Hybrid organic solvent nanofiltration membranes on ceramic and polymeric supports

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September 2013
ECN-L--13-067

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EWM 2013

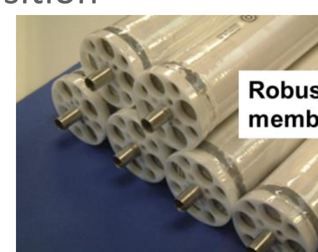
Saint-Pierre d'Oléron

4 September 2013

Contents

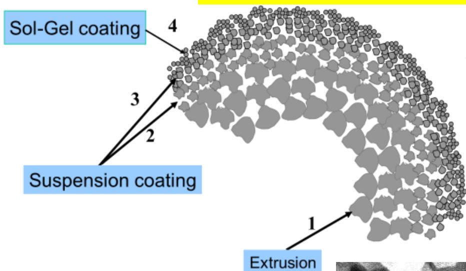
Introduction/background

- Wish for organic solvent stable NF membranes: sharp MWCO 200-500 Dalton
  - Now available: polymeric, ceramic, porous/non-porous, asymmetric, integrally skinned composites
  - No swelling, predictable and stable (but tunable) flux
  - Wide range of solvents (alcohols, ketones, aromatics, aprotics, solvent + water)
  - Cheap + easy to produce
- Our approach: apply solvent stable HybSi® (organic-inorganic layer) on polymeric support
- Project consortium:
  - ECN: HybSi membranes and sol-gel/liquid phase deposition
  - Solsep: membrane + SW module producer, liquid phase deposition
  - TU Eindhoven: (PE)CVD technology/gas phase deposition
  - FujiFilm: membrane producer, roll-to-roll technology
  - Arkema: end-user

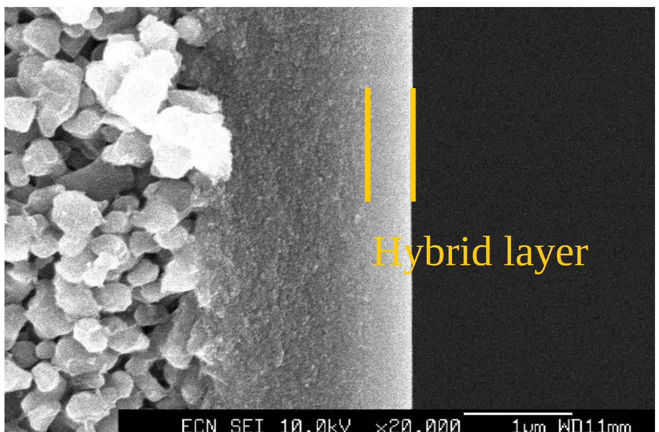


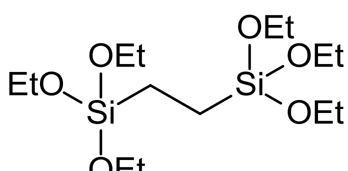
Robustness includes membranes and elements

