Membrane Technology
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Lecture - 07
Composite Membranes: Interfacial Polymerization, Dip-Coating, Plasma Polymerization

Good morning students today is lecture 7 of module 3. In today's lecture will cover about composite membranes preparation, interfacial polymerization, dip-coating method and plasma polymerization. So, interfacial polymerization is one of the most important breakthrough in the inorganic membrane preparation, dip-coating is the usual and very simple technology and plasma polymerization is also very important technology. However, it is bit costly process, but anyway, we will learn one by one about all these processes, their applications, their advantages and disadvantages.

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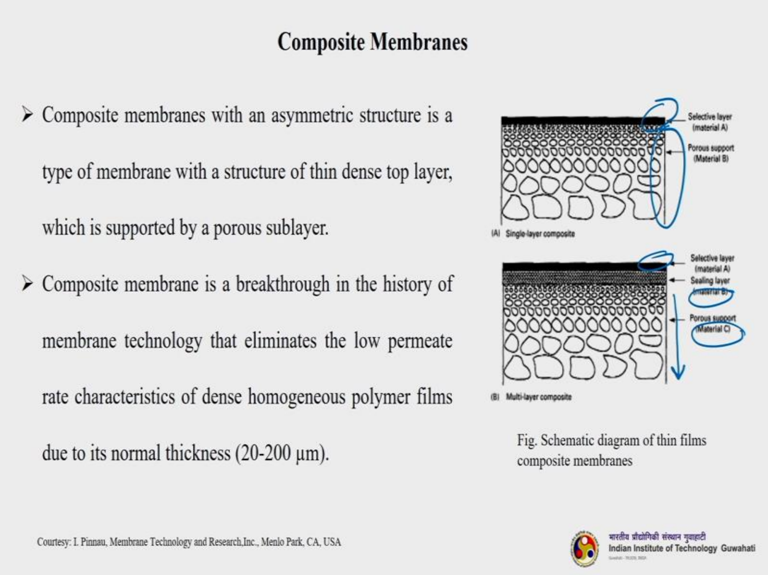

Composite Membranes

- Composite membranes with an asymmetric structure is a type of membrane with a structure of thin dense top layer, which is supported by a porous sublayer.
- Composite membrane is a breakthrough in the history of membrane technology that eliminates the low permeate rate characteristics of dense homogeneous polymer films due to its normal thickness (20-200 μm).

Fig. Schematic diagram of thin films composite membranes

Courtesy: I. Pinnau, Membrane Technology and Research,Inc., Menlo Park, CA, USA

So, let us start begin our lecture today of composite membranes. So, we have discussed earlier also what is composite membranes. So, you can see the picture. So, composite membranes are basically asymmetric membranes having a thin dense top layer which is supported by a porous layer. Now, you can see in these pictures that there we can have either a single layer composite or we can have a multi layer composite.

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So, in single layer composite the porous strut there is only one porous layer struts here and the selective layer the top layer which is doing the separation is only supported by one porous layer but in a multi layer composite. So, here 2 distinct or even more than that porous structures, which are supports, here you can see that below the selective layer this is a selectively which is doing the separation here this is the material b and this is the material c.

There are 2 different porous layers, the material b pore size is lesser than that of the material c. So, as we go down like this so, the pore size of the support increases. So, this is multi layer composite. So, composite membrane is actually a breakthrough in the history of membrane technology which eliminates the low permitted characteristics of the dense homogeneous polymer films.

So, you know, we have discussed about dense membranes which have non porous membranes. So, there are certain applications in which we need dense membranes or non porous membranes. However, the problem is that seems these membranes do not have pores. So, they suffer from very low permeat rate or permeat flux is also very less. So, the separation target is usually not met actually get rid of this.

The composite membrane has come into picture in which there can be a densed or non porous top layer of having a very small thickness on the top layer, followed by single or multi layer porous structures or supports.

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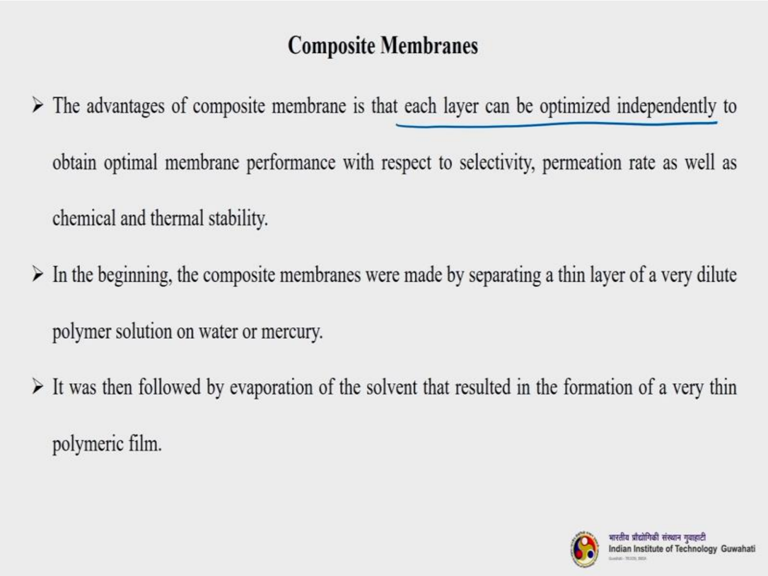

Composite Membranes

- The advantages of composite membrane is that each layer can be optimized independently to obtain optimal membrane performance with respect to selectivity, permeation rate as well as chemical and thermal stability.
- In the beginning, the composite membranes were made by separating a thin layer of a very dilute polymer solution on water or mercury.
- It was then followed by evaporation of the solvent that resulted in the formation of a very thin polymeric film.

The advantage of composite membrane is that each layer can be optimized independently. This is very important as we have shown that this one in our previous slide. That either we can have a single layer composite or we can have a multi layer composite, even if we have a multi layer composite, then also the layers are of distinct pore sizes and we can characterize and optimize them independently.

So, as to obtain a particular targeted separation and to have a optimized membrane performance so, with respect to basically selectivity permeation rate, as well as, chemical and thermal stability. So, these are the parameters which actually are important for any chemical separation process. So, in the beginning composite membranes are made by separating a thin layer of very dilute polymer solution on water or mercury.

So, initially when the composite membrane actually we are manufacture so, it was done by let us say there is a polymer porous structure and our which we are grafting a very thin layer of polymers material. By using water or mercury then it was followed by evaporation of the solvent and resulted in the formation of thin polymer. Basically, what we are doing is that there is already a porous layer and over which we are casting the polymers solutions.

So, in that solution the polymer which will make the top of the top layer is already soluble in the solvent, we have discussed this in our earlier lecture, how to make a polymer solvent and how the solvent evaporates. So, eventually when I cast it on the surface of the polymer support, or even if it is a ceramic support also does not matter. So, after some time, the solvents will start disappearing. Once the solvent evaporates, they will it will form a very thin layer of polymeric film on the support itself. Then we can go for drying or centering whatever process it is required to get the further and final membrane.

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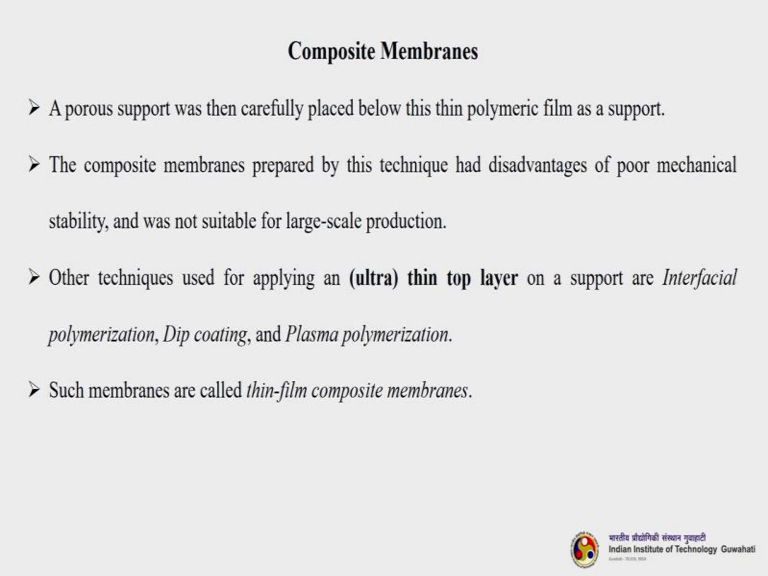

Composite Membranes

- A porous support was then carefully placed below this thin polymeric film as a support.
- The composite membranes prepared by this technique had disadvantages of poor mechanical stability, and was not suitable for large-scale production.
- Other techniques used for applying an **(ultra) thin top layer** on a support are *Interfacial polymerization*, *Dip coating*, and *Plasma polymerization*.
- Such membranes are called *thin-film composite membranes*.

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So, usually a porous support is placed between the thin film I just support the composite membranes are prepared by these technique had disadvantages of poor mechanical stability and was not suitable for large scale application. So, what is the problem is that if the drafting and if the fusing of the polymeric thin layer on the surface of the porous support is not proper, then during the application it will come out from the support.

So, if it is not properly strict or stitch to it then the stability becomes a big problem. So, other techniques used for applying a thin top layer on the support are called interfacial polymerization, dip-coating and plasma polymerization. So, to get rid of this mechanical stability problem so, interfacial polymerization, dip-coating and plasma polymerization came into picture. So, such membranes having a very thin top layer along with the micro porous support or even ultrafiltration support is called thin film composite membranes. So we will discuss little about thin film composite membranes.

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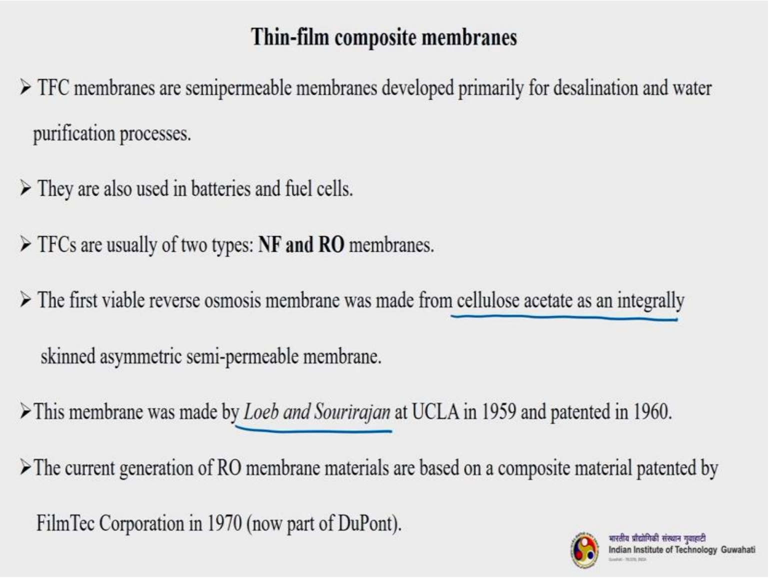

Thin-film composite membranes

- TFC membranes are semipermeable membranes developed primarily for desalination and water purification processes.
- They are also used in batteries and fuel cells.
- TFCs are usually of two types: **NF and RO** membranes.
- The first viable reverse osmosis membrane was made from cellulose acetate as an integrally skinned asymmetric semi-permeable membrane.
- This membrane was made by *Loeb and Sourirajan* at UCLA in 1959 and patented in 1960.
- The current generation of RO membrane materials are based on a composite material patented by FilmTec Corporation in 1970 (now part of DuPont).

So, these membranes are semi permeable membranes developed primarily for desalination and water purification process. So, they are also used nowadays in batteries and fuel cells. So, there are basically we can make either 2 types of membranes from the thin films. So, either they will win the nano filtration range or they will be in the range due to this poor range actually, and that is why the intended applications are mostly water desalination or water purification.

So, the first viable reverse osmosis membrane was made from cellulose acetate. So, it is an integrally skinned asymmetric semi-permeable membrane you remember we discussed in our first class, this membrane preparation from cellulose acetate by Lobe and Sourirajan is one of the most important breakthrough in membrane science that is in University of California, Los Angeles in 1959 and they patented it in 1960.

Now, the current generation of the reverse osmosis membrane materials are based on a composite material patented by the FilmTech Corporation. Now it is a part of DuPont Company. So FilmTech has initially produced such RO membrane composite membranes.

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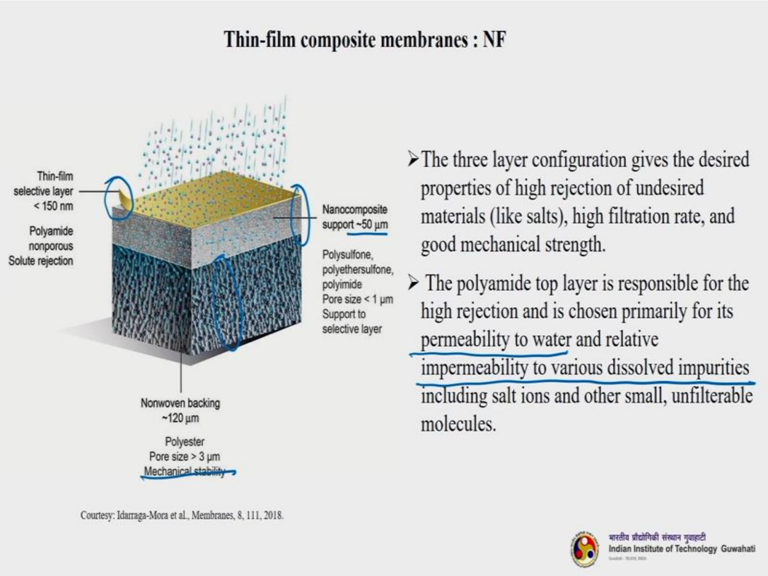

Thin-film composite membranes : NF

- The three layer configuration gives the desired properties of high rejection of undesired materials (like salts), high filtration rate, and good mechanical strength.
- The polyamide top layer is responsible for the high rejection and is chosen primarily for its permeability to water and relative impermeability to various dissolved impurities including salt ions and other small, unfilterable molecules.

Courtesy: Idarraga-Mora et al., Membranes, 8, 111, 2018.

