Methods of polymeric membrane preparation

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Classification of polymeric membranes

- Symmetric membranes
  - have a uniform composition and structure throughout.

- Asymmetric membranes
  - consist of a number of layers each with different structures and permeabilities.
Classification of polymeric membranes

- **Symmetric membranes:**
  - Symmetric nonporous membranes
  - Symmetric microporous membranes

- **Asymmetric membranes**
  - Phase separation membranes
  - Solution-coated composite membranes
  - Interfacial polymerization membranes

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Symmetric nonporous membranes

- are rarely used in membrane separation processes because the transmembrane flux through these relatively thick membranes is too low for practical separation processes.
- are widely used in laboratory work to characterize membrane properties.
- Usually are prepared by solution casting.

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Solution casting

- is commonly used to prepare small samples of membrane for laboratory characterization experiments.

- An even film of an appropriate polymeric solution is spread across a flat plate with a casting knife.
Solution casting

■ After casting, the solution is left to stand, and the solvent evaporates to leave a thin, uniform polymeric film.

■ The polymer solution used for solution casting should be sufficiently viscous to prevent it from running over the casting plate.

■ Preferred solvents are moderately volatile liquids
  - low volatility requires long evaporation times.
  - Rapid evaporation of the solvent cools the casting solution, causing gelation of the polymer. The result is a film with a mottled, orange-peel-like surface.
Solution casting

- Smooth films can be obtained with rapidly evaporating solvents by covering the cast film with a glass plate raised 1 to 2 cm above the film to slow evaporation.
- Machinery used to make solution-cast film on a commercial scale:

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Symmetric microporous membranes

- have much higher fluxes than symmetric dense membranes and are widely used as microfiltration membranes.
- are used as inert spacers in battery and fuel cell applications and as the rate-controlling element in controlled drug delivery devices.

Classification
- Expanded-film membranes
- Template leaching membranes
- Track-etch membranes

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Expanded-film membranes

- are made from semi-crystalline polymers.

- In the first step of the process, polymeric film is produced by extruding polymer at close to its melting point.

- Then the film is stretched a second time, up to 300%.

- Amorphous regions between the crystallites are deformed, forming slit-like voids, 200 to 2500 Å wide, between the polymer crystallites.
Expanded-film membranes

- Typical polypropylene film membrane.
Expanded-film membranes

- Typical expanded polypropylene film membrane.
Template leaching

- This method is applied for preparation of symmetric microporous membranes from insoluble polymers such as polyethylene, polypropylene and poly(tetrafluoroethylene).
- In this process a homogeneous melt is prepared from a mixture of the polymeric membrane matrix material and a leachable component.
- To finely disperse the leachable component in the polymer matrix, the mixture is often homogenized, extruded, and pelletized several times before final extrusion as a thin film.

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Template leaching

- After formation of the film, the leachable component is removed with a suitable solvent, and a microporous membrane is formed.

- The leachable component can be a soluble, low-molecular-weight solid, a liquid such as liquid paraffin, or even a polymeric material such as polystyrene.

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Template leaching

Flow schematic of a melt extruder system used to make polypropylene membranes by template leaching.

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Track-etch membranes

- are prepared by the two-step preparation process.

- Step 1: A thin polymer film is irradiated with fission particles from a nuclear reactor or other radiation source.
Track-etch membranes

- Polymeric film is passed through a solution that etches the polymer, the film is preferentially etched along the sensitized nucleation tracks, thereby forming pores.
Track-etch membranes

- The exposure time of the film to radiation determines the number of membrane pores.

- The etch time determines the pore diameter.

- A feature of the track-etch preparation technique is that the pores are uniform cylinders and have the same diameter.
Asymmetric membranes

- are layered structures in which the porosity, pore size, or even membrane composition change from the top to the bottom surface of the membrane.
- have a thin, selective layer supported on a much thicker, highly permeable microporous substrate.
- Because the selective layer is very thin, membrane fluxes are high.
- The microporous substrate provides the strength required for handling the membrane.

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Methods of asymmetric membranes preparation

- Phase separation membranes
  - Precipitation by solvent evaporation
  - Precipitation by absorption of water from the vapor phase
  - Precipitation by cooling
  - Loeb–Sourirajan technique

- Solution-coated composite membranes

- Interfacial polymerization membranes

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Polymer precipitation by absorption of water vapor

- It is an important method of making microfiltration membranes.
- In this method, there is a combination of solvent evaporation and absorption of water vapor from a humid atmosphere.
Polymer precipitation by absorption of water vapor

- The casting solution is cast onto a moving stainless steel belt and then passes through a series of environmental chambers.
- Warm, humid air is usually circulated through the first chamber, where the film loses the volatile solvent by evaporation and simultaneously absorbs water.
- Dense skin formation is generally prevented by incorporating sufficient polymer non-solvent in the casting solution.

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Polymer precipitation by absorption of water vapor

- After precipitation in the environmental chambers, the membrane passes to a second oven, through which hot, dry air is circulated to evaporate the remaining solvent and dry the film.

