Polymeric Materials of Different Kind
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Lecture - 28
Blends 1

Hello, welcome to this lecture on polymeric blends, we are in week 4, where we are discussing polymeric materials of different kinds, we looked at copolymers, we are going to look at blends and also we will take a closer look at composites. And in all of this we are trying to learn concepts, which are related to the polymeric materials and they are mixtures, whether it is copolymers blends or composites.

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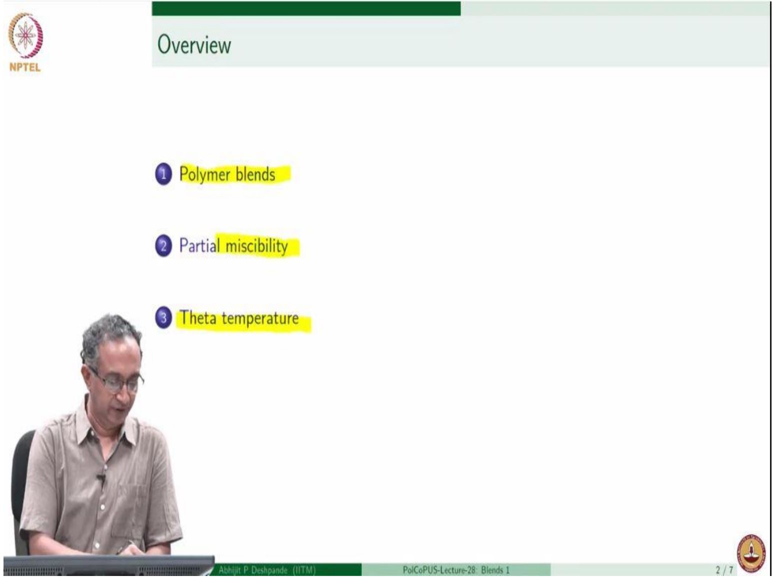

Overview

1. Polymer blends
2. Partial miscibility
3. Theta temperature

And today's lecture, we will first look at briefly what blends are and then look at the concept of partial miscibility we will see that there are miscible blends and immiscible blends as well as some blends where there is range of behavior in terms of full miscibility to partial miscibility to immiscibility. And then we will also look at the context of polymer solvent mixture which is similar in thermodynamic analysis, the concept of theta temperature.

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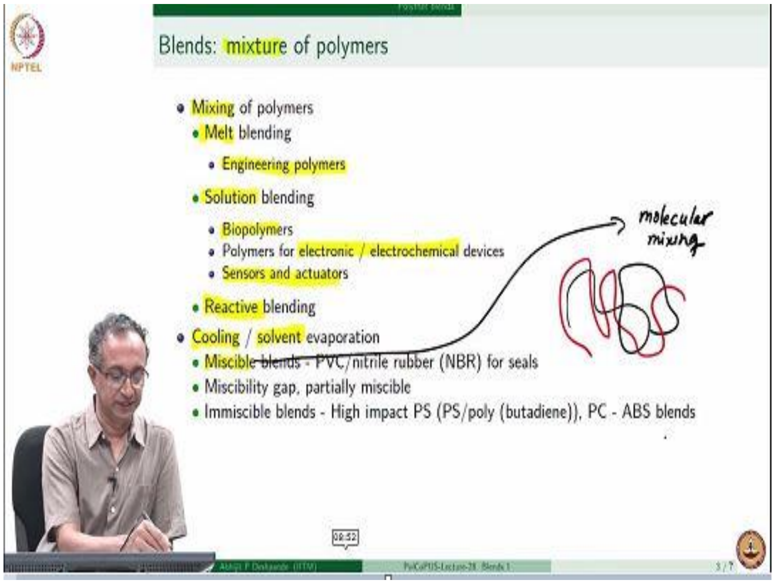