So, let us closely look at this particular diagram or figure or sketch. So, you can see a it is a 3 layer nano filter cum thin film composite membrane, the top layer you can see it is very, very thin. So, it is almost 150 nanometer less than 150 nanometer usually polyamide is being used. The reason for using polyamide is that it will give very high rejection and followed by 2 support layers.

The first layer is the nanocomposite support this one, it is almost close to 50 microns the pore size. So, we can use various materials membrane materials for this either polysulfone, polyethersulfone, polyimide all these things and the pore size is actually less than one micron. So, this is giving the support to the selective layer. So, this nano particular nano composite layer is giving the initial support to the top layer thin film membrane.

Then this is the more porous structure, it is a nonwoven backing almost approximately 120 micron. So, you can use easily polyester there are other materials that can also be used. So, the pore size is usually greater than 3 microns. So, this is providing the measure mechanical stability. So, this 3 layer configuration gives the desired properties of high rejection of undesired materials like salts, and then high filtration rate and good mechanical strength.

The polyamide top layer is responsible for high rejection and is chosen primarily for its permeability to water and relative permeability to water and relative impermeability to various dissolved impurities, including salt ions and others small, unfilterable molecules.

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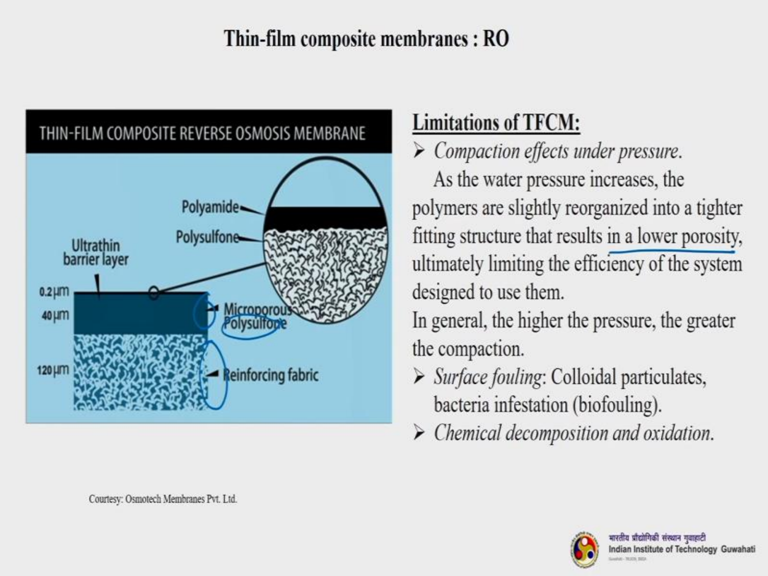

Thin-film composite membranes : RO

Limitations of TFCM:

- *Compaction effects under pressure.*
  As the water pressure increases, the polymers are slightly reorganized into a tighter fitting structure that results in a lower porosity, ultimately limiting the efficiency of the system designed to use them.
  In general, the higher the pressure, the greater the compaction.
- *Surface fouling*: Colloidal particulates, bacteria infestation (biofouling).
- *Chemical decomposition and oxidation.*

Courtesy: Osmotech Membranes Pvt. Ltd.

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So, this is another example which is a TFC a thin film composite membrane, RO membrane reverse osmosis membrane. So, you can see again the top layer is polyamide. So, for the same reason polyamide is being used here. However the structure and the support below support layers 2 distinct support layers can be of different materials here it is the micro porous polysulfone, this layer then followed by the Reinforcing fabric.

So, mostly they are of the same nature and the type. However, the thin film composite membranes also suffer from some limitations. So, 3 distinct limitations or drawbacks has been actually, I am showing here. So, the first one is compaction effects under pressure, as the water pressure increases, the polymers are slightly reorganized into a tighter fitting structure that results in lower porosity.

And ultimately limiting the efficiency of the system designed to use them. So what is happening when the process is on and inside the memory module due to the increasing water pressure system material is polymeric. So they are slightly the matrix itself is slightly getting reorganized.

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So they are getting compacted or they are getting a tight basically we can say in that word, they are getting tighter or tight fitting structure.

So, what is happening by this the permeation rate will decrease (()) (10:25) will also decrease. So efficiency of the system will be decreasing. So, in generally, the higher the pressure the greater the compact zone and another problem is surface fouling. And this actually a comes due to colloidal particles and bacterial infestation, where adulating in the bio fouling characteristics of the membrane and then chemical decomposition and oxidation. So, this all depends upon what type of solutes and the particular membrane is handling.

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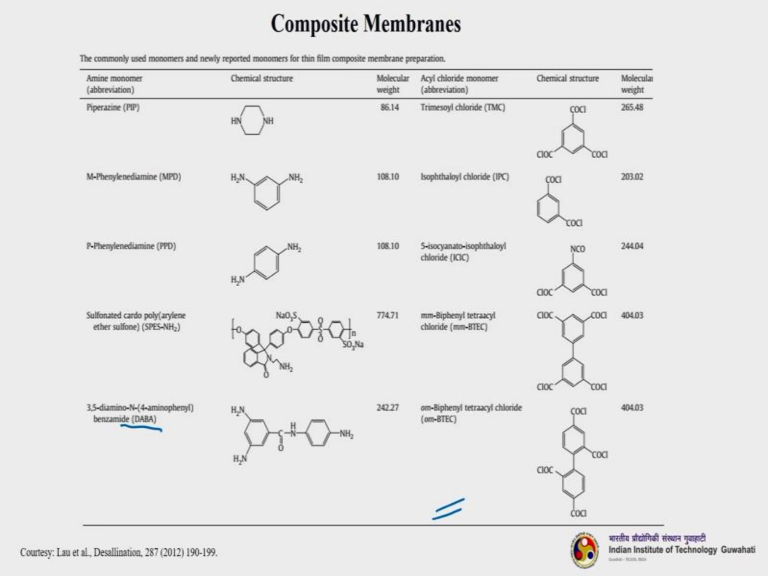

Composite Membranes

The commonly used monomers and newly reported monomers for thin film composite membrane preparation.

Amine monomer (abbreviation)	Chemical structure	Molecular weight	Acyl chloride monomer (abbreviation)	Chemical structure	Molecular weight
Piperazine (PIP)		86.14	Trimesoyl chloride (TMC)		265.48
M-Phenylenediamine (MPD)		108.10	Isophthaloyl chloride (IPC)		203.02
P-Phenylenediamine (PPD)		108.10	5-isocyanato-isophthaloyl chloride (ICIC)		244.04
Sulfonated cardo poly(arylene ether sulfone) (SPES-NH_2)		774.71	mm-Biphenyl tetraacyl chloride (mm-BTEC)		404.03
3,5-diamino-N-(4-aminophenyl) benzamide (DABA)		242.27	om-Biphenyl tetraacyl chloride (om-BTEC)		404.03

Courtesy: Lau et al., Desallination, 287 (2012) 190-199.

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So have a close look at this particular table. So the this is taken from one of the public exam by Lau et al. So, you can see this list out the commonly used monomers and some new reported monomers for this thin film membrane preparation. So, you can have piperazine, we can have MPD which is M-Phenylenediamine then, we can have PPD, we can have sulfonated cardo poly arylene ether sulfone, then we can have DABA dapa people call it as daba.

So, their molecular weights are also given and then there are other materials also like trimesoyl chloride, then isophthaloyl chloride then we can have 5-isocy isophenyl chloride and then BTEC and there are 2 types of-BTEC actually biphenyl tetraacycl chloride. So, either MM type or OM type. So, their molecular routes are also given. So, this right hand side, whatever you are seeing here. So, these are under new monomers and the left hand side monomers are widely used and are also used for commercial membrane preparation.

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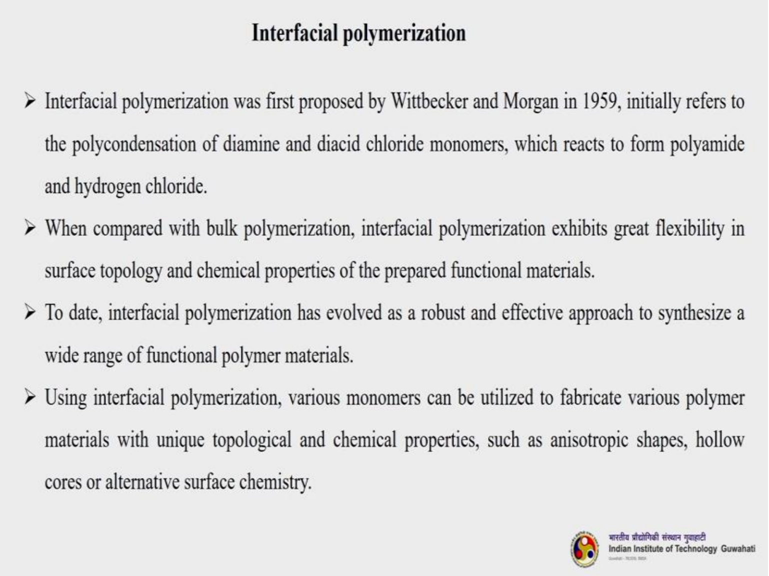

Interfacial polymerization

- Interfacial polymerization was first proposed by Wittbecker and Morgan in 1959, initially refers to the polycondensation of diamine and diacid chloride monomers, which reacts to form polyamide and hydrogen chloride.
- When compared with bulk polymerization, interfacial polymerization exhibits great flexibility in surface topology and chemical properties of the prepared functional materials.
- To date, interfacial polymerization has evolved as a robust and effective approach to synthesize a wide range of functional polymer materials.
- Using interfacial polymerization, various monomers can be utilized to fabricate various polymer materials with unique topological and chemical properties, such as anisotropic shapes, hollow cores or alternative surface chemistry.

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So, let us now understand and learn, what is Interfacial polymerization? As I told you earlier that at the beginning of this particular class that interfacial polymerization is one of the most important breakthrough in membrane preparation or in membrane science and technology. So, it was first reported by Wittbecker and Morgan in 1959, long back. So, initially refers to the polycondensation of diamine and diacid chloride monomers, which reacts to form polyamide and hydrogen chloride.

So, initially the scientists ~~to~~ whoever develop this they call this polycondensation reaction. So, 1-diamine I mean basically, I mean, and another acetic chloride monomer are fused together or reacted together. So, they form a polyamide and a hydrogen chloride once after the reaction so, when compared with bulk polymerization, interfacial polymerization exhibits great flexibility in surface topology and chemical properties of the prepared functional materials.

So, to date interfacial polymerizing has evolved as a robust and effective approach to synthesize a wide range of functional polymer materials. So, many different types of polymeric materials can be used for interfacial polymerization and various types of membrane materials of different grades and sizes can be prepared. So, using interfacial polymerization various monomers can be utilized to fabricate various polymer materials with unique topological and chemical properties such as anisotropic shapes, hollow fiber hollow cores or alternative surface chemistry.

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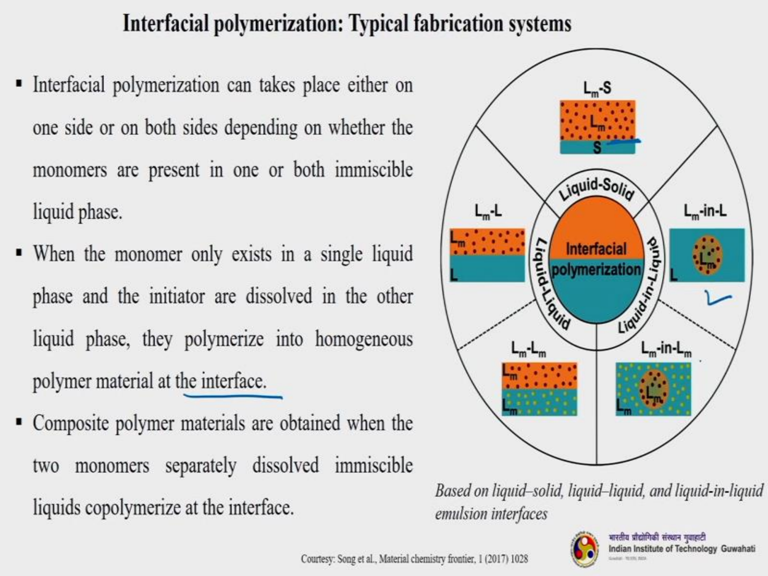

Interfacial polymerization: Typical fabrication systems

- Interfacial polymerization can takes place either on one side or on both sides depending on whether the monomers are present in one or both immiscible liquid phase.
- When the monomer only exists in a single liquid phase and the initiator are dissolved in the other liquid phase, they polymerize into homogeneous polymer material at the interface.
- Composite polymer materials are obtained when the two monomers separately dissolved immiscible liquids copolymerize at the interface.

Based on liquid–solid, liquid–liquid, and liquid-in-liquid emulsion interfaces

Courtesy: Song et al., Material chemistry frontier, 1 (2017) 1028

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So, let us now understand, what are the different types of fabrication systems? That is already in practice for interfacial polymerization. You can closely look at this particular figure given in the right hand side. So, this figure is best on liquid solid, liquid and liquid and liquid emulsion interfaces so, interfacial polymerization can take place either on one side or on both sides depending on whether the monomers are presenting one or both immiscible liquid phases.

So, when the monomer only exists in a single liquid phase and the initiator dissolved in other liquid phase, they polymerize into homogeneous polymer material at the interface. So, the interface is very important and either interfaces only polymerization is happening. Composite polymer materials are obtained when the 2 monomers separately dissolved immiscible liquids copolymerize at the interface. Now, let us see what are the different types of fabrication system.

So, you can have a liquid in monomer and solid system. So, this is the interface actually which I am talking about, the reaction is taking place there, then we can have under liquid-liquid system we can have liquid in monomer and liquid system or we can have liquid monomer and liquid monomer systems both are same then we can have liquid-in-liquid system where we can have a liquid in a monomer in liquid in monomer system.

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Or we can have a liquid in monomer in a liquid system. So, these are basically these and these are emulsion type of interfaces. So, you can see the Global's you can see here, the Global's here and here. So, these are actually emulsions.

