PolCoPUS

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Lecture No -60

Polymers at interfaces

Hello, welcome to this week of lectures where we are discussing interaction of polymers with other materials. So in this introductory course on polymers we have discussed several aspects related to the behavior of polymers and we focus a lot on viscoelasticity, but now as many of these polymeric materials are used in several different environments how they interact with the environment is also very crucial.

So in this particular lecture we will look at those macro molecules which are at interfaces and interfaces could be formed during processing or during service. So what is the role of polymers at interfaces and what are the concepts key concepts which are related to polymer at interfaces.

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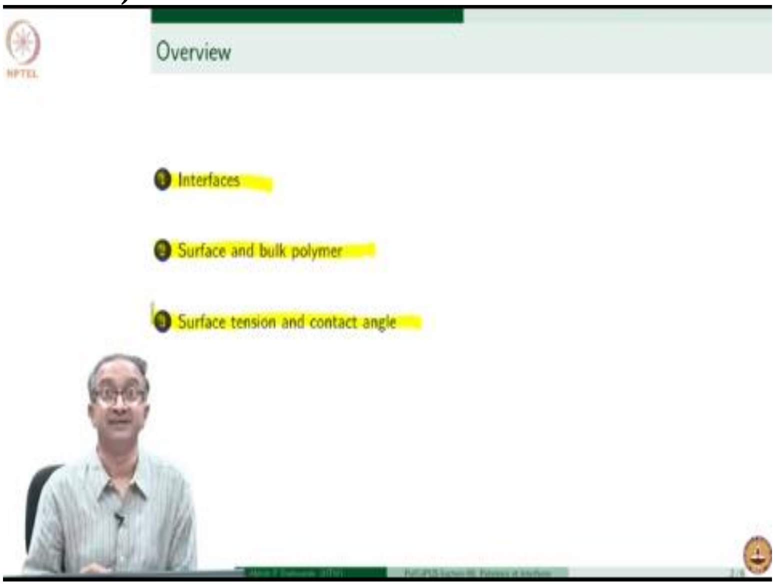

Overview

1. Interfaces
2. Surface and bulk polymer
3. Surface tension and contact angle

And this will be done by first looking at what are the different types of interfaces where we have to look at these macromolecular systems and try to highlight certain features which are related to how surface macromolecules may be different compared to the bulk macromolecules and one quick way of characterizing the macromolecules which are at the interfaces or the polymeric interfaces by measurement of a property.

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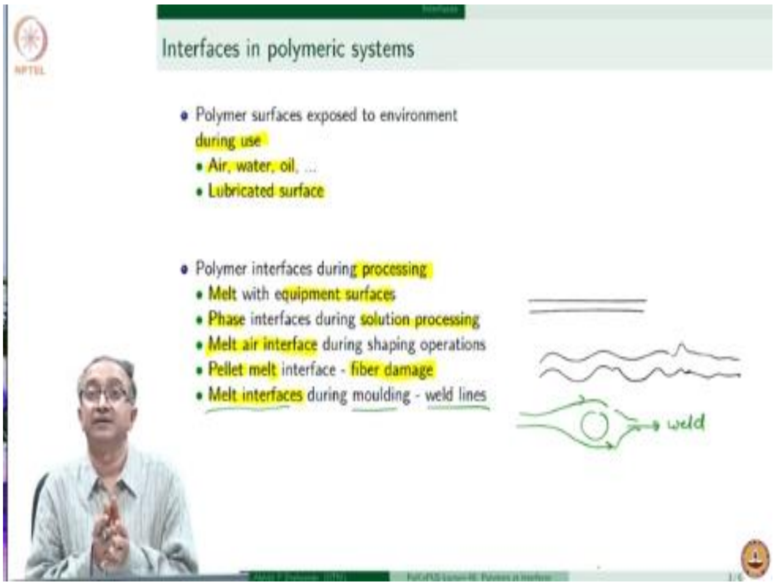

