Zeolite filled polydimethylsiloxane (PDMS) as an improved membrane for solvent-resistant nanofiltration (SRNF)

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Due to the shape-selectivity of the pores and the induced polymer crosslinking, zeolite filled elastomers are excellent solvent-resistant nanofiltration membranes with enhanced fluxes and retentions compared to commercial membranes, allowing use in non-polar solvents and at high temperatures.

A challenge in nanofiltration (NF) and reverse osmosis (RO) is to broaden the applications from aqueous to organic feeds. Using NF and RO, selected applications have already been investigated, like edible oil processing,[1] lube oil refining[2] and catalysis.[3] A more widespread use requires solvent-resistant membranes that preserve their separation characteristics under more aggressive conditions of strongly swelling solvents and elevated temperatures. One material that qualifies is silicone rubber. It was first known as a membrane material in pervaporation (PV) and gas separation (GS). More recently, it was used in RO and NF to remove solutes from organic solvents.[2,4,5] Also the MPF-50 membrane, up to now the most studied SRNF membrane, is linked with patents that describe the preparation of silicone-derived SRNF-membranes.[6,7]

Silicone rubber is chemically and thermally stable, but, like most elastomers, tends to swell excessively in organic solvents, especially in the non-polar. The membrane can swell to such an extent that solutes with high molecular weights start to permeate.[2] To overcome this problem, several solutions have been proposed in the literature. One is the use of halogen-substituted silicone rubber,[2] another the extra cross-linking of the silicone rubber *via* plasma treatment.[8] Both approaches reduce the fluxes.

In general, the addition of fillers in elastomers leads to the reinforcement of polymers and reduced swelling, rendering them mechanically and chemically more stable. For silica and zeolites in PDMS, such reinforcement has been explained by adsorption of the polymer chains on the silanol-groups of the filler surface.[9,10] When the filler interacts well with the polymer, the effective cross-linking density increases and the swelling degree of the polymer network decreases.[11] Montmorillonite,[12] mica,[13] zinc oxide,[14] zeolite A,[15] ZSM-5, zeolite Y and silicalite[10,16] have thus been used to decrease membrane swelling in GS and PV.

Filled elastomers have not yet been applied in pressure driven processes, like RO and NF. The main reason for this is the general assumption that fillers lower the permeability of the films in these processes.[2] The use of porous zeolitic fillers could counter this problem, with the solvent being transported, even selectively, through the pores.

The general utility of the zeolite-filled PDMS membranes† in organic processes, is reflected in the Wilkinson catalyst (952 Da)

rejection data in several solvents, shown in Table 1.[17] In the strongly swelling solvents (see Fig. 1) toluene, ethyl acetate (EA) and dichloromethane (DCM), the catalyst rejections were considerably lower for the unfilled PDMS reference membrane, confirming the limited applicability of PDMS as an SRNF-membrane in these solvents. Zeolite addition improved the separation performance of PDMS in these solvents substantially, as explained by the higher cross-linking density and the resulting reduced swelling of the filled PDMS. Fig. 1 illustrates this reduction of the swelling upon addition of the zeolites.[18] Compared with unfilled PDMS, the available space between the polymer chains is strongly decreased because of the reduced swelling, which consequently reduces the diffusivity of permeating molecules. The diffusivity for high-molecular weight solutes, like the Wilkinson catalyst, is reduced more drastically than for the low-molecular weight solvent molecules, explaining the higher rejections. Moreover, the small pores of the ZSM-5 zeolite do not allow transport of the catalyst through this filler.