HybSi® and hybrid membranes



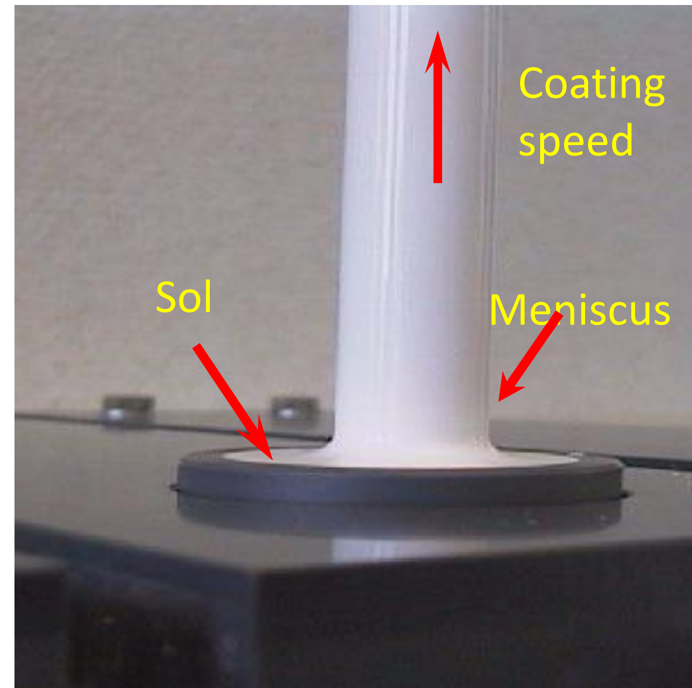
Sol – gel technology





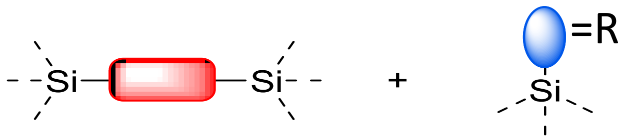
BTESE

Coating step



HybSi®
Pervaporation Membranes

HybSi® and hybrid membranes



BTESE + RTES with R = CH_3, C_3H_7, C_6H_{13}, $C_{10}H_{21}$

- R=None — Water selective (=ECN licenced pervaporation membrane)
- $R=CH_3$
- $R=C_3H_7$
- $R=C_6H_{13}$
- $R=C_{10}H_{21}$

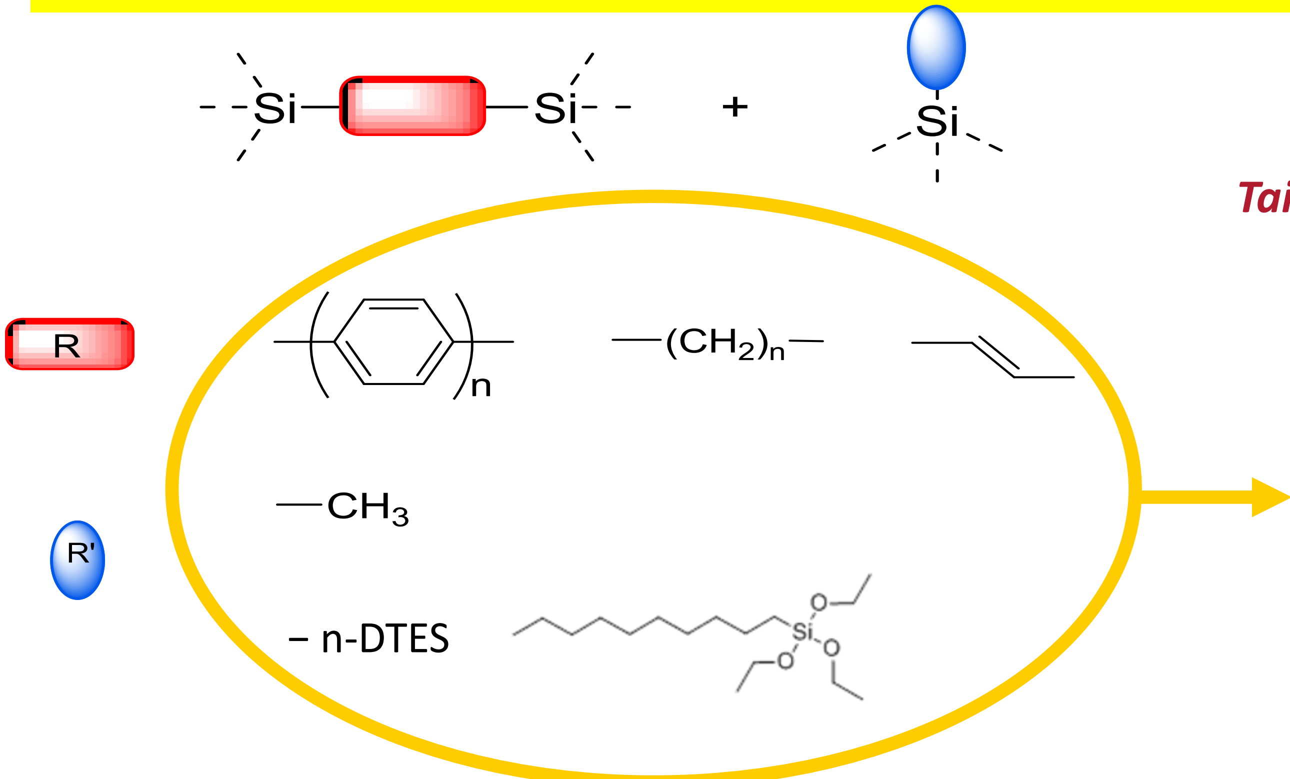
  Transition (developed)