Interfaces in polymeric systems

- Polymer surfaces exposed to environment during use
  - Air, water, oil, ...
  - Lubricated surface
- Polymer interfaces during processing
  - Melt with equipment surfaces
  - Phase interfaces during solution processing
  - Melt air interface during shaping operations
  - Pellet melt interface - fiber damage
  - Melt interfaces during moulding - weld lines

So interfaces in polymeric systems could be due to basically what is happening when the polymer is in service life or it could be due to when polymer is being processed. So for example it could be exposed to different types of phases depending on what is the service if it is a oil storage application then of course there is an oil polymer interface and many of the exchanges of small molecules may happen at this exchange at this interface and we therefore will have to worry about what is the status of macromolecules at the interface.

We could also have polymer being subjected to contact with other solids in case of a lubricated surface so Teflon, for example is used as a machine component or nylon is used as a machine component and then it comes in contact with metallic or other materials. So what happens at the interface between two solid materials? During processing of course melt interacts with the equipment surface and you might think in terms of, why is this important?

Why would melt interaction with the solid surface the solid surface of a mould material or a screw extrusion material? Why is that important? And this can be again important from the point of view of both the phenomenon where polymer remains on the surface of the equipment and does that lead to anything or some of the metallic components, coming out from the metal surface to the polymer.

So what is the nature of interface between polymers and the overall metallic surfaces in case of instruments, does it lead to for example accumulation of these macromolecules on the metallic interface and slowly heating cooling characteristics change which then will lead to problem with processing, later on do the some of these metallic components come into the polymer and then they come into the final part and can be there as impurities or can they lead to some catalytic action which may form cross linking or chain cessation in the polymeric systems and so on.

So you can see that interfaces and interaction during processing can lead to whole lot of possibilities. There is of course phase interface between macromolecule and solvent whenever we have solution processing, whenever polymer is precipitating out of the solvent or in case polymer is dissolving in the solvent there is the interface between polymer rich phase and the solvent rich phase.

We could also have the melt air interface when we are forming a film or when we are forming a fiber I hope you can recognize that when a film is formed it should be of uniform thickness, we do not want this air polymer interface to become like this, in which case we will get very non-uniform thickness and so interface has to remain stable in case of melt air interface in variety of shaping and polymer processing operations.

Similarly you may have a situation where there is a solid pellet of a polymer which is actually molten through the polymer processing operations which we will discuss in 69 lecture, 70 lecture, 71 lecture where we will look at some of these polymer processing operations and we will see that we start with polymer pellets or granules. So many of the polymers are sold as these and then they are melted and then processed mixing and then addition of different additives fibers and then they are finally shaped.

So in this case there is an interface between the melt and the pellet itself, so pellet starts melting slowly as it goes through the processing operation and this sometimes can be very crucial in terms of what happens to the fiber. So whenever we use short fibers to reinforce and make a composite material it is well known that the lot of fiber damage happens during processing.

So while inputting we may be having let us say 4 mm, 5 mm length of a fiber but in the final part because of the what happens to fiber at melt pellet interface, the eventual size of the fiber may be only 2 mm or 1 mm. So lot of fiber breakage happens and this is again an interface between a solid and melt which determines what happens to the fibers and how easily or difficult it is for them to break.

And the interface of melt when flow when there is an object which is let us say has we have an annular disc to be made then what happens is polymer melt will come and go around both sides and then again come and meet. So this there will be a what is called a weld surface or where melt interfaces come and they again join together, so such interfaces can also be there. So all of these are places where macromolecules are there in contact with another macromolecular surface or another small molecule surface like that of gas or liquid.

