



ELSEVIER

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

PDMS grafting of mesoporous γ -alumina membranes for nanofiltration of organic solvents



Cheryl R. Tanardi, Ana F.M. Pinheiro, Arian Nijmeijer, Louis Winnubst*

Inorganic Membranes, MESA⁺ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

ARTICLE INFO

Article history:

Received 24 March 2014

Received in revised form

1 July 2014

Accepted 7 July 2014

Available online 15 July 2014

Keywords:

Solvent

Nanofiltration

PDMS

Alumina

Grafting

ABSTRACT

In this paper grafting of mesoporous γ -alumina membranes with monovinyl terminated polydimethylsiloxane (PDMS), using 3-mercaptopropyltriethoxysilane (MPTES) as a linking agent, is described. The grafting performance of the organic moieties on γ -alumina powders was studied by FTIR. Contact angle measurements and solvent permeability tests were used to characterize the membrane properties. The results indicated that grafting reactions were successfully carried out. The toluene permeability of the membrane was reduced from 5.3 to 2.1 L/m² h bar after grafting with the polymer. No degradation of the membrane material was observed after chemical stability tests in toluene for 6 days at room temperature and at elevated temperatures (up to 90 °C).

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Nanofiltration of organic solvents for solvent recovery is an ideal solution in the quest for more sustainable processes in the pharmaceutical, biochemical, and petrochemical industry. The main driver for applying nanofiltration is that it consumes less energy compared to other separation technologies, such as evaporation and distillation. However, industrial application of this technology demands a robust membrane that is able to endure an aggressive environment such as a continuous exposure towards organic solvents. In order to make the application of solvent nanofiltration technically feasible, a hydrophobic and chemically stable membrane with nanofiltration properties is required.

Membranes have been developed for several decades using polymers as a main ingredient [1]. Polymers are relatively inexpensive and are available with a wide variety of functional groups. They are frequently used as Solvent Resistance Nanofiltration (SRNF) membranes [2,3]. However, currently used SRNF polymeric membranes, such as those made from PDMS (polydimethylsiloxane) [4], PPSU (polyphenylsulfone) [5], and chitosan [6], were reported to swell significantly in organic solvents, like toluene, diethylether, acetone, methylene chloride, hexane, ethyl acetate, methanol, ethanol, isopropanol, or methyl ethyl ketone [4–6]. A loss in nanofiltration performance of these membranes due to swelling was observed after several hours in contact with these

organic solvents [3,7–9]. A need for nanofiltration membranes with less swelling towards organic solvents therefore emerged.

Ceramic membranes exhibit a high chemical stability towards organic solvents [10,11]. In addition to this, ceramic membranes are also mechanically stable under operational pressures of up to at least 20 bars [10], at which most polymers will suffer from compaction. Despite these superior characteristics, ceramic membranes are not suitable for the nanofiltration of nonpolar solvents, because the hydroxyl (OH⁻) groups on the ceramic pore walls hinder the permeation of organic solvents in the nanofiltration regime [12].

A new type of membrane showing (1) high chemical stability, (2) suitable wettability properties, (3) high permeability and selectivity, and are (4) non-swelling and non-compressible, is expected to be interesting for organic solvent nanofiltration applications. To achieve this aim, a method is proposed, in which applying a polymer inside the pores of a ceramic material can provide a win-win solution to obtain in this way a hydrophobic and chemically stable membrane. A mesoporous ceramic, as non-swelling and non-compressible porous material, is rendered suitable to provide a rigid support for polymeric materials grafted inside their pores. If the polymer is confined in the perimeter of the ceramic pores, swelling can be brought to a minimum (being the space left inside the pores as the maximum swelling limit). Besides, the ceramic pore will act as a rigid cylindrical spine which will restrain the movement of the grafted polymers from compaction when high pressures are introduced to the membrane system.

A suitable polymeric material grafted on the ceramic pore walls can give a hydrophobic character to the porous ceramic support, thus allowing better wettability for organic solvents. The effective

* Corresponding author. Tel.: +31 53 4892944; fax: +31 53 4892336.

E-mail address: a.j.a.winnubst@utwente.nl (L. Winnubst).URL: <http://www.utwente.nl/tnw/im> (L. Winnubst).

pore size of the ceramic membrane is reduced, thus increasing the selectivity of the membrane. In this way a porous UF ceramic membrane can be changed into a NF membrane we intended. In the work, as described in this paper, a ceramic membrane is used with a pore size as small as possible but sufficiently large to graft a (small) polymer on the pore walls in order to have the largest benefit of the rigid character of a ceramic membrane system, while changing the hydrophilic property of the inorganic membrane into a hydrophobic structure. Polymer grafting is a process in which a specific organic substance is chemically bonded to an inorganic substrate. The OH- groups of the oxide ceramic surface will react with the hydrolysable groups of the to-be-grafted organic moiety to produce a stable covalent bond.

