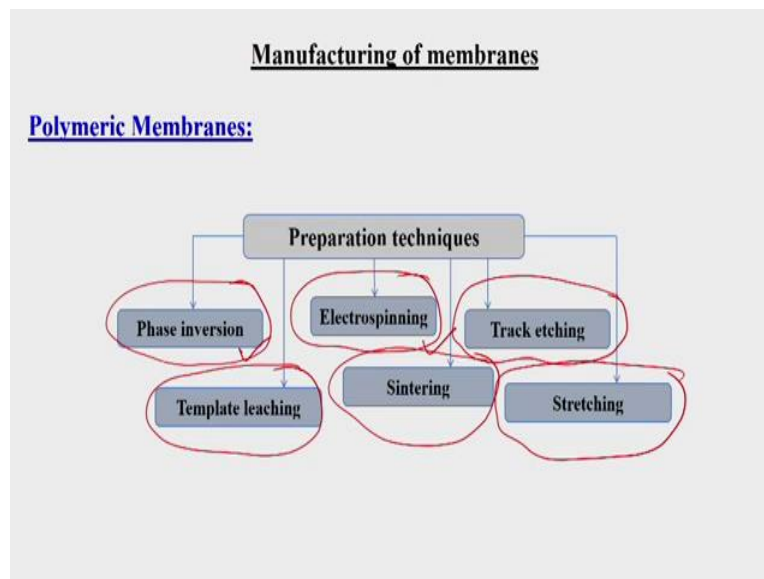


**Mass Transfer Operations II**  
**Professor Chandan Das**  
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**Lecture 19- Manufacturing of Membranes, Advantages of Membrane Separation Processes, Limitations, Approaches To Improve**

Welcome back to Mass Transfer Operations II. In this lecture we will be discussing on the manufacturing of membranes, advantages of membrane separation processes, limitations and approaches to improve the membrane performance.

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We will be discussing first the manufacturing of the polymeric membranes. There are six manufacturing processes for the polymeric membrane fabrication, one is this phase inversion technique, then another is template leaching and one process is electrospinning and another processes sintering and one processes track etching and another process is stretching.

Okay, so out of these we can say we will be discussing mostly this phase inversion techniques and electrospinning processes because these are widely used and new manufacturing processes, whereas we can say this one template leaching, sintering, stretching and track etching, these are all well established studies.

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<b>Manufacturing of membranes</b>			
<b><u>Polymeric Membranes:</u></b>			
<b>Fabrication Technique</b>	<b>Pore Diameter (<math>\mu\text{m}</math>)</b>	<b>Porosity (%)</b>	<b>Membrane properties</b>
✓ Phase inversion	<0.1 - >20	Porous and non-porous	✓ Properties varied according to polymer used ✓ Easy and widely applicable
✓ Electrospinning	Porous	Highly porous (>80)	✓ Highly flux and less tendency to fouling ✓ High surface area
✓ Sintering	0.1-10	10-20	✓ Outstanding chemical, thermal and mechanical stability ✓ Organic and inorganic material can be used
✓ Stretching	1-20	90	✓ High permeability for gases and vapours ✓ Can be produced as flat sheets, tubes
Track etching	0.02-10	Max 10	✓ Low tendency to plug ✓ Good long term flux stability
Template leaching	Min 0.05	✓ Porous	High surface area

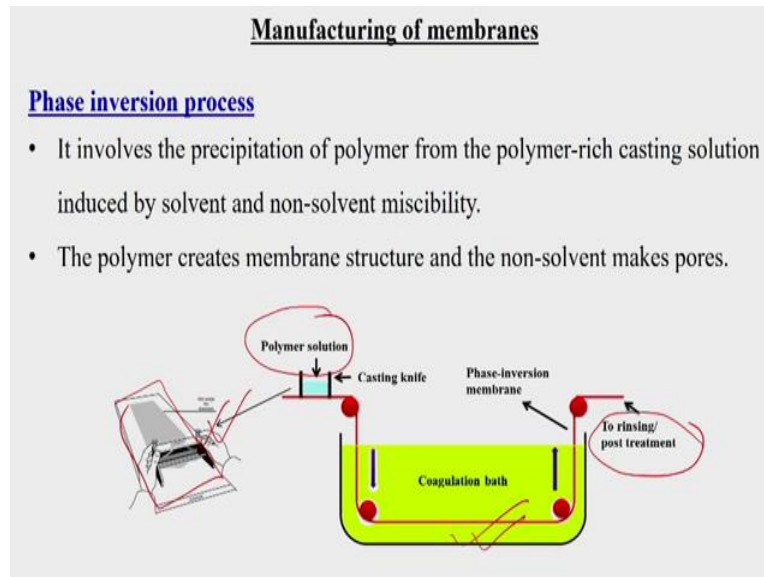
These polymeric membranes like this if we talk about this phase inversion techniques, then we can say the pore diameter will range from less than 0.1 micron to greater than 20 microns, so in the wide range we will be able to manufacture the membrane using this phase inversion techniques and we are able to prepare these both porous and nonporous membrane with the high porosity as well as low porosity and the properties are like this we can say these properties vary according to polymer used and easy and widely applicable.