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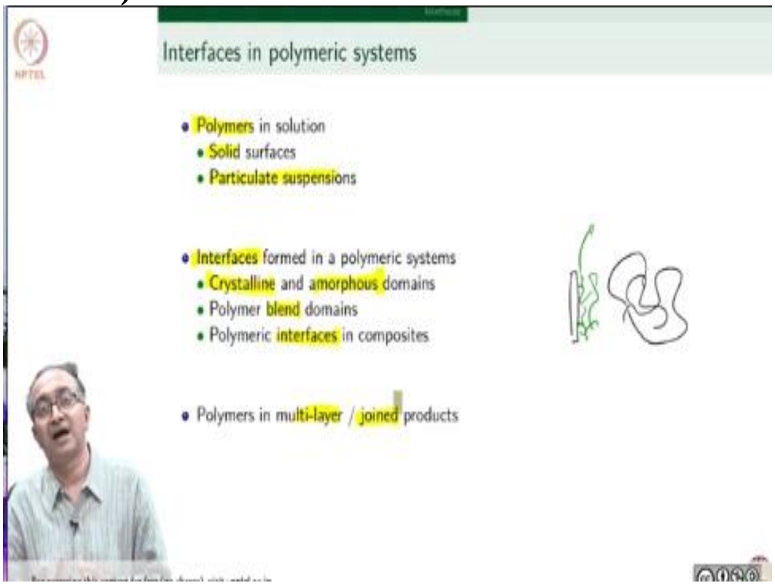

Interfaces in polymeric systems

- Polymers in solution
  - Solid surfaces
  - Particulate suspensions
- Interfaces formed in a polymeric systems
  - Crystalline and amorphous domains
  - Polymer blend domains
  - Polymeric interfaces in composites
- Polymers in multi-layer / joined products

Now what are the different types of interfaces in these situations, so we could have polymers in solution where the polymers are basically in touch with the containers and there can be adsorption between polymers on the surface of these containers. We also could have let us say a particle light suspension, for example paint is a mixture of pigment particles and polymeric materials and solvent and so on.

So polymers could absorb on the paint particles so therefore wherever there are surfaces of either particles or containers, we could have a polymers preferentially reacting with these surfaces. We could also have interfaces which are formed within a polymeric material itself, so for example there is a crystalline domain and an amorphous domain the interface between these regions.

In the crystalline domain there is a definite order of macromolecules there is a lamella there is a unit cell on the other hand in amorphous phase there is random ordering of macromolecules. So there is an interface where there may be mixed behavior we could also have a polymer blend and again interface between two different macromolecules when they are immiscible or compatibilized polymer blends.

We could have a polymer interface in composite itself because whenever we have fiber we will have macromolecules let us say it is an amorphous polymer composite, so macromolecules are randomly distributed but when they come closer to the fiber if there is preferential interaction, there may be a preferential physical interaction between the fiber and the macromolecule and therefore a strong interface may be formed and in fact this is what is desirable if load transfer has to happen from the matrix to the fiber phase as we discussed earlier.

And so interfaces again are involved in case of composite materials and of course many times we will have a multi-layer product by design itself, or polymer may be joined with other materials which could be polymeric or non-polymeric to form a component or to form a overall device. So in this case of course interfaces are involved because by definition heterogeneous materials different materials are bonded together or layered together to form the overall device. So you can see that macromolecules are at interfaces in variety of different ways.

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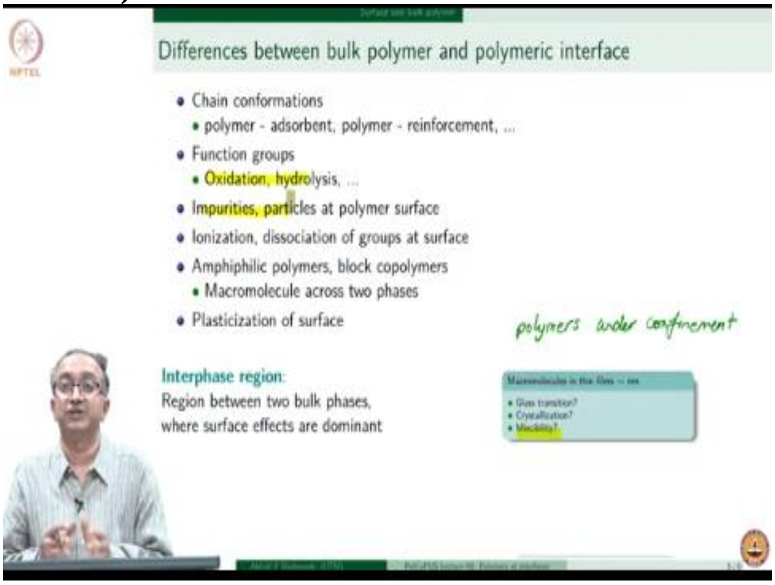