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Precipitation by solvent evaporation

- One of the earliest methods of making microporous membranes.
- **Step 1:** Polymer is dissolved in a two-component solvent mixture consisting of a volatile solvent which the polymer is readily soluble and a less volatile non-solvent, typically water.

- **Step 2:** The polymer solution is cast onto a glass plate. As the volatile solvent evaporates, the casting solution is enriched in the nonvolatile solvent, so the polymer precipitates, forming the membrane structure.
Precipitation by solvent evaporation

- In general, increasing the non-solvent content of the casting solution, or decreasing the polymer concentration, increases porosity.

- Increase in incompatibility of non-solvent with the polymer results in increasing the membrane porosity.
Precipitation by solvent evaporation

- Effect of polymer concentration on the surface morphology of the PAN membranes:

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Polymer precipitation by cooling

- It is the simplest solution-precipitation membrane preparation method.
- Film is cast from a hot, one-phase polymer/solvent solution. As the cast film cools, the polymer precipitates, and the solution separates into a polymer matrix phase containing dispersed pores filled with solvent.
- Because cooling is usually uniform throughout the cast film, the resulting membranes are relatively symmetric microporous structures with pores that can be controlled within 0.1–10 μm.

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Polymer precipitation by cooling

- Low cooling rate (top image) and high cooling rate (bottom image)
Immersion precipitation technique

- is the most important membrane preparation technique.
- is part of the overall membrane preparation procedure for almost all reverse osmosis and ultrafiltration and for many gas separation membranes.
- Reverse osmosis and gas separation membranes made by this technique consist of a completely dense top surface layer (the skin) on top of a microporous support structure.
Stages of immersion precipitation technique

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Membrane formation mechanism

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Membrane formation mechanism

CBT=0 °C, Brij-58 wt.%=0

CBT=0 °C, Brij-58 wt.%=2

CBT=0 °C, Brij-58 wt.%=4

CBT=0 °C, Brij-58 wt.%=6

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Immersion precipitation membrane casting machine
Empirical approach to membrane formation by immersion precipitation technique

- Over the years several rules of thumb have developed to guide producers of solution precipitation membranes. These rules can be summarized as follows:
  - Choice of polymer
  - Choice of casting solution solvent
  - Precipitation medium
  - Using suitable additives

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Choice of polymer (What is ideal polymer?)

- Tough
- Amorphorous: If the polymer is crystalline or a rigid glass, the resulting membrane may be too brittle and will break if bent during later handling.
- Soluble in a suitable water-miscible solvent
- Glass transition temperature more than 50 °C above the expected use temperature.
- Polymers with higher molecular weights are usually preferable (more than 30000 Da).
- Polymers that meet these specifications include cellulose acetate, polysulfone, poly(vinylidene fluoride), polyetherimide and aromatic polyamides.

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Choice of casting solution solvent

- Aprotic solvents:
  - such as dimethyl formamide, N-methyl pyrrolidone and dimethyl acetamide
  - are the best casting solution solvents and dissolve a wide variety of polymers.
  - Casting solutions based on these solvents precipitate rapidly when immersed in water to give porous, very asymmetric membranes.

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Choice of casting solution solvent

- Casting solutions using low solubility-parameter solvents, such as tetrahydrofuran, acetone, dioxane and ethyl formate, result in slow precipitation and give relatively nonporous membranes.
Precipitation medium

- Water is almost always the casting solution precipitation medium.
- Some work has been done with organic solvents, particularly to form hollow fiber membranes.
- Organic-based solvent precipitation media such as methanol or isopropanol almost always precipitate the casting solution more slowly than water, and the resulting membranes are usually denser and lower flux than membranes precipitated with water.
- Generally low-temperature precipitation produces lower flux, more retentive membranes.
Precipitation medium

- Effect of coagulation bath temperature on the surface morphology of the PSF membranes:

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Precipitation medium

- Effect of coagulation bath temperature on the cross-sectional morphology of the PES membranes:

  a) 0 °C  
  b) 25 °C  
  c) 50 °C

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Precipitation medium

- Effect of coagulation bath temperature on the cross sectional morphology of the CA membranes:

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Effect of polymer concentration

Effect of polymer concentration on the surface morphology of the PAN membranes:

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Effect of polymer molar weight

- Effect of polymer molar weight on the cross sectional morphology of the PAN membranes:

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Effect of using suitable additives

- Pore former

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Effect of using suitable additives

- Increase/decrease in porosity
Effect of annealing temperature

Annealing Temperature = 70 °C
Annealing Temperature = 80 °C

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Effect of using suitable additives

- Increase in the membrane hydrophilicity
- Increase in the thermal/chemical stability of the prepared membrane

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Solution-coated composite membranes

- A thin (0.5–2.0 μm) selective layer on a suitable microporous support.
- A dilute polymer solution in a volatile water-insoluble solvent is spread over the surface of a water-filled trough.
Solution-coated composite membranes

- The main problem with this method is the transfer of the fragile, ultrathin film onto the microporous support.

- This is usually done by sliding the support membrane under the spread film. With care, small pieces of membrane as thin as 200 Å can be made.

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