Towards a truly hybrid membrane for organic solvent filtration

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@OSN Aachen 2013

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SolSep BV

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- TUE
- Solsep BV

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SolSep BV

SolSep BV

SolSep is an independent membrane producer (since 2000)

Focus on organic solvents

- mainly organic solvents
- some aqueous with x% solvent

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- produces membranes and SW elements
- not an equipment builder
- helps with development of applications (Organic solvent)

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Proven robustness in solvents

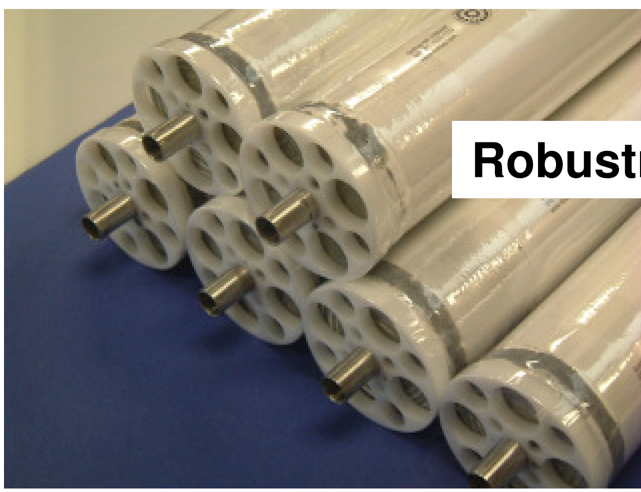
Technical grade solvents - may include water

All technical solvents:

hexane,ethyl acetate, acetone, MEK
ethanol, toluene, benzene, propylene oxide…..

aprotic solvents NMP, THF, DMF, DMAc

water plus 10-20% solvent (EA, EthylE, polyether)



Robustness includes membranes and elements

SolSep Membranes

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Solvent systems	Ultrafiltration		Nanofiltration					
	010104	010706	010306	010206(S)[1]	030306	080105[2]	030705	030306F
Alcohols	X	X	X	X	X	X	X	X
Esters	X	X	X	X	X			
Ketones	X		X		X	X	X	X
Aromatics	X		X		X		X	X
Chlorinated			X	X	X	X		X
Red.Atmos.			X		X			

1. stabilized version for e.g aprotics
2. mainly for decolorization

Applications (decolorization-color harvesting)

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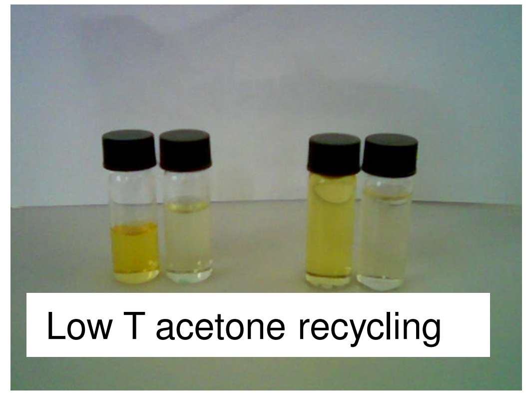
-Membranes are part of the solution