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Interfacial polymerization: Typical fabrication systems

- In a *liquid-solid interface*, polymerization begins at the interface, and results in a polymer attached to the surface of the solid phase.
- In a *liquid-liquid interface with monomer dissolved in one phase*, polymerization occurs on only one side of the interface, whereas in *liquid-liquid interfaces with monomer dissolved in both phases*, polymerization occurs on both sides.
- An interfacial polymerization reaction may proceed either stirred or unstirred.
- In a stirred reaction, the two phases are combined using vigorous agitation, resulting in a higher interfacial surface area and a higher polymer yield.
- Most interfacial polymerizations are synthesized on a porous support in order to provide additional mechanical strength, allowing delicate nano films to be used in industrial applications.

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In a liquid-solid interface, polymerization begins at the interface, and results in a polymer attached to the surface of the solid phase. So, this is a solid interface let us say I have a polymeric support material solid material over which I will try to carry out the polymerization reaction. So, I pour my desire this one I mean as well as the acid chloride on the surface of this particular solid support and the reaction will happen at the liquid and solid interface.

That means the polymerization reaction, so, that is how it happens in a liquid-solid interface. Whereas, any liquid-liquid interface with monomer dissolved in one phase polymerization occurs only one side of the interface whereas, in liquid-liquid interfaces with monomer dissolved in both the phases, polymerization occurs in both sides. So an interfacial polymerization reaction may proceed either stirred or unstirred.

So, you can either stirred the process or we do not need stirring at all. So, in a stirred reaction, the 2 phases are combined using vigorous agitation, resulting in higher interfacial area and higher polymer yield, always stirring is a better solution for achieving a better result. Whether it is a mass transfer or whether it is a reaction and most interfacial polymerization are synthesized on a porous support in order to provide additional mechanical strength.

That is what actually the TFC is are mostly the interfacial polymerization happening with the liquid-solid interface that is what it is telling it is easy to carry out and the solid porous material is already providing a mechanical support. To the thin film that is going to be developed at the interface.

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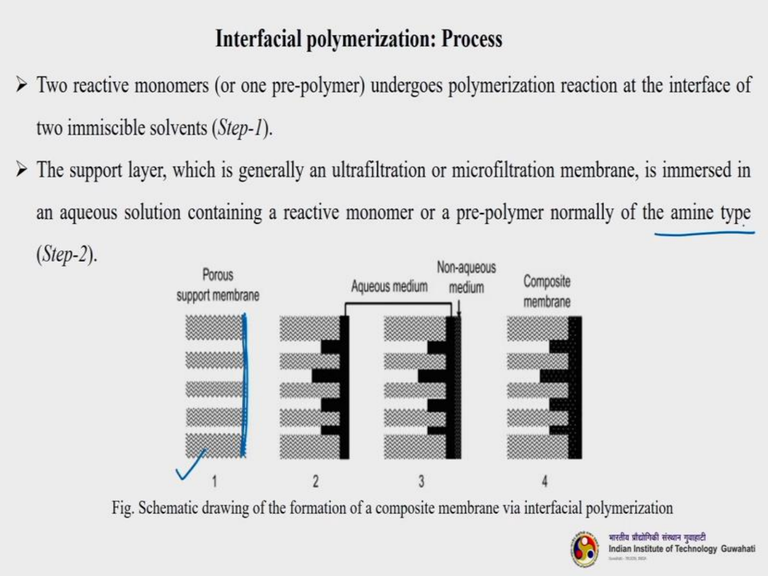

Interfacial polymerization: Process

- Two reactive monomers (or one pre-polymer) undergoes polymerization reaction at the interface of two immiscible solvents (*Step-1*).
- The support layer, which is generally an ultrafiltration or microfiltration membrane, is immersed in an aqueous solution containing a reactive monomer or a pre-polymer normally of the amine type (*Step-2*).

Fig. Schematic drawing of the formation of a composite membrane via interfacial polymerization

So, let us try to understand now how the process happens, 2 reactive monomer or we can have one pre polymer undergoes polymerization reaction at the interface of 2 immiscible solvents. So, you can see the first one is that this is a porous support membrane and this is the interface on which we are talking about that our reaction will take place. So, the support layer which is generally an ultrafiltration or microfiltration membrane.

So, which one to choose? That is depending upon what is the intended application. So, you can either go for ultrafiltration membrane as a support or we can go for a microfiltration membrane as a just support. So, this membrane or porous support is immersed in an aqueous solution containing a reactive monomer or a pre polymer normally of the amine type. So, either we can usually have it amine type. So, once you immerse then the amine actually get inside the pores you can see from here.

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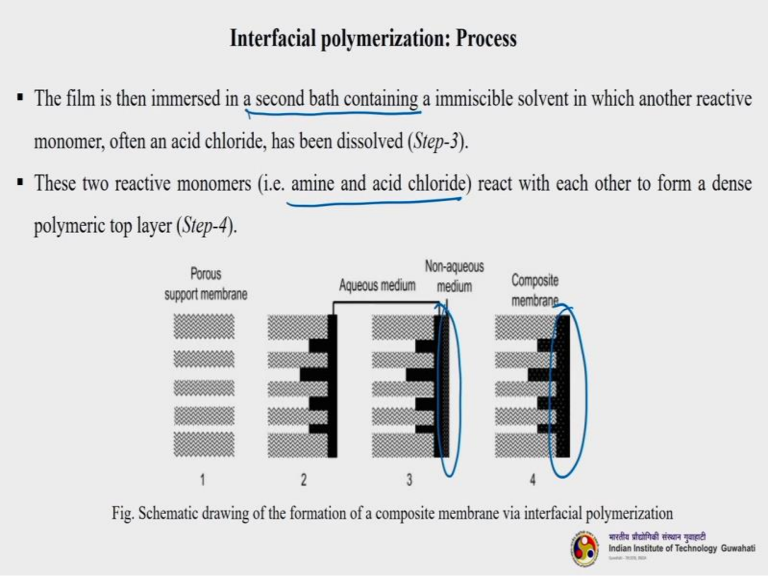

Interfacial polymerization: Process

- The film is then immersed in a second bath containing a immiscible solvent in which another reactive monomer, often an acid chloride, has been dissolved (*Step-3*).
- These two reactive monomers (i.e. amine and acid chloride) react with each other to form a dense polymeric top layer (*Step-4*).

Fig. Schematic drawing of the formation of a composite membrane via interfacial polymerization

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The film is then immersed in a second bath. We are going for a second bath containing a immiscible solvent in which another reactive monomer often an acid chloride, has been dissolved. So, basically what we are doing we are taking an amine solution and putting it in the said that amine solution we are dipping our membranes support either it is a ultrafiltration or microfiltration then once it is done the pores are filled with the amine then we take it out.

And then put it in another bath, which is having a immiscible solvent and in that that di-aceyl chloride or acid chloride whatever it is already dissolving. So, you can see now this is a non aqueous medium or which is getting in contact with the polymeric support on already containing the amine solution inside it is pore. So, these 2 reactive monomers that is amine and acid chloride react each other to from dense polymeric layer.

So, the exam is proceeding here, then we can get a dense polymeric layer here, so this is a very thin layer we obtain from this method. So this can be done in a lab scale also, only have to be very careful that what are the solvents you are choosing and what is the amine and what is the acid chloride that is choosing and you have to do it very carefully. So that the thickness of the membrane that is finally is coming out soon within so, that there will be a proper separation.

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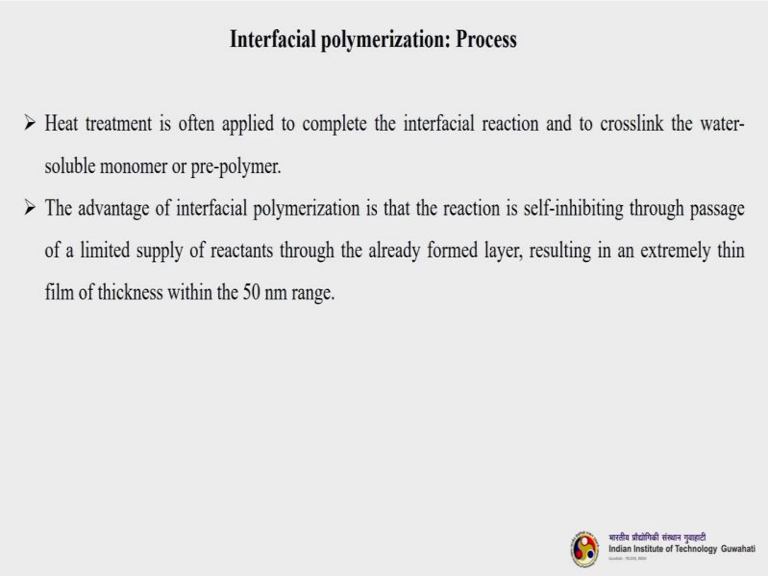

Interfacial polymerization: Process

- Heat treatment is often applied to complete the interfacial reaction and to crosslink the water-soluble monomer or pre-polymer.
- The advantage of interfacial polymerization is that the reaction is self-inhibiting through passage of a limited supply of reactants through the already formed layer, resulting in an extremely thin film of thickness within the 50 nm range.

So, heat treatment is often applied to complete the interfacial reaction and to crosslink the water soluble monomer or pre polymer. So, usually once it is the polymerization is over, it is not the end of the process then the membrane is taken out dried and it goes for a further this was heat treatment either in a dried chamber or it can be sintered at a particular desire temperature. So, that this one the water soluble monomer or pre polymer will get crosslink.

The advantage of interfacial polymerization is that the reaction is self-inhibiting, through passage of a limited supply of reactants through the already formed layer, resulting in an extremely thin film thickness with the almost 50 nanometer range.

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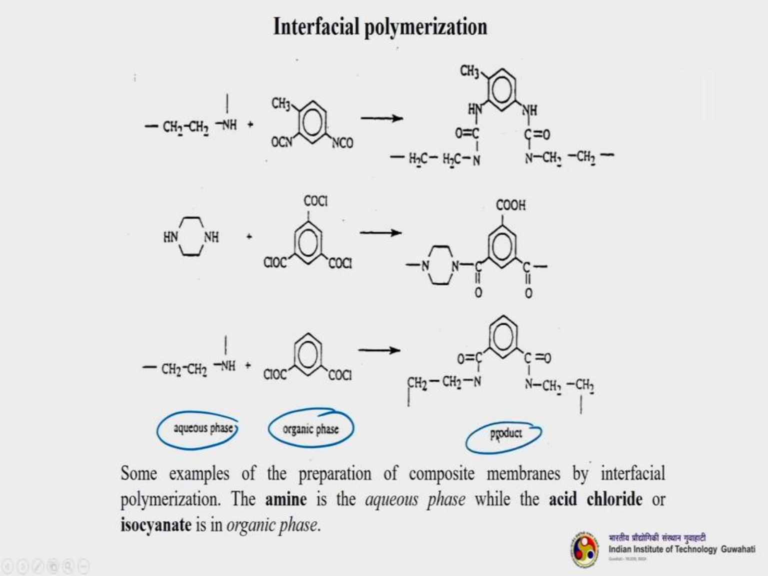

Interfacial polymerization

Some examples of the preparation of composite membranes by interfacial polymerization. The **amine** is the *aqueous phase* while the **acid chloride** or **isocyanate** is in *organic phase*.

So, these are some of the examples of the preparation of the composite membranes by interfacial polymerization and the amine is the aqueous phase here, the aqueous phase these are all a amines, you can see then NH containing group then the acid chloride or isocyanate is in the organic phase. So, the first one is the aqueous phase which is containing the amine, the second is organic phase which is containing either the acid chloride or isocyanate. And it can be anything else also, depending upon what type of membrane you want to actually prepare and then resultant is the product. This is the polymerization product.

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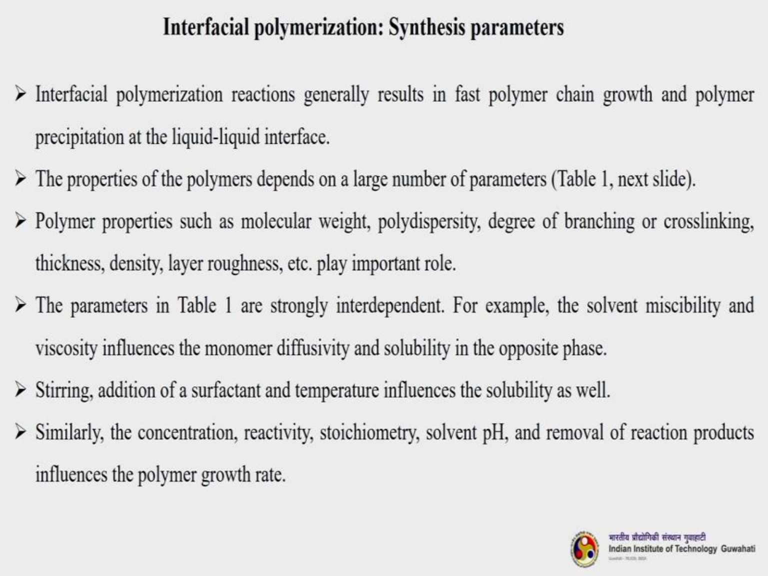

Interfacial polymerization: Synthesis parameters

- Interfacial polymerization reactions generally results in fast polymer chain growth and polymer precipitation at the liquid-liquid interface.
- The properties of the polymers depends on a large number of parameters (Table 1, next slide).
- Polymer properties such as molecular weight, polydispersity, degree of branching or crosslinking, thickness, density, layer roughness, etc. play important role.
- The parameters in Table 1 are strongly interdependent. For example, the solvent miscibility and viscosity influences the monomer diffusivity and solubility in the opposite phase.
- Stirring, addition of a surfactant and temperature influences the solubility as well.
- Similarly, the concentration, reactivity, stoichiometry, solvent pH, and removal of reaction products influences the polymer growth rate.

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Interfacial polymerization reactions generally result in fast polymer chain growth and polymer precipitation at the liquid-liquid interface. So it is a very fast instantaneous reaction. And you know that it does not need any anything to start the reaction it is a self starting reaction. Basically, the properties of the polymers depend on a large number of parameters; will see it in the next slide.