In case of the electrospinning, this is we can say it is a highly porous, so we will be discussing this one it is done by electro winning and porosity maybe sometimes like this more than 80 percent or so and flux values is very high and less tendency to fouling and high surface area. In case of the sintering we can say, we will be able to get the pore diameter from 0.1 to 10 micron, here also be we can say this one wide range of membrane pores manufacturing using this sintering process and porosity varies from 10 to 20 percent. So we can say this one it has outstanding chemical, thermal and mechanical stability and organic and inorganic materials can be used actually for the separation.

And stretching, this one using this stretching also we are able to make the pore diameter from 1 to 20 micron and porosity is also very high to 90 percent porosity is observed and high permeability for gases and vapors can be produced as flat sheets and tubes. And for track etching we can say the pore diameter ranges from 0.02 to 10 micron like this and maximum 10 percent porosity is observed, it has this low tendency to plug and good long-term flux stability is observed. And for template leaching we can say this one minimum pore is

observed like 0.05 micron and it is highly porous and high surface area is available using this template leaching, okay?

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So in phase inversion techniques we can say it involves the precipitation of polymer from the polymer-rich casting solution induced by solvent and non-solvent miscibility. So the polymeric creates the membrane structure and non-solvent makes the pores. Suppose we have this polymer solution, it is dissolved in suppose one organic solvent and then whenever it is mixed properly for a long period of time, then it is now placed in the glass plate and then using this digital film applicator or casting knife we are able to make a film using this polymeric solution.

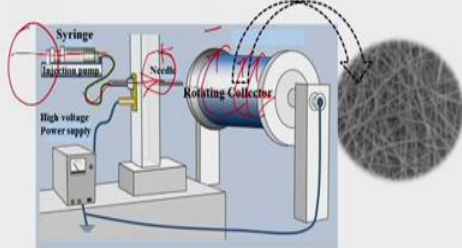
Then say we need to put inside this then we can say inside this film the polymer as well as this organic solvent is there. Now we are using one coagulation bath say where we have we use water or cold water as the phase inversion medium. So whenever it will be coming then polymer from the liquid will be converting into the solid phase, so that phase will be inverted here and then we can say this phase inverted membrane actually will go for this we can say rinsing as well as this post treatment, then drying is done in different temperature zones.

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**Manufacturing of membranes**

**Electrospinning Process**

- A fiber spinning technique depending on the **electrostatic forces**.
- An **electric field** is created between the needle tip and collecting plate by applying high voltage supply.
- Produced fibers in **nanometer to micrometer** diameter ranges.
- The polymer chain entanglements within the solution prevents the electrospinning jet from breaking up.



And in case of this electrospinning process, say a fiber spinning technique depending on the electrostatic force of attraction is used for the preparation of electro spun nano fibers membrane. An electric field is created between the, suppose this we have this one feed here and using this syringe or we can say the injection palm suppose this membrane, nano-fiber as fiber, this membrane actually is now injected and suppose this needle of this syringe is made by a positively charged pole.

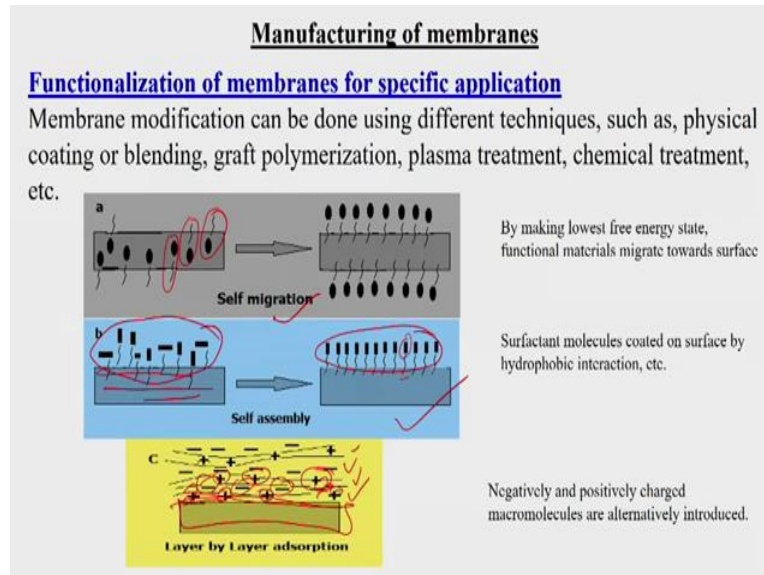
And there is one rotating disk collector, suppose it is rotating in say maybe in a cyclic, we can say this one in the clockwise direction or anticlockwise direction and then needle actually will be moving from the one side of this rotating disk collector to the other side of the rotating disk collector and at the same time rotating disk collector will be rotating in the either we can say this one clockwise direction or anticlockwise direction.