-Often combination of techniques

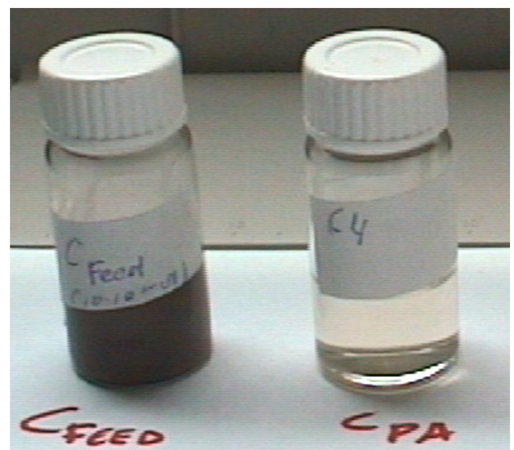
Fractionationation of colors

In acetone and ethylalcohol

Natural colorant harvesting



Low T acetone recycling



Recovery of ethyl acetate

Processing examples

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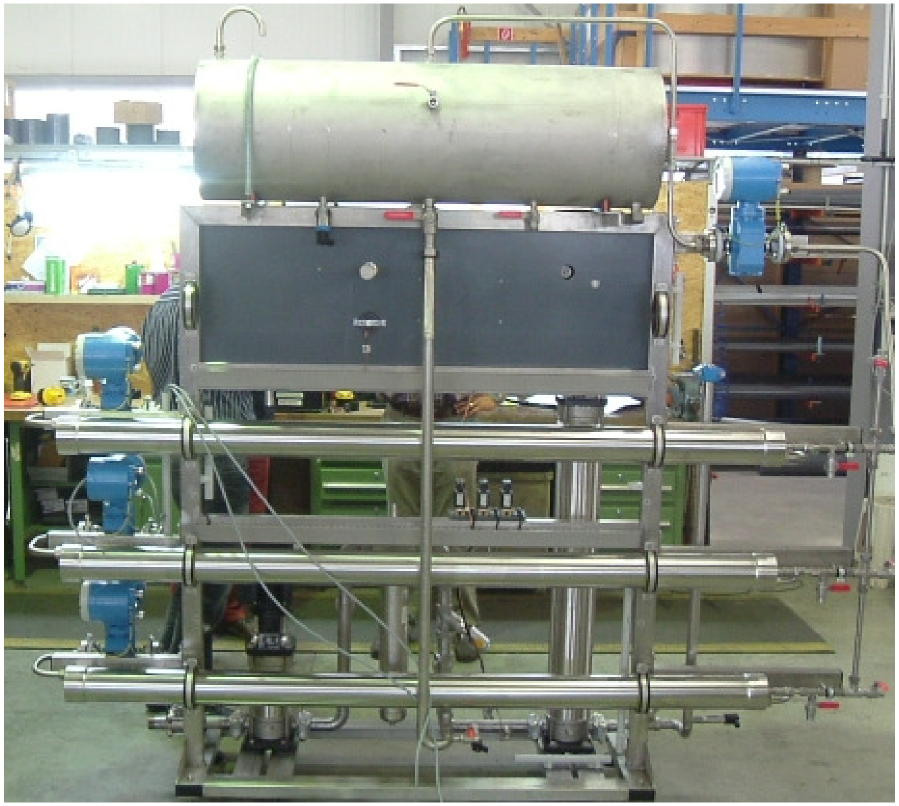
Output 5-100 l/h



Output 200-2000L/h

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NF Membranes for organic solvents:
what's there now

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Polymeric membranes

Ceramic membranes

Porous

Non-porous

- asymmetric

    integrally skinned
    composites

What could be improved..?

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Better agreement “expected” and real separation

partly not possible: see membranes in aqueous systems

partly improved by forecastable behavior

Causes of uncertainty (list is not complete…)

variable interaction in solvent-solute-membrane - swelling

pore-molecular “size” aspects

filtration/process aspects (CP, fouling)

Can we solve the problems?

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Probably only partly

but we can check what is possible in some areas.

In this work: materials

combination of polymeric and ceramic

Lead: “Hybsi®” concept for pervaporation

HybSi® was developed for pervaporation (dehydration)

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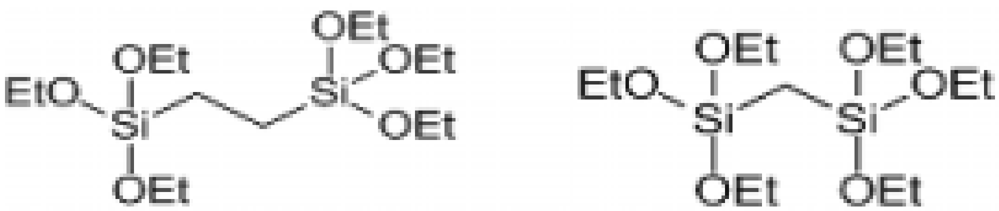
HybSi ® = organic-inorganic hybrid silica-based amorphous material



BTESE BTESM

Very tight microporous materials
as such not useable as NF membrane

But –expected- to be very stable (in solvents)