So, polymer properties such as molecular weight, polydispersity degree of branching or cross linking, thickness, density, layer ~~of~~ roughness etc. play a very important role. So, these are the parameters listed under table 1 are strongly interdependent. For example, the solvent miscibility and viscosity influences the monomer diffusivity and solubility in the opposite phase.

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Stirring, additional of a surfactant and temperature influences the solubility as well. If we stir it and or add some surfactant or you been you go for certain temperature application then it will affect the solubility. Similarly, the concentration reactivity stoichiometry, solvent pH and removal of reaction products influences the polymer growth rate.

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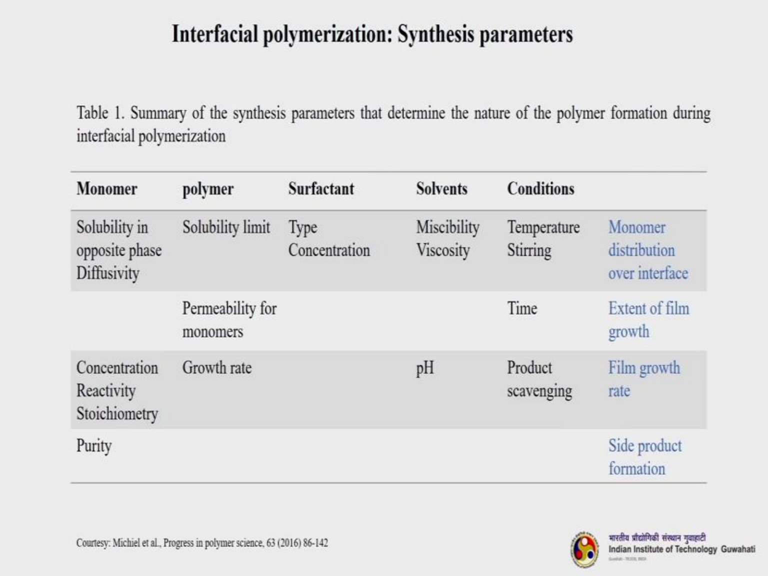

Interfacial polymerization: Synthesis parameters

Table 1. Summary of the synthesis parameters that determine the nature of the polymer formation during interfacial polymerization

Monomer	polymer	Surfactant	Solvents	Conditions	
Solubility in opposite phase Diffusivity	Solubility limit	Type Concentration	Miscibility Viscosity	Temperature Stirring	Monomer distribution over interface
	Permeability for monomers			Time	Extent of film growth
Concentration Reactivity Stoichiometry	Growth rate		pH	Product scavenging	Film growth rate
Purity					Side product formation

Courtesy: Michiel et al., Progress in polymer science, 63 (2016) 86-142

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So, this table was referring to so, this is a summary of synthesis parameters that determine the nature of the polymer formation during the interfacial polymerization, so solubility in the opposite phase diffusivity, concentration reactivity, stoichiometry and purity for the monomers and similarly the solubility limit permeability per monomers a growth rate of the polymer and if we use any surfactant, then its type and concentration.

And the solvents characteristics picture like pH viscosity miscibility and the conditions if we are carrying out the reaction under a atmosphere temperature or do we are heating it, we are stirring it, what is the time? residence time we are allowing and what is the product that is forming an are we scavenging it. So, depending on the types of product will for either monomer distributed our interface or extent of the film growth will takes place or film growth will be very faster and side product formation, will takes place.

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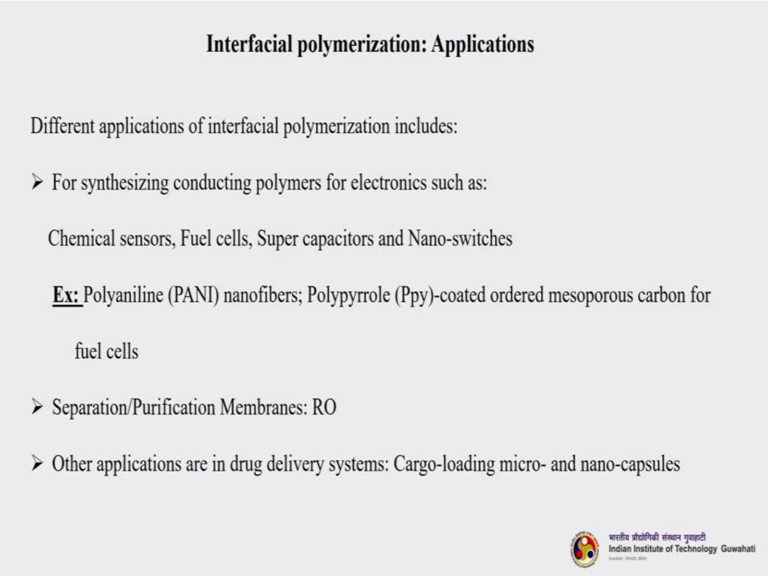

Interfacial polymerization: Applications

Different applications of interfacial polymerization includes:

- For synthesizing conducting polymers for electronics such as:

  Chemical sensors, Fuel cells, Super capacitors and Nano-switches

  Ex: Polyaniline (PANI) nanofibers; Polypyrrole (Ppy)-coated ordered mesoporous carbon for fuel cells
- Separation/Purification Membranes: RO
- Other applications are in drug delivery systems: Cargo-loading micro- and nano-capsules

So, different applications of interfacial polymerization includes for synthesizing conducting polymers for electronics, such as chemical sensors, fuel cells, super capacitors and nano switches. For example PANI, so it is used to prepare nanofibers then Ppy coated ordered mesoporous carbon for fuel cells application PPY is Polypyrrole and then it is also used for separation in purification membranes. As for example, RO membrane preparation, other applications are in drug delivery systems, cargo-loading micro and nano-capsules which are already in practice and commercialized also.

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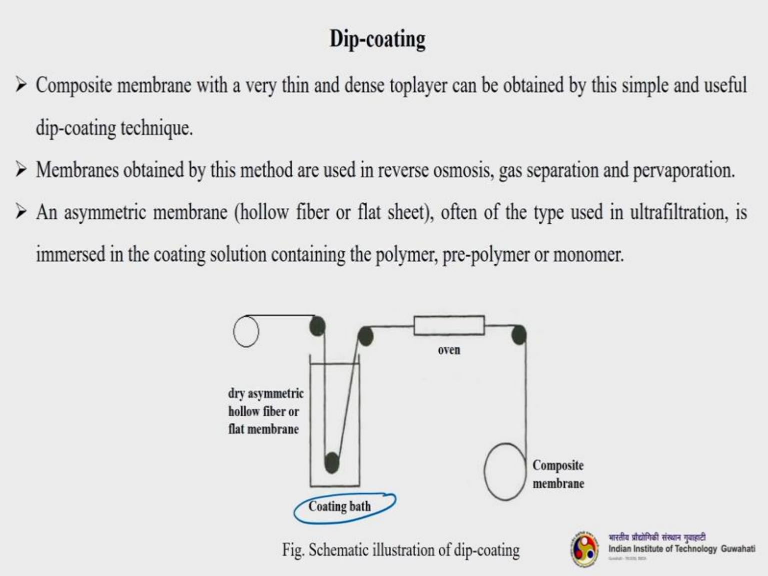

Dip-coating

- Composite membrane with a very thin and dense toplayer can be obtained by this simple and useful dip-coating technique.
- Membranes obtained by this method are used in reverse osmosis, gas separation and pervaporation.
- An asymmetric membrane (hollow fiber or flat sheet), often of the type used in ultrafiltration, is immersed in the coating solution containing the polymer, pre-polymer or monomer.

Fig. Schematic illustration of dip-coating

The student, the next method that we are going to discuss is Dip Coating. This is one of the most easy simplest method and it is a crude method also. Now in the crude way basically we can do it in a lab scale, we have done it in many times, and it is very easy to do. However, in the industry, it is done using of course, different machines. So, composite membrane with a very thin and dense top layer can be obtained by this simple and useful Dip Coating technique.

Now membranes obtained by this method are used in reverse osmosis, gas separation and for evaporation and asymmetric membrane hollow fiber or flat sheet either you can use hollow fiber or flat sheet membrane does not matter or often of the type used in ultrafiltration , is immersed in the coating solution containing the polymer, pre polymer or monomer. Now, you can see this scheme. So, we have a dry asymmetric hollow fiber or flat membrane.

I am putting it inside a coating bath. So, this bath actually is containing the material it can be pre polymer, polymer or monomer which we actually want to coat over the surface of the hollow fiber flat membrane once it is dipping so, dip then you can take it out slowly then it goes to the open for the drying and then we get a composite membrane.

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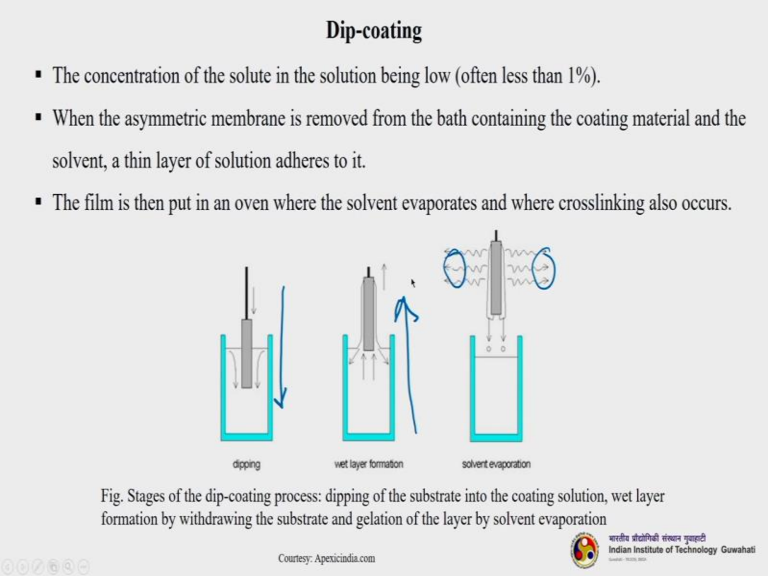

Dip-coating

- The concentration of the solute in the solution being low (often less than 1%).
- When the asymmetric membrane is removed from the bath containing the coating material and the solvent, a thin layer of solution adheres to it.
- The film is then put in an oven where the solvent evaporates and where crosslinking also occurs.

Fig. Stages of the dip-coating process: dipping of the substrate into the coating solution, wet layer formation by withdrawing the substrate and gelation of the layer by solvent evaporation

Courtesy: Apexicindia.com

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So, the concentration of the solute in the solution being low upon less than 1% actually, when the asymmetric membrane is removed from the bath containing the cotton material, and the solvent, a thin layer of solution adheres to it, so actually, you can see this particular example or the figure, you can see the stages of the dip coating process. So, initially the dipping of the substrate in the coating solution, so, you are dipping it.

So, slowly you are putting it inside that bath which contains the polymer pre polymer are here this one monomer. Then you allow it some residents time basically so, that the coating actually happens properly then you take it out slowly in this way. So, you can do it in hand we have done it okay it is very easy to do it only thing is that you have to dip it slowly and further slowly you have to dip out.

And once it is done, you can see that it comes out of this one then if we allow it. Then what will happen is that in the ambience only the solvent will evaporate. See, these are the solvent evaporation happening and then cross linking start.

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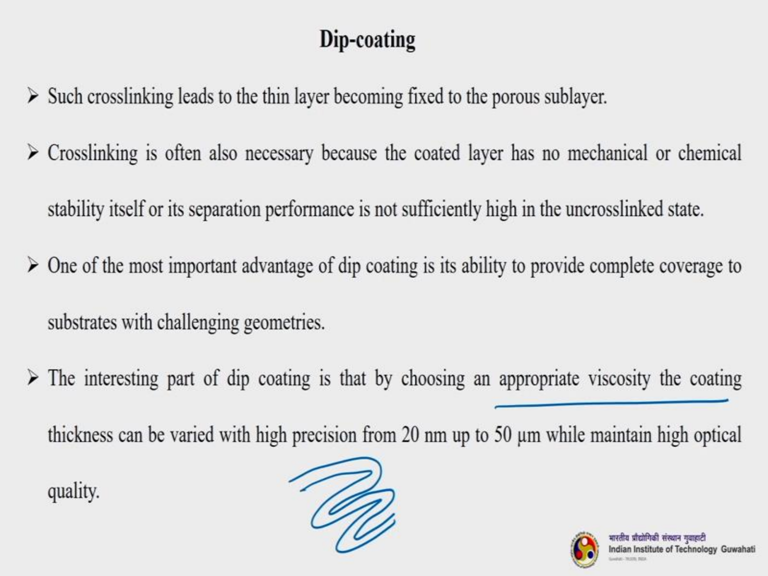

Dip-coating

- Such crosslinking leads to the thin layer becoming fixed to the porous sublayer.
- Crosslinking is often also necessary because the coated layer has no mechanical or chemical stability itself or its separation performance is not sufficiently high in the uncrosslinked state.
- One of the most important advantage of dip coating is its ability to provide complete coverage to substrates with challenging geometries.
- The interesting part of dip coating is that by choosing an appropriate viscosity the coating thickness can be varied with high precision from 20 nm up to 50 µm while maintain high optical quality.

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So, such cross linking leads to a thin layer becoming fixed to the porous sub layer. So, cross linking is open necessary, because the coated layer has no mechanical or chemical stability itself or its separation from performance is not sufficiently high in the uncross linked state, it will see basically w are talking about cross linking. If it is not crosslink and thus layer which is attached or coated on the surface of the polymeric membrane or even let us talk about a ceramic membrane it will come out during the application.

So, one of the most important advantage of dip coating is its ability to provide complete coverage to the substrates with challenging geometries. So, if we have a very different types of geometry, so, let us say I have a geometry something like this. So, s tubeless structures. So, how do I repair a thin film membrane. So, dip coating is the only way ~~to~~ so enter this material I can put it in the bath, so it will get coated then I take it. And I can go for the solvent evaporation, cross linking some heat treatment or whatever it is.