So in this case there are two different types of movements, one movement is from suppose one side of this rotating disk collector to the other side, that is we can say this one movement of the needle of the syringe, another movement is this cyclic rotation either clockwise or anticlockwise, that is the direction or rotation of the rotating disk collector, okay? And then due to this winding actually we can say this one the membrane film actually will be produced.

So produced fibers in the nanometer to micrometer range actually will be there, it is depending on so many parameters. And the polymeric chain entanglements within the solution prevent the electrospinning jet from the breaking up. And then whenever say we

have so many rounds of the rotating disk and say from the needle of the syringe we can say the jet is coming out and this suppose this rotating disk is negatively charged, so due to this charged distribution whenever the polymeric fiber will be coming out it will be wound on the rotating disk collector and ultimately it will be obtained as the film.

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And say we have some we can say functionalization of the membrane for specific applications like this membrane modification can be done using different techniques, such as we can say this polymeric coating or blending, graft polymerization, then plasma treatment, then chemical treatment etc. Like one is the self migration by making lowest free energy state of these functional materials that migrate towards the surface. Suppose some functional materials are required for a particular application, suppose polymer is formed then we can say if we make this lower, lowest free energy state then this will be we can say oriented on the top surface of the polymeric membrane. So this is due to the self migration.

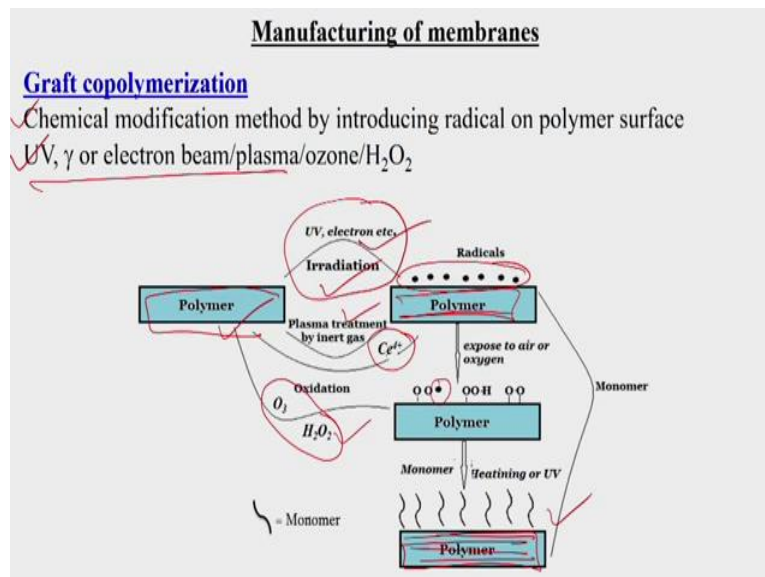
There is one another method called self assembly, like say surfactants molecules coated on the surface by hydrophobic interaction, so suppose this is the polymeric membrane and these are all surfactants then if these are placed or coated on the top of this polymeric membrane due to their we can say this one hydrophobic interaction this will be oriented in the regular fashion.

And it has a particular application like this, so it is we can say this one hydrophobic tail and hydrophilic head is there. So for that case we can say if it is cationic surfactants, if it is an anionic surfactant or if it is zwitter-ionic, if it is non-ionic surfactant, depending on the we

can say this one surfactant property we will be able to selectively separate a particular component using that type of self-assembly polymeric membrane.

The third type is called layer by layer adsorption membrane like this, so negatively and positively charged micro-molecules like this, these are placed like this. In the beginning suppose on the membrane surface if the positively charged micro molecules are placed then and the second layer will be negatively charged like this, this will be placed one by one and this alternatively we will be able to code this again positively charged micro molecules and we will be getting this different and depending on the requirement we will be able to quote what type of charged membrane we require. Based on that we can quote say maybe 1, 2, 3, 4, 5 like this, so how many layers actually are required based on that we will be doing this.

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And another method of the manufacturing of polymeric membrane using graft copolymerization process, this is we can say the specific application, for the specific application of the polymeric membrane that is done like chemical modification method by introducing radicals or on the polymer surface and then we can say this one UV, gamma or electron beam or plasma or ozone or hydrogen peroxide, these are used as the grafting.

