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► To cite this version:

Marwen Moussa, Tojo Ivan Andrianirina, Cédric Plessis, Florent Allais, Sandra Domenek. Effect of incorporating cellulose nanocrystals on the mechanical, thermal, morphological and transport properties of nanocomposite poly(vinyl alcohol) membranes. International Meeting on Material/Bioproduct Interaction (MATBIM 2015), Jun 2015, Zaragoza, Spain. , 1 p., 2015. hal-01195514

HAL Id: hal-01195514

<https://hal.science/hal-01195514>

Submitted on 17 Oct 2022

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Effect of incorporating cellulose nanocrystals on the mechanical, thermal, morphological and transport properties of nanocomposite poly(vinyl alcohol) membranes

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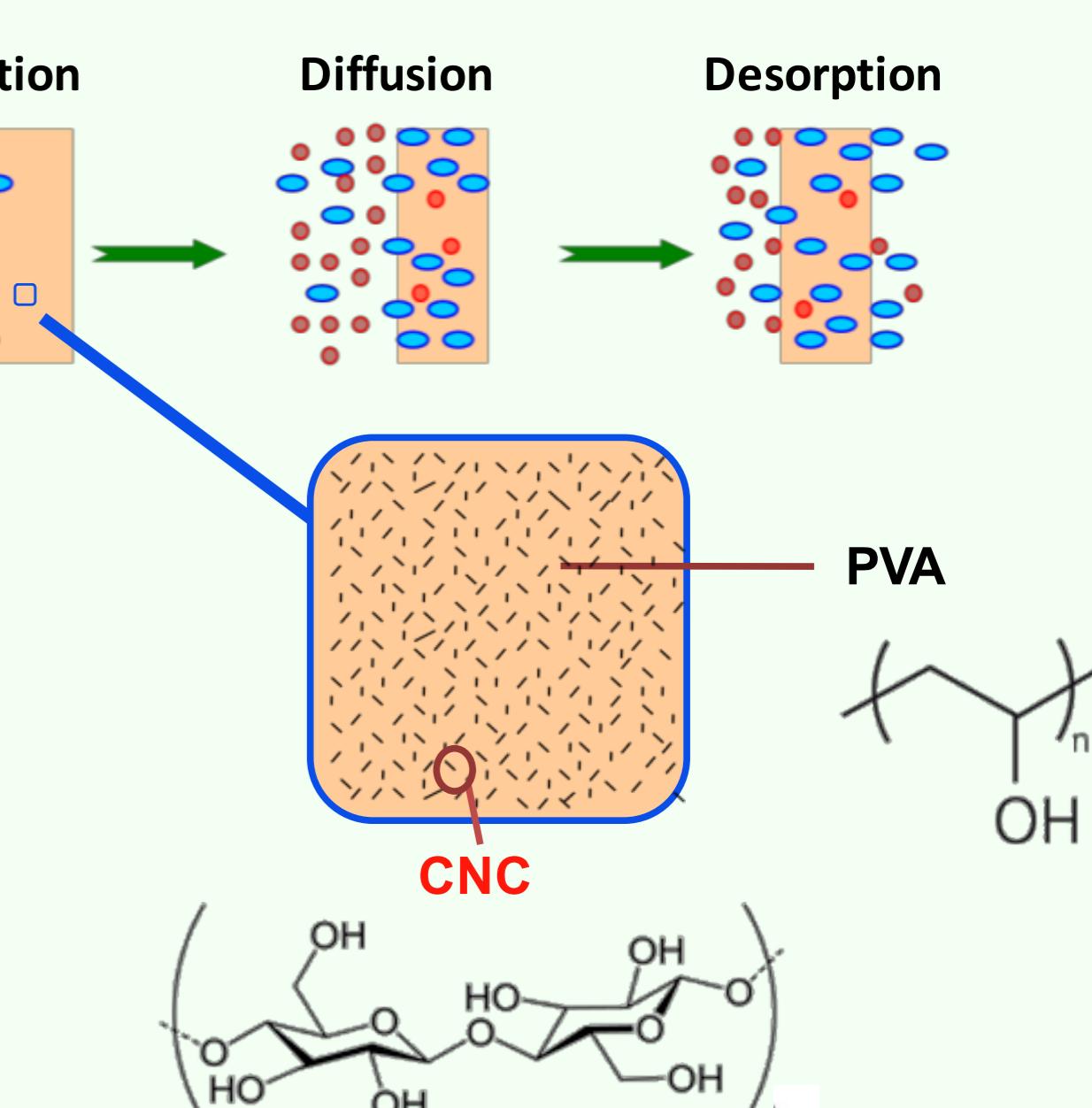
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Context

