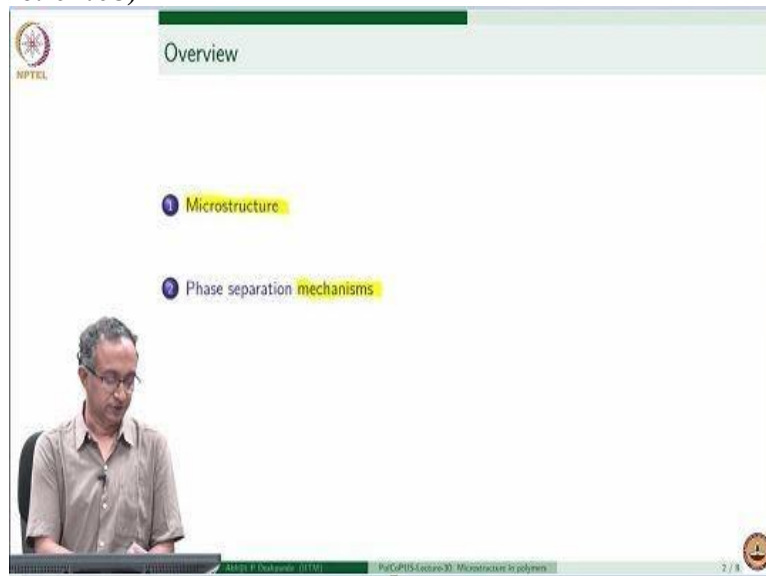


**Blends and Composites**  
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**Lecture - 30**  
**Microstructure in Polymers**

Hello welcome to the lectures on polymers in this lecture we are going to look at microstructure in polymers through this course on polymers in which we have looked at the concepts related to polymers, we are looking at the properties we are looking at several interesting applications. And of course we are also discussing the overall sustainability aspects. In this week we will start looking at the properties of polymers in the first couple of lectures though we still have to look at the polymeric materials of different kind. And we will finish our analysis and understanding of the blends and composites. And so the focus in this lecture will be on learning concepts related to what is meant by microstructure in polymers. And specifically we will also see some mechanisms of microstructure formation.

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So we will look at what are different microstructures and then we will survey quickly the mechanisms which are of interest when we talk about microstructure.

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**Polymeric materials: microstructure**

- Amorphous, glassy → orientation
- Semi-crystalline Polymers → crystal morphology, orientation
- Blend → Domain size and shape
- Copolymer → Domain size and shape
- Composite → Distribution and orientation

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Match the characterization technique with the most appropriate property

Characterization technique	Property
P. infrared spectroscopy	1. melting point
Q. thermo-gravimetric analysis	2. functional group
R. transmission electron microscopy	3. degradation temperature
S. differential scanning calorimetry	4. morphology

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

So polymeric materials what is the different set of microstructure or structures at the microscopic scale that are of interest. And so if we look at let us say just the amorphous or glassy polymer then the chain orientation is what is of interest. So for example if the molecules are oriented towards one direction and we saw this that orientation is a very important aspect related to applications of polymeric films. Similarly if we have a semi-crystalline polymer then the crystal morphology and orientation of crystals is important.

So the dimensions of crystal we saw that the polymer chain folds itself and this fold leads to formation of what is called a lamella. And so what are the dimensions of this lamella and more importantly how is this lamella distributed itself like we saw in case of a spherulite. So what is the spherulitic size for example? So these are all aspects related to morphology of crystallization over and above if there is an orientation associated with, so in the case of ferrolite basically the ribbon like lamella are distributed completely isotropically throughout the sample but if we plastically deform this sample then all the lamellas may get stacked on each other and then there is a preferred orientation. So orientation not just of the chain itself we may have orientation of the crystal lamella also. So both of these orientations are important from a microstructure point of view. And one of the things that you can immediately notice is this lamella will have an anisotropic property.

If you look at in this direction there is covalent bonds but in these directions basically there is only the polymer chains which are stacked with each other and there is only energy of interaction which is secondary interactions. And so the spacing also, the lattice dimensions as we have seen earlier A B and C will be different and so that again indicates that crystal is an anisotropic entity, which has consequences both for mechanical properties diffusion and all the other performances.

So therefore orientation of these lamella will definitely determine what the overall performance is. Now if we mix the 2 polymers as we saw in case of polymer blends and we have partial miscibility or immiscibility then what is the sizes of the A rich or A lean phase. Or if it is A and B completely immiscible then what are the domains and shapes of A and B. Similarly in case of a copolymer especially when it is a block copolymer or a graft copolymer then again what are the domain sizes and shape?