- R=other — Organic selective (aimed for)

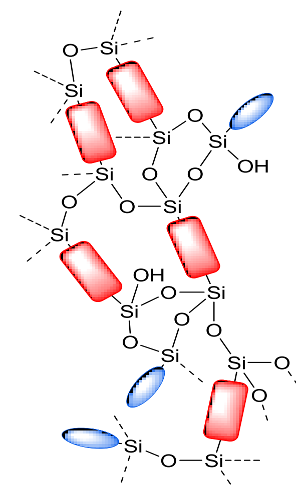
Increasingly hydrophobic

OSNF membrane preparation and results

HybSi® and hybrid membranes: OSNF



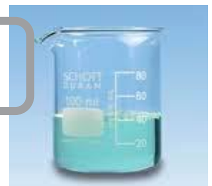
Tailored network

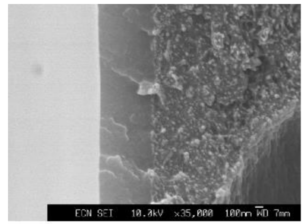


Apply on polymeric supports

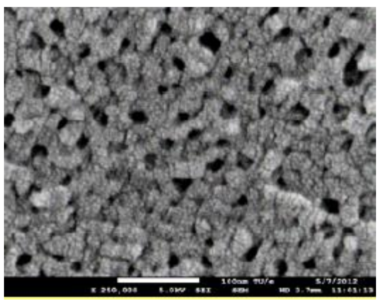
Block scheme of membrane preparation + testing

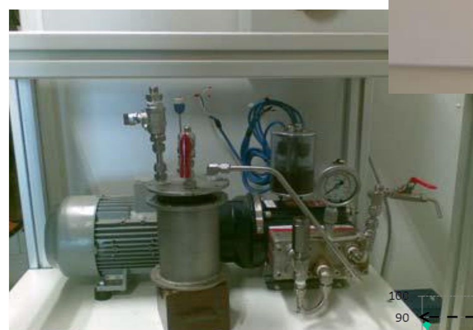
Wet phase route



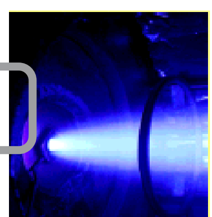


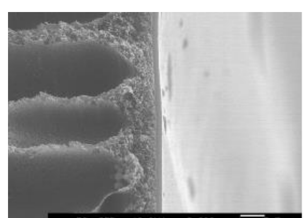
PI1109-0.3 (590 nm)



