

**PolCoPUS**  
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**Lecture No -59**  
**Porous polymers/ membranes**

Hi, welcome to the course on polymers. In this lecture we will focus on uses of polymeric materials and we will focus on porous polymers or membranes and in the week we are looking at interaction of polymers with different materials and whenever we have porous polymers or membranes one of the important application is in terms of permeation or preventing permeation or in terms of protecting the material and so therefore interaction with other materials is involved.

In this course we are looking at not only uses but concepts and properties and also sustainability aspects.

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So we will look at both membranes and porous materials in the form of foams.

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## Membranes Polymeric separation membranes: mechanisms

- Solution diffusion mechanism
  - Separation based on diffusivity and / or solubility
- Knudsen diffusion
  - Porous membrane
  - Separation based on molar mass
- Molecular sieve
  - Porous membrane
  - Separation based on molecular size and / or interaction with pore surface

What are the advantages of using polymeric materials in these membranes?

Flexibility - processing to make the porous membrane

Use of other separation:

- polymer-polymer
- polymer-solvent
- polymer-solvent/other solute



And so polymeric separation membranes are very important class of materials these days, from water to gas separations or production of various fine chemicals we use polymeric materials as membranes, which are useful for separating one set of molecules from other set of molecules and there are different mechanisms by which polymeric materials can do this and that is why they are used so often.

So depending on the substances which have to be separated we can have access to different types of mechanisms and since we have different mechanisms selectivity can be manipulated we can manipulated the rates of permeation and of course there is an overall advantage associated with polymeric system in terms of their flexibility and other mechanical properties or viscoelastic properties which are very useful.

So one of the mechanisms which is common is called solution diffusion in which case absorption has to happen or solubilization has to happen from a gas phase or a liquid phase into the polymer and then diffusion has to happen. So therefore both solubility and diffusivity are involved and permeation in this case, therefore permeability will be related to diffusion coefficient and solubility, both of these properties are involved.

So this is the diffusion coefficient and this is a solubility, so permeation is high if a substance can solubilize easily in the polymeric membrane. Similarly if diffusivity is high then the diffusion flux will be higher and permeation will be higher. So we could if it is a good separation membrane where we want to prevent then solubility also has to be low and diffusion coefficient also has to be low, but more importantly it is the product of these two it needs to be lower.

The other mechanism is when we have a porous membrane, but the pore size is so small that it is the same order of magnitude as the mean free path of the molecule. I am sure all of you recall that a gas or liquid molecule basically goes randomly bouncing around and between two collisions we have the mean free path and if this is the same order of magnitude as the pore size. So what can we say in that case?

We can state that on average the molecule will collide with the walls of the pore more often than colliding with other molecule itself. If mean free path is very small compared to the pore size then what we have is we have a pore size which is very big and lots and lots of molecules,

so therefore mean free path is much smaller than the overall pore size. So this situation is analogous to the bulk while this situation is called Knudsen diffusion.

Because interactions with the wall of the pore are very important Knudsen diffusion case and so generally whenever we have Knudsen diffusion, the molar mass of the substance which is diffusing is very crucial. We can also have materials being separated based on the size of the molecule with respect to the size of the pore. So anything which is bigger just does not go through the pore and this is like sieving and only thing is since we are sieving molecules it is called molecular sieves.

So which again can be porous materials and separation in this case is based on molecular size in addition what we can do is we can make the pore hydrophilic in that case hydrophobic substances will find it more difficult to go, we can make the pore surface hydrophobic then maybe hydrophilic substances may find it more difficult to go. So therefore based on the size of the pore and its characteristic we can look at the separation phenomena.

And so just ponder over the fact that you know what are the advantages, I have already talked about you know flexibility of polymers what other features that you can think of as to why polymeric materials are very important membrane materials. So there are ceramic membranes also there are inorganic other inorganic and organic materials which are used as part of the membranes.