Table 1 Filtration of Wilkinson catalyst from different solvents (0.225 mM, 30 °C, 15 bar)

	Permeance (l m^{-2} h^{-1} bar^{-1}) (Rejection (%))			
	PDMS[a]	ZSM-5[b]	USY[c]	MPF-50
Toluene	1.15 (78)	0.58 (98)	0.22 (98)	0.47 (81)
EA	1.14 (62)	0.55 (97)	0.20 (94)	0.50 (76)
DCM	1.71 (81)	0.71 (93)		
THF		0.85 (80)		0.50 (55)

[a] 6 ± 1 μm, [b] 19 ± 2 μm, [c] 31 ± 1 μm. [d] Top-layer thickness.
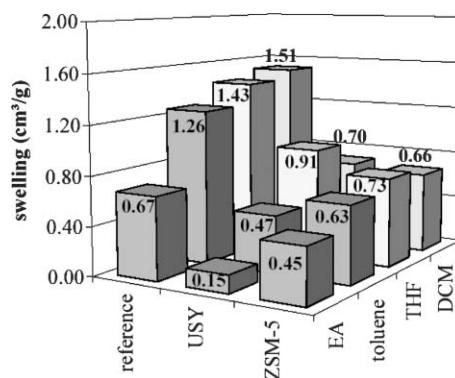
Fig. 1 Swelling of the different types of membrane materials in the solvents used in this work.
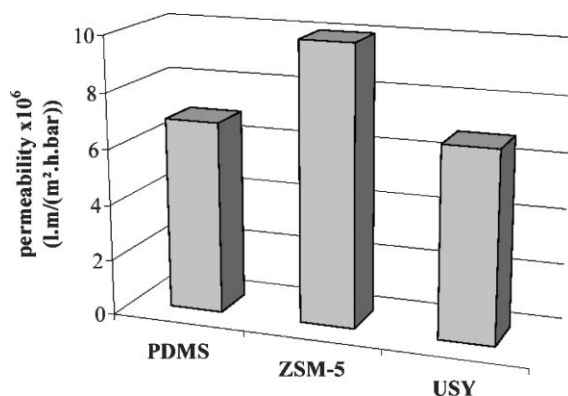
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Fig. 2 Toluene permeability of the different membrane materials (0.225 mM Wilkinson catalyst, 30 °C, 15 bar).

Table 2 Influence of temperature on Wilkinson catalyst filtrations (0.225 mM, toluene, 15 bar)

| | Permeance (l m^{-2} h^{-1} bar^{-1}) (Rejection (%)) | | |
	30 °C	50 °C	80 °C
PDMS	1.15 (78)	1.50 (0)	
ZSM-5	0.58 (98)	0.72 (98)	0.84 (88)
USY	0.22 (98)	0.27 (98)	

Fig. 2 indicates the toluene permeability of the three types of membranes. Since the permeability is independent of the thickness, it allows the comparison of the membranes. The calculation is done assuming a generally accepted reciprocal proportionality between SEM-measured top-layer thickness and flux, which seems appropriate under these experimental conditions. The permeability of the ZSM-5 filled membrane is higher than for the unfilled membrane, indicating an additional selective solvent transport through the zeolite pores. The effect is less pronounced with USY incorporated, where physical pore intrusion by PDMS-chains is likely to appear because of the wider pores of the filler.[10]

Table 1 also compares the laboratory-prepared membranes with the commercially available MPF-50, which has a silicone based top-layer too. The performance of MPF-50 was found to be strongly dependent on the pretreatment given. Used as such after being taken from the EtOH/H$_2$O storage solution, the toluene permeance was only 0.072 l m^{-2} h^{-1} bar^{-1}. A pre-conditioning step in 2-propanol increased the permeance to 0.47 l m^{-2} h^{-1} bar^{-1}.[19] With all other permeance values in Table 1 also measured applying a 2-propanol conditioning, all rejections measured for MPF-50 in toluene, EA and tetrahydro-furan (THF) were all lower than the ones for the filled PDMS membranes, confirming their excellent and enhanced utility in SRNF. Even though a further decrease of the zeolite filled membrane top-layer thickness is still under investigation, the permeance of the ZSM-5 filled membranes already exceeds the one of the commercial membrane.

The generic aspect of zeolite filled elastomers as high-rejection SRNF-membranes is illustrated with EPDM-based membranes where the addition of USY increased Wilkinson rejections in EA at 30 bar from 38 to 79%. The permeability decreased from 1.48 × 10^{-6} to 0.94 × 10^{-6} l m m^{-2} h^{-1} bar^{-1}.