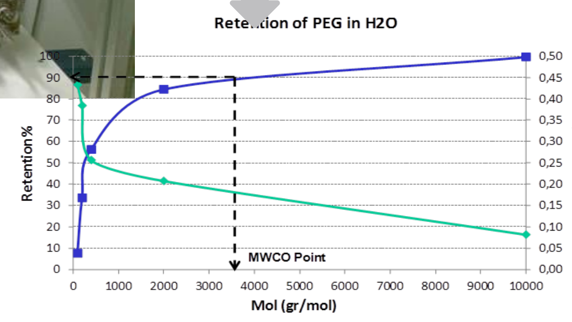


Gas phase route



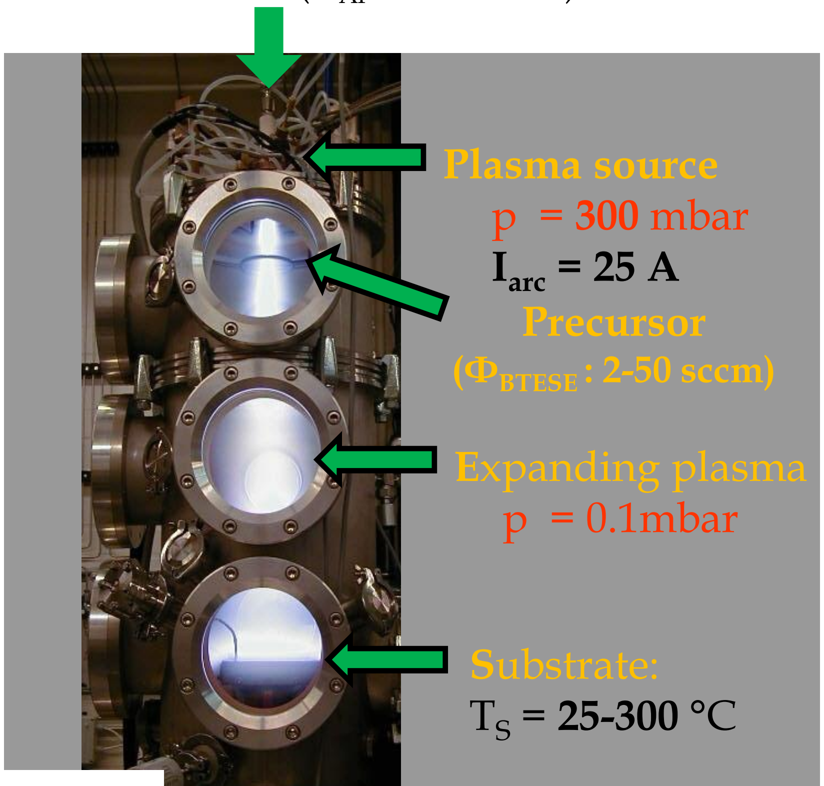


B (240 nm)



Gas phase deposition

Ar (Φ_{Ar}= 1200 sccm)



Organosilicon/ Ar Plasma chemistry

1- Charge exchange reaction

$$M + Ar^{+} = M_1^{+} + Ar$$

but also $M + Ar^{+} = M_1^{+} + M_2 + Ar$

2- Dissociative recombination reaction

$M^{+} + e^{-} = M_3 + M_4$

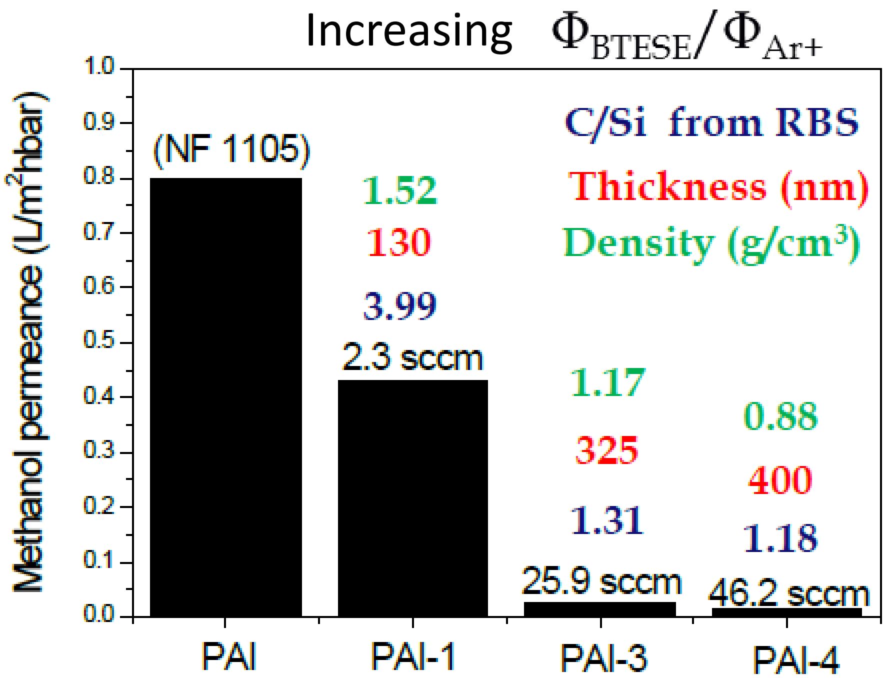
M_2, M_3 and M_4 are radicals

M: Organosilicon precursor

* sccm: standard cubic centimeter per minute

Gas phase deposition

First results

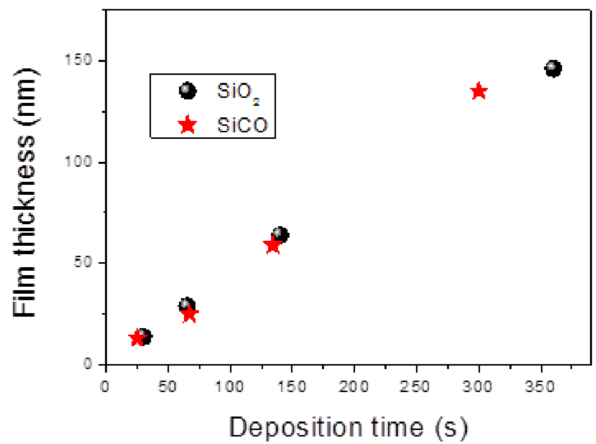


- Very low methanol permeance (too dense films)
- Partial decolorization of Methyl red (MW:269) in methanol