“glassy polymer” were interaction playes an important role

“Common” silicium containing polymers

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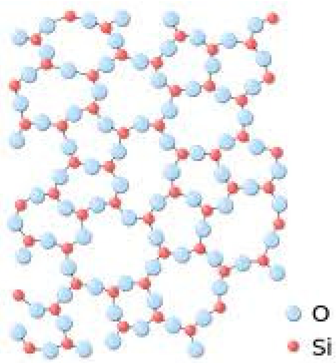
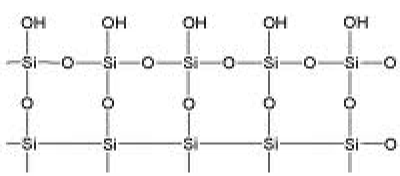
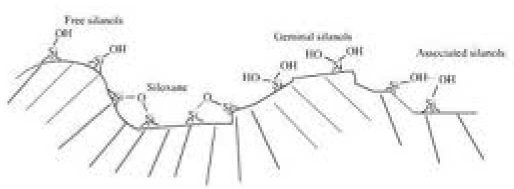
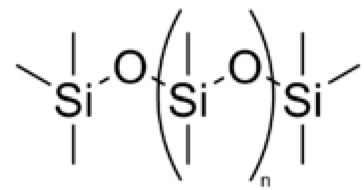
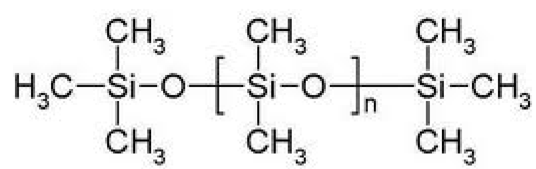






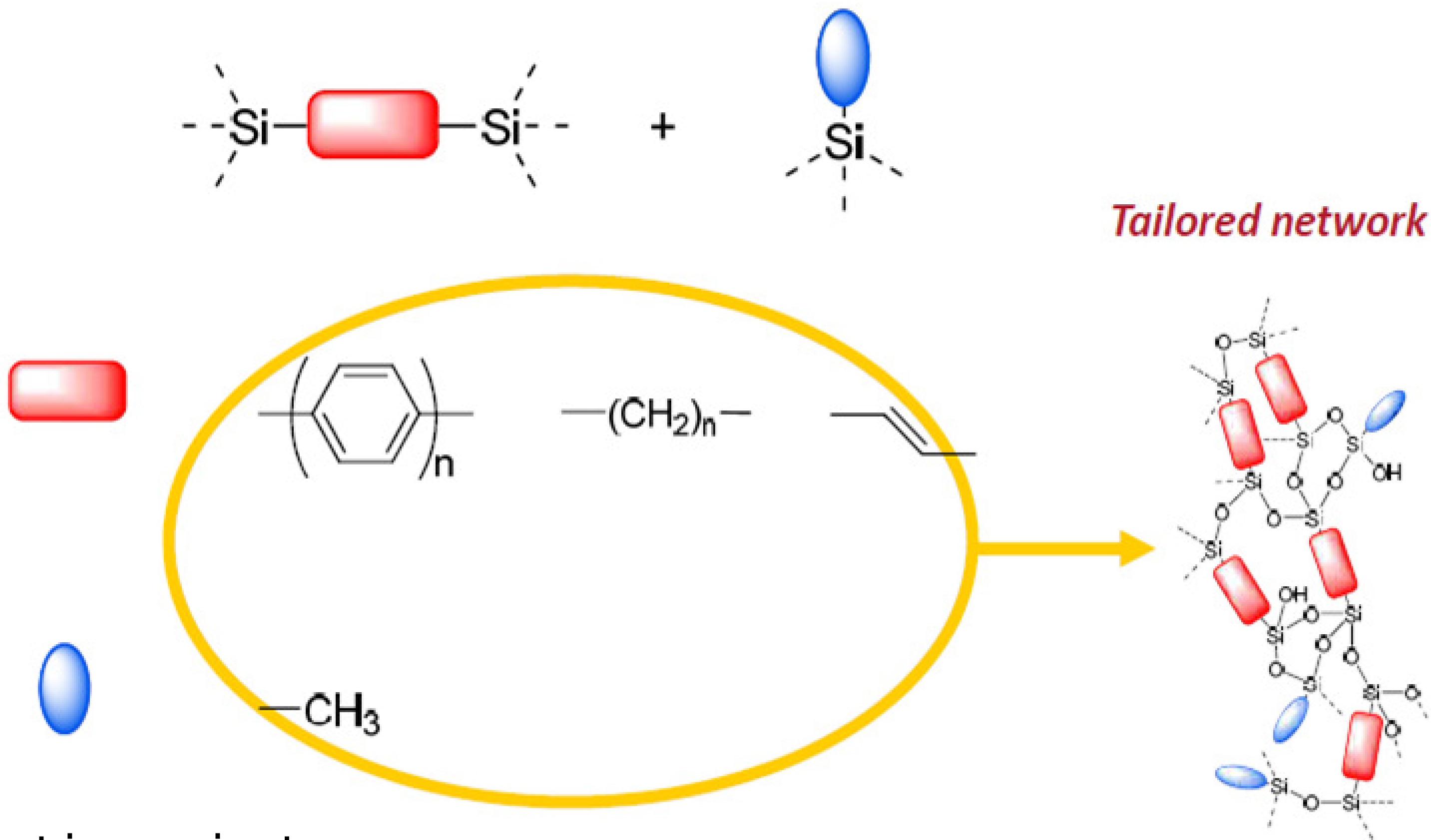
silica particle





siloxane

Precursors



Concept in project:

- HybSi types on polymeric substrates>>>scale up to SWEs
- vary blocks
- use two deposition technologies

HybSi® in Pervaporation

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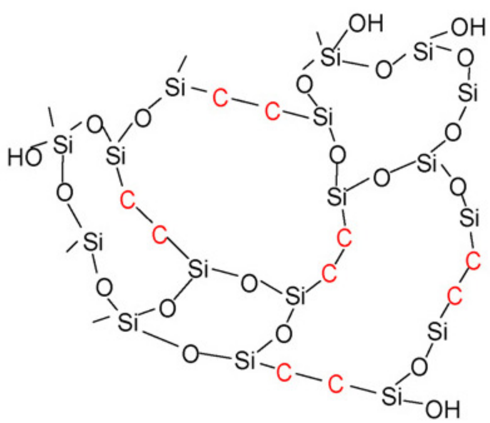
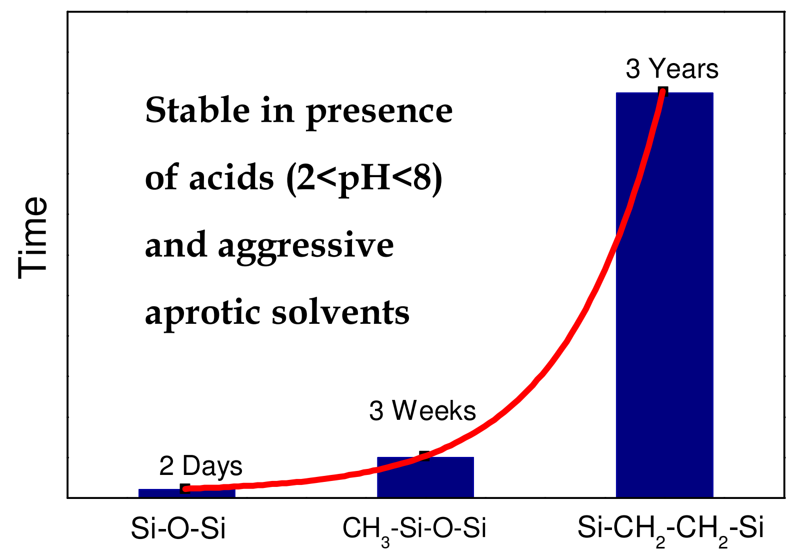
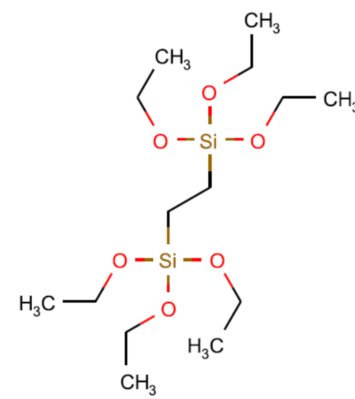


Hybrid silica network





1,2-Bis(triethoxysilyl)ethane
(BTESE)

H.M. van Veen et al.; Journal of Membrane Science 380 (2011) 124-131.

Si-CH_2-CH_2-Si bonds improve the properties of the silica network.

Can we make good membranes of "hybrid materials" on polymeric supports (better cost perspectives…) for NF??

Critical steps in synthesis

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1) Sol-gel route “classical for membranes”

   Sol synthesis (ECN)
   Deposition on polymer sublayer >>semi ceramic system high T required
   Post treatment

2) Plasma route “classical for polymer coats”

   Reactive plasma (TUE)
   Deposition on stable layer (T, Chem stable)
   Consistency in composition (initially close to HySi®)

