



## Coupled-PDMS grafted mesoporous $\gamma$ -alumina membranes for solvent nanofiltration



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### ABSTRACT

In this paper grafting of mesoporous  $\gamma$ -alumina membranes with hydride terminated polydimethylsiloxane is described. Vinyltriethoxysilane is used as linking agent and tetrakis(vinyltrimethylsiloxy)silane as a coupling agent, to create a dense network structure that is grafted in the ceramic pores. Grafting performance of the organic moieties on  $\gamma$ -alumina powders was analyzed by FTIR and TGA. The results indicate that grafting reactions were successfully carried out. Contact angle analysis on the grafted membranes showed that grafting occurs on the  $\gamma$ -alumina layer and that the resulting membrane surface had a water contact angle of 108°. From permeability and rejection tests using Sudan Black in toluene, ethyl acetate or isopropanol, the use of a coupling agent was found to result in a more dense network structure grafted in the gamma alumina pores. This resulted in a higher rejection for nanofiltration of solvents but at the cost of a lower solvent permeability, when compared with PDMS-grafted alumina membranes where no coupling of PDMS was applied.

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### 1. Introduction

Organic Solvent Nanofiltration (OSN) is a potential technology to recover solvents [1,2]. For this application, a chemically stable membrane is required that can endure continuous exposure towards organic solvents. Grafting of porous ceramic substrates by an organic moiety is an interesting way to prepare chemically and mechanically stable membranes for nanofiltration of solvents [3,4]. During organic grafting of oxide ceramic membranes the OH- groups, that are present at the oxide surface, react with hydrolysable groups from an organic moiety to produce a stable covalent bond. Most work done in this area describes a two-step reaction, in which the surface hydroxyl groups are first reacted with organosilanes to provide reactive sites for the organic moiety to be grafted [3–9]. Previously only organosilanes have been used to increase the hydrophobic nature of ceramic membranes. Examples include the grafting of alkyl silanes to silica-zirconia membranes (pore diameters of 1–3 nm) by Tsuru et al. used for solvent filtration applications [10]. Sah et al. used chlorosilanes to graft  $\gamma$ -alumina membranes [11], while Rezaei et al. grafted n-alkyl silanes to titania membranes (pore diameter of 1 nm) [12]. In all

these cases an increase of membrane hydrophobicity as well as a higher permeation of nonpolar solvents was observed.

Several examples of membrane preparation by organic grafting of ceramic membranes are given in the literature [3–9,13]. Pinheiro et al. [3] and Tanardi et al. [4] graft low molecular weight (MW) PDMS to silylated  $\gamma$ -alumina porous supports (pore size 5 nm) for the fabrication of nanofiltration membranes. Here a “grafting to” method was used, in which a low MW polymer was grafted to the ceramic mesoporous substrate without additional growing of the organic chain from the surface of the pore wall. Another way of grafting is the “grafting from” method where the polymer chains are synthesized from the monomer molecules by initiating chain growth from an active centre on the ceramic surface, e.g., via free radical polymerization between the organic molecules in order to result in a as small as possible membrane pore diameter [5–7]. Faibish and Cohen [5] used free-radical graft polymerization of vinylpyrrolidone monomers to grow the organic layer during grafting of silylated zirconia membranes for the fabrication of ultrafiltration membranes. This way of grafting resulted in a reduction in pore size of around 25%. Yoshida and Cohen made a layer of a terminally bonded polymer via free radical graft polymerization of vinyl acetate or vinyl pyrrolidone monomers on the silylated surface of gamma alumina tubular support (pore size 5 nm) [6] and silica membranes (pore size of 20 nm) [7] for pervaporation application. Besides free-radical polymerization, another way to increase the thickness of the grafted organic layer is by means of

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reactions between organic molecules and a coupling agent. Popat et al. [8] and Lee et al. [9] employed a catalyzed covalent reaction between low MW poly(ethylene glycol) and a coupling agent (in this case silicon tetrachloride) so that the organic chain was grown from the surface of the pore wall during the grafting of straight pore alumina (“anodisc”) membranes to be used for ultrafiltration.