Suppose the polymer is there we will be using this for a particular application, then we can say we can do this UV or electron beam or some irradiation and by plasma also we can do and then maybe selenium also is used, then on the polymer surface we can say this one radicals are generated and then using this ozone or hydrogen peroxide we can say this one

some radicals are now grafted with different functional groups. And then finally one grafted copolymerized one membrane will be formed which will be used for a particular application.


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**Manufacturing of membranes**

**Fabrication of Cellulose acetate-modified-Titanium dioxide (TiO<sub>2</sub>) nanoparticles electrospun composite membranes**

- Solutions of CA and CA-TiO<sub>2</sub> membranes were prepared
- The mixed solution was stirred for 4 h at 200 rpm speed
- Sonicated for 3 h in order to ensure the optimum distributions of the TiO<sub>2</sub> NPs in the CA solution

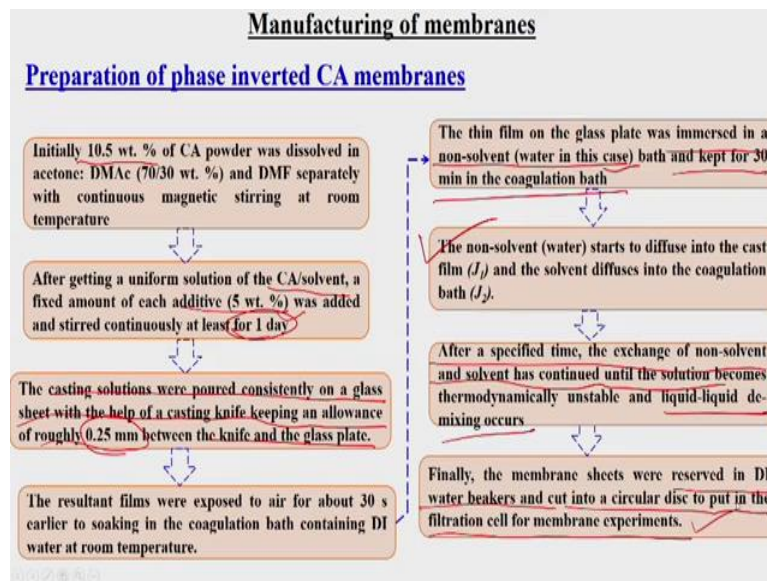
Membrane	CA (wt. %)	TiO <sub>2</sub> (wt. %)	AC/DMAc (wt. %)
M <sub>1</sub>	13.5	0	86.5
M <sub>2</sub>	13.5	1.0	85.5
M <sub>3</sub>	13.5	2.5	84.0
M <sub>4</sub>	13.5	4.5	82.0
M <sub>5</sub>	13.5	6.5	80.0



And another one is the fabrication of cellulose acetate-modified-titanium oxide nanoparticles electrospun composite membrane, that is also used for a particular application, okay? So for that case suppose this is a cellulose acetate solution and this is cellulose acetate titanium dioxide solution and then say the mix solution was stirred for 4 hour at 200 rpm speed and then sonicated for 3 hour in order to ensure the optimum distributions of the TiO<sub>2</sub> nanoparticles in the cellulose acetate.

And then say we can say this one for the fabrication of different membranes like M1, M2, M3, M4, M5, so many membranes, suppose different compositions of cellulose acetate, titanium dioxide and acetone DMAc these are added and then these are again electrospun to get a particular say film like this. So if the concentration of cellulose acetate is fixed and then concentration or dose of this titanium dioxide is changed as well as this we can say the solvent and co-solvent also is altered then the property of the membrane also will be varied. Okay, so based on that, based on the particular application or depending on a particular application the membrane will be fabricated.

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And regarding this manufacture of the cellulose acetate membrane using this phase inversion technique and then by applying this digital film applicator or casting knife, so this is a typical procedure actually of the manufacture of phase inverted cellulose acetate membrane. Suppose initially 10.5 wt percent cellulose acetate powder was dissolved in acetone DMAc mixture that is 70 is to 30 and DMF separately with continuous magnetic stirring at room temperature.

And then after getting a uniform solution of the cellulose acetate solvent mixture, a fixed amount of each additive, suppose different additives are added and then stirred continuously at least for one day, okay? After that the casting solution were poured consistently on a glass sheet with the help of one casting knife keeping an allowance of roughly say 0.2 millimeter or whatever the required thickness of the membrane, so we need to keep that gap, then this knife actually is moved from one side of this glass plate to the other side.

The resultant film were, this one films were exposed to air for about 30 seconds earlier to soaking in the coagulation bath and for this one bath containing deionized water at room temperature. Then the film actually on the glass plate was immersed on a non-solvent like water in this case and kept for 30 minute in the coagulation bath. So there we can say this phase inversion will take place, up to this it was like this in the liquid phase and inside the solvent, suppose this solvent is suppose DMAc and suppose acetone DMAc DMF, these are there, so now we are placing this one in water. So then what will happen? This non-solvent like this water starts to dissolve, diffuse actually into the cast film.