- Bioethanol dehydration using pervaporation process is considered as more flexible, cleaner and requiring less energy than azeotropic distillation and molecular sieves [1].
- During the last decade, considerable efforts have been put in the development of innovative membranes in the quest of better chemical, hydrothermal and mechanical stability and optimized perm-selectivity performances [2].
- With the increasing drive towards the valorization of environmentally friendly biopolymers, the use of cellulose nanocrystals (CNC) as nanosized reinforcements in PVA has attracted considerable attention to replace the traditional mineral fillers and take advantage of the large specific surface area and interesting mechanical properties of CNC [3,4].

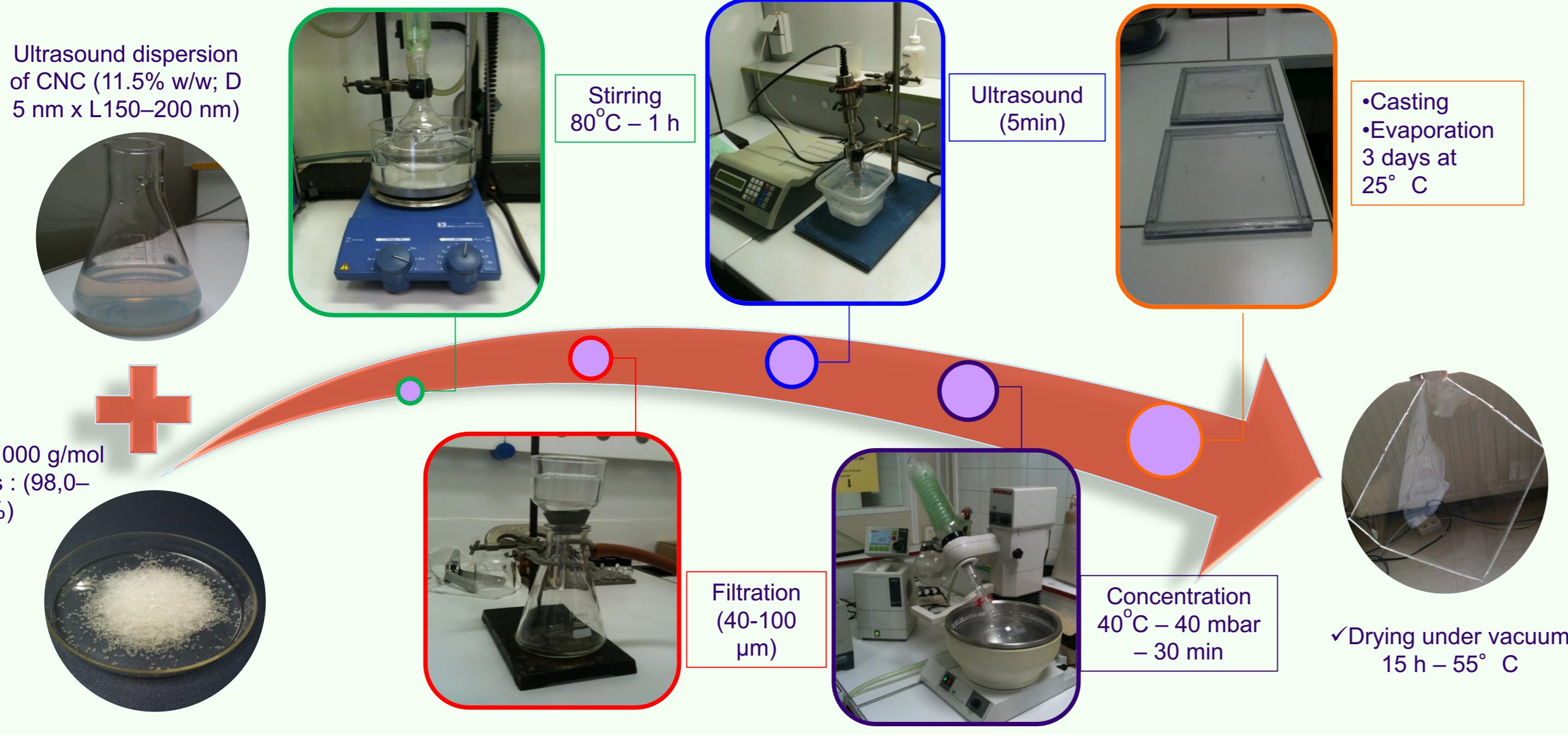
Aims

- To study the characteristics of dense nanocomposite membranes based on PVA and CNC according to the sorption-diffusion mechanism.
- Different techniques were used : thermogravimetric analysis, differential scanning calorimetry, morphological and mechanical analyses, sorption and pervaporation experiments.



Material & Methods

Membrane preparation:



Thermo-gravimetric analysis

- Heating rate = 10° C·min⁻¹
- Temperature range: 25° C → 550° C

Tensile properties

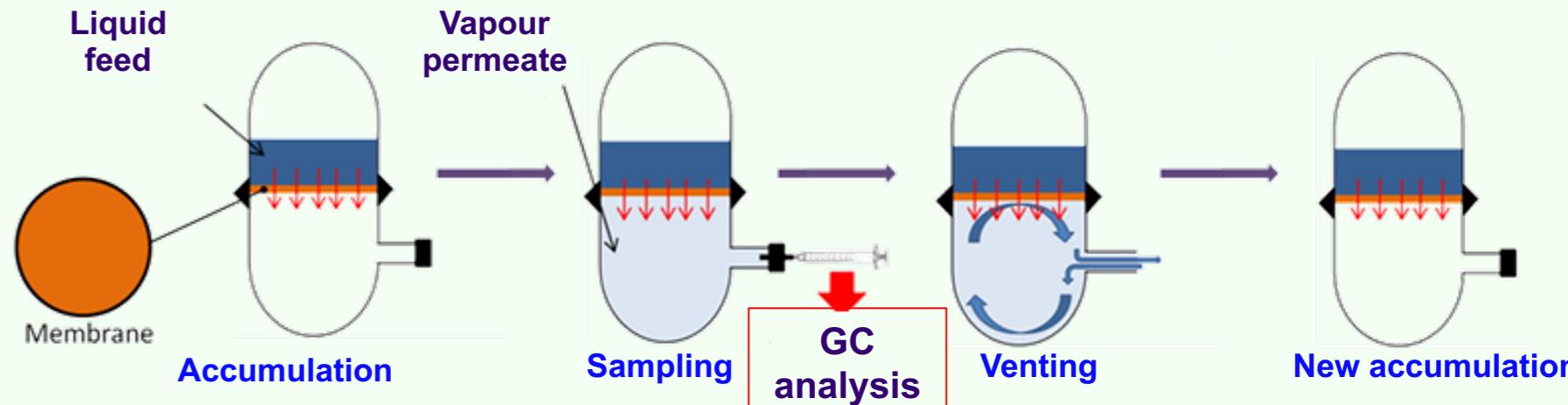
- Using the UNI ISO 527-3 standard

DSC analysis

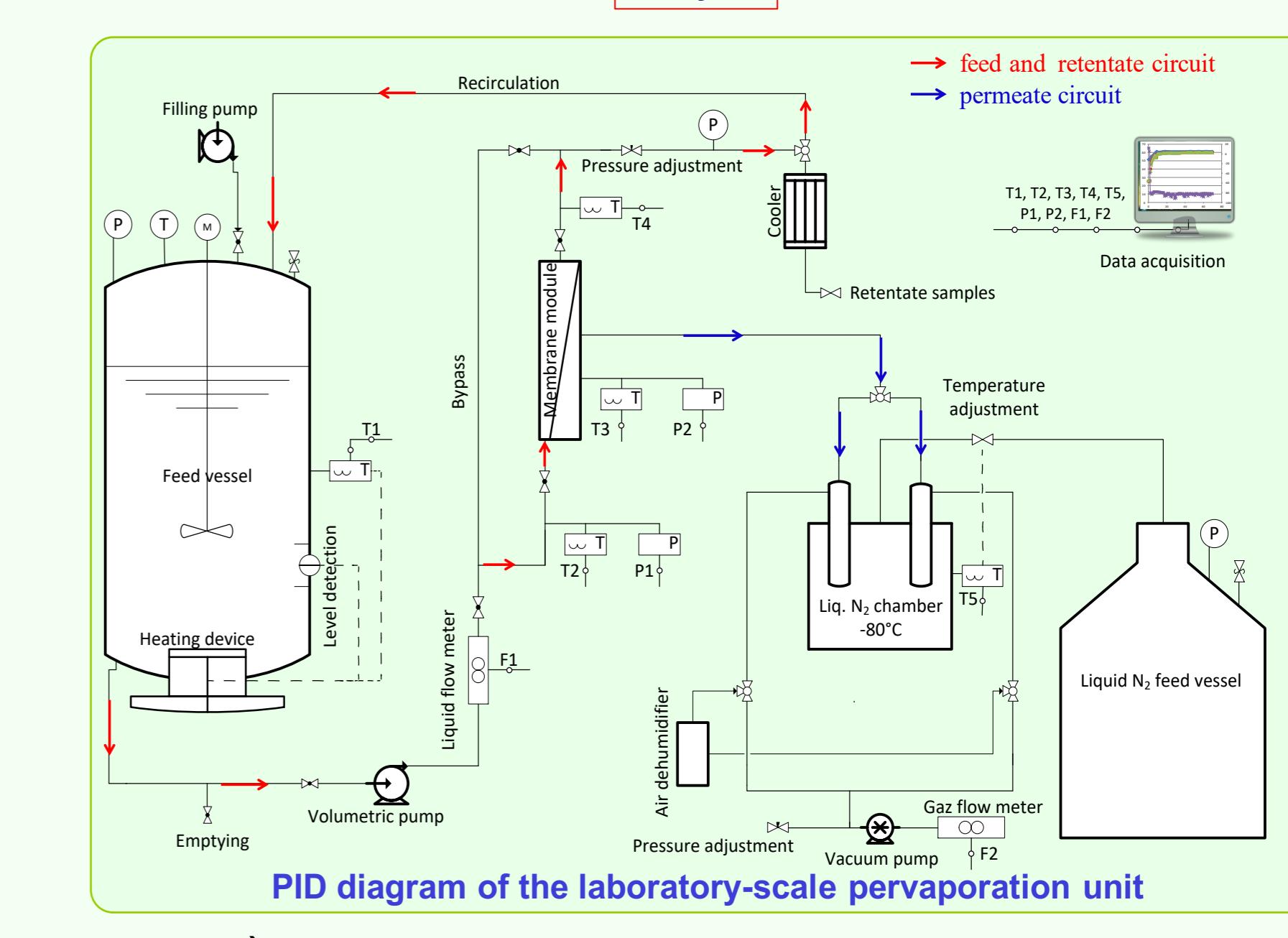
- Heating rate = 10° C·min⁻¹ (50° C → 250° C)
- Cooling at 5° C then annealing

Pervaporation experiments:

- Trials using permeation cell: performed using a laboratory-scale unit in static mode; feed temperature = 60° C; PVA and PVA-CNC membranes (flat area of 34.21 cm²).



- Pilot plant trials: performed using a pilot unit; feed flow rate = 100 kg·h⁻¹; feed temperature = 60° C; permeate pressure = 300 Pa. PVA and PVA-CNC membranes (flat area of 170 cm²).



Membrane performances:

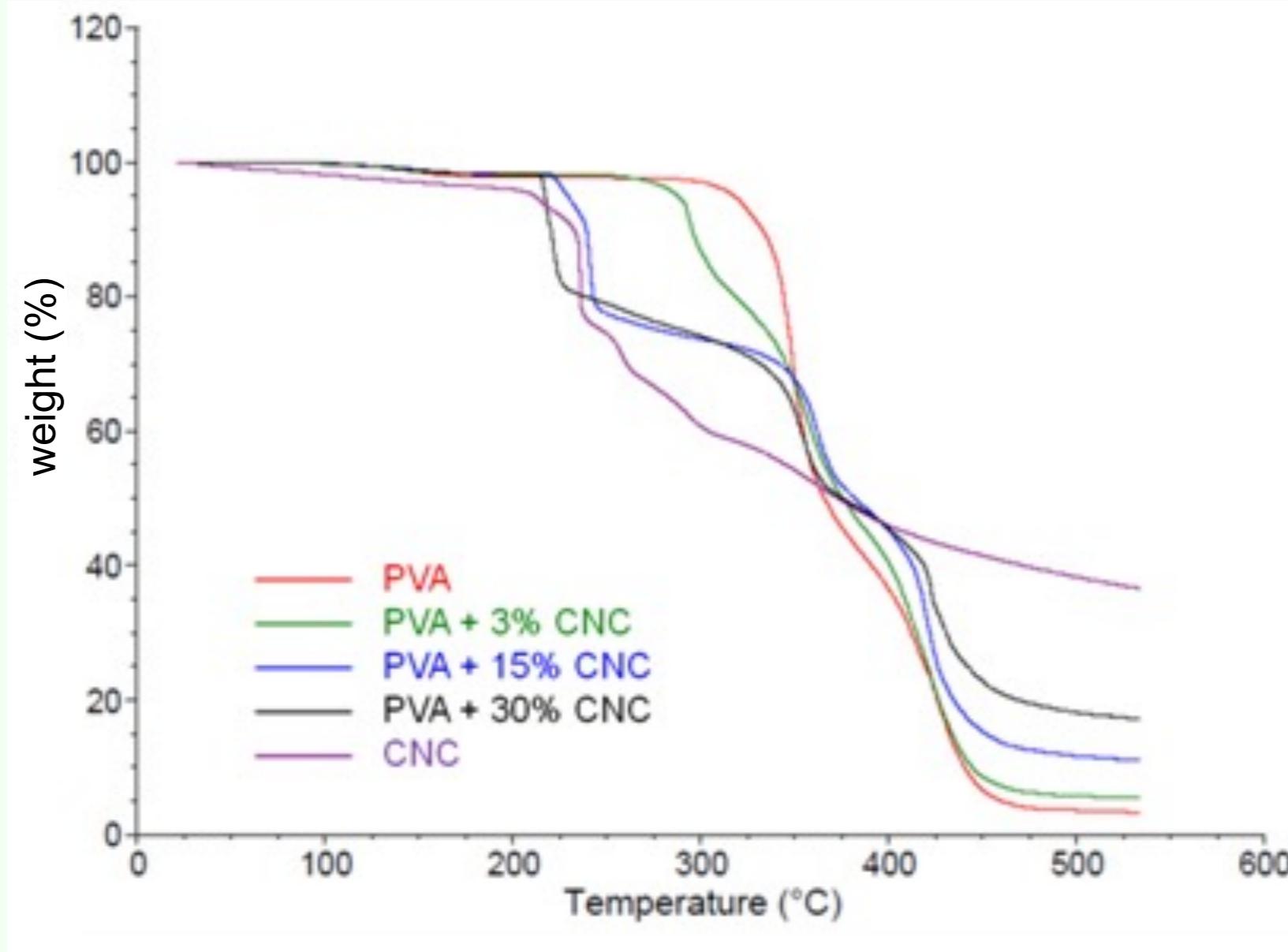
$$\text{Flux} : \begin{cases} J_i = \frac{D_i S_i}{m z} (p_{i,f} - p_{i,p}) = P_i (p_{i,f} - p_{i,p}) \\ J = \frac{A t}{At} \end{cases}$$

J (J_i) = total (partial) flux z = membrane thickness
m = permeate weight D_i = diffusion coefficient
A = membrane surface area S_i = sorption coefficient
 P_i = permeance t = permeation time

Results & Discussion

PVA membranes with CNC loading levels between 3 and 30% w/w were successfully prepared. Average thickness was about 35±5 µm.

