1/2}$)
(C) acetone ($\delta = 19.9\ \mathrm{MPa}^{1/2}$)
(D) methanol ($\delta = 29.7\ \mathrm{MPa}^{1/2}$)

So, therefore let us look at what is this macromolecular recycling through dissolution. So, the idea is to dissolve the polymer from waste and of course this is not trivial because we have a mixture of polymers generally it is a mixed waste plastics, there are multiple polymers there, not only that there are lots of additives from compatibilizers to pigments to UV stabilizers, we have seen the whole gamut of small molecules and oligomers and macromolecules which could be part of a commercial polymeric system.

And so generally what we would have to do is look at a combination of solvents and for precipitation anti-solvents or co-solvents and non-solvents. So, that we can devise a proper strategy of dissolving precipitating. So, for example toluene acetone or xylene hexane are known good solvent systems for polyethylene and polypropylene. Of course one of the problems in this process from a point of view of sustainability would also be the impact of the solvent itself.

So, we could have organic solvents which are being used and the problem with them is related to the environmental impact. But therefore there is lot of work which is going on related to ionic liquids or plant based green solvents or super critical fluids to minimize the impact during this dissolution recovery process. So, the stages that we can see in this are following, that there is dissolution and then there is a filtration and then there is a crystallization precipitation to get the polymer and then solvent has to be recovered. So, that it can be again used back in dissolution.

Now just to highlight how we can devise solvent non-solvent system and how do we design this kind of a process which is very effective we will have to start looking at interactions between solvent and macromolecular systems. And of course we have seen that solubility parameter is one way to figure out what may be a good solvent system for a given polymer and this exam question asks you know which is one among the solvents which are given, which is the best one for polyethylene. So, having knowledge about solubility parameter you should be able to quickly get the answer to this.

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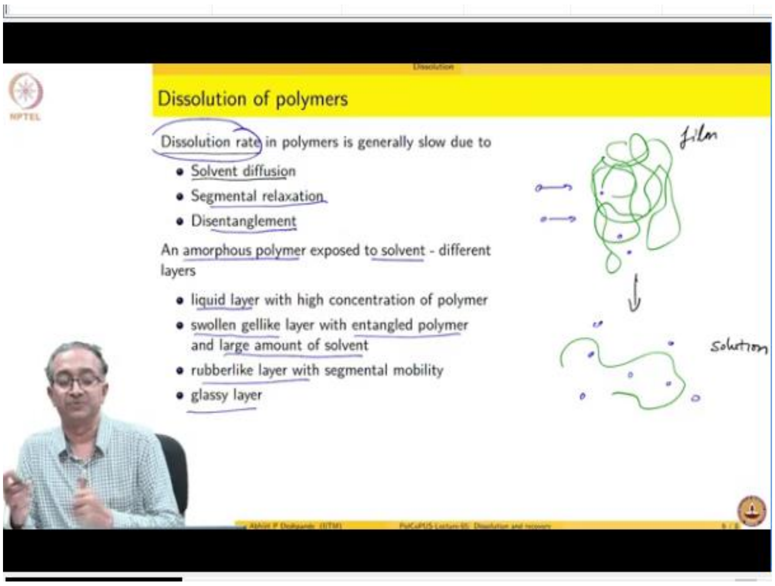