Differences between bulk polymer and polymeric interface

- Chain conformations
  - polymer - adsorbent, polymer - reinforcement, ...
- Function groups
  - Oxidation, hydrolysis, ...
- Impurities, particles at polymer surface
- Ionization, dissociation of groups at surface
- Amphiphilic polymers, block copolymers
  - Macromolecule across two phases
- Plasticization of surface

polymers under confinement

Interphase region:
Region between two bulk phases,
where surface effects are dominant

- Glass transition?
- Crystallization?
- Miscibility?

And what can we summarize as the main differences between the bulk polymer and the interface in which there are macromolecules and so generally what could happen is the chain conformation can change. For example if macromolecules are close to a fiber surface and there is very favorable interaction, the macromolecules may lie parallel to the fiber. So in that case what we are doing is a macromolecule which can be otherwise random starts orienting itself parallel to the fiber.

So depending on how the polymer absorb on a surface or polymer interacts with a reinforcement the chain conformations will be very different at the interface compared to the bulk polymer. We could also have functional groups which are different at the interface. So because macromolecule at the interface is let us say exposed to more moisture or more air in case it is exposed to environment then some of the macromolecular functional groups may change and oxidize or hydrolyze and therefore the functional groups at the interface will be very different compared to bulk.

And so this is something very important for us to consider, for example when we think of a glass particle is just S_iO_2, but many times the glass interface can also contain what are called silanol groups S_iOH, because of interaction with environment, water and so on. So you can see how the bulk of the particle will only be glass but surrounding on the surface will be some S_iOH groups. So we cannot think of glass particle only by focusing on the S_iO_2.

We have to look at the interface and see what is the distribution of molecules, similarly in case of a polymer surface the bulk may be polyethylene but on the surface there may be few oxidized chains available, in which oxygen has been incorporated along with the chains and so the behavior of interface will be very different compared to what we imagine it to be if it was just CH_2-CH_2-CH_2 polyethylene chain.

Additionally the complication is that polymer surfaces may adsorb various other impurities, it could be small molecules it could be large molecules it could be bacteria viruses it could be particles, so all these can be absorbed at the polymer interface and again modifying the behavior of polymer interface with respect to what could be the bulk response of the polymer. Depending on the environment and let us say if we have a polar solvent water is one example of course.

But there are several polar solvents used in case of processing of polymers NMP, DMSO so you can go and look at why some of these solvents are polar but whenever a solvent is polar it can lead to ionization of charge groups. So dissociation of ions can happen and ionization can happen and this can again happen because solvent is there at the interface while bulk of the material no ionization happens.

So again interface is ionized while bulk may not be, we can have the reverse situation in which case the bulk has let us say water absorbed so therefore there is lot of ionization but the interface is exposed to oil. In this case because the interface is exposed to oil ionization may not happen. So all different possibilities in which interface is very different compared to the surface, the bulk polymer.

We could have an amphiphillic polymer an amphiphillic substance for example surfactant is amphiphillic so it has both hydrophobic hydrophilic character so if you have a block copolymer or an amphiphillic copolymer what may happen is the bulk of the polymer there may be one distribution of different blocks but on the surface there may be different distribution. So in general macromolecules which are across two different phases may be distributed differently depending on the nature of what surrounding these macromolecules.