Flow scheme HybPON project

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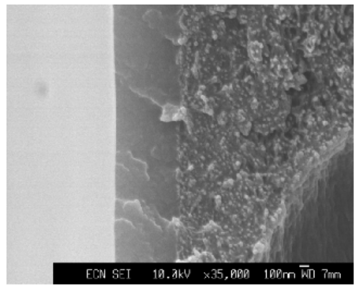
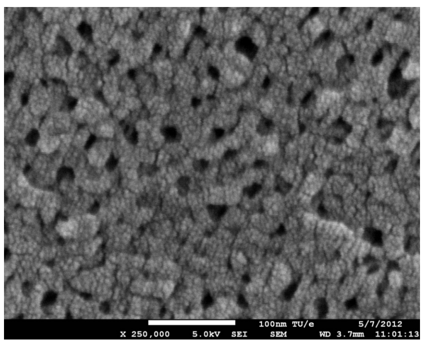
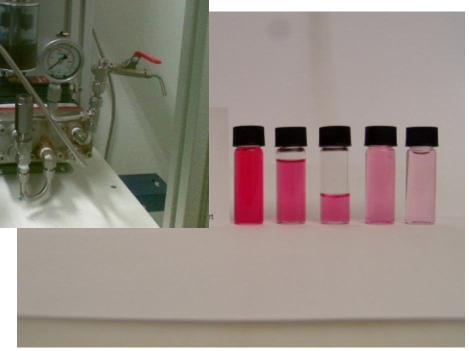
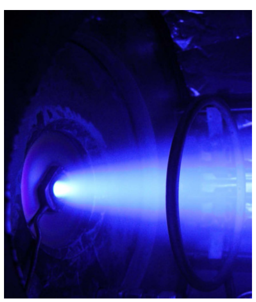
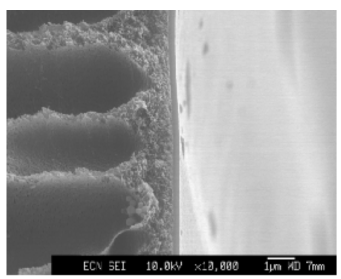


PI1109-0.3 (590 nm)









B (240 nm)

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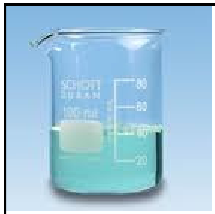
Method #1: wet chemical deposition



Membranes via sol-gel-Wet chemical deposition

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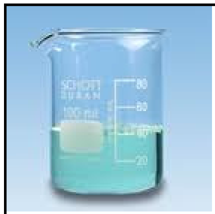
- **HybSi (BTESE)**
  - Layers can be made
  - Sublayers were made that “survive” 150+degC
  - Very low P in NF
  - Have selectivity in PV

- **HybPON (BTESE + n-DTES) <-> stability of sol**
  - Layers can be made
  - Thin enough to give flexible stable membranes
  - Reasonable P, good-reasonable R in some solvent

- **Up-scaling**
  - Roll coating
  - Proof of principle



Coating – layer thickness

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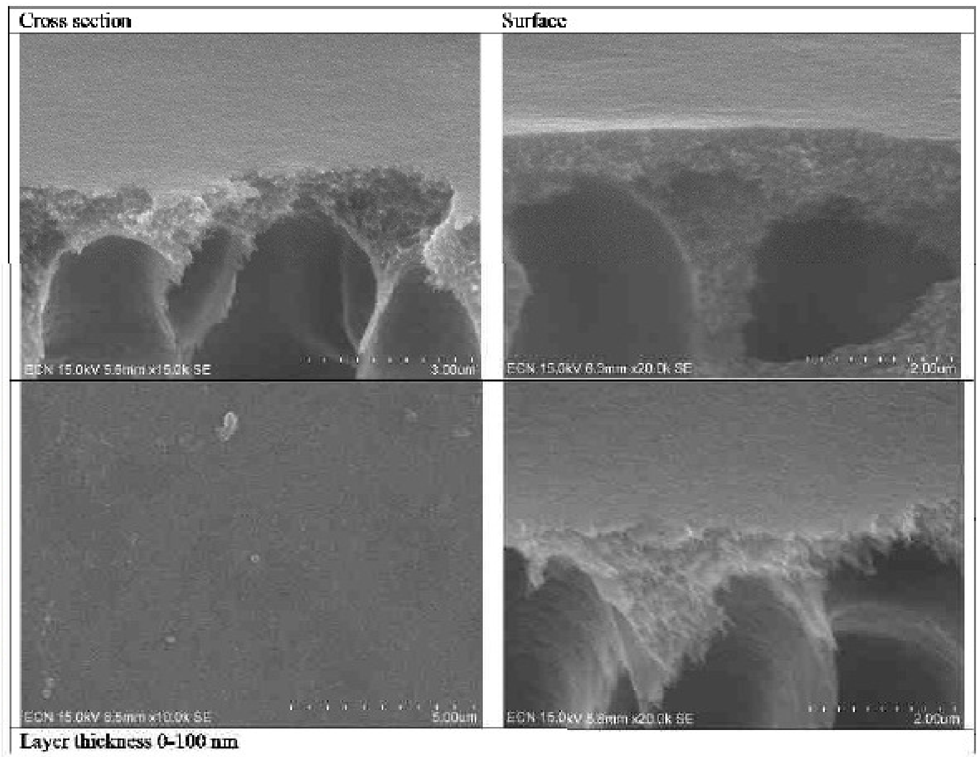
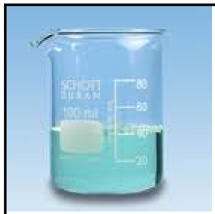
1112-SOL BTESE+NDTES