So, the entire substrate material is covered by this process. The interesting part of dip coating is that by choosing an appropriate viscosity the coating thickness can be varied with high precision from 20 nanometer to 15 micron while maintaining high optical quality. So, you have to choose the appropriate viscosity of the coating material. So, if it is a very low viscous material or the solvent then what will happen that film will be very thin and the chances of it coming out during the application is also more. So, you have to decide the thickness there is no thumb rule.

Basically you have to prepare certain you have to optimize it doing some experiment only you have to prepare a 10 or 15 membranes with different viscosities and we will find that one particular viscosity suits here particular application, this is how actually it is done in lab and also in commercial scale before we go for a full pledged production.

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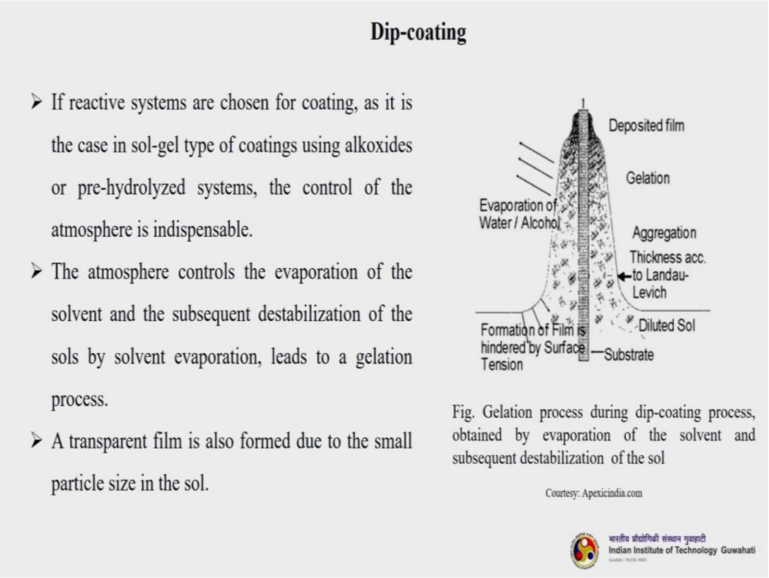

Dip-coating

- If reactive systems are chosen for coating, as it is the case in sol-gel type of coatings using alkoxides or pre-hydrolyzed systems, the control of the atmosphere is indispensable.
- The atmosphere controls the evaporation of the solvent and the subsequent destabilization of the sols by solvent evaporation, leads to a gelation process.
- A transparent film is also formed due to the small particle size in the sol.

Fig. Gelation process during dip-coating process, obtained by evaporation of the solvent and subsequent destabilization of the sol

Courtesy: Apexicindia.com

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If reactive systems are chosen for coating as it is the case in sol-gel type of coating like alkoxides or pre-hydrolyzed system, the control of the atmosphere is indispensable. The atmosphere controls the evaporation of the solvent and the subsequent destabilization of the sols by solvent if evaporation leads to a gelation process. A transparent film is also formed due to the small particle size in the sol. So, you can see this particular figure. So, this is a gelation process during dip coating obtained by evaporation of the solvent and subsequent destabilization of the sol. So, particle size of the sol plays a very important role here.

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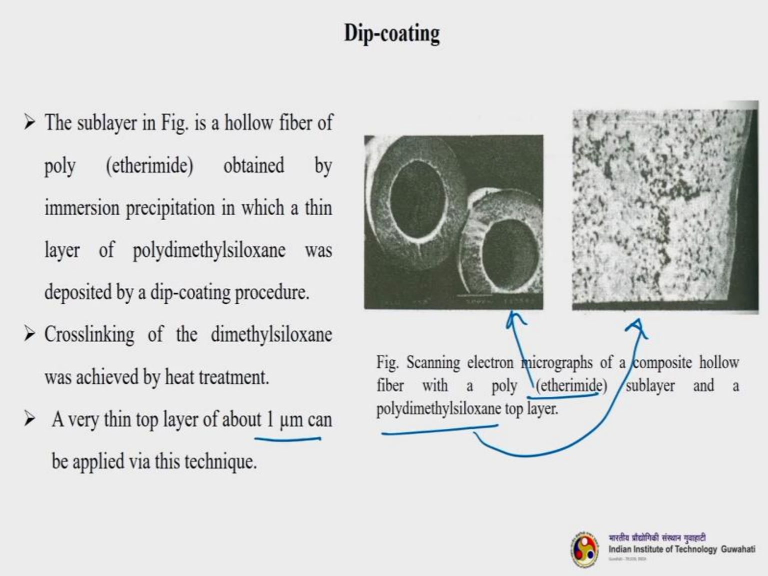

Dip-coating

- The sublayer in Fig. is a hollow fiber of poly (etherimide) obtained by immersion precipitation in which a thin layer of polydimethylsiloxane was deposited by a dip-coating procedure.
- Crosslinking of the dimethylsiloxane was achieved by heat treatment.
- A very thin top layer of about 1 μm can be applied via this technique.

Fig. Scanning electron micrographs of a composite hollow fiber with a poly (etherimide) sublayer and a polydimethylsiloxane top layer.

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So, you can see 2 scanning electron microscope images of a composite hollow fiber membrane with a polyetherimide sub layer and a polydimethylsiloxane top layer so, this is polyetheriamide this one and this is polydimethylsiloxane top layer. The sub layer is a hollow fiber of polyetherimide obtained by immersion precipitation in which a thin layer of polydimethylsiloxane was deposited by a dip-coating procedure. Cross linking of the dimethylsiloxane was achived by heat treatment and a very thin top layer of about one micron can be applied via this technique.

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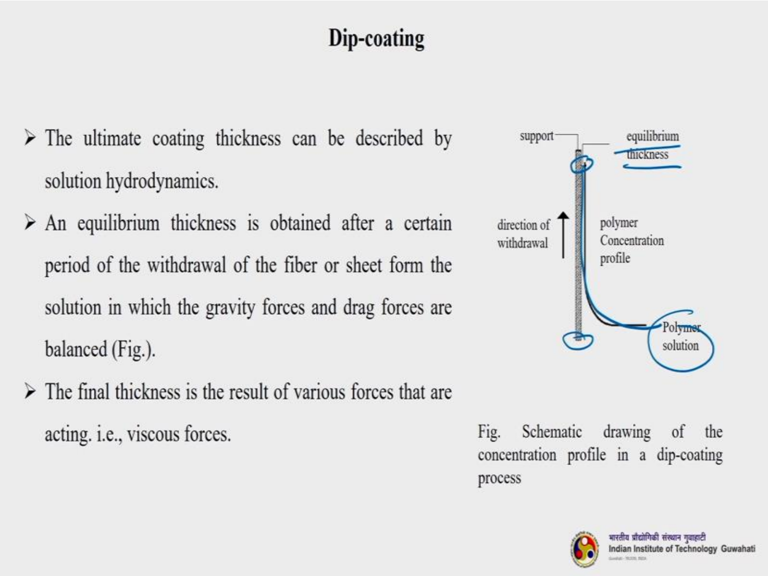

Dip-coating

- ➢ The ultimate coating thickness can be described by solution hydrodynamics.
- ➢ An equilibrium thickness is obtained after a certain period of the withdrawal of the fiber or sheet form the solution in which the gravity forces and drag forces are balanced (Fig.).
- ➢ The final thickness is the result of various forces that are acting. i.e., viscous forces.

Fig. Schematic drawing of the concentration profile in a dip-coating process

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The ultimate coating thickness can be described by solution hydrodynamics. And equilibrium thicknesses is obtained after a certain period of withdrawal of the fiber and sheet that form the solution in which the gravity forces and drag forces are balanced, you please see this particular figure where you can see the direction of withdrawal. So, this is actually the supported the substrate here the polymer solution is there.

So, I have dipped it, then I am taking it out slowly. So, this is the direction of the withdrawal you can see and the polymer concentration profile actually happens like this it is pulling like this. And whatever the thickness is, that is getting resultant and that is called the equilibrium thickness. The final thickness is the result of various forces that are acting so, viscous forces basically.

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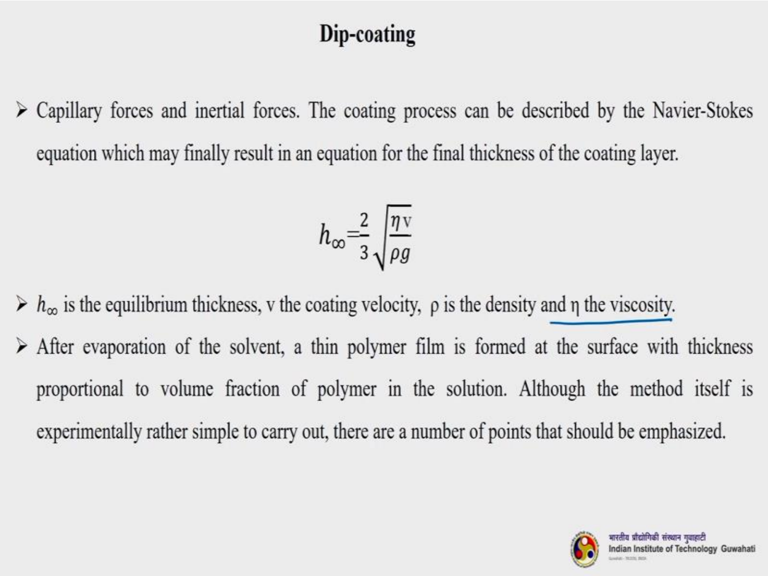

Dip-coating

- Capillary forces and inertial forces. The coating process can be described by the Navier-Stokes equation which may finally result in an equation for the final thickness of the coating layer.

$$h_\infty = \frac{2}{3}\sqrt{\frac{\eta \mathrm{v}}{\rho g}}$$

- h_∞ is the equilibrium thickness, v the coating velocity, ρ is the density and η the viscosity.
- After evaporation of the solvent, a thin polymer film is formed at the surface with thickness proportional to volume fraction of polymer in the solution. Although the method itself is experimentally rather simple to carry out, there are a number of points that should be emphasized.

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So, capillary forces and inertial forces. It is only not the viscous forces, but the capillary and inertial process also plays an important role. The coating process can be described by Navier-Stokes equation was finally resulting in equation for the final thickness of the coating layer so, you can see this equation h infinities 2 / 3 eta v by rho g under root. So, h infinity is the equilibrium thickness, V is the coating velocity, rho is the density and this is the is the viscosity.

And after evaporation of the solvent and thin polymer film is formed at the surface with thickness proportional to volume fraction of polymer in the solution. Although the method itself is experimental rather simple to carry out there are a number of points that should also be emphasized.

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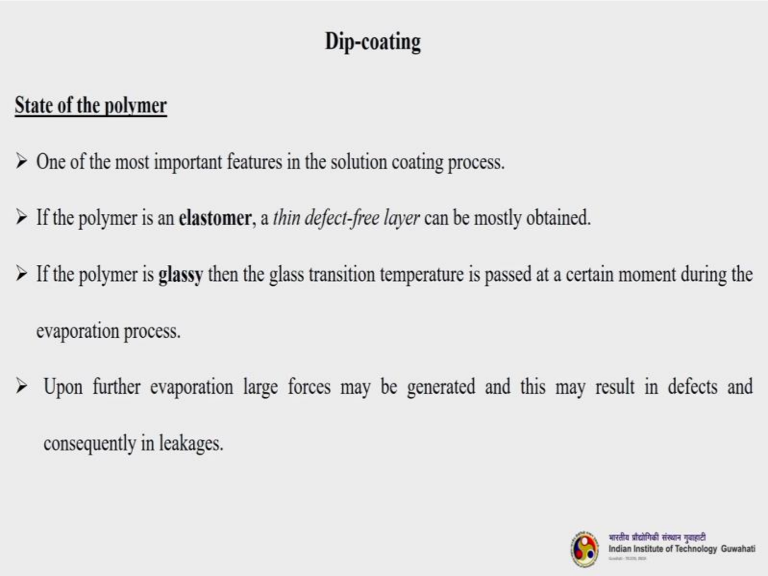

Dip-coating

State of the polymer

- One of the most important features in the solution coating process.
- If the polymer is an **elastomer**, a *thin defect-free layer* can be mostly obtained.
- If the polymer is **glassy** then the glass transition temperature is passed at a certain moment during the evaporation process.
- Upon further evaporation large forces may be generated and this may result in defects and consequently in leakages.

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So, the first one is the state of the Polymer. So, one of the most important features in the solution coating process what is the type of polymer basically. If the polymer is an elastomer, then a thin defect-free layer can mostly be obtained, mostly elastomer is used to get a very, very thin and a defect-free layer. If the polymer is glassy, that glass transition temperature is passed at a certain moment during the evaporation process. And upon further evaporation large forces may be generated. This may result in defect and subsequently and consequently in leakages the cracks will develop.

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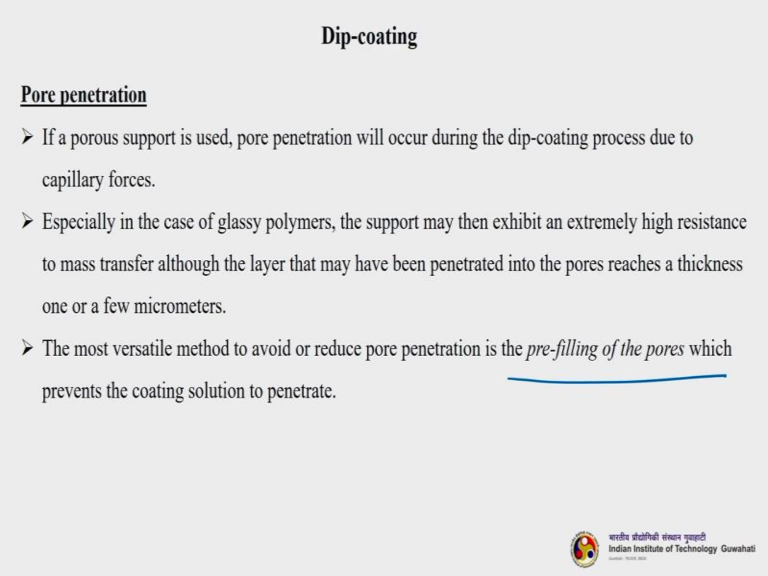

Dip-coating

Pore penetration

- If a porous support is used, pore penetration will occur during the dip-coating process due to capillary forces.
- Especially in the case of glassy polymers, the support may then exhibit an extremely high resistance to mass transfer although the layer that may have been penetrated into the pores reaches a thickness one or a few micrometers.
- The most versatile method to avoid or reduce pore penetration is the *pre-filling of the pores* which prevents the coating solution to penetrate.