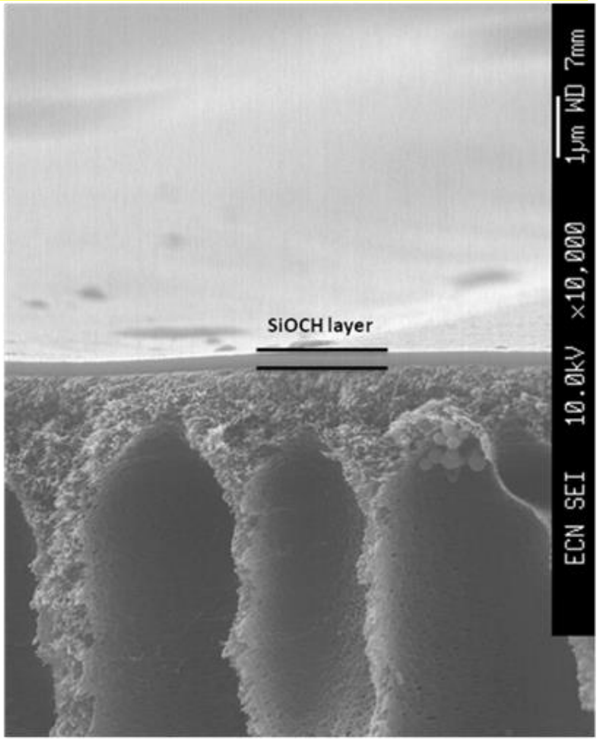
Gas phase deposition

Optimizations

- More open sublayer
- Optimize sublayer vs. top layer thickness



- Improve film porosity
- Use of gutter layer: PDMS gave best results



Cross-sectional SEM image of the polyamideimide-supported hybrid silica layer

Gas phase deposition

- Permeances of plasma deposited BTESE on ultrafiltration membrane sublayer with PDMS as gutter layer: need for smooth surface
- PAI-1, PAI-3 and PAI-18 refer to different PE-CVD conditions. PDMS is the reference membrane, without BTESE (R=retention)

Solvent	Solute	Mw	PDMS (l/m2hrbar)	PAI-1 (l/m2hrbar)	PAI-3 (l/m2hrbar)	PAI-18 (l/m2hrbar)
Methanol			0.2	0.06	0.05	
Hexane			8	0.02	0.05	
Toluene			12	0.1	005	0.47
	Sun flower oil	900	7 R=33%	0.04 R=0%	0.02 R=42%	0.14 R=100%

Promising results in toluene

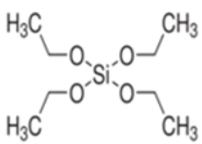
Gas phase deposition

There is pervaporation performance!

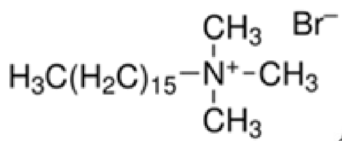
Membranes	WF (wt %)	α (H2O/BuOH)	Water Flux (kg/m^2 h)	T(^oC)
PVA ('industrial standard')	5	<200	< 1.5	100
This work (Polymer-supported hybrid silica)	5	1133	2	95
Hybsi® (Ceramic-supported hybrid silica)	5	4700	3.6	95

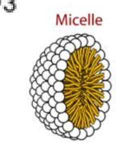
Sol-gel - wet phase deposition

On ceramic supports

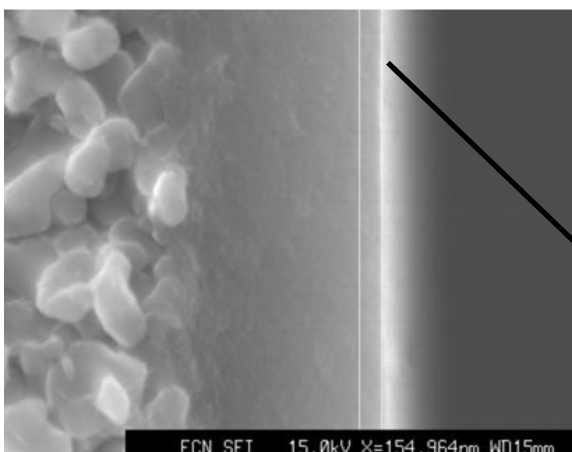


TEOS



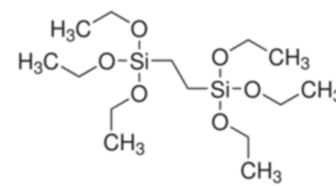


CTAB
(a surfactant)