Performance BETSE + n-DTES membrane on UF/NF supports

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			HybPON 0.3 M BTESE + n-DTES		SolSep 010206	
Solvent	**Solute**	**Mw**	**Permeance**	**Retention**	**Permeance**	**Retention**
Methanol			0.5			
	Methyl Red	269	0.3	adsorption	0.8	yes
	Bengalerose	1018	0.1	yes		
Hexane			0		0	
	Sun Flower	900				
Toluene			0.3		0	
	Sun Flower	900	0.1	100%		
Acetone			1.3		2	
	Sun Flower	900	1.2	33%	1	100%

Permeance [l/m2.hr.bar]

- **HybPON membrane shows promising results in toluene**
- **Limited P**

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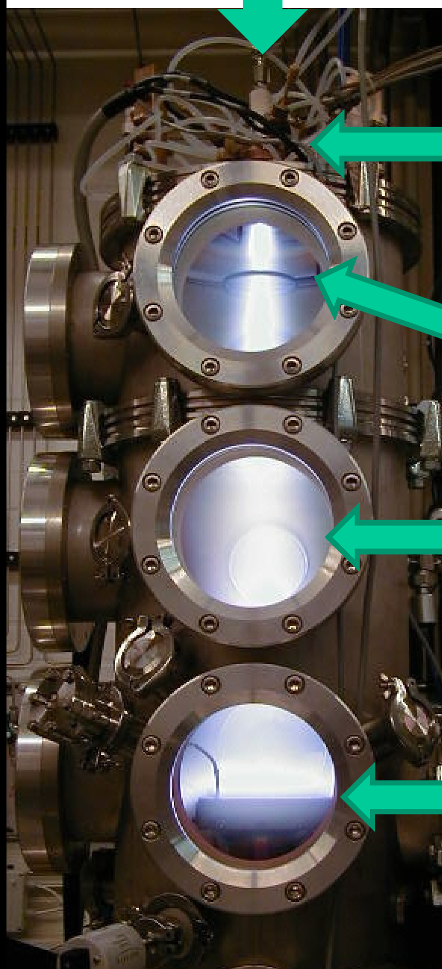
Method #2 Plasma coating

Experimental: The expanding thermal plasma - CVD

Ar (Φ_{Ar}= 1200 sccm)