Blends: mixture of polymers

- Mixing of polymers
  - Melt blending
    - Engineering polymers
  - Solution blending
    - Biopolymers
    - Polymers for electronic / electrochemical devices
    - Sensors and actuators
  - Reactive blending
- Cooling / solvent evaporation
  - Miscible blends - PVC/nitrile rubber (NBR) for seals
  - Miscibility gap, partially miscible
  - Immiscible blends - High impact PS (PS/poly (butadiene)), PC - ABS blends

So, blends are basically mixtures of polymers. And both of these polymers can exist themselves as, homopolymers as single polymers, where we mix them in required proportions to optimize or to tune properties. And this mixing can be done by 2 ways, we can do melt blending, where we take both of the polymers or if it is a blend of 3 polymers and take all 3 polymers to the melting temperature and above and then we can do the mixing.

And many of the engineering polymers and commodity classes that we see around us are blended using this method, we could also dissolve both the polymers in a solvent where both are soluble, and that is called solution blending. So, we make a solution of both the polymers in a solvent and then by evaporating the solvent we can achieve a blend and many of the bio polymers that are blended are usually water soluble and if they are water soluble then solution blending is an option, solution blending has also become more important for many of the device applications.

Whether it is membrane making whether it is thin coating required for a transistor or a photovoltaic device, then we use solution blending. One reason is also that many of the polymeric materials which are used for such devices have melting temperature, which is higher than their degradation temperature. So, if you want to take them to a molten state, where they can start flowing degradation reactions starts happening.

So therefore, solution blending is a method of progression. Similarly, for sensor and actuator devices also. So, from a traditional plastics point of view, melt blending is what is usually done but from modern devices point of view, solution blending is becoming more and more important. In solution blending we have a ternary system. So even if there are 2 polymers the third solvent is also there. While in case of melt blending we are looking at a binary system.

Sometimes we may also end up doing reactive blending, in which case we carry out reactions at the same time as blending. And so in the blending process, we actually cool if it is a melt blending or we evaporate the solvent if it is solution blending and then finally get the product which is a blend and this polymer blend could be miscible. In which case, if we have 2 polymer molecules, basically they will be intermixed and there will be molecular level mixing. So, in case of miscible blends, we have molecular level mixing, but if we have a case of immiscible blend, then what we will have is 2 domains. So, if we have any misicible blend.

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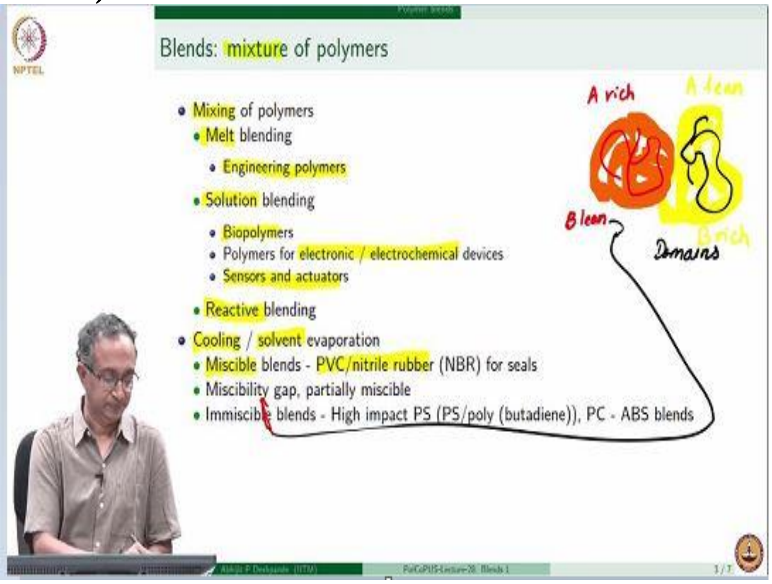

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In that case, what we will see is so let us look at the case of immiscible blend in this case, what will happen is there will be one domain of polymer 1 and another domain of polymer and so within this each domain, there will be molecules of one kind. So molecules have one kind, and this one will have molecules of other kind. So therefore, in this case, we have domains. And so we have domains. And it is partial miscibility, then what we have is in both of these domains, both the polymers will be there.