Dissolution of polymers

Dissolution rate in polymers is generally slow due to

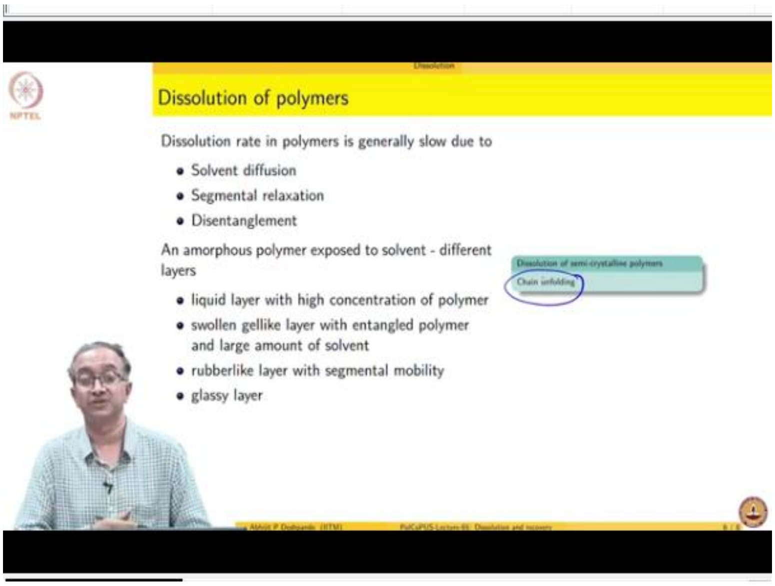
- Solvent diffusion
- Segmental relaxation
- Disentanglement

An amorphous polymer exposed to solvent - different layers

- liquid layer with high concentration of polymer
- swollen gellike layer with entangled polymer and large amount of solvent
- rubberlike layer with segmental mobility
- glassy layer

Now the having a good solvent is not the overall thing because dissolution rates in case of polymers are generally very slow and this is because what you have is basically a macromolecular system which is most likely in a glassy state and then you have the small molecule which is trying to diffuse. Eventually what our goal is to get a system where the macromolecule is molecularly mixed with the solvent system. So, we want a solution from let us say a film using this solvent. So, what has to happen in this process is first solvent has to get absorbed and diffuse. So, solvent should be able to diffuse through the macromolecular network. So, that is a crucial requirement first. So, some amount of solvent has to go, then once the solvent starts interacting with the macromolecular segments segmental flexibility goes up. And therefore segmental relaxations can start happening and once sufficient segmental relaxations can happen disentanglement can happen because in the end we want polymer in the solution form. So, therefore when we look at any amorphous polymer which is exposed to a solvent there is a very complex set of processes which are there and there are different layers that you can see in terms of the film which is there and the solvent which is there. So, there is a very next to the film itself there is a liquid layer where there is a very nice segmental mobility of polymers and solvent and polymer molecules are well mixed. Next to that there is large amount of solvent. So, therefore there is a swollen gel like layer, but the polymer is still entangled and that is why the performance is still gel like and large amount of solvent is there.

Beyond that still small amount of solvent is there and therefore there is a rubber like layer with small amount of segmental flexibility and then finally there is the glassy layer of the polymer film which we were trying to dissolve. So, you can see that dissolution rate therefore is going to be very slow, because the polymer molecule is not having any segmental mobility to get the finally dissolved polymer we need not just segmental mobility we need disentanglement also. **(Refer Slide Time: 15:50)**



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Dissolution of semi-crystalline polymers

Chain unfolding

So, therefore if you have a semi crystalline polymer there is an even bigger phenomenon of crystal melting because of solvent. So, chain has to unfold the secondary interactions which are very important during formation of the lamella have to be overcome and therefore dissolution of semi crystalline polymers again will be a slow process.

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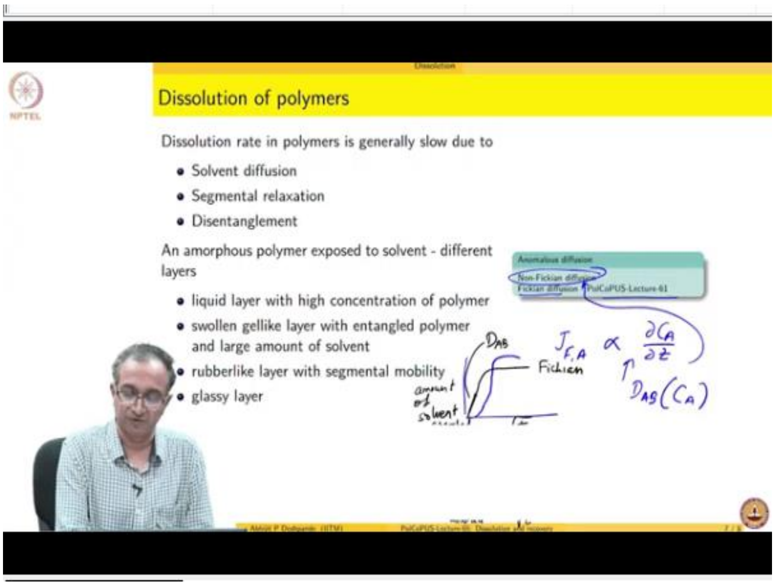