Many potential SRNF applications, *e.g.* the removal of homogeneous catalysts from reaction mixtures or the work-up of synthesized fine chemicals, require membranes with good separa-tion properties at higher temperatures. According to the technical information,[20] MPF-50 can not be applied above 40 °C. When used at 50 °C, the unfilled PDMS membranes also failed to retain the Wilkinson catalyst in toluene (Table 2). The zeolite-filled PDMS membranes on the other hand, successfully kept their separation characteristics intact at higher temperatures. Even then,

the diffusivity of the Rh-catalyst thus remained low enough to be well retained, thanks to the decreased chain mobility and the intact catalyst exclusion from the narrow zeolite pores.

In conclusion, addition of fillers turned elastomers into highly useful SRNF-membranes, with applications extended to tempera-tures as high as 80 °C and in solvents that induce very high swelling. The problem of reduced permeability upon filler addition is avoided by the use of zeolites with porous structure that do not allow polymer intrusion. At the same time, these zeolites enhance the membrane selectivity by increasing transport of solvent molecules and excluding sterically the larger solutes.

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Notes and references

† *Experimental*: The PDMS (RTV-615 A en B) and the adhesion promoter (SS 4155) were obtained from General Electric Corp. (USA). Component A contains a prepolymer with vinyl groups. Component B has hydrosilyl groups and acts as cross-linker. EPDM (Keltan 578) was kindly provided by DSM. ZSM-5 (CBV-3002) and USY (CBV-780) were supplied by PQ-corporation and dried at 110 °C before use. ZSM-5 has typical pores with a diameter of 0.55–0.58 nm and a particle size of 1–1.5 μm, while USY-pores are less regular with diameters all above 0.78 nm. The particle size of USY ranges from 0.4–0.8 μm. The polyacrylonitrile (PAN) support was kindly provided by VITO, Belgium. *PDMS membrane preparation*: A PDMS solution (RTV A/B = 10/1) was prepolymerised for 1 h at 60 °C. The support was saturated with water and glued to a glass or INOX plate. The excess of water was wiped away with a humid tissue and the support was treated with adhesion promoter, before coating the PDMS solution on the impregnated support. The plate was tilted to a defined angle and the polymer solution was poured over the support. After evaporation of the hexane, cross-linking was completed in a vacuum oven at 100 °C. *Filled PDMS membrane preparation*: The filler was dispersed in hexane. To improve the dispersion, a treatment of one hour in an ultrasonic bath was applied to break crystal aggregates. The cross-linker was added to the zeolite dispersion and this mixture was stirred for two hours at 40 °C. Finally, the prepolymer was added and the mixture was stirred for another hour at 60 °C. The filler fraction in the membrane is kept constant at 30 wt.%. The PDMS/filler solutions were coated the same way as described above. *EPDM membrane preparation*: The EPDM-PAN membranes were prepared in a similar way.

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17 Filtrations were done in a stainless steel dead-end pressure cell with 15.2 cm^2 membrane surface area. The feed solution was poured in the cell, heated to the desired temperature and subsequently pressurised with nitrogen. Permeate samples were collected in cooled flasks as a function of time, weighed and analyzed. The permeance is defined as volume permeate (l)/(time of permeation (h)·membrane surface (m^2)·applied pressure (bar)). The permeability is defined as the permeance multiplied with the thickness of the membrane top-layer (m). All reported values are equilibrium measurements. Wilkinson catalyst (925 Da) was chosen as test solute. To determine the concentration, the samples were analysed for Rh with an atomic absorption spectrometer of Varian Techtron (type IL 651 AA/AE). Rejection is defined as (1 − (concentration in permeate/concentration in feed)).
18 Dried pieces of PDMS slabs were weighed and immersed in the solvent. After equilibrium, the membranes were quickly wiped with a tissue to remove the solvent from the external surface before weighing. The additional weight of the membrane was recalculated to the amount of solvent sorbed (cm^3) per gram of membrane.
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