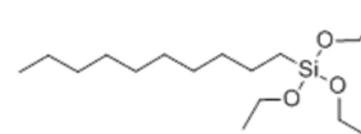


TEOS + CTAB
membrane layer
Thickness: 150 nm

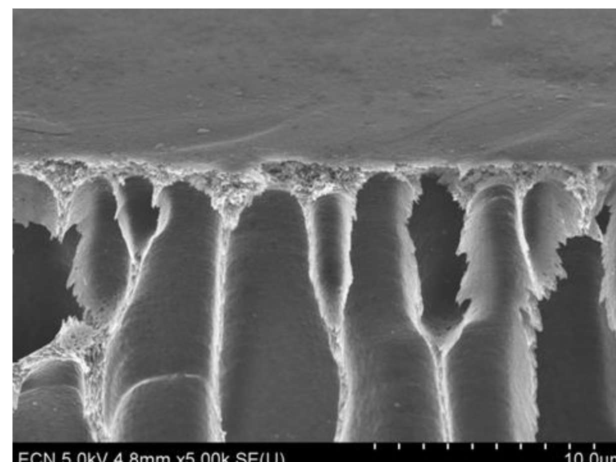
On polymeric supports



BTESE



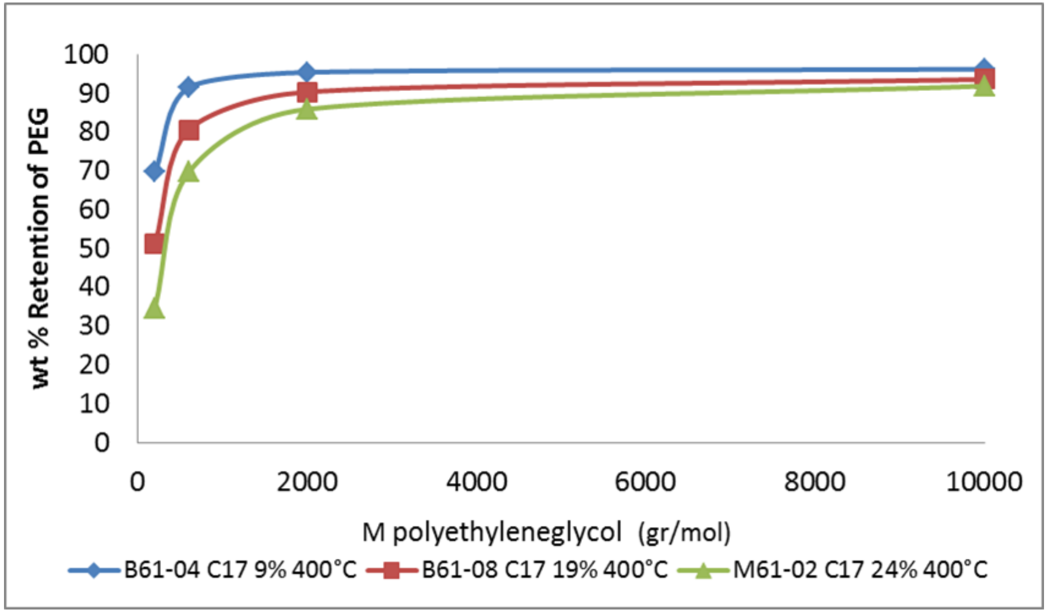
n-DTES



BTESE + n-DTES
membrane layer
Thickness: 115 nm

Sol-gel - wet phase deposition

On ceramic supports: retention of PEG molecules in water



More template leads to higher cut off values and higher flux.
Fluxes are still low.