Different from [3,4], in which a low MW PDMS was grafted to the ceramic mesoporous substrate, without additional covalent coupling for growing of the organic chain from the pore wall, in this work a covalent reaction between PDMS molecules and a coupling agent was used in order to result in a more dense organic network grafted inside the pores. It is expected that this method may lead to a smaller membrane pore diameter compared to the results given in [3,4] to accommodate the need for removing very small impurities during solvent recycling.

In this paper the grafting of mesoporous  $\gamma$ -alumina membranes with hydride terminated polydimethylsiloxanes is described. Vinyltriethoxysilane is used as linking agent and tetrakis(vinyltrimethylsiloxy)silane as coupling agent, in order to generate a membrane for solvent nanofiltration. The grafting behaviour of the organic moiety was studied by Fourier Transform Infrared spectroscopy (FTIR) and TGA. Contact angle measurements and SEM-EDX analyses were used to characterize the grafted membrane properties. Permeation tests with toluene, isopropanol, and ethyl acetate, as well as rejection tests with Sudan Black B were performed to characterize the membrane performance.

## 2. Experimental procedure

Anhydrous toluene, ethyl acetate, and isopropanol were obtained from Sigma-Aldrich. Vinyltriethoxysilane and tetrakis(vinyltrimethylsiloxy)silane were purchased from ABCR. Hydride terminated polydimethylsiloxane (PDMS), with an average number of repeating monomers ( $n$ ) of 10, was purchased from Gelest. All chemicals were used as received. Flat  $\alpha$ - $\text{Al}_2\text{O}_3$  supported  $\gamma$ - $\text{Al}_2\text{O}_3$  membranes with a diameter of 39 mm were purchased from Pervatech. The mean pore diameter of the 3  $\mu\text{m}$  thick  $\gamma$ - $\text{Al}_2\text{O}_3$  layer and the 1.7 mm thick  $\alpha$ - $\text{Al}_2\text{O}_3$  support were 5 nm and 80 nm, respectively [14,15]. The  $\gamma$ - $\text{Al}_2\text{O}_3$  powder was bought from Alfa-Aesar, having a BET surface area of 84.38  $\text{m}^2/\text{g}$ .

The unmodified  $\gamma$ - $\text{Al}_2\text{O}_3$  membranes were soaked in an ethanol/water (2:1) solution for 24 h at ambient temperature to remove dust and provide suitable hydroxylation. The membranes were then dried at 100 °C for 24 h under vacuum and stored at room temperature under nitrogen atmosphere until further use.

Inside a glove box, under nitrogen atmosphere, a 100 ml toluene solution of 25 mM of the linking agent, vinyltriethoxysilane, was prepared in a 250 ml five-necked round flask. After removing the linking agent/toluene solution from the glove box a  $\gamma$ - $\text{Al}_2\text{O}_3$  membrane was placed in a sample holder located a few centimeters above the vinyltriethoxysilane solution. The solution was stirred and heated to perform the grafting reaction between vinyltriethoxysilane vapor and  $\gamma$ - $\text{Al}_2\text{O}_3$  at 90 °C for 4 h under nitrogen flow. Details on this Vapor Phase Deposition (VPD) method are provided elsewhere [3,16]. After the reaction mixture was allowed to cool down to room temperature, the membrane was retrieved from the sample holder and rinsed with toluene before being dried in a vacuum oven at 100 °C for 2 h.

Grafting of PDMS combined with the coupling agent tetrakis(vinyltrimethylsiloxy)silane was performed through hydrosilylation [17] on the vinyl grafted membranes by a solution phase deposition (SPD) method. A 100 ml solution of 37.5 mM of hydride terminated PDMS in toluene was added under stirring at room temperature to a 500 ml flask containing a vinyl-grafted membrane, submerged in toluene. A 100 ml solution of 12.5 mM tet

rakis(vinyltrimethylsiloxy)silane was added under stirring to this solution, and subsequently 10 mg of a Pt catalyst (50% of Pt-divinyltetramethyldisiloxane complex and 50% of Pt-cyclovinylmethylsiloxane complex, Fluka) was added to this solution under stirring. The mixture was heated under reflux at 60 °C for 0.5 h to initiate the addition reaction between the vinyl groups of the linker and coupling agent with the hydride terminated PDMS. Afterwards, the membrane was retrieved from the solution and rinsed three times with toluene, dried overnight in a fumehood and further dried at 100 °C in a vacuum oven for 2 h.