www.SolSep.com

sccm: standard cubic centimeter per minute

OTB SOLAR

Industrial setup

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

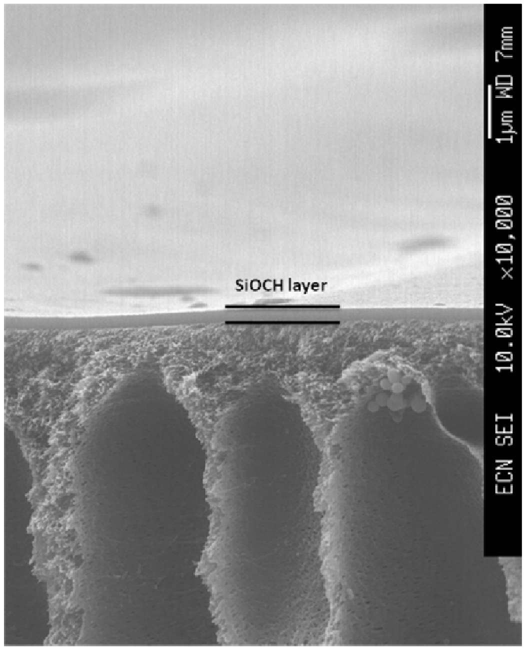
$M^{+} + e^{-} = M_3 + M_4$

M_2, M_3 and M_4 are radicals

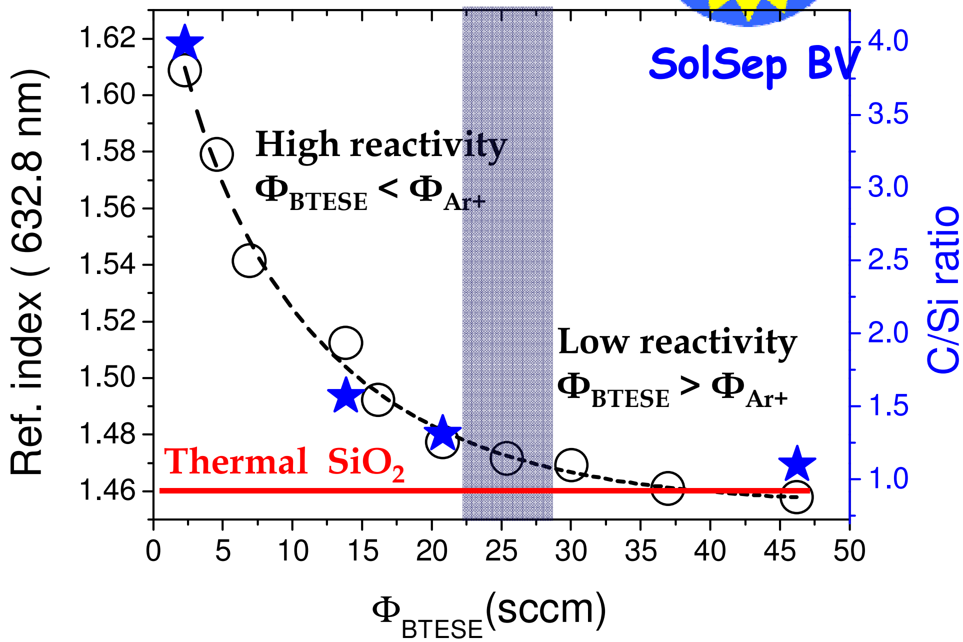
M: Organosilicon precursor

TU/e Technische Universiteit Eindhoven University of Technology

Optical and chemical properties



Cross-sectional SEM image of the polyamide-imide-supported hybrid silica layer.



C/Si ratio is determined by Rutherford Back Scattering and the refractive index by Spectroscopic Ellipsometry.

As Φ_{BTESE} increases:

- Limited reactivity of the BTESE precursor
- Reduced film density and carbon content

<u>Film density:</u>

ρ = 1.52 g/cm^3 @ 2.3 sccm
ρ = 0.88 g/cm^3 @ 46.2.sccm
ρ = 2.27 g/cm^3 (Thermal SiO_2)

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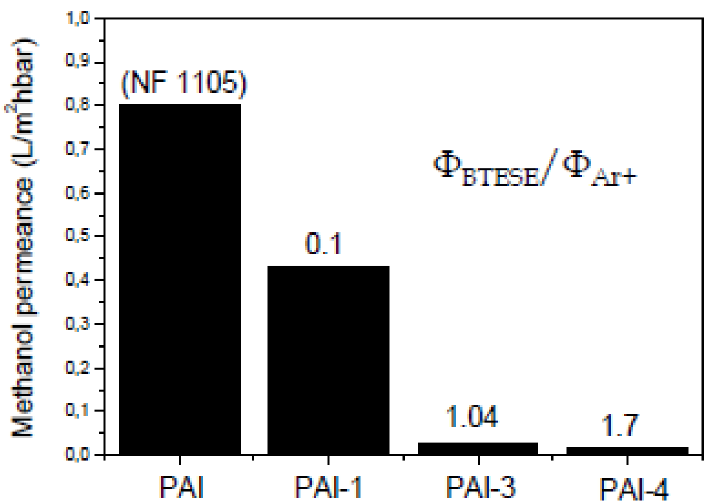
NF properties