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Second one is pore penetration. So, a porous support is used for pore penetration will occur during the dip coating process due to the capillary forces. Especially in the case of glassy polymers, the support may then exhibit an extremely high resistance to mass transfer although the layer that may have been penetrated into the pores, which is a thickness of one or few microns so, actually what is happening pore penetration is good or also bad also.

Why it is good because then linking or the sticking of the material on the thin layer over the surface of the support will be better because it has penetrated into the pore so, the support will be more. However, it is blocking the pores of the support also thereby restricting the free flow of the material which is separated by the top layer. So, the most versatile method to avoid or reduce pore penetration is pre filling of the force so, which prevents the solution.

So, what is being done is that so, when you are taking the support, you pre fill the forces of this support using some solvent, which can later be evaporated or been taken out through the opposite side of the membrane. So, that was the field then nothing will get inside the pores once again. So, there will be no more pore penetration basically.

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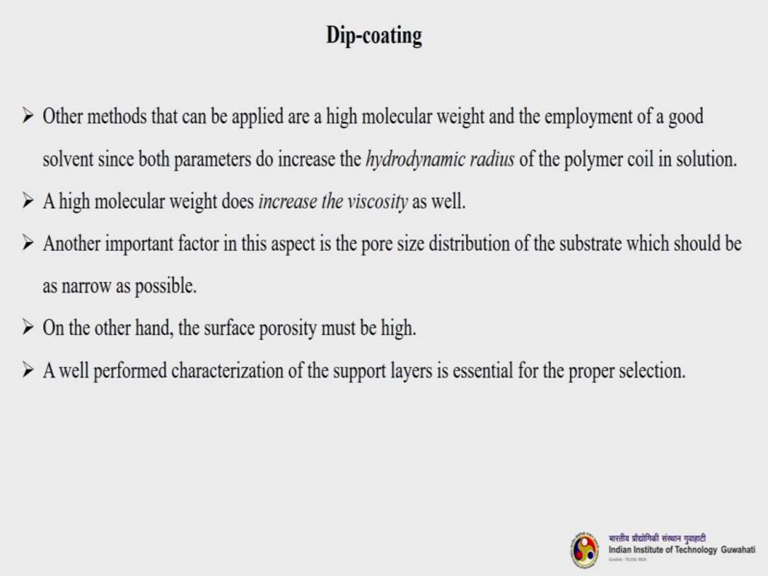

Dip-coating

- Other methods that can be applied are a high molecular weight and the employment of a good solvent since both parameters do increase the *hydrodynamic radius* of the polymer coil in solution.
- A high molecular weight does *increase the viscosity* as well.
- Another important factor in this aspect is the pore size distribution of the substrate which should be as narrow as possible.
- On the other hand, the surface porosity must be high.
- A well performed characterization of the support layers is essential for the proper selection.

So, other methods that can be applied are a high molecular weight and employment of a good solvent. Since both parameters increase the hydrodynamic radius of the polymer coil in the solution. So, what is the molecular weight using here if the molecular weight is very high than it is favourable. So, a high molecular weight does increase the viscosity as well that is also very important. And another important factor in this aspect is the pore size distribution of the substrate which should be narrow as possible. So, on the other hand surface porosity must be high, while perform characterization of the support layers is essential for the proper selection.

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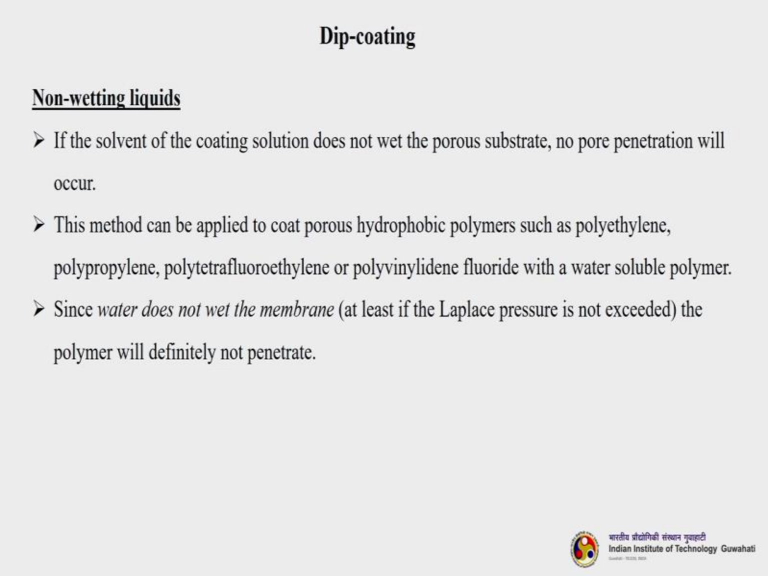

Dip-coating

<u>Non-wetting liquids</u>

- ➢ If the solvent of the coating solution does not wet the porous substrate, no pore penetration will occur.
- ➢ This method can be applied to coat porous hydrophobic polymers such as polyethylene, polypropylene, polytetrafluoroethylene or polyvinylidene fluoride with a water soluble polymer.
- ➢ Since *water does not wet the membrane* (at least if the Laplace pressure is not exceeded) the polymer will definitely not penetrate.

Then, comes the non-wetting liquids the importance of the non wetting liquids. So, if the solvent of the coating solution does not wet the porous substrate no pore penetration will occur. This method can be applied to coat porous hydrophobic polymers such as polyethylene, polypropylene, polytetrafluoroethylene or polyvinylidane fluoride with a water soluble polymer. Now, since water does not wet the membrane or at least if the Laplace pressure is not exceeded, then the polymer will definitely not penetrate.

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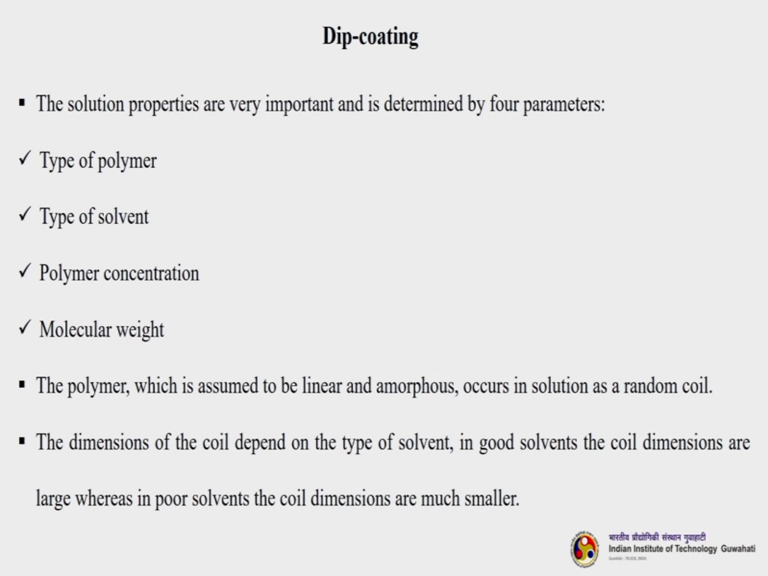

Dip-coating

- ▪ The solution properties are very important and is determined by four parameters:
- ✓ Type of polymer
- ✓ Type of solvent
- ✓ Polymer concentration
- ✓ Molecular weight
- ▪ The polymer, which is assumed to be linear and amorphous, occurs in solution as a random coil.
- ▪ The dimensions of the coil depend on the type of solvent, in good solvents the coil dimensions are large whereas in poor solvents the coil dimensions are much smaller.

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So, the solution properties are very important and is determined by 4 parameters. So, those are type of polymer, type of solvent, polymer concentration and molecular weight. So, the polymer which is assumed to be linear and amorphous occurs in solution as a random coil and the dimension of the coil depend on the type of solvent in good solvents that coil dimension are large whereas, in poor solvents the coil dimension solvents are very smaller.

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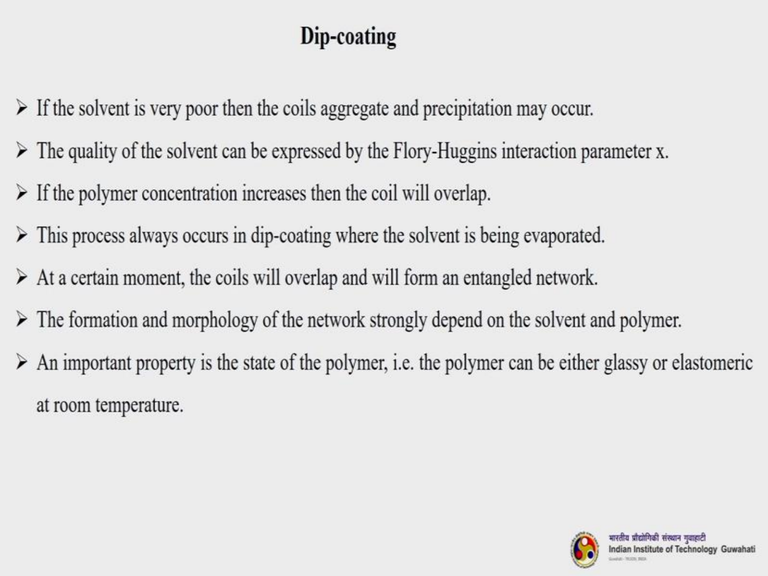

Dip-coating

- If the solvent is very poor then the coils aggregate and precipitation may occur.
- The quality of the solvent can be expressed by the Flory-Huggins interaction parameter x.
- If the polymer concentration increases then the coil will overlap.
- This process always occurs in dip-coating where the solvent is being evaporated.
- At a certain moment, the coils will overlap and will form an entangled network.
- The formation and morphology of the network strongly depend on the solvent and polymer.
- An important property is the state of the polymer, i.e. the polymer can be either glassy or elastomeric at room temperature.

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If the solvent is very poor than the coils aggregate and precipitation may occur. So, that is another actually thing that has to be actually taken care of the quality of the solvent can be expressed by the Flory-Huggins interaction parameter x, if the polymer concentration increases, then the coil will overlap that is another problem. So, this process always occurred in dip coating where the solvent is being evaporated.

And at a certain moment the coils will overlap and will form an entangled network. The formation and morphology of the network strongly depend on the solvent and the polymer. And important properties in the state of the polymer that we just discussed. If it is a elastomer, and what will happen if it is a glassy polymer then what may happen?

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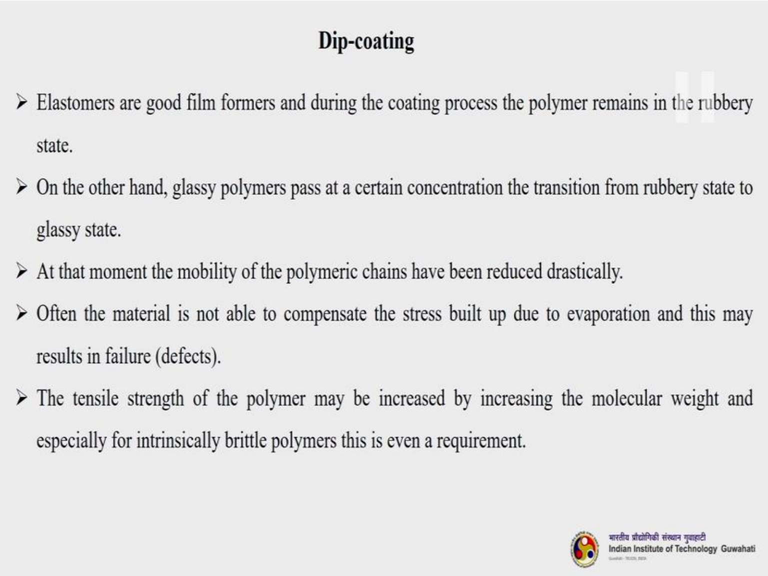

Dip-coating

- Elastomers are good film formers and during the coating process the polymer remains in the rubbery state.
- On the other hand, glassy polymers pass at a certain concentration the transition from rubbery state to glassy state.
- At that moment the mobility of the polymeric chains have been reduced drastically.
- Often the material is not able to compensate the stress built up due to evaporation and this may results in failure (defects).
- The tensile strength of the polymer may be increased by increasing the molecular weight and especially for intrinsically brittle polymers this is even a requirement.

Elastomers are good film formers and during the coating process, the polymer remains in the rubbery state. On the other hand, glassy polymers pass at a certain concentration and the transition from rubbery state to glassy states. So, when that transition is happening so, certain temperature we are applying, so that may result in some crack formation. So, at that moment the mobility of the polymeric chains have been reduced drastically upon the material is not able to compensate the stress built up due to evaporation.

And this may result in failure. So, the tensile strength of the polymer may be increased by increasing the molecular weight and especially for the intrinsically brittle polymers this is even a requirement.

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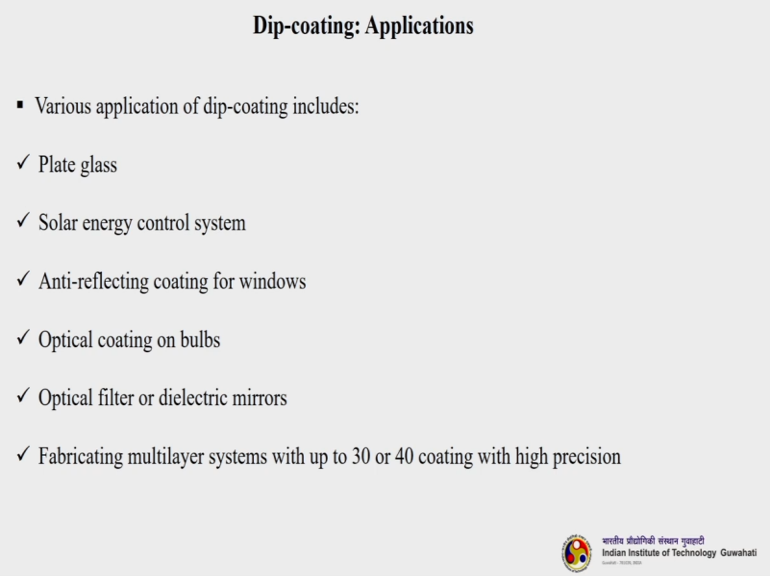

Dip-coating: Applications

- Various application of dip-coating includes:

✓ Plate glass

✓ Solar energy control system

✓ Anti-reflecting coating for windows

✓ Optical coating on bulbs

✓ Optical filter or dielectric mirrors

✓ Fabricating multilayer systems with up to 30 or 40 coating with high precision

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Various application of dip coating includes plate glass, solar energy control system, anti reflective coating for windows, optical coating on balls, optical filters or dielectric mirrors, fabricating multi layer systems with up to 30 or 40 coating with very high precision.