So inside this film water will be trying to enter and at the same time the entrapped acetone DMAC DMF will be trying to come out or diffuse from the coagulation bath. So after the specified time the exchange of the non-solvent and the solvent has continued until the solution becomes thermodynamically unstable and liquid-liquid de-mixing occurs. Finally the membrane sheets were reserved in deionized water and cut into a circular disk or maybe the whatever the desired shape to put in the filtration cell for membrane experiment but sometimes that treatment also is done.

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**Manufacturing of membranes (Examples)**

**Preparation of phase inverted CA membranes**

- ❖ Coagulation bath = DI Water
- ❖ Coagulation temperature = 25 °C
- ❖ Evaporation time = 30 sec
- ❖ Phase inversion time = 30 min

Membrane	CA wt. %	PEG wt. %	PVP wt. %	AC: DMAc (70/30 wt. %)	DMF wt. %
CA0	10.5	-	-	89.5	-
CA1	10.5	5	-	84.5	-
CA2	10.5	-	5	84.5	-
CA3	12.5	-	-	-	89.5
CA4	10.5	5	-	-	84.5
CA5	10.5	-	5	-	84.5

The diagram illustrates the casting process. A casting solution is applied to a glass plate. The solvent (H<sub>2</sub>O and Solvent: J<sub>2</sub>) evaporates from the surface, leaving a membrane. The membrane is then immersed in a coagulation bath (H<sub>2</sub>O). The diagram shows the exchange of solvent and co-solvent, leading to the formation of pores in the membrane.

A photograph of a circular membrane disk, showing its texture and color.

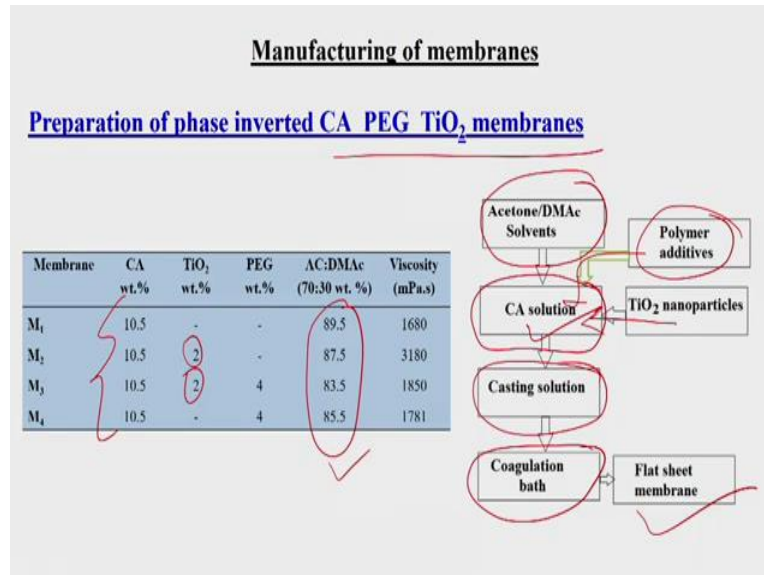
So this is a typical we can say this is a composition of this cellulose acetate and we can say polymeric membrane. Suppose the different membranes are there and then cellulose acetate concentration is fixed at 10.5 and sometimes this 12.5 also and then PEG concentration also is kept sometimes 5 percent, then PVP also is taken like these additives and then acetone DMAc is taken as sometimes 89.5 percent, somewhere it is 84.5 percent and then DMF also is taken sometimes at 89.5 sometimes it is 84.5.

So there are so many combinations but the optimum composition is shown here, then what is happening inside this coagulation bath? Say inside suppose this is the membrane and suppose we can say the solvent is there inside this one, so solvent will be coming to this water and water will be entering into this membrane. So due to this exchange of the solvent and co-solvent we can say pores are formed, okay?

So like coagulation bath is now deionized water and coagulation temperature is maintained at 25 degree Celsius, evaporation time is only 30 seconds and then phase inversion time is 30