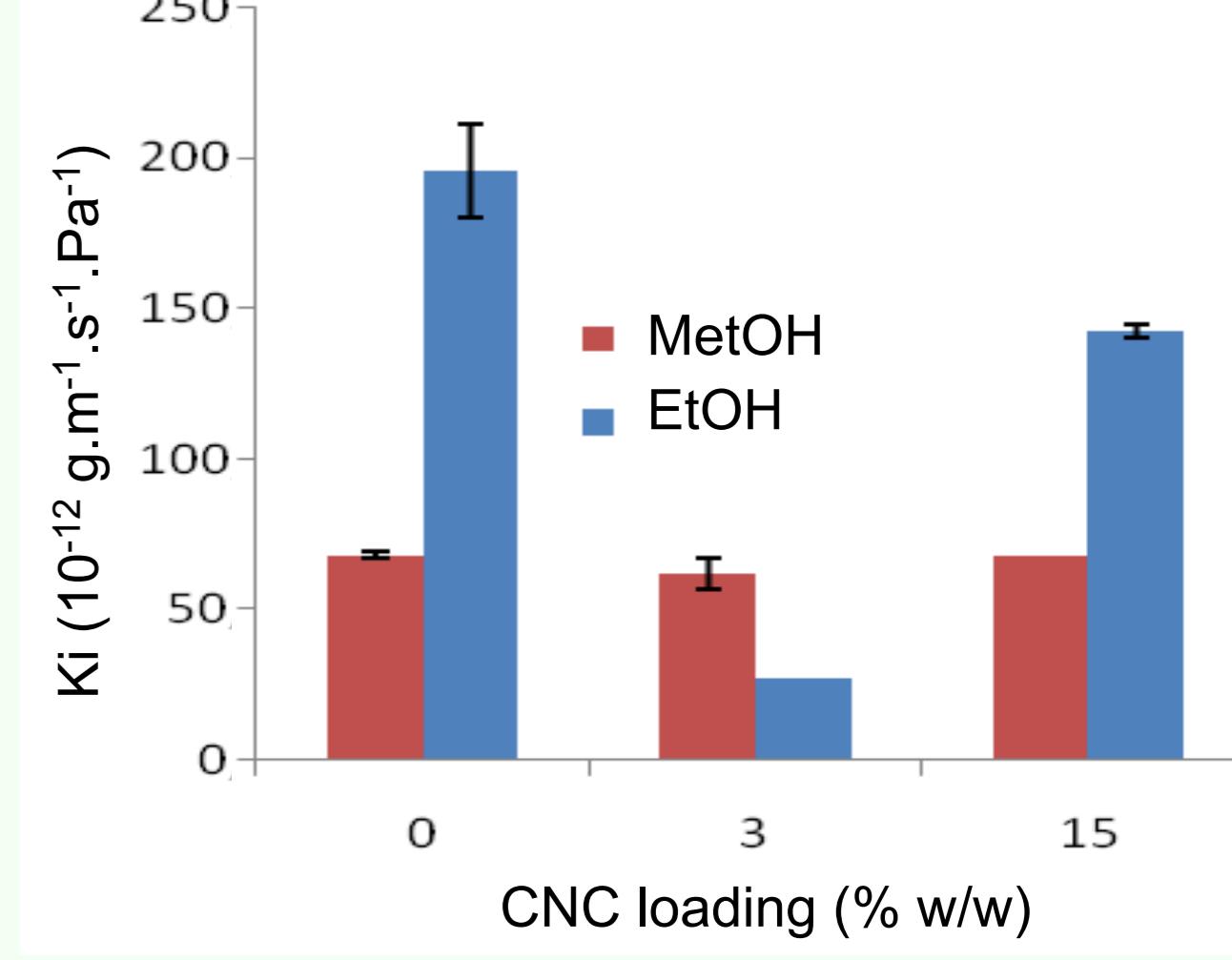
DSC results showed that CNC loading did not change Tg (about 55° C) and crystallinity degree (about 40%).



TGA analysis data show:

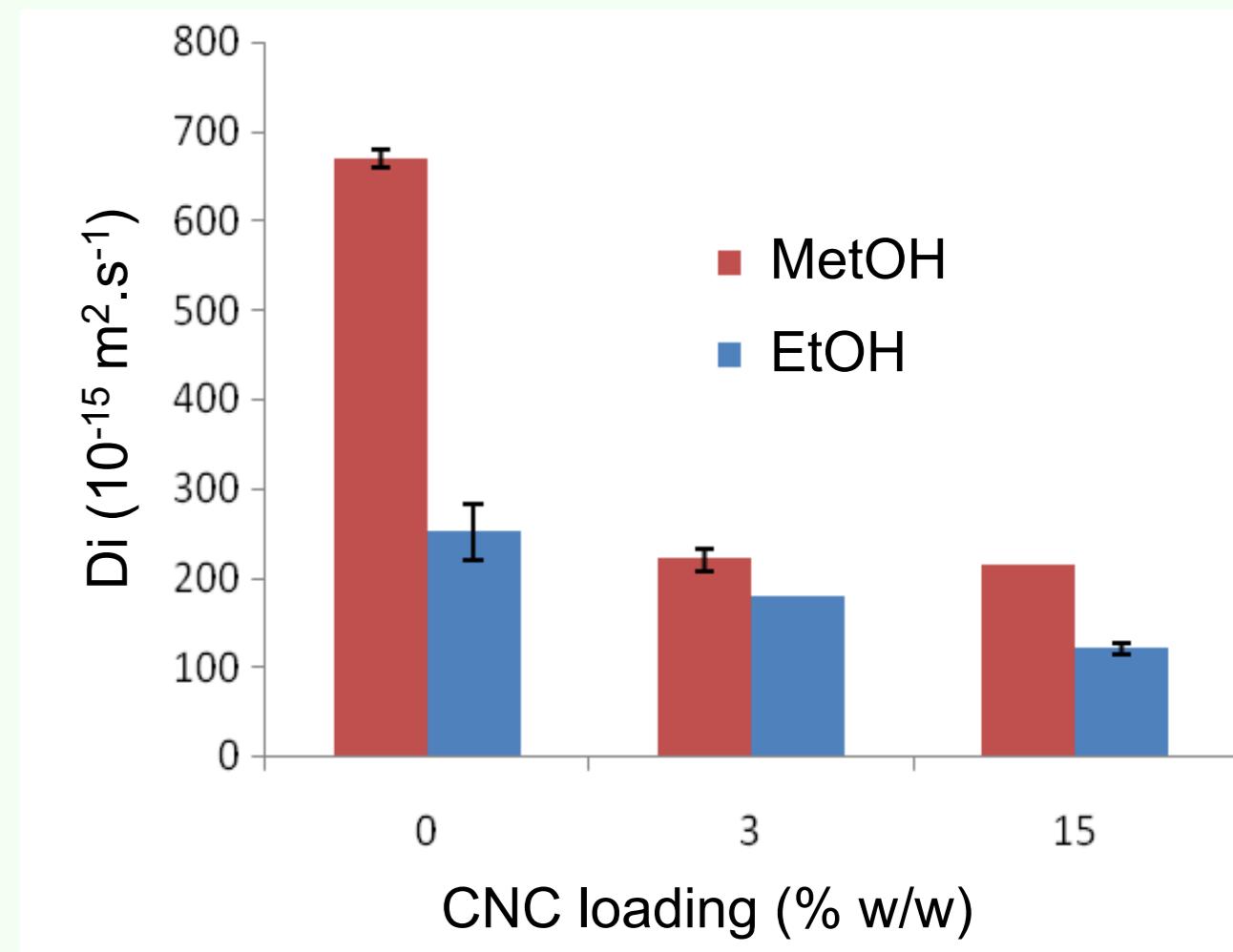
- CNC were decomposed prior to the PVA
- Thermal decomposition of PVA/CNC membranes shifted towards lower temperature

Membrane permeability decreased at 3% CNC for EtOH but remained constant for MetOH