And this we have repeated several times that a polymer blend and a block copolymer or a graft copolymer have certain behavior which is similar because we have basically segments of A and B. In one case they are reacted with each other as a block copolymer but in other case they are free but in terms of molecular level picture both of these have some similarities. In case of a composite when we add either a particle or a fiber or a fabric then basically the distribution and orientation of again fibers is important.

If it is a spherical particle then of course only distribution is important because it is a spherically symmetric filler. But in case of fibrous or any other disc like any object which itself is anisotropic we will need to look at the orientation in the final polymer composite part. So you can see that there is a wide ranging variety from molecule level to particle level that we have to look at when we discuss microstructure of polymeric systems.

And in this question for example morphology which is what we mean by microstructure can be looked at using microscopy. There are several types of microscopies we can look at optically using optical microscope, we can have a scanning electron microscope so there is atomic force microscopy so all of these are ways to look at what is the distribution on surface or in case of transmission electron microscopy since we use a very thin sample we can look at the overall sample itself.

And we can know the what is the distribution of different components so we know basically the morphology of the sample. And clearly then other techniques are useful for determining other parts of the structure of a polymeric system or its behavior.

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Phase separation mechanism

**Phase separation: crystal/melt and A-rich and A-lean regions**

- Depending on the conditions, the mechanism of phase separation differs
- The mechanism depends on the second derivative of Gibbs free energy
- Compositions fluctuations exist in a system, and depending on the response to these fluctuations, the phase separation mechanism would differ
- The temperature composition diagram can be used to describe different regions with different phase separation mechanisms

In terms of energy of crystallization or energy change of mixing,

$$\delta G = \frac{1}{2V} \left[ \frac{\partial^2 \Delta G_{mix}}{\partial \phi^2}(\phi_0) \right] \delta \phi^2 d^3 r. \quad (1)$$

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So one of the things that are important when we look at crystal melt transition to a solid phase because we in case of a semi crystalline polymer we are going from a molten state which is completely random to a semi crystalline state where we will have a distribution of glassy and crystalline states. Or in case of a blend where we look at the 2 domains of the blend it is of interest to know what is the distribution of these crystalline amorphous regions or A rich A lean phase.

Those of you who are familiar with phase equilibria and have looked at let us say vapor liquid equilibria or liquid liquid equilibria may not have come across this and can you guess what why is the reason that in case of vapor liquid equilibria we do not really look at these phase

separation mechanisms in as much detail. If you think in terms of vapor structure or in terms of liquid structure the phase separation mechanism is not as relevant because in the end the phase separated structure is identical because there is sufficient molecular flexibility mobility for the phase separation mechanism to remain relevant for the final properties. But in case of polymers we are going to be in the final state which is a glassy state and therefore whatever phase separation mechanism can do to the distribution of macromolecules it will get frozen there.

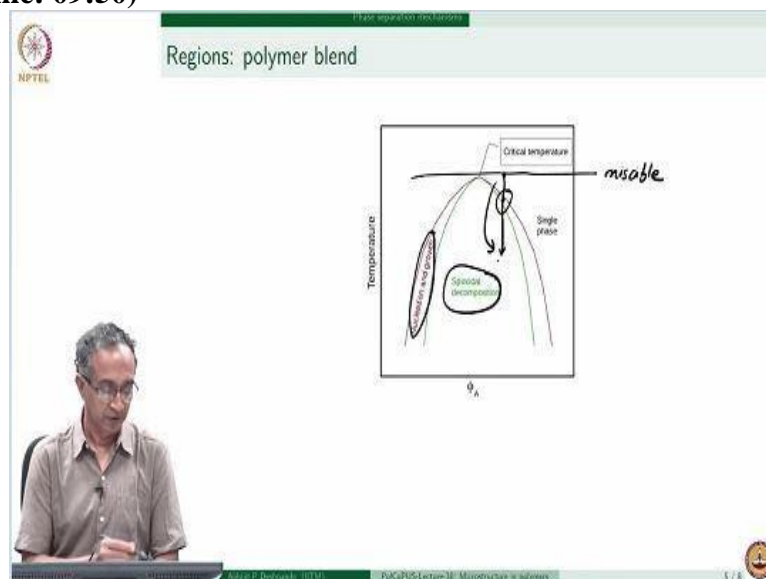
And so it depends a lot on how the phase separation was done and given that macromolecules are also very slow in terms of their response and given that they are entangled with respect to each other more often than not it is the kinetics of phase separation which determines the overall phase separation boundaries of the domains. And so therefore phase separation is very crucial for polymeric systems because it completely determines the microstructure in the final performing part.

