Formation of poly(vinylidene fluoride) hollow fiber membranes: Kinetic and thermodynamic investigations

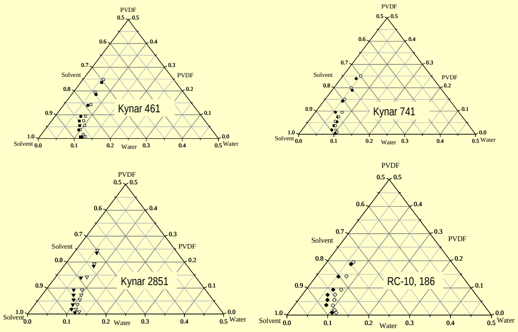
Andy C. Sun[1], Xianshe Feng[1] and Walter Kosar[2]
[1]Dept. of Chemical Engineering, Univ. of Waterloo, Waterloo, ON, Canada N2L 3G1
[2]Technical Polymers, Arkema Inc., 900 First Avenue, King of Prussia, PA, USA 19406

1. Objectives

- Thermodynamics (phase diagram) and kinetics (solvent evaporation and polymer precipitation) relevant to formation of poly(vinylidene fluoride) (PVDF) hollow fiber membranes by phase inversion.
- Fabrication of hollow fibers using different grades of PVDF to produce membranes with different structures for various applications

2. Results

- Thermodynamic data – Phase diagrams (23ºC)



- Solvent: N-methyl-2-pyrrolidinone (NMP)
- Additive: LiCl
- Open and solid keys represent the data for PVDF/NMP/water systems with and without additives, respectively.

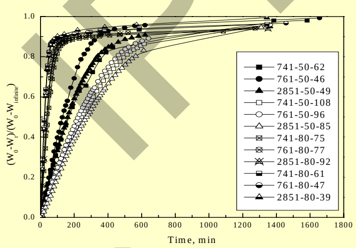
- Amount of water imbibed in polymer affects porosity of resulting membranes.
- Quantity of water to induce phase separation is different for different grades of polymers.
- Presence of additive affects water content at phase separation, and the additive thus acts as a pore controller.

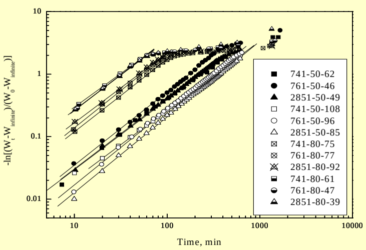
- Solvent evaporation in the "dry" step

- Solvent evaporation occurs in the "dry" step during membrane formation by the "dry-wet" phase inversion.
- Quantification of solvent evaporation rate is important in determining the length of air gap in fiber spinning.
- Experiments conducted for casting solutions with PVDF : LiCl : NMP = 18 : 3.6 : 78.4
- The numbers in the Legend represent polymer grade - temperature - thickness of cast film (μm). For example, 741-50-62 means solvent evaporation at 50°C with Kynar 741 at a membrane thickness of 62 μm.
- The solvent evaporation rate at the early stage of evaporation (which is of interest to membrane formation) can be quantified empirically by

$$\frac{W_0 - W_t}{W_0 - W_\infty} = 1 - \exp(-bt^n)$$

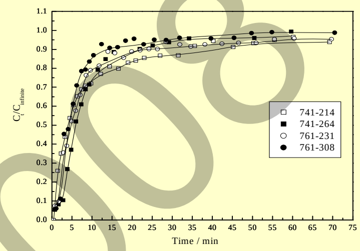
where W_0 = initial weight of the cast film
W_t = weight of the cast film at time t
$W_{infinite}$ = value of W_t at complete evaporation
b and n = empirical parameters



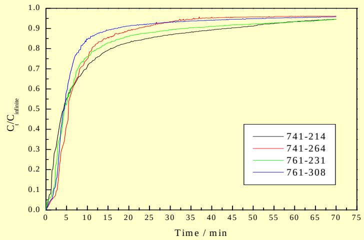


- Solvent-nonsolvent exchange and additive leaching in the "wet" step

- Solvent-nonsolvent exchange and additive leaching occur in the "wet" step during membrane formation.
- Solvent-nonsolvent exchange and additive leaching rates represent kinetics of polymer coagulation/precipitation in gelation bath, which also affect membrane structure.
- The numbers in the Legend represent polymer grade - thickness of cast film (μm).



Solvent concentration in gelation bath vs time.

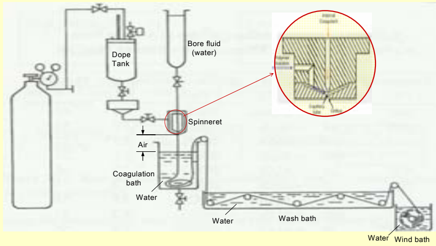


Additive concentration in gelation bath vs time.

- Diffusive exchange between solvent and nonsolvent determines rate of polymer precipitation.
- Fast additive leaching is an indication of porous structure of the membrane, and a sharp decrease in leaching rate with time indicates structural gradient in the membrane.

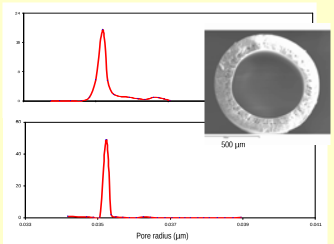
- Hollow fiber fabrication

Fiber spinning conditions
Temperature of dope solution: 50ºC
Temperature of inner coagulant: 22 ºC
Temperature of outer coagulant: 33 ºC
Dope solution extrusion rate: 2.9~5.7 ml/min
Air gap: 10 cm
Fiber take-up speed: 8.3 m/min:
Inner coagulant flow: 23.6 m/min



- Membrane characterization

- Porosity
- Mean pore size
- Pore size distribution



3. Summary

- Thermodynamics (phase diagram) and kinetics (solvent evaporation and polymer precipitation) for formation of poly(vinylidene fluoride) hollow fiber membranes were investigated.
- Hollow fibers with different structures for various targeted applications were prepared using different grades of PVDF polymers.

- Acknowledgement: Research support from Arkema Inc. is gratefully acknowledged.