And so, generally what we will happen is one of the polymer will be rich and one of the polymer will be lean. So if we have an AB system, so, this could be A rich face, while the other one could be A lean or it since it is an AB system, so, this is B rich. And this one is B lean. So, this is for partial miscibility. So, we have now, all the 3 possibilities for many of the systems for example, commercial system of PVC nitrile rubber, it is a miscible blend, we have to be careful.

Sometimes when we talk about miscibility and immiscibility and partial miscibility, because many of these are dependent on the scale with which we talk about and also the overall conditions. So, though PVC nitrile rubber is considered a miscible blend, we have seen research where it has been shown that it is partially miscible under some conditions. So, therefore, many of these things depend a lot on what is the interaction between 2 polymers and what are the conditions under which the blend is reformed.

And in this lecture and next, we will also try to get a sense of why blending is such a difficult task and how critical the conditions of blending are.

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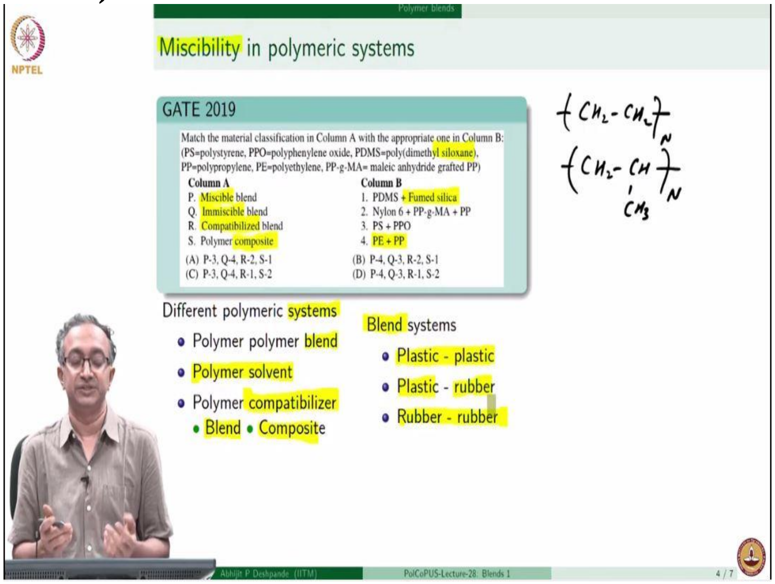

Polymer blends

Miscibility in polymeric systems

GATE 2019

Match the material classification in Column A with the appropriate one in Column B: (PS=polystyrene, PPO=polyphenylene oxide, PDMS=poly(dimethyl siloxane), PP=polypropylene, PE=polyethylene, PP-g-MA= maleic anhydride grafted PP)

Column A	Column B
P. Miscible blend	1. PDMS + Fumed silica
Q. Immiscible blend	2. Nylon 6 + PP-g-MA + PP
R. Compatibilized blend	3. PS + PPO
S. Polymer composite	4. PE + PP

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

$-\!\!\left(CH_2-CH_2\right)\!\!-_N$

$-\!\!\left(CH_2-\underset{CH_3}{\underset{|}{CH}}\right)\!\!-_N$

Different polymeric systems

- Polymer polymer blend
- Polymer solvent
- Polymer compatibilizer
  - Blend
  - Composite

Blend systems

- Plastic - plastic
- Plastic - rubber
- Rubber - rubber

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So, let us just look at one of the questions while we are considering this issue of miscibility in polymeric systems. So, we can have a miscible or immiscible blend as we discuss, if we have an immiscible blend, we can compatibilize it, which means A and B which do not like to mix with each other, we can add another 3rd component which will then induce some amount of interaction between A and B and therefore, we have made A and B compatible.