And so depending on the conditions of phase separation the mechanism can differ. The mechanism generally depends on the second derivative again because this determines the stability of the system as we saw in the 29th lecture where depending on the curvature of the delta G curve with respect to composition we have stability, meta stability and instability. And so the basic picture that we have of why the mechanism differs is based on what happens in a situation where there is a thermodynamic driving force for phase separation.

But just because the thermodynamic driving force is there it does not mean that phase separation will always happen according to same mechanism it also depends on what is the level of fluctuations and how the different driving force such as thermal energy, the interface whenever we create A rich A lean phase or a crystal amorphous phase what is the energy associated with that so all of these determine what is the mechanism.

So we have already seen in the 29th lecture that a temperature composition diagram can be used to describe different regions and in terms of the second derivative of Gibbs free energy so this is what will determine what is the mechanism in terms of phase separation.

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And what we saw was that if I take a blend which is under this condition and if we maintain the temperature then it is completely miscible all the time no matter what is the composition.

But if I cool the blend then there is a possibility of doing phase separation by spinodal decomposition or if I cool it slowly then the phase separation may happen through nucleation and growth. So generally phase diagrams will also tell us about the mechanisms of the phase separation.

And in case of macromolecules there is a kinetics aspects involved also because it may not be always feasible to cool or quench extremely rapidly so that we reach spinodal decomposition. Nucleation and growth may already set in based on the cooling rate that we see and most often because of this nucleation and growth being the phenomena which is immediately started many of the practical systems we see nucleation and growth as the dominant feature.

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**Nucleation and growth**

Energy change when a nucleus is formed,

$$\Delta G(r) = \frac{4\pi}{3}r^3\Delta g - 4\pi r^2\gamma_{cm} \quad (2)$$

- Overall change in energy is positive initially, and increases with  $r$
- Only beyond a certain  $r$ , the change in energy is lower with increase in  $r$
- A critical  $r$  to be a nucleus

The barrier height to be crossed for nucleation,

$$\Delta G_b = \frac{16\pi}{3} \frac{\gamma_{cm}^3}{\Delta g^2} \quad (3)$$

Nucleation is an activated process with nucleation density as  $\nu_{nuc} \sim \exp\left(-\frac{\Delta G_b}{RT}\right)$

A rich region crystal

interfacial

critical size

So let us look at that a little bit closely the idea is that everywhere there are thermal fluctuations and because of which the molecules are randomly changing conformations since there is a thermodynamic driving force for either crystal formation or phase separation locally polymer chains are organizing themselves so that A rich region is formed or a crystal is formed however as soon as these regions are formed we create an interface. And since we create an interface there is an interfacial energy which is proportional to the area  $4\pi r^2$ . Let us say so if we have a domain of this kind with a size  $r$  and this domain could be either a crystal or let us say A rich region then the interfacial energy associated with this is given by this which is the interfacial energy. Which is proportional to the area and then of course there is a thermodynamic driving force which is related to the Gibbs free energy change and it is related to the size the volume of this particular A rich region or a crystal.

So the overall Gibbs free energy is some of these so there is a driving force to form the crystal but there is a interfacial energy term which is making sure that the crystal will melt again and so this dynamic process keeps on happening everywhere if we are above the melt temperature then basically this term itself is not conducive there is no thermodynamic driving force and therefore no crystal is formed. Only when the sample is brought below the melting temperature or below the critical solution temperature LCST or UCST or whichever are the critical transition temperatures then only if the thermodynamic driving force is there. We will have a driving force for having the phase separation or crystallization. So therefore because of this the overall change is energy is positive and it in fact also increases with  $r$ . So if you look at this delta G as a function of  $r$  you can put some numbers here for delta G and gamma c m and you can see that this is how the variation will be as you change with respect to  $r$ .

So in initial region what happens is in fact  $\Delta G$  overall increases if the crystal starts growing or A rich region starts growing. So as soon as due to thermal fluctuation somewhere a small crystal or A rich region is formed there is a tendency for this to again melt back because that is how the  $\Delta G$  is lowered but if you go in this region then you see that  $\Delta G$  will spontaneously decrease so there is a critical size of this crystal or A rich region required.

And that is what we call a nucleus only when it goes beyond this crystal size our description says that okay a nucleus has formed and now growth can happen. And that is why the 2 different stages that there has to be a nuclei first there is a tendency of crystallization everywhere or there is a tendency of forming A rich phase everywhere but certain places only nuclei formed. Because of this competition between Gibbs free energy change which is the driving force for the crystal or A rich formation and then the interfacial energy.