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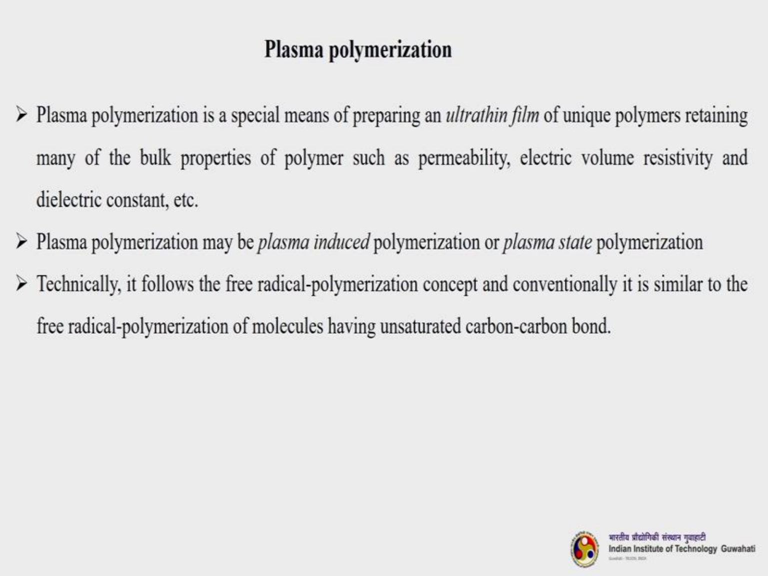

Plasma polymerization

➢ Plasma polymerization is a special means of preparing an *ultrathin film* of unique polymers retaining many of the bulk properties of polymer such as permeability, electric volume resistivity and dielectric constant, etc.

➢ Plasma polymerization may be *plasma induced* polymerization or *plasma state* polymerization

➢ Technically, it follows the free radical-polymerization concept and conventionally it is similar to the free radical-polymerization of molecules having unsaturated carbon-carbon bond.

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So, the students the next process of preparing the thin film membrane is plasma polymerization. So, plasma polymerization is a special means of preparing an ultra thin film of unique polymers retaining many of the bulk properties of the polymer such as permeability, electric volume, resistivity and dielectric constant. The plasma polymerization maybe plasma induced polymerization or plasma state polymerization either of this one type will be used. So, technically it follows the free radical polymerization concept and conventionally. It is similar to the free radical polymerization of molecules having unsaturated carbon-carbon bond.

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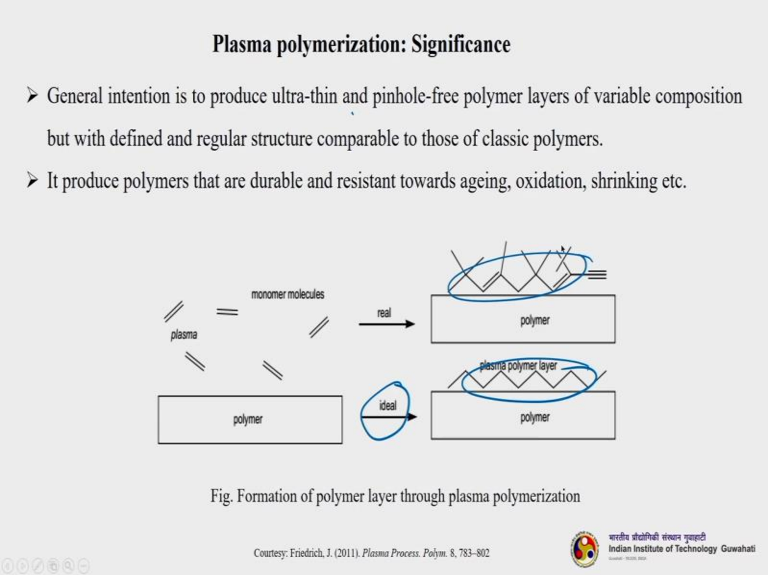

Plasma polymerization: Significance

- General intention is to produce ultra-thin and pinhole-free polymer layers of variable composition but with defined and regular structure comparable to those of classic polymers.
- It produce polymers that are durable and resistant towards ageing, oxidation, shrinking etc.

Fig. Formation of polymer layer through plasma polymerization

Courtesy: Friedrich, J. (2011). *Plasma Process. Polym.* 8, 783–802

Let us see how it happens. So, the general intention is to produce ultra thin and pinhole free polymer layers, so, no defect actually, we do not want any defective layer here and thin polymeric layers of variable composition with the well defined and regular structure that is what actually we want. Then it produces polymers that are durable and resistant towards ageing, oxidation and shrinking.

And now, you can see the how the formation of polymer layer through plasma polymerization is happening. So, the ideal condition would be the polymer and then plasma polymer layer the position happening like this, but actually in real it never happens like this. So, you can see because the monomer molecules are available in this type of form. So when it is getting deposited using the plasma, so the deposited something like this, it is a random structure basically, it is not a very planned structure.

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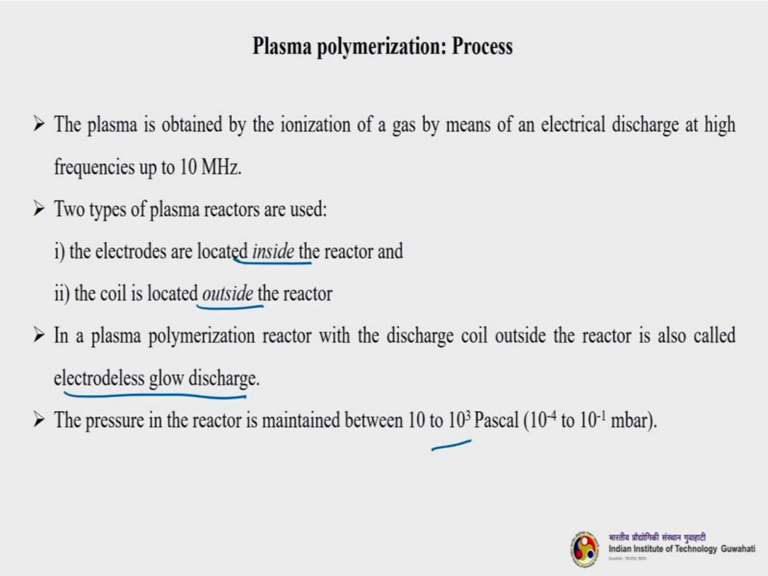

Plasma polymerization: Process

- The plasma is obtained by the ionization of a gas by means of an electrical discharge at high frequencies up to 10 MHz.
- Two types of plasma reactors are used:
  i) the electrodes are located *inside* the reactor and
  ii) the coil is located *outside* the reactor
- In a plasma polymerization reactor with the discharge coil outside the reactor is also called electrodeless glow discharge.
- The pressure in the reactor is maintained between 10 to 10^3 Pascal (10^{-4} to 10^{-1} mbar).

So, the plasma is obtained by the ionization of a gas by means of an electrical discharge at high frequencies up to 10 megahertz, 2 types of plasma reactors are used in one type, the electrodes are located inside the reactor, in another one, the electrodes or the coils are located outside the reactor. In a plasma polymerization reactor with the discharge coil outside the reactor is also called the electrode less glow discharge. If it is outside, many books you will find this particular topic. The pressure in the reactor is maintained between 10 to 10 to the power 3 Pascal.

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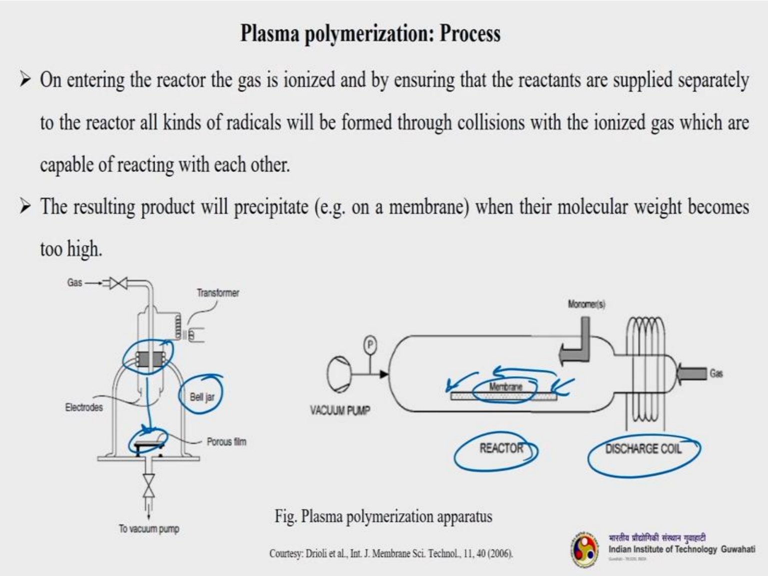

Plasma polymerization: Process

- On entering the reactor the gas is ionized and by ensuring that the reactants are supplied separately to the reactor all kinds of radicals will be formed through collisions with the ionized gas which are capable of reacting with each other.
- The resulting product will precipitate (e.g. on a membrane) when their molecular weight becomes too high.

Fig. Plasma polymerization apparatus

Courtesy: Drioli et al., Int. J. Membrane Sci. Technol., 11, 40 (2006).

You can see the sketches of the plasma polymerization apparatus on entering the reactor. That the gas is ionized and by ensuring that the reactants are supplied separately to the reactor all kinds of radicals will be formed through collisions with the ionized gas which are capable of reacting with each other. So, the resulting product will precipitate on a membrane when their molecular ~~rate~~ weight becomes too high.

So, this is a bell jar type of system and this is another reactor. Here the discharge coil is located outside. Here the discharge coil is also located outside but electrode is little pushed here. So, what is happening here this is the membrane here the porous film or the membrane is located then when the ionization taking place the monomer is ionized and actually there, this one coming and depositing on the surface of this particular membrane. So they are flowing like this and the coating the deposition should be uniform otherwise will get a various thickness membrane.

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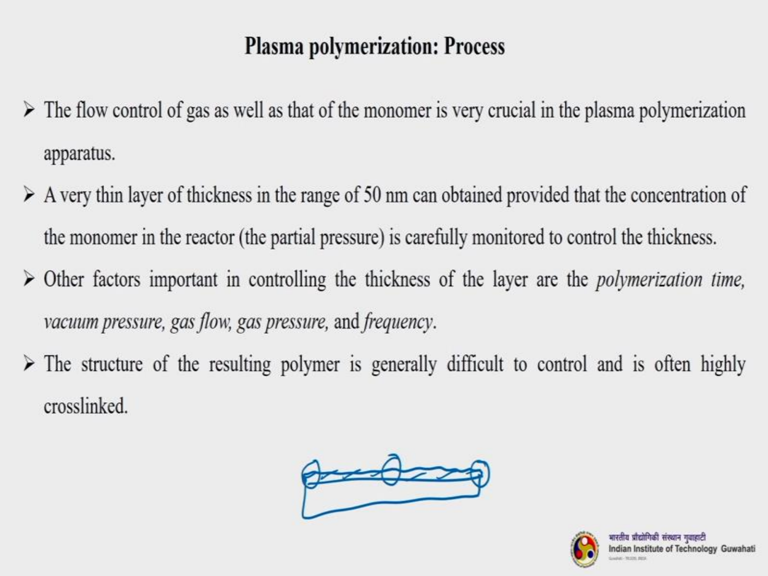

Plasma polymerization: Process

- The flow control of gas as well as that of the monomer is very crucial in the plasma polymerization apparatus.
- A very thin layer of thickness in the range of 50 nm can obtained provided that the concentration of the monomer in the reactor (the partial pressure) is carefully monitored to control the thickness.
- Other factors important in controlling the thickness of the layer are the *polymerization time, vacuum pressure, gas flow, gas pressure,* and *frequency*.
- The structure of the resulting polymer is generally difficult to control and is often highly crosslinked.

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So the flow control of gas as well as that of monomer is very crucial in the plasma polymerization apparatus, a very thin layer of thickness almost 50 nanometer can be obtained provided the concentration of the monomer in the reactor is carefully monitored to control the thickness, this is what I was talking about, if this is not been taken care now, what will happen? So, let us see.

This is the porous support about which you have a having a thin layer deposition. So, what will happen? Here the thickness is very less, here the thickness is more, here the thickness is different. So, it should not happen it should be uniform. So, other factors important in controlling the thickness are polymerization time vacuum pressure, gas flow, gas pressure and frequency these are you can see there are so many parameters. Which actually eventually decide the thickness of the layer. So, the structure of the resulting polymer is generally difficult to control and is upon highly cross linked to.