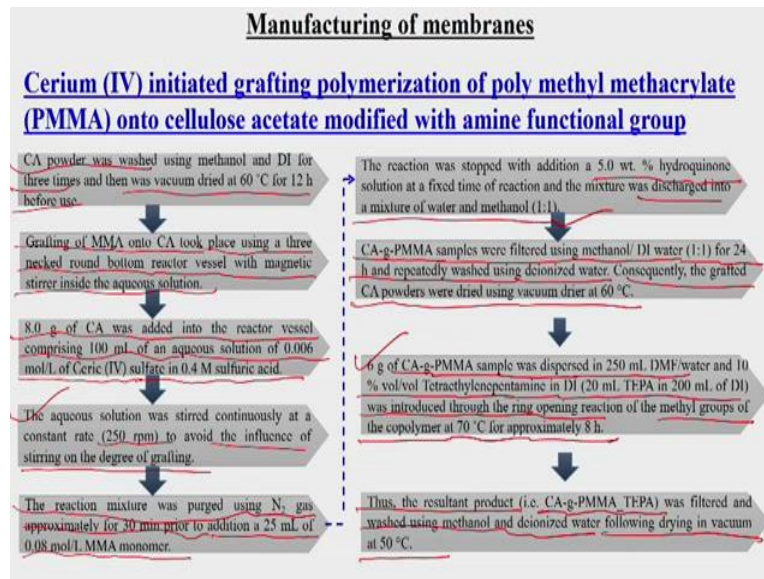
minutes, so in 30 minutes this we can say acetone DMAc and DMF this will be coming out and will be mixing with water whereas this water will be entering into this membrane film, so that actually takes place in 30 minutes. So if we allow more than that time also then after that it will not help anyway and finally we will be getting that polymeric film.

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So now this one sometimes this phase inverted cellulose acetate, PEG, TiO<sub>2</sub> membrane also can be formed. So in that case TiO<sub>2</sub> will be added during this we can say this one cellulose acetate dissolution in this acetone and DMAc and so then we can say this one like acetone DMAc solution is there. Then, we can say this one in the cellulose acetate solution we need to put some polymer additives like this PEG or PVP like this and then TiO<sub>2</sub> nanoparticles also were added and then it is mixed properly, then we can say this one we will be getting casting solution and then once it is prepared then we need to put in the glass plate and then using this casting knife or this film applicator we will be getting the film. Then it will be placed in the coagulation bath, finally we can get flat sheet membrane. So depending on the requirement we can make this one either circular or maybe we can get the rectangular membrane sheet.

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And now we can get this one cerium initiated grafting polymerization of poly methyl methacrylate (PMMA) into cellulose acetate modified with amine functional group also. In that case we can say this we can, we need to take the cellulose acetate powder that will be say we need to wash using this methanol and deionized water for three times and then was vacuum dried at 60 degree Celsius for 12 hours before this use.

Then grafting of this methyl methacrylate into cellulose acetate will take place using three necked round bottom reactor vessel with magnetic stirrer inside this aqueous solution, once this we can say solution is prepared, then 8 gram of the cellulose acetate was added into the reactor vessel comprising 100 ml of aqueous solution of 0.006 mole per liter of ceric sulfate in 0.4 molar sulfuric acid.

The aqueous solution now was stirred continuously at a constant rate of we can say 250 rpm to avoid the influence of the stirring on the degree of this grafting. Then the reaction mixture was purged using this nitrogen gas approximately for 30 minutes prior to the addition of we can say this one in a 25 ml of 0.08 mole per liter MMA monomer.

Then the reaction was stopped with addition of this 5 weight percent of this hydroquinone solution at a fixed time of the reaction and the mixture was discharged into a mixture, water and methanol of 1 is to 1 volume is to volume. Then cellular acetate grafted PMMA samples were filtered using this methanol deionized that is also 1 is to 1 volume is to volume mixture for 24 hours and repeatedly washed using this deionized water, consequently the grafted cellulose acetate powders were dried using vacuum dryer at 60 degree Celsius.

Then 6 gram of this cellulose acetate grafted PMMA sample was dispersed in 250 ml DMF water and 10 volume percent we can say this one TEPA in deionized water and that was introduced through the ring opening reaction of the methyl group of the copolymer at 70 degree Celsius for approximately 8 hours. Then the we can say this one resultant product, that is we can say this one CA grafted PMMA TEPA was filtered and washed using methanol and deionized water following drying in the vacuum at 50 degree Celsius. So this we can say this that type of polymeric membrane is formed this one for a particular application.

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**Manufacturing of membranes**

**Preparation of Ceramic Membranes**

- **Suspension preparation:** Where the starting powders are mixed with a suitable binding liquid.
- **Forming:** This includes shaping of the prepared suspension according to some predetermined method.
- **Heat treatment:** This means using high temperatures to bind the membrane particles through a sintering process.

Now we will be discussing about the preparation of the ceramic membrane, so the steps like this: suspension preparation, where the starting powders are mixed with a suitable binding liquid, so we can say it is a, that is a suspension preparation. Then we need to do the forming, this includes shaping of the prepared suspension according to that we can say predetermined method. Then heat treatment is required at the end, so this means using high-temperature to bind the membrane particles through a sintering process, okay?