So, therefore, this question tries to pose you know, what is the difference? What are these 3 different sets of materials? And of course, as we have already seen several time composites is where we will need to add a component which is quite often non polymeric or in a particle fiber form. And so, maybe some of you can spot that fumed silica is a particle which is added and so that is PDMS composite. But what about the other 3? So, what is your guess? Will polyethylene and polypropylene be miscible blend or immiscible blend?

If it is considered polyethylene and polypropylene are chemically very similar hydrocarbons and very similar sets of interactions. So, do we expect them to be miscible or immiscible and it would be surprised to find that, in fact, polyethylene and polypropylene are immiscible. So, what causes the immiscibility in polymers, so, in general, polymers are immiscible unless there is an interaction which is favorable between the 2 polymers. And this we will try to understand by looking at thermodynamics of mixing.

So, in general, we can have a different polymeric system in which this mixing between one component and other component is valid. And so, this system could be a blend, it could be a polymer solvent system or it could be a compatiblize system, in which case we add a compatibilizer which is valid both for a blend or composite. So, for example, in this question here PDMS and fumed silica, if you see both of them are silicon based.

So, we have siloxane, which is a silicon based polymer and then silica, of course, so, in this case compatibilizer in this composite may not be required, but if you have a lets say glass fiber and polyester, then it may be useful to have compatibilizer. In terms of the blend systems, we can traditional type of we could have a plastic mix in plastic and polycarbonate has been blended with several other plastics to achieve superior performance.

We could have a plastic rubber, in which case the advantages of rubber in terms of improving impact strength can be added or we could just have a rubber-rubber bland also, many times the rubber formulations will have some certain strength in terms of lets say damping performance or in terms of weather resistance but they may lack resistance to acid or some other condition. So, therefore, we can blend the 2 rubber systems to achieve the most optimum performance.

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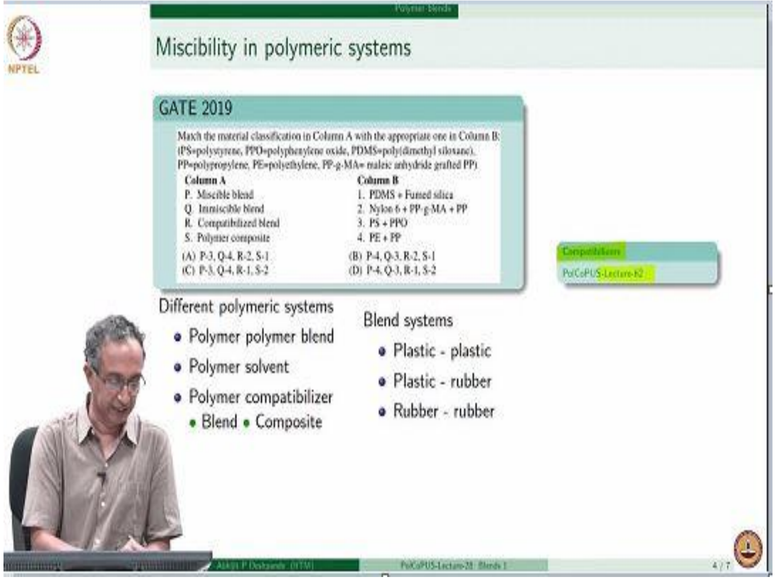

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Blend systems
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Compatibilizers
PolCoPUS-Lecture-82

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So, in general in the compatibilizer is a very useful set of chemicals, which could be polymeric or which could be small molecules, which are added to blends and composites. And we will take a closer look at these in a future lecture.