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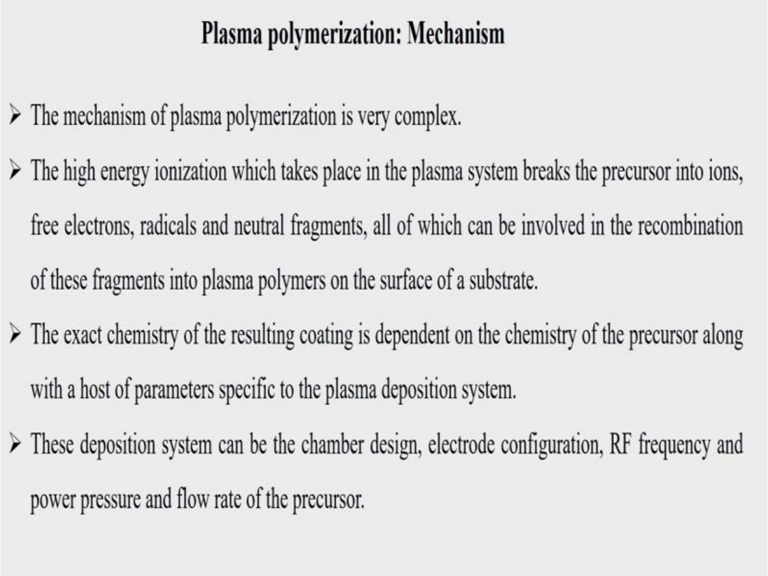

Plasma polymerization: Mechanism

- The mechanism of plasma polymerization is very complex.
- The high energy ionization which takes place in the plasma system breaks the precursor into ions, free electrons, radicals and neutral fragments, all of which can be involved in the recombination of these fragments into plasma polymers on the surface of a substrate.
- The exact chemistry of the resulting coating is dependent on the chemistry of the precursor along with a host of parameters specific to the plasma deposition system.
- These deposition system can be the chamber design, electrode configuration, RF frequency and power pressure and flow rate of the precursor.

Let us understand the mechanism. Actually the mechanism of plasma polymerization is very complex, the high energy ionization which takes place in the plasma system. So, breaks the precursor into various irons, free electrons, radicals and natural fragments. All of which can be involved in the recombination of these fragments into plasma polymers on the surface of the substrate.

So, that means, in various forms the plasma system as a precursor is being deposited on the surface of the support. So, the exact chemistry of the resulting coating is dependent on the chemistry of the precursor along with a host of parameters specific to the plasma deposition system. So, this deposition system can be the chamber designed, electrode configuration. The RF frequency and the power ~~of~~ pressure and flow rate of the precursor. So, many things that actually finally, deciding upon actually it is very complex the mechanism.

The reason is that the precursor is getting fragmented into various types of things, it may be ions, it may be pre electrons, radicals and some neutral fragments. So, that is the reason why the mechanism is very complex.

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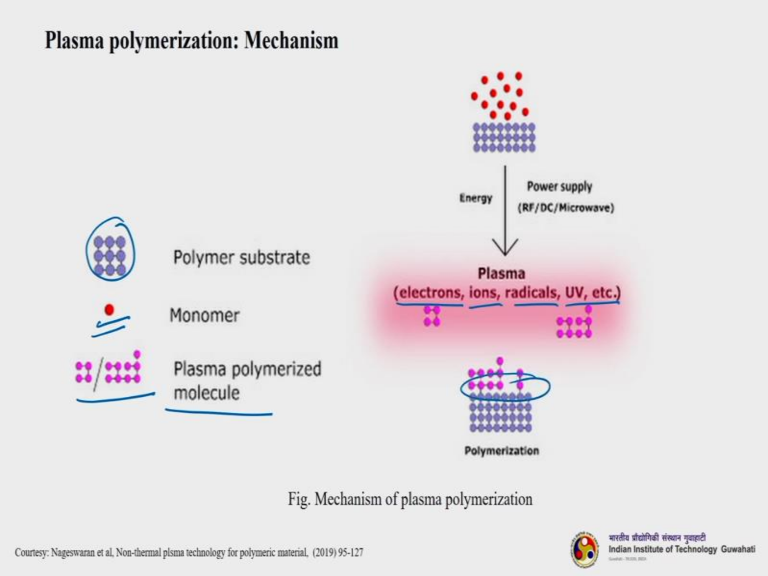

Plasma polymerization: Mechanism

Fig. Mechanism of plasma polymerization

Courtesy: Nageswaran et al, Non-thermal plsma technology for polymeric material, (2019) 95-127

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So, student this is one of the plasma polymerization mechanism you can see the see the polymer substrate how it looks like? This is the monomer, this monomer is getting divided into various types of ions, and free radicals, then when the polymerized, so we will get something like this cross linking line, right? So we can have either electrons, ions, radicals, you be all these things. All of them are getting deposited on the surface. And then once they are depositing they are getting cross linked.

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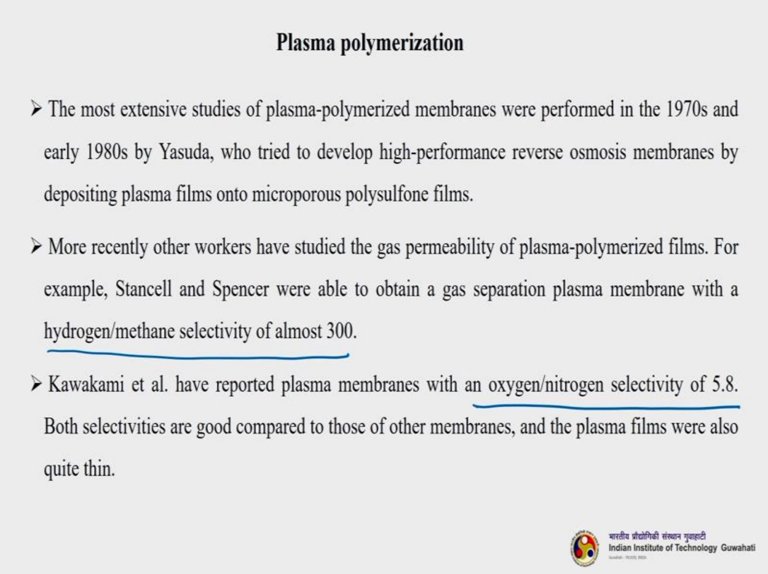

Plasma polymerization

- The most extensive studies of plasma-polymerized membranes were performed in the 1970s and early 1980s by Yasuda, who tried to develop high-performance reverse osmosis membranes by depositing plasma films onto microporous polysulfone films.
- More recently other workers have studied the gas permeability of plasma-polymerized films. For example, Stancell and Spencer were able to obtain a gas separation plasma membrane with a hydrogen/methane selectivity of almost 300.
- Kawakami et al. have reported plasma membranes with an oxygen/nitrogen selectivity of 5.8. Both selectivities are good compared to those of other membranes, and the plasma films were also quite thin.

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So, the most expensive studies of plasma polymerized membranes were performed in the 1970s and 80s by Yasuda, who tried to develop high performance RO membranes by depositing plasma films onto microporous polysulfone films. So, long back it was done. That is not a very new technique that is developed. But the only problem with this is that this very costly process. And more recently other workers also studied, have studied gas permeability of plasma polymerized films.

For example, stancell and Spencer were able to obtain a gas separation plasma membrane with a hydrogen methane selectivity of almost 300. You can imagine the very high selectivity that to separate hydrogen methane then Kawakami et al have recently reported plasma membranes with an oxygen nitrogen selectivity of 5.5.8. Both the selectivity's compared to less than but still with respect to oxygen and nitrogen it is very high but please try to understand that oxygen nitrogen both are getting separated from the air. So, both selectivity's are good compared to those of other membranes, and the plasma films are also very, very thin.

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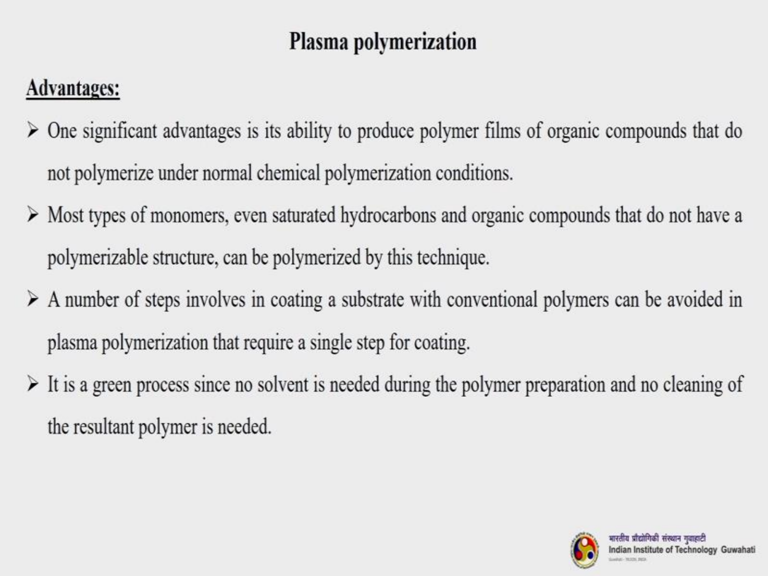

Plasma polymerization

Advantages:

- One significant advantages is its ability to produce polymer films of organic compounds that do not polymerize under normal chemical polymerization conditions.
- Most types of monomers, even saturated hydrocarbons and organic compounds that do not have a polymerizable structure, can be polymerized by this technique.
- A number of steps involves in coating a substrate with conventional polymers can be avoided in plasma polymerization that require a single step for coating.
- It is a green process since no solvent is needed during the polymer preparation and no cleaning of the resultant polymer is needed.

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So, the advantage of plasma polymerization is its ability to produce polymer films of organic compounds that do not polymerize under normal chemical polymerization condition. So, students try to understand that there are certain polymers which we are having very good property to form a particular membrane. However, they are not getting polymerized under standard reaction conditions or other processes.

That is why plasma polymerization helps. So, most of the ammonium are even saturated hydrocarbons and organic compounds that do not have a polymerizable structure can be polymerized by using this technique. So, this is the beauty of this particular process and number of steps ~~in~~ involving coating a substrate with conventional polymers can be avoided in plasma polymerization that require a single step for coating, it is a green process.

So, you need to understand that green process as there is no solvent is being used, however, and no cleaning of the resultant polymer is needed. It is also needed, it is almost getting crosslink during the process, then you just take it out, just leave it for some time for a dry that is the finished. Membrane basically, only the cost of energy involve is very high.

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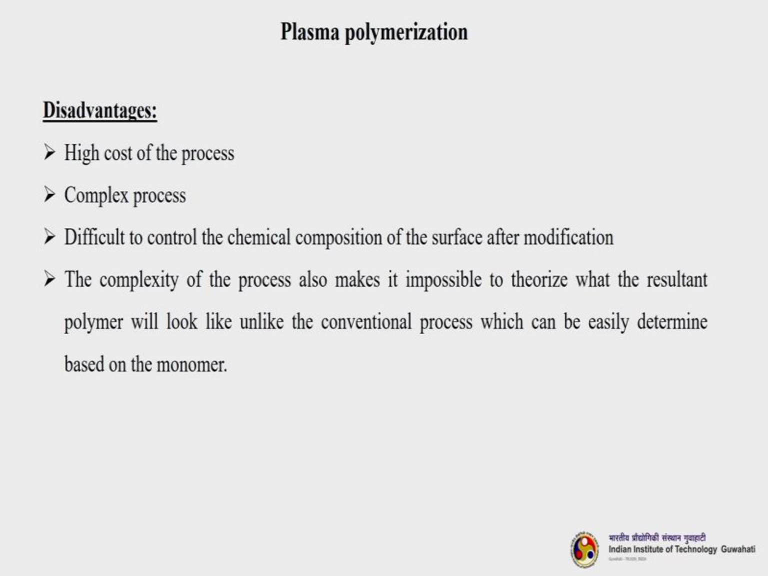

Plasma polymerization

Disadvantages:

- High cost of the process
- Complex process
- Difficult to control the chemical composition of the surface after modification
- The complexity of the process also makes it impossible to theorize what the resultant polymer will look like unlike the conventional process which can be easily determine based on the monomer.

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And disadvantages is the high cost of the process, this is the most important thing actually. Complex process the mechanism is very ill understood and difficult to control the chemical composition of the surface after modification once it is done, you cannot do any modification. And the complexity of the process also makes it impossible to theorize what the resultant polymer will look like, or unlike.

The conventional process which can be easily determine based on the monomer, so if I know what is the monomer that I am going to deposit on the surface of a support in other processes like interfacial polymerization and dip coating. I can predict what type of layer that will be deposited on the surface of the support. But I cannot predict that at least even theoretically during plasma polymerization, because the ionization is making the monomer or fragmenting the monomer into various different types of ions and this one radicals and UV also.

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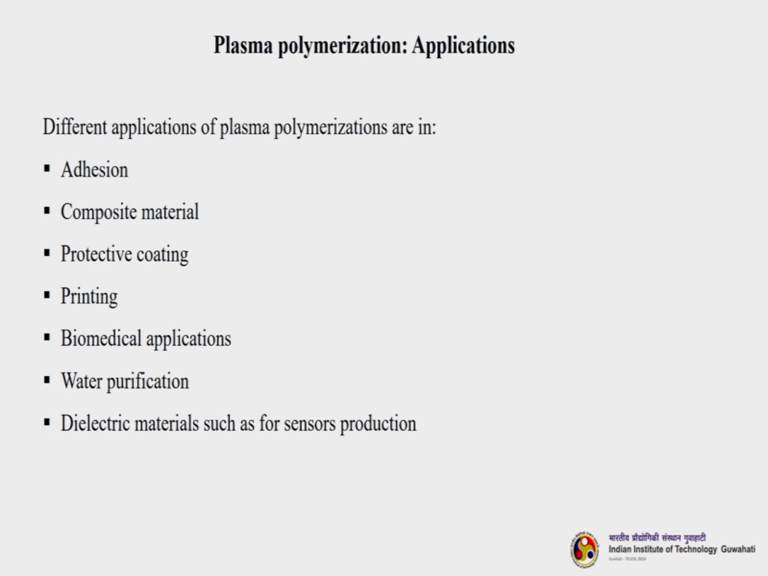

Plasma polymerization: Applications

Different applications of plasma polymerizations are in:

- Adhesion
- Composite material
- Protective coating
- Printing
- Biomedical applications
- Water purification
- Dielectric materials such as for sensors production

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So, different application are, it is of composite material, protective coating, printing, biomedical applications, water purification, dielectric material such as sensor production.

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I will show you also how you can prepare ceramic membrane in lab scale. And then we will discuss about membrane modification also. So, thank you very much. So, in case you have any query, and do write to me at kmohanty@itg.ac.in and I will definitely reply to your queries. Thank you very much.