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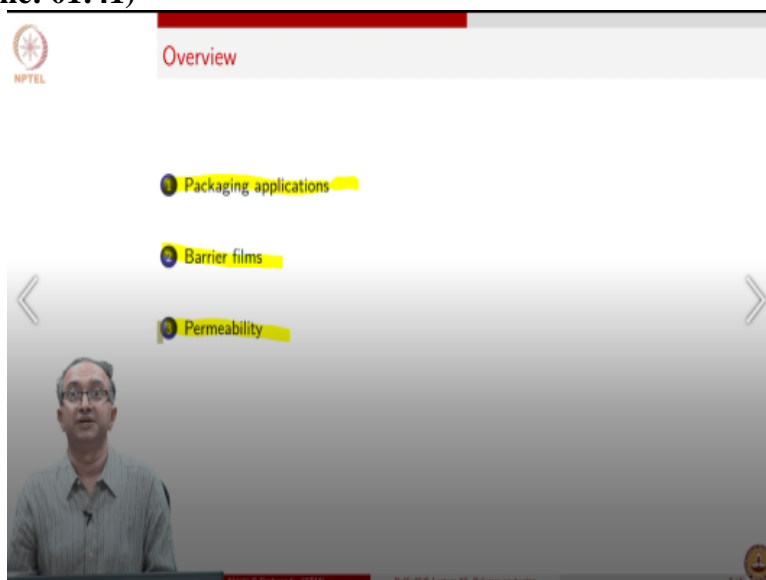
**Lecture No -58**  
**Polymer packaging**

Hello, welcome to the course on polymers. What you would have noticed over the weeks that we have been trying to discuss various concepts and properties related to polymers. That in the last couple of weeks we have started looking more from applications point of view. Having covered the ground in terms of the concepts and properties we have now focus little more on applications.

And see how some of the concepts that we have learnt are actually very useful in terms of analyzing the applications of these polymers. So, along the same lines will continue where we will look at applications of polymers in packaging. And what we will see is a lot of things that we discuss in this particular week will be related to interaction of polymers with other materials. And packaging of course is a case where a polymeric material is trying to protect something on one side.

It could be food or it could be another component which should not be broken from the external environment, which could be in terms of oxygen or UV radiation it could be in terms of mechanical load and so. Therefore, packaging is like a separation media between what has to be protected from the external environment. And so, interaction of polymers both to the inside as well as outside is extremely important.

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And so, the focus will remain on uses and we will look at what are different packaging applications in which polymers are used. Especially the barrier films which prevent small molecules going back and forth across this polymer packaging. And in this we will also have to discuss polymer being permeable to various species and what is meant by permeability of a polymer.

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Packaging application

## Examples of applications

Packaging sector ~40% of overall polymeric materials' use  
 PE, PP, PET and PS ~ 95 % of polymers used in packaging applications

(Nair et al., 2015)

- Barrier films
  - Protection, storage
- Impact resistant packaging
  - Transport
- Secondary packaging
  - Aesthetic appeal
  - Printability
- Electronic packaging
  - Providing electrical connection
  - Isolation of devices from one another
  - Heat conduction away from devices

Recycling of packaging?  
 Renewable / biodegradable:

- Cellulose and starch
- Chitin, chitosan
- Proteins: casein, gluten
- Poly (lactic acid) (PLA), Poly (hydroxybutyrate) (PHB)

So, example of applications which relate to packaging are multiple. Infact packaging sector probably accounts for 40% of overall polymeric materials used. So, it is a very significant amount of polymers which get used in terms of packaging. And if you look at polyethylene and polypropylene, PET and polystyrene, basically 95% are these 4 polymers. So, these 4 polymers pretty much dominate the packaging applications of polymers.

And you should not be surprised because you are all very familiar with these polymers regardless of our technical education. Because these are something which we hear in common parlance. And the applications which can be there, we can think in terms of a barrier film which is for protection and storage of goods and items. It could be impact resistance packaging which isolates the mechanical loading which comes from external environment.

And protects the item which is being stored or the material which is being stored. And so, for example in transport this would be very crucial. There can be secondary packaging which may not have a role in terms of either protection or in terms of impact resistance but it may be related to aesthetic appeal or it could be related to the fact that you need information to be carried and the component itself cannot carry the information.

So the package is what carries the information so, printability and so on. Also, in components like in case of electronics. You need some of these polymeric materials for sometimes providing electrical connections or sometimes isolation of device from one another in terms of insulation. It can also play a very important role in terms of heat conduction or heat insulation depending on what the application is. So, packaging when we say the it encompasses all of these.