And of course some of these things may lead to segmental mobility be completely altered at the interface compared to the bulk. So you can see that there are large number of ways in which interfaces are very different compared to bulk and therefore it is important to focus on the interface and their properties when we are trying to analyze many applications where the role of interface is very crucial.

Many times interface can also be a region and then it is called an inter-phase region because it is not just a small nanometer scale length but because conformation changes are different near the interface some of those effects are much larger than what the interface might be and therefore it is a region between two bulk phases, so there is a fiber phase there is a macromolecule phase and then there is an interphase.

Because of interaction between fiber and micro molecule the behavior in that interface is different compared to either the fiber phase or the macromolecule phase and this is where the surface effects or the interface effects are very dominant. So one of the things that you can think about is what happens when the film of polymer itself is very small, because we have highlighted by whole number of ways in which interfaces are different.

Now if I make a polymer film which is let us say few nanometers thick then there is no bulk, the whole behavior of the film is pretty much influenced by the interface effects because the size of the film is so small and basically interface region and interface effects are going to be completely dominating. So what happens to macromolecules in such films? This is also called for example you might hear especially in the research literature terms polymers under confinement.

And this is very practical also you might think that very few nanometer thick films may not be relevant, but think about coatings, think about biological applications very thin films are involved where macromolecules are. So macromolecules under confinement or in thin films is a very important topic where we need to understand the response of macromolecules which can be very different compared to bulk.

So just looking at let us say glass transition and of course we know glass transition is related to segmental flexibility. So what happens to segmental flexibility when we make a film which is very thin and therefore this thin film is exposed to the environment and can influence if oxygen water is there in air in which this thin film is they can interact. So will segmental mobility increase or decrease when we make a film very thin and in fact because of the specific interaction between small molecules and environment.

And the polymeric film and because of the interface and interface effect there are all kinds of results possible and it depends on a particular polymeric system and the environment in which the film is being tested. So in fact glass transition can increase or decrease compared to the bulk polymer when we make a very thin film. These are actually very fascinating research and application topics where we need to understand the behavior of thin films vis-à-vis the bulk behavior.

And again crystallization which is nothing but arrangement of segments into crystal lamella, this process can get influenced based on segmental mobility. So we may observe that in a thin film crystallization is enhanced or reduced again depending on what happens to segmental mobility and similarly the cases with miscibility because there are surface groups there are impurities on the surface miscibility may have a completely different behavior compared to bulk miscibility.

So you can see how polymers and thin films is very important for us to understand from both fundamental as well as applications point of view. However given the nature of ways in which interface can be different we have to be careful in terms of analyzing a system. So lot of mechanisms are specific to one particular case and therefore we cannot generalize and make a very broad remark regarding how interface is different compared to bulk.

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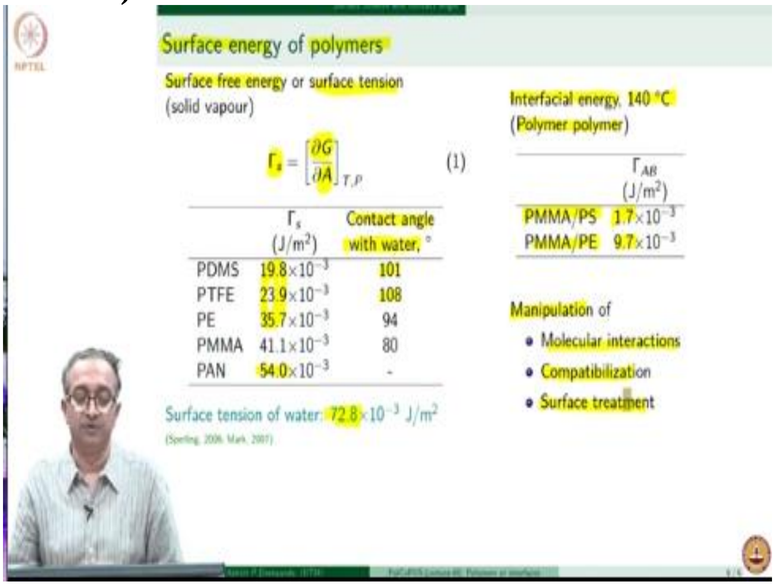