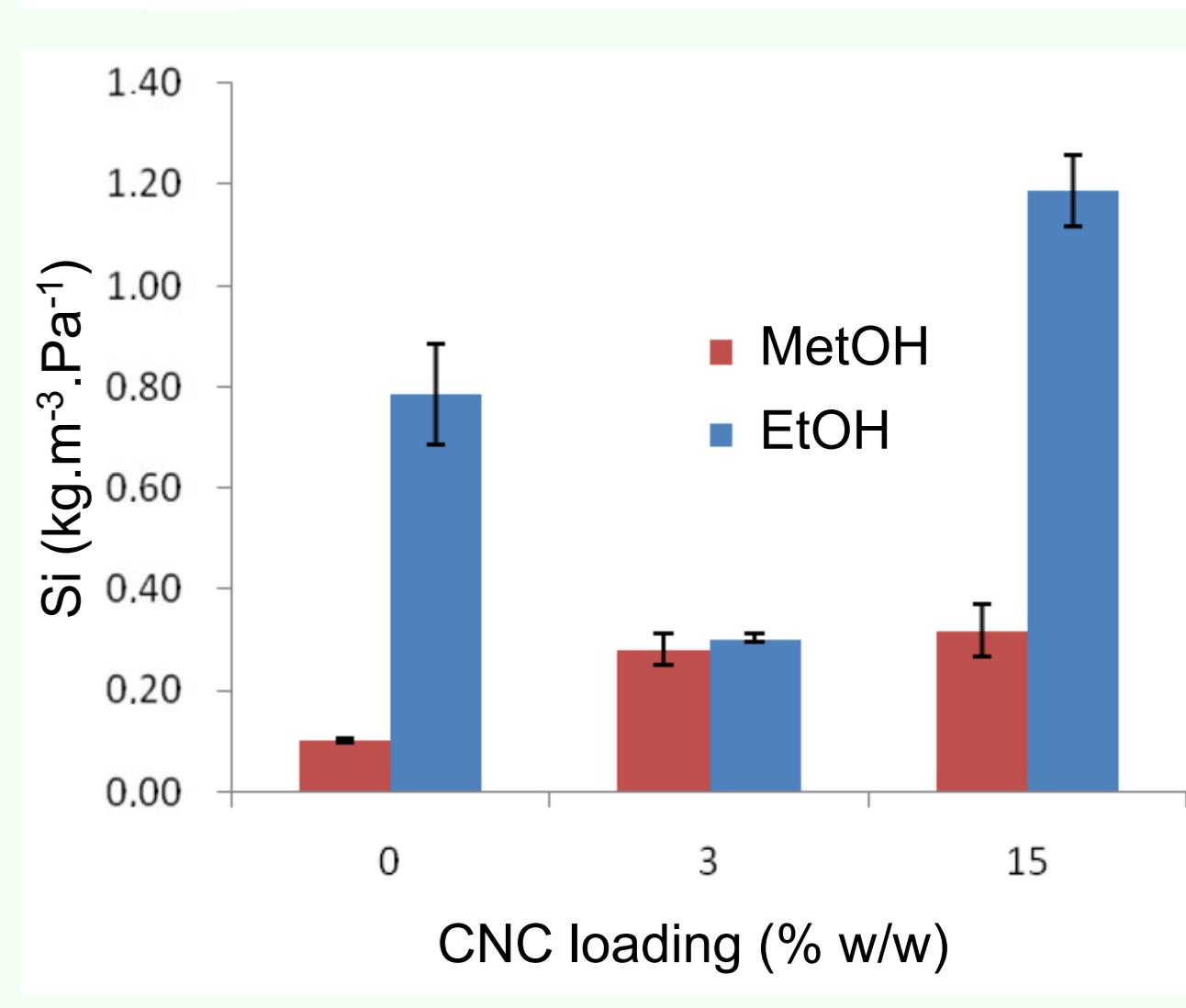
Diffusion coefficient data show:

- Higher values for MetOH than for EtOH. Indeed, methanol has smaller molecular size.
- For both EtOH and MetOH, D decreased with the increase of CNC loading:
→ tortuosity effect



Sorption coefficient data show:

- Higher values for EtOH than for MetOH except at 3% CNC loading level.
- $S_{MetOH} < S_{EtOH}$ even though MetOH is more hydrophilic than EtOH.
- S_{EtOH} was the lowest at 3% CNC: this loading level is close to the percolation threshold.
- At 15% loading level, CNC aggregates would limit the sorption capacity.



PVA membranes with 15% CNC proved to be stable during pilot plant trials. The total fluxes obtained for PVA and PVA/CNC membranes were quite the same ($9.5 \cdot 10^{-6}$ kg·m⁻²·s⁻¹) and compare well with commercial PVA membranes.

Conclusion & Prospects

- CNC allow for increase of mechanical stability of PHV membranes
- Optimization of CNC/PVA permeability and long term stability by adapting CNC content
- Reactive CNC surface allows for surface grafting to obtain higher compatibility

	MW (g.mol ⁻¹)	Hydrophobicity (Log P at 25°C)
Ethanol	46.07	-0.14
Methanol	32.04	-0.63
Water	18.02	--

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