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The other thing that in this diffusion description that I have described to you is the fact that how important solvent polymer interactions are and the diffusion of solvent is very strongly influenced by solvent and polymer interactions. This is generally referred to as anomalous or non-Fickian diffusion, because we saw Fick's law in case of 61st lecture where the flux was related to the concentration gradient. And then there was a constant which specified that how much will be the flux the diffusion coefficient. But in case of polymeric systems since the solvent is interacting with macromolecule and changing the free volume or changing the segmental flexibility the diffusion coefficient starts changing as more and more solvent comes in. So, therefore this is a function of how much solvent is there.

And so this leads to what is called the non-Fickian diffusion. So, diffusion is no longer based on Fick's law where DAB is a constant value and because of the macromolecular relaxations, because of the segmental conformational changes in macromolecules the phenomena is referred to as anomalous diffusion. Because when you look at how fast or slow the solvent molecule diffuses in it shows a very different behavior. So, for a Fickian response generally there is an increase and then becoming constant. So, what I am plotting here is the amount of solvent absorbed in the polymer as a function of time and generally this is plotted as a square root of time, because then this becomes a straight line and the slope of this in fact gives us DAB. So, this is for Fickian diffusion. But for non-fiction diffusion we have cases like this where diffusion is very slow initially and then it becomes very fast and then it becomes constant.

So, that is why we call it anomalous diffusion or non-Fickian diffusion. So, at a fundamental level also the process of dissolution is very much influenced by these diffusive processes and the interaction between solvents and polymers.

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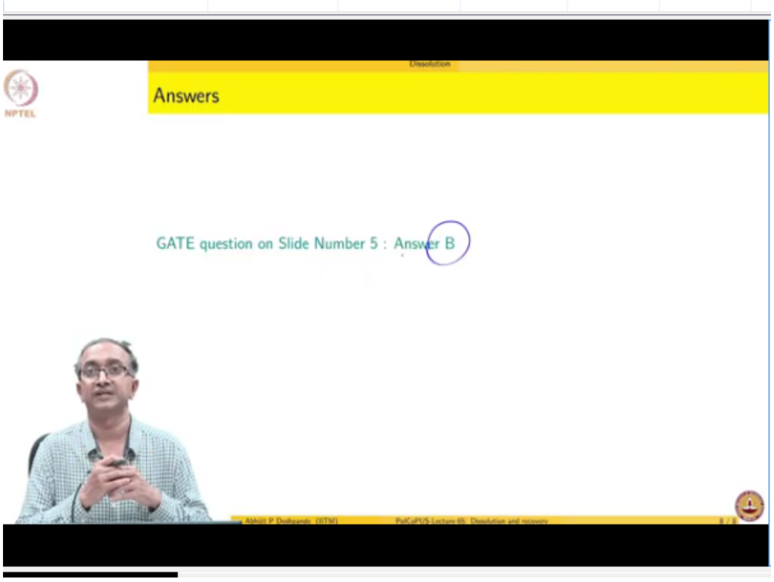

Dissolution

Answers

GATE question on Slide Number 5 : Answer B

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It is very interesting from the point of view of understanding. So, I hope based on the solubility parameter you have been able to arrive at the answer that wherever solubility parameter is very close between 2 substances then they are likely to be having favorable interactions and miscible with each other. So, with that we will close this lecture, thank you.