Of course with time our understanding of nucleation and growth has become much better but for our course purposes this gives us a basic idea as to why there is a certain set of places where nucleation forms. And then the growth can occur simultaneously and so this barrier height to nucleation can also be estimated mathematically by just finding a maximum of this  $\Delta G$  and it depends on the surface energy and the overall driving force.

And nucleation therefore is dependent on what is this barrier energy if thermal energy is more in terms of the difference between the transition temperatures and wherever you are then there will be a higher degree of nucleation.

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The slide content is as follows:

- Phase separation mechanisms
- Processing and microstructure
- Flow induced- and influenced by flow (shear induced, flow field assisted)
  - Orientation
  - Crystallization
  - Phase separation
- Field-assisted microstructure manipulation
  - Electric field
  - Magnetic field
  - ...

Handwritten notes on the slide include 'quiescent' with two irregular shapes, 'flow' with an arrow and two elongated shapes, and 'electrospinning'.

The other phase separation mechanism of spinodal decomposition as I mentioned is less prevalent and it needs to generally be continuous. Because there is an unstable phase separation formation what happens is there is co-continuously everywhere A rich region and A lean region will be there or polymer crystals will be spread throughout and it is observed only in either lab conditions or for very few specific systems.

So generally one of the things that we have to be very cautious about is how is the processing being done on a polymeric system affecting its microstructure because in the final part it is the microstructure which is very important but the processing will have a large influence on it. And during processing we basically will make the polymeric material flow into a mould or we will

press it between rollers or we will stretch it using a spinning machine, so all of these are operations in which we deform and make the material flow.

And so is there any flow induced or influenced structure for example chains will orient in the flow direction crystals can also orient in the flow direction phase separation the domains may also so if we have a domain of A rich region which is largely this if we create it under what is called a quiescent condition. Quiescent condition implies no flow or stationary phase and so in this case we may observe spherical domains but if we have now a flow then the domains may get elongated like this.

So therefore chain orientation or crystals or the domains of blends will get affected based on the processing conditions. And the shear rates which are involved the stresses which are involved will significantly influence what is the microstructure that we get in the end. And in fact this is a very important tool available to us to manipulate the microstructure of polymeric systems so that we get the desired performance.

The other interesting thing about many of these macromolecular structure is depending on the chains or the crystals or the domains if they respond to other fields then we can in fact achieve microstructure by applying electric or magnetic field. So for example electro spinning is a method of making fibers using an electrical field also so when we apply electric fields and if macromolecules have charges then they will respond very differently to it compared to some other macromolecules which have less dipoles and less charges on them.

So therefore field assisted microstructure manipulation is also important in many of these applications so in a nutshell microstructure is very important. Because final polymeric part will basically perform according to the microstructure that is present and this is what we had mentioned when we talked about processing structural property. So in case of polymeric materials the 3 are interwoven with each other very intricately and when we want to understand the behavior of polymers we have to look at all these 3 aspects.

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Phase separation mechanism

Answer

GATE question on Slide Number 3 : Answer D

Infra-red (IR, FTIR, NIR) spectroscopy : vibration/stretching of covalent bonds  
Thermo-gravimetric analysis (TGA) : weight change with temperature  
Transmission electron microscopy (TEM) : observation with few nm resolution  
Differential scanning calorimetry (DSC) : heat flow with temperature or time

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PaCoPUS-Lecture 30: Microstructure in polymers 6 / 8

And so morphology of course we have seen that microscopy is used and in transmission electron microscope we can get results up to few nanometers and then we will see also that like mechanical spectroscopy with rheology or dynamic mechanical analysis dielectric

spectroscopy we have molecular spectroscopy where vibration stretching of covalent bonds tells us about which are the functional groups present.

So one can identify quickly whether this is a polypropylene or whether this is a polyethylene terephthalate or it is a polystyrene sulfonate by looking at the groups which are present. Weight change with temperature is a very good way of estimating the thermal stability of the system of course it is a only aggregate or gross measurement because even without weight change certain reactions can take place and therefore degradation can set in earlier than what is indicated by TGA.

But from a gross measurement point of view it is a very important technique and we will have a lot more to talk about differential scanning calorimetry especially when we look at glass transition crystallization polymerization so many transitions that happen have a thermal signatures. And so all of these techniques are extremely useful in determining the polymeric properties as well as polymeric microstructures so with this we will close this lecture. Thank you.