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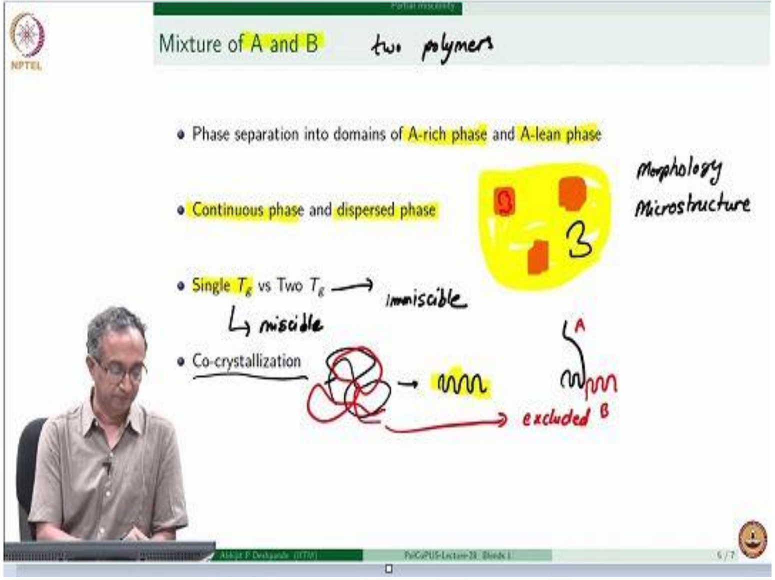

Partial miscibility

Mixture of A and B two polymers

- Phase separation into domains of A-rich phase and A-lean phase
- Continuous phase and dispersed phase
- Single T_g vs Two T_g → immiscible
  ↳ miscible
- Co-crystallization

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So, now, let us look at a mixture of A and B, A and B are the 2 polymers. And so, we would consider what happens when we have partial miscibility or complete miscibility in case of complete miscibility A and B basically just intermingled with each other, but when we have partial miscibility, then we have as we discuss A rich phase and A lean phase. And also we will have some phase which is continuous and some phase which is this was generally a polymer blend.

If we look at depending on the proportion of the components added, we may have certain morphology like this. So, this is a term which we have used earlier also and we will continue to use it called morphology or microstructure, how the 2 polymers A and B are distributed with respect to each other. If it is a miscible blend, then microstructure is only related to molecular arrangements, but if they split into domains of A rich phase and domains of B rich phase.

Then we it is our interest to know where is A rich phase and what it is shape and where is B rich phase and what is its shape. It is quite often we may have continuous and disperse phases. Whenever we have miscibility in the system, then we have a single T g. So, single T g generally implies the segments of 2 polymers are closely interacting with each other. So, whether segmental mobility is present rubbery phase and segmental mobility is absent glassy phase will happen at the same time.

So, therefore, there will be only one single T g .On the other hand, if we have domains like this, where the segments are in one domain and segments here another domain both of them will undergo glass transition under their own respective thermal conditions. And so, in the immiscible case, we will generally have 2 glass transition. So, this is one way of finding out whether the blend is miscible or immiscible is trying to see the segmental mobility of the polymers.

If they are molecularly mixed with each other, then both of them will have similar segmental mobility and they will undergo only one glass transition, but if they are space separated, then we will have different glass transition and bridges. The other interesting thing about polymer blends is what if we have crystallization that is possible. So, as we know if is a molecule and it has to undergo crystallization chain folding has to happen.

Now, what we have is another molecule also. And if it is miscible blend, then for this crystallization to happen, the red molecule first has to get excluded and then only the chain folding can happen. So, therefore, crystallization quite often is much more tricky in case of blends, there is only some if both the chains are so, similar that we can have chain folding of one and then in that another chain can get incorporated which is B.

For this to happen, both A and B need to be exactly same size in inorganic crystals also, you might be familiar with that if we add impurity, which is atom of a very different size, then it is not possible for it to go and occupy the lattice positions. But if atoms are similar size and similar interactions, then it is possible for lattice to be occupied by an impurity. So, therefore, co-crystallization is again not very common, and crystallization is in fact quite often suppressed whenever we do blending, because of these complications where the other polymer has to be excluded before single polymer can form crystals.