But polymers are a very significant component as far as membrane materials goes. So in addition to the fact that they are flexible and observe a rich diversity of mechanical response can you think of any other feature which allows polymeric materials to be used so effectively and my hint would be to think in terms of processing to obtain these membranes. One of the features that we can capture very again easily is the fact that we can tune the polymer microstructure by modifying the phase separation.

So porous membranes when we are trying to prepare or we are trying to prepare the separation membranes with a variety of permeation behavior we can manipulate the microstructure by understanding the phase separation. Phase separation could be one polymer with another polymer, phase separation could be based on a polymer and a solvent system or it could be based on polymer solvent and a non-solvent is added so that polymer separates out.

Whenever we have a solvent which is solubilizing polymer if I add a non-solvent then this non-solvent solvent mixture interacts with each other and excludes the polymer, by which the polymer starts precipitating or phase separating. So by manipulating temperature concentrations and the environment in which this phase separation is happening solvent evaporation rates and so on we can get a rich diversity of microstructures.

We can also manipulate the mechanisms whether its nucleation and growth or spinodal decompositions and again get different shapes and sizes of domains which effectively can lead to pores or very effective set of properties.

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We will close this lecture by just looking at couple of concepts related to polymeric foams and like Styrofoam, of course we are very familiar with it does a very excellent job of impact resistance as well as insulation and so it is used quite widely again we must bring in the issues

related to sustainability, whenever we have such very large scale and Styrofoam is a problem material from the point of view of its recycling and reuse and sustainability.

So polymeric foams can be of open cell type or closed cell type in case they are open cell type then they allow substances to permeate through them, close cell on the other hand from pore the substance has to absorb into the foam material let us say polystyrene or polyurethane which may be the foam material then again it has to desorb into another pore and then that is how it has to go. So therefore the permeation characteristics of open cell foam and closed cell foam are very different and sometimes depending on the application we may want one or the other.

And generally since pores are so central to defining the overall characteristic we could have a uniform or non-uniform distribution through the foam. For example we can make a material which has pores more confined to the center and then less, so lot more pores in the center and then very few pores in the periphery. So sometimes if we do a processing operation and have the blowing agent within the polymer then depending how the distribution of the blowing agent is and how the processing is happening we may get a natural non uniform distribution.

And so this part of the polymer will play a more mechanical role, while this part of the polymer will serve the purpose of permeation. So it can be something like this where you design non-uniform distribution of pores in a foam material or you could have a uniform foam material and so you could also do this by processing induced variation, by having the blowing agent play its role at different stages of processing with flow and deformation being imposed on the material and so we can manipulate the overall distribution and size of pores which is achieved.

We could also do a sandwich construction in which case we make a foam and then sandwich it between two other layers to so that mechanically it is handleable and can be used and utilized in way as a component in any overall device and of course applications of these foams are in sound absorption in impact resistance packing or as thermal and electrical insulation and generally to obtain a size and size distribution.

And uniformity or non-uniformity of pores we have to pay close attention to the phase separation, how gas polymer phase separation happens? And so this is a gas polymer system in which initially there will be a solution of gas and polymer and then gas will separate out and foam the pores and so nucleation in growth and spinodal decomposition can happen as we have seen in case of polymer blends or in case of crystallization of polymers.

And generally the blowing agents which are used which lead to the generation of the gases can be physical in which case they are volatiles or gases which are first molecularly mixed with the polymer and because of the pressure change or temperature change, they get phase separated or we could also have additives which react during processing and produce the gas and then the gas again phase separates from the overall polymer melt or polymeric resin and then leads to foaming.

So there is a decomposition reaction involved which leads to formation of gas species and generally the foams which most commonly used are polystyrene, polyurethane. In fact polyurethane foams are very close to us in terms of their usage because of their use in mattress materials. Polypropylene is also very commonly used. So with this we will close our quick review of porous materials in terms of membrane and foams, thank you.