In literature several examples are given on modification of porous inorganic membranes by grafting for various applications. Leger et al. [13] used silicone oil (viscosity 545 mPa) to graft the surface of alumina membranes with a pore size of 5 nm and studied its gas permeation and pervaporation performance. The membrane was shown to be chemically stable in toluene, acetone and THF. Faibish et al. [14] grafted polyvinylpyrrolidone on zirconia membranes for oil-in-water emulsion treatment. Here grafting was performed by free-radical polymerization, using a vinyl silane as linking agent to the zirconia membranes. The authors claim a reduction in pore size of around 25% after grafting but no pore size values are given in this paper. Yoshida et al. [15] grafted γ -alumina (pore size 5 nm) by using vinyl acetate or vinyl pyrrolidone monomers and made a layer of terminally bonded polymers on the surface of the γ -alumina tubular support. In another paper Yoshida et al. [16] grafted vinyl acetate or vinyl pyrrolidone to silica membranes (pore size of 20 nm) by free radical graft polymerization for pervaporation of methyl-tert-butyl ether from water. Popat et al. [17] grafted polyethylene glycol to straight pore alumina membranes (“anodisc”) using a silane coupling agent. Lee et al. [18] used polyethylene glycol to graft straight pore alumina membranes for the application of anti-fouling membrane for biomolecules. The pore size of the bare alumina, as used in [17,18], are in the order of 25–80 nm, while the grafted membranes are in the ultra-filtration range. Pinheiro et al. [19] developed nanofiltration membranes by grafting PDMS in γ -alumina porous supports (pore size 5 nm) using aminopropylethoxysilane (APTES) as linking agent and (mono(2,3-epoxy) polyether terminated polydimethylsiloxane with an average number of repeating monomers (n) of 10 and a viscosity of 10–50 mPa.

The work described in this paper is on grafting a mesoporous (pore size 5 nm) γ -alumina layer, supported on macro porous α -alumina, with 3-mercaptopropyltriethoxysilane (MPTES) as linking agent. Subsequently, the system is grafted with monovinyl-terminated polydimethylsiloxane (PDMS) in order to generate a membrane for solvent nanofiltration. The grafting behavior of the organic moieties on the γ -alumina is studied by Fourier Transform Infrared spectroscopy (FTIR). Contact angle measurements and solvent permeability tests are used to determine the membrane properties. Chemical stability tests in toluene at elevated temperatures are performed as well.

2. Experimental procedure

Anhydrous toluene was obtained from Sigma-Aldrich. 3-mercaptopropyltriethoxysilane (MPTES) was purchased from Fluka. Monovinyl terminated polydimethylsiloxane (PDMS) was purchased from ABCR with an average number of repeating monomers (n) of 39 and a viscosity of 80–100 mPa s. An azobisisobutyronitrile catalyst was purchased from Sigma Aldrich. All chemicals were used as received. Flat α - Al_2O_3 supported γ - Al_2O_3 membranes with a diameter of 39 mm were purchased from

Pervatech. The mean pore diameter of the 3 μm thick γ - Al_2O_3 layer and the 1.7 mm thick α - Al_2O_3 support were 5 nm and 80 nm, respectively [20,21].

The unmodified γ - Al_2O_3 membranes were soaked in an ethanol/water (2:1) solution for 24 hours 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 solution of 12.5 mM MPTES in anhydrous toluene was prepared in a 500 ml five-necked round flask. A soaked and dried γ - Al_2O_3 membrane was placed in a sample holder located a few centimetres above the MPTES solution. The solution was stirred and heated to perform the grafting reaction between MPTES vapor and γ - Al_2O_3 at 80 °C for 4 h under nitrogen flow. Details on this Vapor Phase Deposition (VPD) method are given elsewhere [19,22,23]. After 4 h the reaction mixture was allowed to cool down. Immediately after the cooling down, the membrane was retrieved from the sample holder and rinsed with toluene and dried under vacuum at 100 °C for 24 h.

PDMS was grafted on the MPTES linker by a Solution Phase Deposition (SPD) method. A 100 ml solution of 12.5 mM PDMS in toluene was prepared in a 500 ml five-necked round flask. The MPTES-grafted γ - Al_2O_3 membrane was then immersed into the PDMS/toluene solution on a sample holder and kept in the solution throughout the reaction. As catalyst, 5% (n/n) Azobisisobutyronitrile (ABN) was added. The grafting reaction between monovinyl terminated PDMS and the MPTES-grafted γ - Al_2O_3 was carried out under continuous stirring at 70 °C for 24 hours under nitrogen flow. After 24 h the reaction mixture was allowed to cool down. The membrane was then retrieved from the mixture and soaked overnight in toluene to remove any physically adsorbed PDMS. The membrane was further rinsed by isopropanol and ethanol before drying under vacuum at 100 °C for 24 h.