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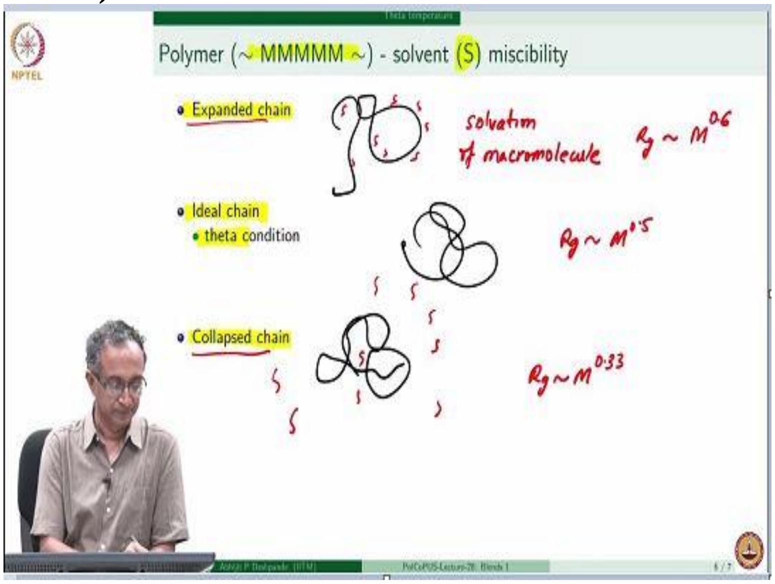

Theta temperature

Polymer (~ MMMMM ~) - solvent (S) miscibility

- Expanded chain
- Ideal chain
  - theta condition
- Collapsed chain

So, let us now finish this lecture by just looking at similar system where this polymer the other one is small molecule solvent. So, the polymer will be let us say monomer monomer repeated several times and then solvent and we have already seen the 2 models where we have the expanded chain because in this case, the solvent is basically next to the polymer chain. And so there is a solvation of the polymer chain. And in this case, we have already seen that the size is proportional to molecular weight or molar mass M to the power 0.6.

And that is why it is called an expanded chain. Now, if we look at the other extreme, where if we reduce the temperature or if we increase the temperature or we remove the solvent, in such cases, what will happen is the polymer would like to start interacting with each other segments and then this will exclude all the solvent molecules. So, the solvent molecules in general will be excluded.

And therefore, now, what we have is a collapse chain and in this case, the radius of gyration is much more stronger that is why it is called as collapse chain.

So, this is like what happens in case of precipitation, where macromolecule would like to interact with other segments of macromolecule and not with the solvents and in between, what is called theta condition is where we have ideal chain, where the macro molecule behaves as if it is not interacting with each other. And in this case, we know that radius of gyration is based on gaussian chain approximation and the random walk model that we saw earlier and the size of the molecule is proportional to molecular weight to the power 0.5.

So, therefore theta condition is an important condition which tells us about what is the interaction between polymer and solvent if interaction between polymer and solvent is very favorable, then we will have an expanded chain if polymer in solvent interactions are not favorable, and then we will have a collapse chain or in other words, polymer will exclude the solvent from its surrounding and there is a condition in between where the polymer behaves as if it is not interacting at all and he ideal chain behaviour is observed.