And in case of electronic it is called packaging because several devices are being packaged in an integrated circuit and in a chip. So, therefore it is again referred to as a packaging material. And given the amount of use that we have in terms of polymers in these packaging applications, and given that there are few materials which are predominantly used lot of sustainability issues have to be related to these applications.

And so, recycling of packaging is a very challenging task. Also, because packaging come sometimes very thin film forms packaging comes as multi-phase materials. And so, generally there is lot of emphasis in terms of replacing packaging by renewable and sustainable or

biodegradable polymers. So, for example cellulose and starch based materials, chitin and chitosan based materials, casein and gluten based films.

So, all of these people are working on and trying to see if we can replace many of the packaging applications. Including biodegradable polymers such as hydroxybutyrate and lactic acid based polymers. So, lot of work is going on to try to get biopolymers and degradable polymers as well as compostable and renewable polymers in terms of their usage in packaging applications. So, bulk of sustainable polymer activity is towards this single application related to packaging. (Refer Slide Time: 05:51)

The slide is titled "Important phenomena associated with barrier films" and is presented by NPTEL. It lists several phenomena and properties of interest:

- Diffusion**
  - Flux of molecules due to chemical potential gradient  $\rightarrow$  concentration gradient
- Absorption, sorption, solubilization (solubility)**
  - Phase transfer from gas/liquid to polymer
- Permeation**
  - Flux due to pressure gradient
  - Convection - flow
  - Absorption, diffusion and desorption
- Adsorption**
  - Polymer surfaces
- Leaching**
  - Migration from polymer phase

**Properties of interest:**

- Thermodynamic : phase equilibria**
  - Solubility, concentration at saturation
  - Adsorbed concentration
- Transport**
  - Diffusion coefficient
  - Permeability

Small molecules in with polymeric materials:

- Separation membranes: PoC&PUS-Lecture-59
- Diffusion: PoC&PUS-Lecture-61
- Swelling: PoC&PUS-Lecture-62

Now the important phenomena which happen during let us say barrier film. So, we will look at one example of barrier film. Though polymers are used in several packaging application in case of barrier as the name suggests the small molecules are prevented from going one way or the other. Sometimes it may be selective barrier. So, in the sense that it allows oxygen to permeate but stops carbon dioxide or it may allow moisture to go, but stop carbon dioxide and oxygen or it may stop water but allow oxygen to go through. So, depending on the application we may have several such possibilities. In some cases it may prevent any of the small molecules from going. So, that we protect the material from getting exposed to any of the other smaller molecules. So, generally the phenomena which happen is first related to the diffusion.

Given that the material has a certain concentration of these small molecules and outside has certain other concentrations. So, if we think in terms of food item we may not want the food item to get dried. So, in that case we do not want water to go from food to the surrounding. The reverse also can be there that we do not want the food to get wet or hygroscopic materials which absorb moisture. We do not want them to start absorbing moisture.

So, therefore we do not want water to go from outside to inside. So, therefore barrier role is to manipulate the flux of molecules which go through this barrier film with through diffusion. And diffusion is basically flux of molecules due to a concentration gradient. It is based on the chemical potential gradient and chemical potential is defined in terms of change in Gibbs free energy per unit mole.

And so, diffusion happens whenever there is a concentration difference of these small molecules. And barrier film prevents diffusion. You could also have absorption so for example barrier film is exposed to vapour phase or barrier film is exposed to a liquid phase. Then first

the molecule has to transfer from the liquid or air phase to the polymer and that phenomenon is called absorption or also called sorptions at times or what we also have is solubilization.

So, a small molecule; let us say water from the atmosphere is getting solubilized into a polymer and so this is basically phase transfer from gas liquid to polymer. This also has to happen before diffusion can happen within the polymer phase. The reverse of this is also possible which is called leaching, especially in the context of liquid where migration from polymer phase to the liquid phase.

So small molecules which are there in the polymer can go over to the other phase. And this is something again worrisome let us say from the point of view of packaging in food application. So, if the polymer packaging contains a plasticizer or a catalyst or an additive which can be harmful in terms of its ingestion. Then we have to ensure that the small molecule does not interact with the food item and get food item does not absorb it from polymer or it leaches out from the polymer.

And so, overall what we are interested in is permeation phenomenon. Permeation in a English language sense just says that something being permeated from one side to the other permitted to go from one side to the other. And but permeation as a phenomenon is defined generally whenever we have flux due to pressure gradient. So, permeability of a material is classically is defined for a porous material.

So, if we have let us say sand particles and then there are pores and so what can happen is liquid can permeate through this porous medium. And the way permeation will happen is because we have a pressure gradient and  $P_1 > P_2$ , so this is called permeation. But we use this general term to also talk about any flux which is going from one side of the membrane to the other.