Membrane code	Permeance (l/m²hrbar)	Layer thickness (nm)	MWCO (Dalton)
B61-04 C17 9% 400°C	0.027	270	500
B61-08 C17 19% 400°C	0.075	175	1800
M61-02 C17 24% 400°C	0.107	270	6500

Sol-gel - wet phase deposition

On polymeric supports

			HybPON 0.3M BTESE+nDTES		Solsep 010206
Solvent	Solute	Mw	Permeance (l/m^2hrbar)	Retention	Permeance (l/m^2hrbar)
Methanol			0.5		
	Methyl Red	269	0.3	Adsorption	0.8
	Bengalerose	1018	0.1	yes	
Toluene			0.3		0
	Sun Flower oil	900	0.1	100%	
Acetone			1.3		2
	Sun Flower oil	900	1.2	33%	1

Promising retention in toluene, permeance still rather low

Scale up/outlook, summary and conclusions

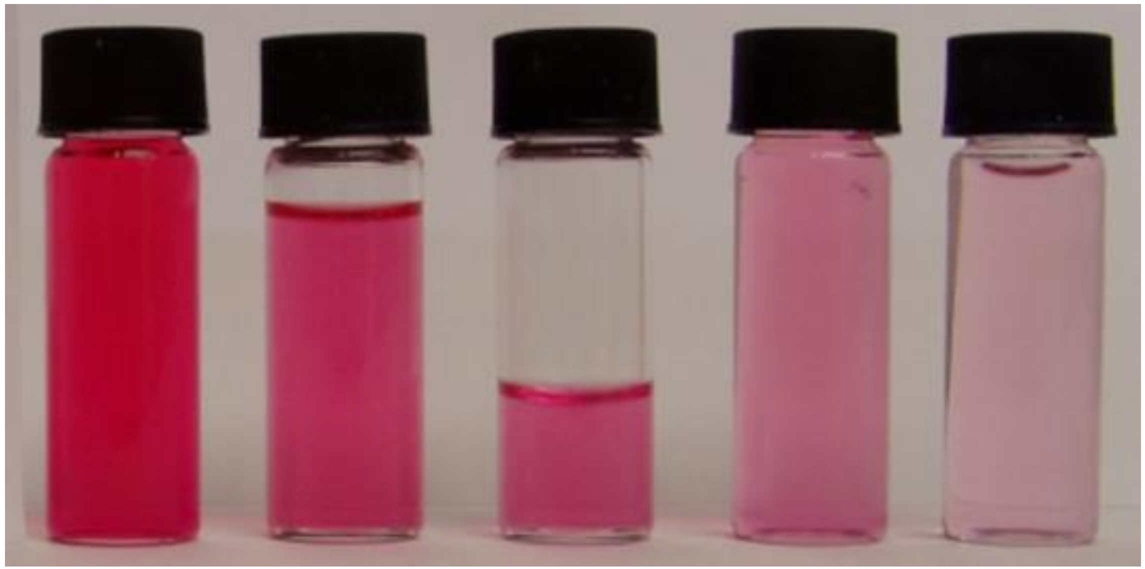
Scale up and outlook

Wet phase: BTESE + n-DTES membranes made via dip coating and roll coating

Solvent	Solute	Mw	0.3M dip (l/m^2hrbar)	Roll coating (l/m^2hrbar)
Toluene			0.23	4.0
	Sunflower oil	900	0.06 R=100% N=2	0.6 R=76% N=4

Roll coated composite membrane performance acceptable for a first trial

Colorful summary of results



Filtration of methyl red (molar mass = 269) in methanol for different membranes. From left to right: feed, permeate for a polymeric UF membrane, a 100 nm thick gas phase deposition membrane, a 130 nm thick gas phase deposition membrane, a liquid phase deposition membrane (BTESE + nDTES)

Conclusions

- Hybrid ceramic precursors can be tailored towards NF membranes
- It is possible to apply these membrane layers on polymeric supports (cost effective) via - at least - 2 methods
  - Via gas phase deposition good pervaporation membrane: first time seen and big step forward
  - Via wet phase: pore size and affinity can be tuned
  - Both methods: good retention properties (< 900 Dalton) in some solvents: toluene!
- This opens up roll – to – roll and spiral wound manufacturing of hybrid OSNF membranes on polymeric supports

Thank you for your attention

This presentation is part of the project ‘HybPON’ performed by ECN, TU Eindhoven, Solsep BV, Arkema and FujiFilm.

The project was sponsored by the Dutch Ministry of Economic Affairs via the EOS-LT program managed by Agentschap NL.

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