In order to study the grafting performance of  $\gamma$ - $\text{Al}_2\text{O}_3$  by means of FTIR, a  $\gamma$ - $\text{Al}_2\text{O}_3$  powder was used as starting inorganic material. The grafting procedure of the  $\gamma$ - $\text{Al}_2\text{O}_3$  powder was nearly the same as for grafting the  $\gamma$ - $\text{Al}_2\text{O}_3$  membranes. Here the 100 ml toluene solution of 25 mM of the linking agent was prepared in a 250 ml two-necked round flask. After removing from the glove box, the round flask was connected with an U-shaped glass tube to another 250 ml round flask in which 600 mg of  $\gamma$ - $\text{Al}_2\text{O}_3$  powder was placed. Both flasks were heated at 90 °C for 4 h under nitrogen flow to allow the grafting reaction between vinyltriethoxysilane vapor and  $\gamma$ - $\text{Al}_2\text{O}_3$ . Details on this powder vapor phase deposition (VPD) method are given elsewhere [18]. After 4 h of reaction, both flasks were cooled to ambient temperature. Immediately after, the modified powder was retrieved and rinsed with toluene to remove any physically adsorbed vinyltriethoxysilane. The powder was further dried for 2 h at 100 °C the vacuum oven. Further grafting with PDMS, coupled with tetrakis(vinyltrimethylsiloxy)silane, was performed by the same SPD method as described for the  $\gamma$ - $\text{Al}_2\text{O}_3$  membranes.

### 2.1. Characterization

FTIR analysis was performed using a Bruker Optik GmbH Tensor 27 TGA-IR spectrometer equipped with a universal ATR polarization accessory. The FTIR spectra were recorded at room temperature over a scanning range of 700–3000  $\text{cm}^{-1}$  with a resolution of 4.0  $\text{cm}^{-1}$ . The grafted  $\gamma$ - $\text{Al}_2\text{O}_3$  powder sample is considered to have the same chemical characteristics as the actual  $\gamma$ - $\text{Al}_2\text{O}_3$  membrane and therefore can be used to describe the chemical reactions that occur between ceramic membrane and grafting agent.

Thermogravimetric analysis on the PDMS-grafted powder was conducted from room temperature until 700 °C in nitrogen. The measurement was performed at a heating rate of 10 °C/min.

Water contact angles of the membrane surfaces were measured by the sessile drop method to evaluate the surface wettability for grafted and ungrafted membranes. 5  $\mu\text{l}$  Millipore Q2 water was dropped at a speed of 2  $\mu\text{l s}^{-1}$  on a membrane surface using a Hamilton Microliter syringe. The water contact angle data were collected by the Data Physics Optical Contact Angle instrument (OCA 20).

Morphologies of the membranes were observed by scanning electron microscopy (SEM-EDX, Thermo NORAN Instruments).

Solvent permeation tests were carried out at room temperature using a dead-end pressure cell made from stainless steel. Membranes to be tested were soaked in the organic solvent for 12 h prior to each experiment for preconditioning. The cell was filled with the feed solution and helium was used to pressurize the cell. Solvent permeation values were obtained by measuring the weight of the collected permeate as a function of time. Three different membrane samples were analyzed for each data point to ensure reproducibility and measurements were performed three times for each sample.

Rejection tests using Sudan Black B were performed in a batch mode using the same dead-end pressure cell at 50% recovery. The cell was filled with feed solution and helium was used to pressurize the cell. The feed solution was constantly stirred at a speed

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