Methanol permeance



Nanofiltration test

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

Increase NF Permeance + R

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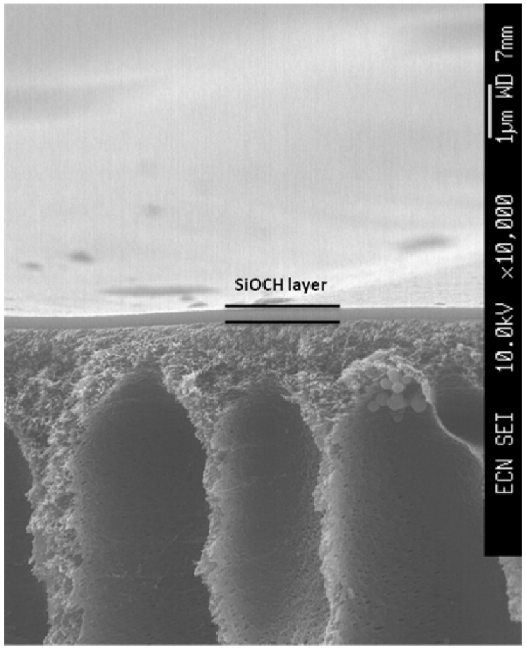
- Optimize sublayer vs top layer thickness

- Small pores ………….no pores (gutter layer)
- High porosity
- Low resistance
    - Large pores yield pin holes
    - Very thin layer gives more problems



Improving surface properties-effect on membrane

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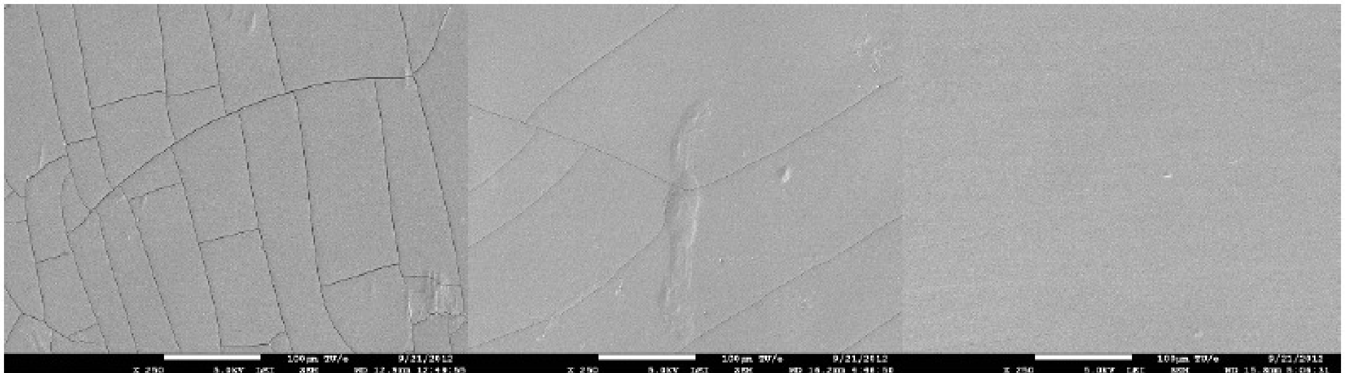
SiO2 (≈ 0.5 µm) | SiO2 (≈ 0.5 µm)/ PAI-3 (≈ 250 nm) | SiO2 (≈ 0.5 µm)/ PAI-3 (≈ 600 nm)



SiO2 (≈ 0.5 µm)/ PAI-3 (≈ 1 µm)

More cracks/defects at thicker layer

Use of intermediate layer >>

decreases cracks

Results
Plasma deposition on UF/PDMS

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Permeance [l/m2.hr.bar] **Sublayer 1209S (UF/PDMS)**

Solvent	Solute	Mw	PDMS	PAI-1	PAI-3	PAI-18
Methanol			0.2	0.06	0.05	
Hexane			8	0.02	0.05	
Toluene			12	0.1	0.05	0.47
	Sun Flower	900	7	0.04	0.02	0.14
			R=33%	R=0%	R=42%	R=100%

- **Promising for toluene**
- **Plasma deposition on UF/BTESE+n-DTES deteriorated in methanol and acetone**

By the way- there is PV performance!

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Membranes	WF (wt %)	$\alpha_{W/b}$	Water Flux (Kg/m^2 h)	T(^oC)	PSI*
PVA	5	<200	< 1.5	100	< 300
This work (Polymer-supported hybrid silica)	5	1133	2	95	2003
Hybsi ® (Ceramic-supported hybrid silica)	5	4700	3.6	95	16920

Final remarks

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- Semi-ceramic systems can be tailored towards NF membranes (HybPON vs HybSi®)
- Possible to make such systems onto polymeric supports – cost effective
- Can be done via -at least- 2 methods
- This opens up spiral wound manufacturing
- Good retention properties in some solvents
- Still not (yet?) "universal "

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