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**Manufacturing of membranes**

**Common Methods**

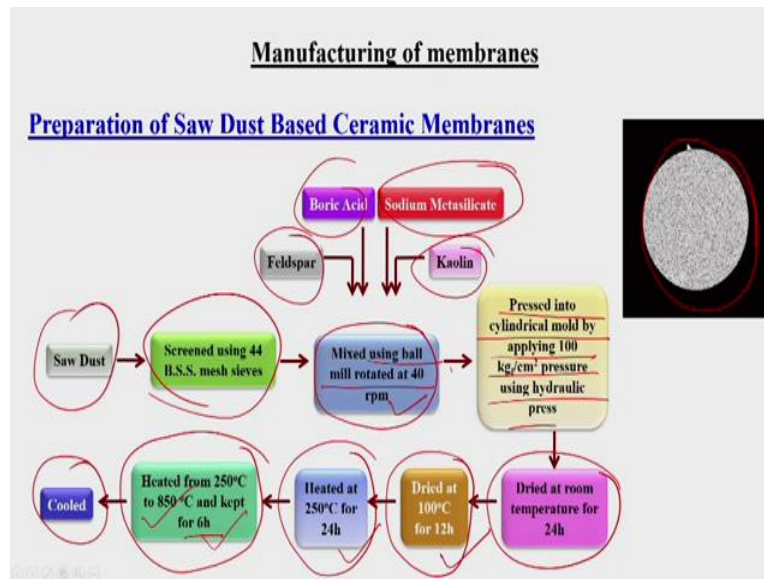
- **Paste Method:** Precursors are mixed together with water/solvent to form paste. Proper shape is provided followed by heat treatment.
- **Dry Compaction Method:** Precursors are mixed together in dried form. The resulting powder is fed into a mold to give it a proper shape. The obtained structures are finally sintered.
- **Dip Coating:** Ceramic supports are dipped in a polymer solution and then calcined.
- **Extrusion:** Ceramic mixtures are mixed with water/solvent and fed in an extruder. The resulting structures are then sintered

And the common methods are like this: so there are four common methods, one is this paste method, another one dry compaction, the third one is the dip coating method and the fourth one is the extrusion. So paste method that is also widely used like precursors are mixed together with water or solvent to form paste and then proper shape is provided followed by heat treatment.

When we will be talking about the dry compaction method, their precursors actually are mixed together in dried form, so there is no need of adding any solvent and the resulting powder actually is fed into the mold to give it a proper shape, whatever the shape we need depending on that actually we need to make the mold. Like if we want to get a particular say disc shape then the mold will be of the disc shape, if we want to make a tubular shape then we can say mold also will be the tubular shape. The obtained structures are finally sintered.

Another one is the dip coating, so ceramic supports are dipped in the polymer solution and then this one calcined or heated. And the fourth one is the extrusion, the ceramic mixtures are mixed with water or solvent and fed in an extruder, the resulting structures are then sintered, okay?

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And there is one specific we can say this common the specific application of the ceramic membrane using this saw dust based membrane. So in general for the preparation, for the generation of the membrane pores, the pore forming materials are used like some carbonates. So here the pore forming material is used as the saw dust. So there we can say this saw dust is taken then it is screened through say 44 B.S.S. mesh sieves and then it is mixed you can say this one it is using this ball mill actually rotated at 40 rpm say the saw dust is mixed with this feldspar, boric acid, sodium meta-silicate, kaolin, okay?

Then the mixture actually is pressed into the cylindrical mold by applying 100 Kg force per centimeter square pressure using this hydraulic press and then it is dried at room temperature for 24 hours, then it will be again dried at 100 degree Celsius for 12 hours, then it will be heated at 250 degree Celsius for 24 hours and then it will be heated this one from 250 to 850 degree Celsius with a particular we can say this one heating rate and it will be kept at for 6 hours and then it will be cooled and then final membrane actually will be formed like your disc shape like this.

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#### Advantages of membrane separation processes over conventional process

- ✓ 1. Physical separation process
- ✓ 2. No chemicals are used
- ✓ 3. Generally less energy requirement
- ✓ 4. Treatment of heat sensitive materials, e.g., fruit juice
- ✓ 5. Mild operating condition (operable under ambient temperature)
- ✓ 6. Almost no damage to the species under processing
- ✓ 7. No phase change
- ✓ 8. Less capital and running cost
- ✓ 9. Easy to scale up (modular in nature)
- ✓ 10. Process management simple (low man power)

And the advantages of membrane separation processes over the conventional processes are huge, so firstly we can say it is a physical separation process, then no chemicals are used and generally less energy requirement compared to the conventional separation processes, and treatment of the heat sensitive materials like fruit juice et cetera will be done, and mild operating conditions like this operable under ambient temperature, then almost no damage to the species under processing, and no phase change, and the less capital and running costs, easy to scale up and we can say this process management is very simple with the low manpower.