So, for example, it could be that there is a pressure difference then this membrane will permeate or there could also be a concentration difference. So, permeation in general is used in a little more general sense in the context of polymeric membrane. So, generally from a fundamental point of view it is the flow and convection which implies permeation. And generally, permeation is accompanied in case of polymer case because polymer can have pores in which case this analogy with sand is very similar.

But let us say polymers does not have pore and there is a pressure gradient like this. Then what has to happen is let us say carbon dioxide or oxygen which is here in large quantities, first has to absorb, first has to solubilize in the polymer medium then it has to diffuse and then finally desorb or come out of the polymer phase. So, permeation in case of polymers depending on what is the type of polymer may involve flow through pores like in case of sand or it may involve what is called a solution diffusion mechanism, as in case of a solid polymeric membrane.

Additionally, we can have surfaces being involved. So, absorption of small molecules on polymer surfaces that also can happen. So, a packaging film can, if it is a packaging film it can accumulate either dust particles or let us say larger amount of water molecules on the surface. And this can influence its packaging performance. For example, we see that if water has accumulated more on the surface it may lead to a biofilm formation, a mould formation or a growth can start happening.

So, therefore adsorption itself can also be a very critical phenomenon which determines the overall response of packaging applications of barrier films. So, these are you can see that there are so many features associated with how small molecules interact with polymeric systems. And general properties of interest based on all these discussions are twofold. One is in terms of the thermodynamic property where we are looking at interactions between small molecules and macromolecules.

And basically equilibrium, the distribution of small molecules in polymer phase with respect to either the liquid or the air phase which it is exposed to. So, therefore in these cases things like solubility how soluble is a molecule in polymer phase. How soluble is the same molecule in the liquid phase which is surrounding and so on. And in case of surfaces what is the equilibrium adsorption concentration.

So, there are these phenomena which are related to phase equilibrium between polymer phase and other phases. In case of a barrier film, where which is let us say multiple polymers this phase equilibrium will be between multiple polymer phases also. And the other side of the properties which we are interested are related to transport or flux of these molecules. And in that case properties like permeability diffusion coefficient are what are of relevance.

So, generally performance of barrier films is assessed based on the solubility and phase equilibria properties as well as permeability and diffusion coefficient and transport properties. And generally all of this we will discuss in more detail for example for separation membranes. We will take a look at what are the mechanisms the phenomenon of diffusion as well as phenomenon of swelling. We will also discuss in lectures later on.

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**Permeation**

- When a polymeric material is exposed to gas/liquid medium, it allows substances to go from one side to another
- Permeation rate =  $\frac{\text{Amount}}{\text{area} \times \text{time}}$  : flux ( $J_{r,i}$ )
  - For gases, with amount in volume: permeation rate units -  $\frac{\text{cm}^3}{\text{cm}^2 \cdot \text{s}}$
- Permeability ( $P_{p,i}$ )
  - property of polymer/substance (i) pair

$$J_{r,i} = \frac{P_{p,i}}{l_i} (P_1 - P_2) \quad (1)$$

- Units:  $\frac{\text{cm}^3 \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg}}$  (1 barrer =  $10^{-10} \frac{\text{cm}^3 \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg}}$ )
- Selectivity - relative permeabilities for two substances

$$\alpha_{ij} = \frac{P_{p,i}}{P_{p,j}} \quad (2)$$

So, let us focus on permeation because that central to how small molecules move across. So, we can have let us say reverse osmosis in which case we want to selectively remove particles and again permeation is involved. We can have a barrier film which prevents motion of small molecule. So, in all of these cases permeation is an important property that has to be measured. And so when a polymeric material is exposed to gas or liquid medium it allows basically these substances small molecules to go across each other.

And in case of let us say biological system we may be also interested in allowing some proteins to go through and so even macromolecules to go through. In case of a separation involving

colloidal particles sometimes we may allow colloidal particles to go through or filter out the colloidal particles. So, many of these things substances could be small molecules, macromolecules or particles also.

And generally when we talk of a permeation rate what we are interested is the amount of this substance which is going through per unit area, per unit time. So, that is a measure of how much is being allowed to go through the membrane, which is either a separation membrane or a barrier membrane. And generally for gases we try to express this permeation rate in terms of volume of gas which is going through per unit area of the membrane and per unit time.

And based on the historical usage and based on earlier industrial applications one way in which this is expressed is based on the volume and it is these are cgs units but this is what is used quite commonly in terms of a unit called barrer. And what we are trying to do in each of these cases is to say that there is a flux of polymeric material allowing a substance to go through it. And the flux depends on the permeability of polymer to species  $i$ .