Surface energy of polymers

Surface free energy or surface tension
(solid vapour)

$$\Gamma_s = \left[\frac{\partial G}{\partial A}\right]_{T,P} \qquad (1)$$

	Γ_s (J/m^2)	Contact angle with water, °
PDMS	19.8×10^{-3}	101
PTFE	23.9×10^{-3}	108
PE	35.7×10^{-3}	94
PMMA	41.1×10^{-3}	80
PAN	54.0×10^{-3}	-

Surface tension of water: 72.8×10^{-3} J/m^2

(Sperling, 2006; Mark, 2007)

Interfacial energy, 140 °C
(Polymer polymer)

	Γ_{AB} (J/m^2)
PMMA/PS	1.7×10^{-3}
PMMA/PE	9.7×10^{-3}

Manipulation of

- Molecular interactions
- Compatibilization
- Surface treatment

So given all these myriads of ways in which polymer interfaces are different can we not characterize and measure properties of interfaces and yes certainly we can and one way to talk about the properties of an interface is to talk in terms of what is the surface energy of polymers? And so the surface tension or surface free energy is one common way of measuring the properties.

This can also be measured in terms of what happens when a different liquid is placed on a polymeric substrate and what does it do in terms of a drop, does it form a nice spherical drop and remain most of you might have seen that if thermometer breaks and mercury comes out it remains like a ball and goes around, because it does not wet the surface. On the other hand water on many substrates will just fall and then just spread completely.

So contact angle is an important way to assess the wettability of substances on a polymeric substrate and other substrates also and so the surface free energy is defined as the change in free energy with respect to the change in area given temperature and pressure are constant and here what we are looking at is surface free energy for several different materials and you can see that polymers in general are low surface energy materials.

Water for example has a higher surface energy, in this case when we say surface tension of water it is water in equilibrium with its vapour air mixture, because when we have air on top there is some amount of water molecules also there in the equilibrium. So that is the interfacial tension of water interface of liquid and vapour, while these quantities are again interface of polymer with gas phase since PDMS and PMMA and all these polymers are non volatile, there is no macromolecule in the other phase.

But you can see polyacrylanitrile which is a water soluble polymer has a surface energy which is on the higher side. So you can see the surface energy gives you a very good indication already about hydrophobic or hydrophilic nature of a surface and the same can be looked at by looking at contact angle also larger the contact angle more hydrophobic it is, because this is with respect to water.

I can do similarly by measuring a contact angle of oil on a surface and then whenever it is a hydrophobic surface oil will spread and form a low contact angle. Whenever it is a hydrophilic surface, oil will not spread and form a larger contact angle. We can also look at interfacial energies when we have a polymer-polymer interface in case of blends mixing processing such melt interfaces may be very important.

And in this case at a high temperature poly methyl methacrylate and its interfacial energy is given and you can see that it can be an order of magnitude difference between the interfacial energies and so these interfacial energies can be modified by manipulation of molecular interactions we can compatibilize by adding another substance and we can also do surface treatment by grafting by adding functionalization and so on.

So this is a rich field which is very useful from the point of view of applications and there is a lot to understand here in terms of basics.

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Mark, J., editor (2007). *Physical Properties of Polymers Handbook*. Springer.

Sperling, L. (2006). *Introduction to Physical Polymer Science*. Wiley.

So with this we will close the lecture related to the interface and polymers, I hope you have been able to get an idea that why interfaces are different compared to bulk and how using surface tension and contact angle we can characterize some of the differences of polymeric interfaces, thank you.