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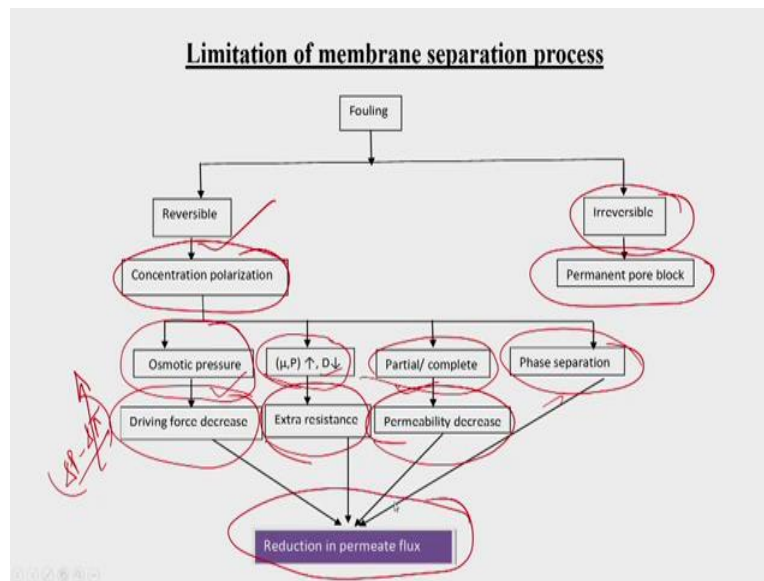
#### Limitations of membrane separation process

Despite considerable progress, a membrane process has certain limitations that prevent its widespread applicability.

- ✓ There are two primary factors namely, reversible fouling and irreversible fouling, which result in a decline in permeate flux.
- ✓ This decline is direct consequence of change in membrane permeability.
- ✓ The decline in flux is extremely rapid initially and become gradual later on.

Progress, a membrane process has certain limitations that prevent its widespread applicability. Like this there are two primary factors that is we can say reversible fouling and irreversible fouling which result in the decline in permeate flux. This decline is direct consequence of the change in membrane permeability, so with time membrane permeability goes on decreasing. And decline in flux actually extremely rapid initial and becomes gradual later on.

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So there are we can say this one the consequences of the fouling like this for reversible fouling we can say this one concentration polarization and for irreversible fouling we can say this permanent pore blocking, due to permanent pore blocking we can say permeability of the membrane is lost permanently. But for reversible fouling due to the concentration gradient we can say polarization, this osmotic pressure increases and viscosity pressure increases as well as the diffusivity value decreases and partial or complete we can say pore blocking actually starts and the phase separation also starts.

And due to the osmotic pressure we can say driving force decreases because driving force is  $\Delta P - \Delta \pi$ . As the  $\Delta \pi$  increases then we can say this one driving force actually decreases and extra resistance is generated and we can say permeability decreases, as a result we can say this one reduction in the permeate flux.

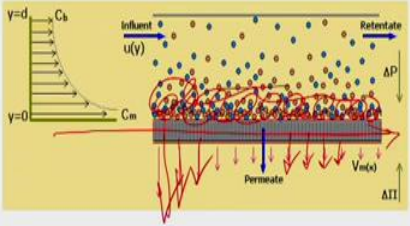


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**Limitations of membrane separation process**

**Concentration polarization:**

It is defined as the accumulation of solute of the upstream surface of the membrane.



- Accumulation of solute particles on the membrane surface  
↑ Flow resistance, ↓ Throughput, ↑ Fouling

So there are so many in terms of we can say this one concentration polarization it is defined as the accumulation of the solute of the upstream surface of the membrane, like this separation process is going on and then say permeate actually is collecting, in the beginning permeation rate is very high but with time as these solutes are deposited on the membrane surface, so we can say this one permeate flux will go on decreasing, okay? So due to we can say this one flow resistance increases, then throughput decreases, and fouling increases, okay? So this is regarded as the concentration polarization.

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***Ways to reduce concentration polarization and fouling***

It can be noted here that concentration polarization cannot be avoided completely; it can be controlled only.

- **Modification of the membrane surface**
  - Plasma treatment
  - Ion beam irradiation etc.
- **Change of hydrodynamic conditions in the flow channel**
  - Increased turbulence
  - Introduction of turbulent promoter
  - Pressure pulsation etc.
- **Change of chemical environment of the solution**
- **Application of external body force**
  - d.c. electric field
  - Magnetic field etc.

So ways to reduce the concentration polarization and fouling, so it can be noted here that the concentration polarization cannot be avoided completely but it can be controlled only, so

there are so many steps like, this modification of the membrane surface using plasma treatment or ion beam irradiation, and change in hydrodynamic conditions in the flow channel like this increased turbulence, then introduction of turbulence promoters or wires, then pressure pulsation in the pumping system. And change in the chemical environment of the solution also, then application of external body force like DC electric power supply, then magnetic field et cetera, okay.

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So, thank you very much, and in the next class we will be discussing various models and application and some design aspect.