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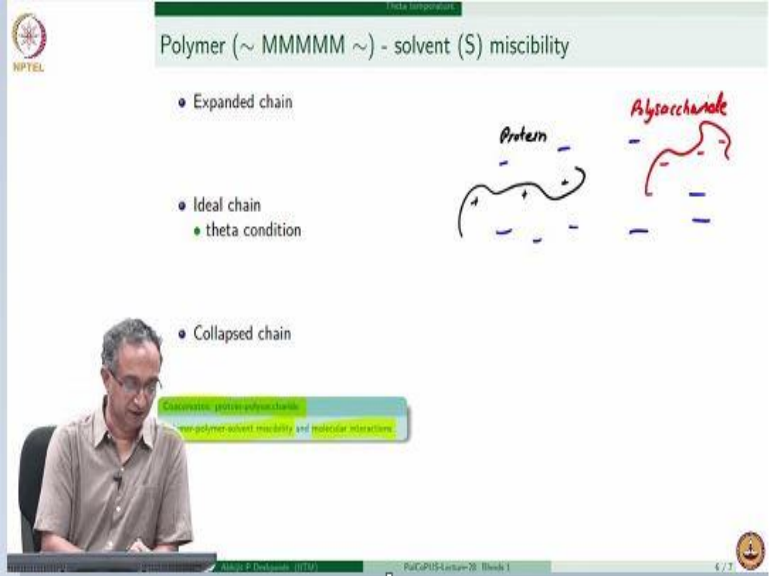

Polymer (~ MMMMM ~) - solvent (S) miscibility

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So, one of the interesting things that you can look up are coacervates and these are become extremely important in biomedical and drug delivery application, and here the combination of molecular interactions macro molecular behavior is very beautifully tuned to achieve a property. So, let us say if we have a protein molecule and that may have plus charges on it, and then we have a polysaccharide molecule. So, we have a protein molecule, which is cationic, and then a polysaccharide both of these are there in our cell systems.

Which have and then of course, there is a solvent water. So, if you have ternary system of this kind where there is a positively charged macro molecule, negatively charged macro molecule and you have solvent, what happens to the macro molecular arrangement, such coacervates are very important for drug delivery other applications. So, in this case, you will be able to see what we have is a polymer-polymer solvent miscibility.

And what decides this miscibility is the molecular level interactions, and it is possible that you will have protein polysaccharide complex which is what is called coacervate and therefore, water will be excluded. Other possibilities, we will only have a protein rich solution and a polysaccharide rich solution or we have a perfectly miscible system we have protein polysaccharide and water are extremely well distributed and molecularly makes throughout it is a very interesting system.

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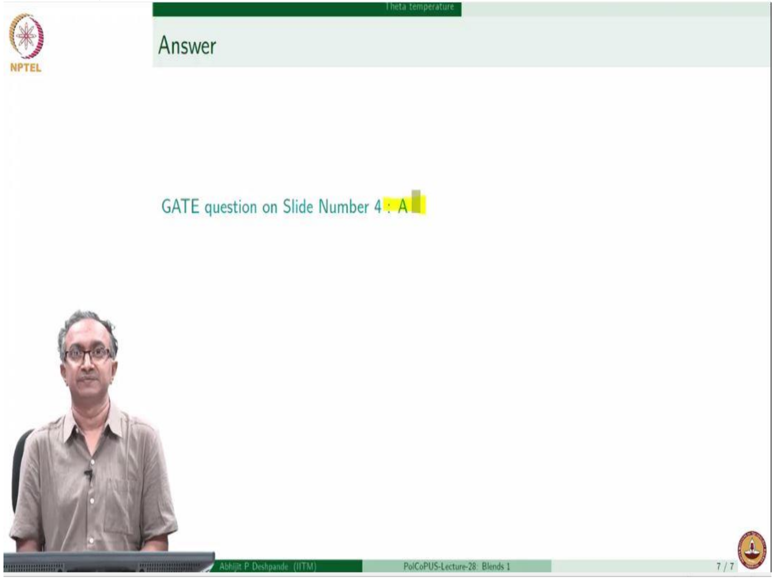

Answer

GATE question on Slide Number 4 : A

To think in the context of blending of polymers and we will close this lecture and I am sure that given that polyethylene polypropylene are immiscible systems, the what we need is a favorable interactions and so polystyrene and polyphenylene oxide, the benzyl group interactions between the 2 polymer chains makes it miscible. So, you need certain favorable interactions or polymeric systems to be miscible so with that message. In the next lecture, what we will try to do is to look at thermo dynamics of mixing. Thank you.