So, that is why we have 2 subscripts describing permeability; polymer and the substance which is permeating. And this depends on the pressure difference across the polymeric membrane and the thickness of the polymeric membrane. And quite often we are also interested in selectivity. Especially so in case of separations where we want to separate out one component preferentially but not separate the other.

So, in that case we are interested in knowing the ratio of permeabilities of the same polymer to two different species  $i$  and  $j$  in this case.

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The slide displays two tables of permeation data for common polymers. The first table lists Oxygen Transmission Rate (OTR), Carbon Dioxide Transmission Rate (COTR), and Water Vapour Transmission Rate (WVTR) in units of cm<sup>3</sup>/m<sup>2</sup>·day, cm<sup>3</sup>/m<sup>2</sup>·day, and g/m<sup>2</sup>·day respectively. The second table lists permeability (P<sub>p,i</sub> × 10<sup>11</sup>) in units of cm<sup>3</sup>·cm/cm<sup>2</sup>·s·cm Hg for O<sub>2</sub> and g·cm/cm<sup>2</sup>·s·cm Hg for H<sub>2</sub>O.

	Representative data for permeation rate			Permeability ( $P_{p,i} \times 10^{11}$ )	
	OTR ( $\frac{\text{cm}^3}{\text{m}^2 \cdot \text{day}}$ )	COTR ( $\frac{\text{cm}^3}{\text{m}^2 \cdot \text{day}}$ )	WVTR ( $\frac{\text{g}}{\text{m}^2 \cdot \text{day}}$ )	$P_{p,O_2}$ ( $\frac{\text{cm}^3 \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg}}$ )	$P_{p,H_2O}$ ( $\frac{\text{g} \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg}}$ )
LDPE	8000	2000	20	2930	0.83
HDPE	2000	5	5	10.8	0.42
PP	900	200	15	0.42	3.2
PET	10	10	25	0.0001	5000
PVA	4		$2.5 \times 10^8$		

So, generally when we look at permeation rate one of the important substances which has to be prevented from going from one side to the other is oxygen. Because oxidation of materials has to be prevented and that is one of the roles that packaging can do. And so, this is measured in terms of let us say oxygen transmission rate. Similarly carbon dioxide transmission rate or water vapour transmission rates are also measured.

And this slide shows some of the example data for common polymers. What you can see is polyethylene is not very good in terms of oxygen transmission. So, it allows a fair amount of oxygen to go through, but water is very small for both polyethylenes. On the other end

polyvinyl alcohol which is a water soluble polymer in fact allows lot of water to go through but it is excellent in terms of stopping oxygen.

Infact polyvinyl alcohol is a very common example in many of the separation membranes. Because also can be processed in variety of microstructures in a film form which is easy to handle. So, we can these are industrial tests which measure in you can see the units on these. So, these are again trade tests and that is why they have a specific name called OTR, COTR and any packaging polymer which is sold where a company is trying to advertise very suitable materials for to be made into packaging, they will try to include these parameters in their trade sheets.

So you can look at some commercial websites and try to find OTR and COTR for some of the materials which they are trying to sell through their data sheets. On the other hand, we can also express the permeation from a fundamental point of view as we defined in the last slide. And again, what you can see is oxygen permeability is very high in case of ethyl polyethylene but very low in case of polyvinyl alcohol.

Reverse is true as far as water is concerned. That polyethylene has a very low permeability for water but PVA has very high permeability. And so, one of the questions that we can think about as a way of futuristic thought process is can these packaging material not do something little more actively. In terms of either changing their performance if let us say they are being subjected to lot more water then can they increase their barrier properties or can they allow oxygen to be permeated for certain amount of time and then they switch over which is based on requirement.

And such applications and so one of the thoughts with which we can stop this lecture, is in terms of thinking about active packaging. And what do I mean by active packaging? Can packaging do little more than just be a passive barrier film. So, for example if the amount of water that is barrier film is exposed to suddenly increases quite a lot can the barrier properties also increase. Or can a active packaging material indicate to us in addition to doing the barrier job.

The concentration of what may be some of the substances or can it be a barrier for certain amount of time and then non barrier for certain other amounts of time. So, these are some examples of research problems which people are working on where packaging material due to the polymeric materials which are forming it can perform certain other actions in terms of not only doing the barrier film job but providing us information.

Or smartly changing its behavior depending on the requirement. So, you can try thinking about some of these applications and what may be ideas based on your own experience.

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So, with this we will close this lecture on polymer packaging thank you.