In order to study the grafting performance of γ - Al_2O_3 by means of FTIR, porous γ - Al_2O_3 flakes were used as starting inorganic material. The γ - Al_2O_3 flakes were prepared from a boehmite sol which was dried and calcined at 650 °C for 3 h at a heating rate of 1 °C/min. To remove dust and provide suitable hydroxylation, the γ - Al_2O_3 flakes were soaked in an ethanol/water (2:1) solution for 24 h at ambient temperature. The flakes were then dried at 100 °C for 24 h under vacuum and stored under nitrogen atmosphere prior to grafting. Grafting of the γ - Al_2O_3 flakes was performed as follows. Inside a glove box, under nitrogen atmosphere, a 100 ml solution of 12.5 mM MPTES in anhydrous toluene was prepared in a 250 ml two-necked round flask. The round flask was removed from the glove box and connected with a glass tube to another 250 ml round flask where 600 mg of γ - Al_2O_3 flakes were placed. Both flasks were heated at 80 °C for 4 h under nitrogen flow to allow the grafting reaction between MPTES vapor and γ - Al_2O_3 . Details on this vapor phase deposition (VPD) method are given elsewhere [22,23]. After 4 h, both flasks were cooled to ambient temperature. Immediately after, the modified flakes were retrieved and rinsed 3 times in toluene to remove any physically absorbed MPTES. The flakes were further dried for 24 h at 100 °C under vacuum.

PDMS was grafted on the MPTES linker by a solution phase deposition (SPD) method. A 100 ml solution of 12.5 mM PDMS in toluene was prepared in a 250 ml two-necked round flask. The MPTES-grafted γ - Al_2O_3 flakes were then immersed into the PDMS/toluene solution and kept stirred in the solution throughout the reaction. 5% of ABN catalyst was added. The grafting reaction between monovinyl terminated PDMS and the MPTES-grafted γ - Al_2O_3 was carried out at 70 °C for 24 h under nitrogen flow. After 24 h the reaction mixture was allowed to cool down. Immediately after, the flakes were retrieved from the mixture

and centrifuged 3 times in toluene to remove any physically adsorbed MVPDMS. The flakes were further dried at 100 °C for 24 h under vacuum.

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 600–4000 cm^{-1} with a resolution of 4.0 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.

Contact angles were measured by the sessile drop method to evaluate the hydrophobicity of the membrane after the modification was carried out. 5 μL 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 a Data Physics Optical Contact Angle instrument (OCA 20).

Toluene permeation tests were carried out at room temperature using a dead-end pressure cell made from stainless steel. Three different membrane samples were analyzed to ensure reproducibility. Prior to the solvent permeation test the membranes were soaked for preconditioning in the organic solvent for 12 h. The cell was filled with the solvent and helium was used to pressurize the cell. Permeate fluxes were obtained by measuring the weight of the collected permeate as a function of time. The membrane permeability was calculated in $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ unit according to the equation below:

$$\text{Permeability} = J/\Delta P \text{ where } J = V/At,$$

J is the flux in $\text{L m}^{-2} \text{h}^{-1}$, V is the permeate volume in L, A is the effective membrane surface area in m^2 , t is the permeation period in h, and ΔP is the trans-membrane pressure in bar.

Chemical stability tests were done by immersing 0.1 gr of grafted $\gamma\text{-Al}_2\text{O}_3$ powders into 40 ml of toluene for 6 days at 30, 60, 80 or 90 °C under continuous stirring. After immersion, the system was cooled down to room temperature and retrieved from the solvent by centrifuge. The retrieved powder was three times washed by centrifuging with respectively ethanol and water and subsequently dried in a vacuum oven. Afterwards FTIR analysis were done to check whether there is any degradation of membrane material, marked by appearance of new bands or absence of characteristic absorption bands as compared to the FTIR spectra of freshly-grafted powders.

3. Results and discussion

3.1. Chemical reaction background

In this work chemical grafting was carried out using two consecutive steps. The first step was the attachment of 3-mercaptopropyl-triethoxysilane (MPTES) onto the pore wall of the γ -alumina.

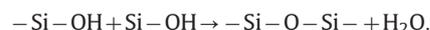
The silylation of the porous ceramic substrate by Vapor Phase Deposition (VPD) provides a more uniform and homogeneous distribution of products as compared to a Solution Phase Deposition (SPD) method and results in a monolayer or near-monolayer silane coverage on the pore wall [19,22,23]. The grafting reaction proceeds by hydrolysis of the alkoxy groups of the MPTES followed by a condensation reaction upon meeting the hydroxyl groups on the membrane surface, resulting in a stable covalent Al–O–Si bond between the oxide surfaces and the MPTES. In this reaction,

moisture from the substrate acts as a catalyst for the hydrolysis [23,24]. For the silanes to access the hydroxyl groups on the membrane surface, no more than 2 or 3 monolayers of water should exist on the substrate surface [24]. In order to limit the amount of moisture present on the substrate to be grafted, the substrate was kept in nitrogen atmosphere before grafting. To limit the amount of moisture present in the grafting process, the reaction was performed in a dry atmosphere and anhydrous solvents are used. The grafting reaction between the $\gamma\text{-Al}_2\text{O}_3$ pore surface and MPTES is depicted in step 1 of Fig. 1. The hydroxyl groups on the γ -alumina surface act as the active sites for the grafting reaction.

After this first reaction step, the S–H group from the linker will react with the vinyl group from the Monovinyl terminated polydimethylsiloxane to form a stable S–C bond. PDMS was chosen due to its highly hydrophobic character and good chemical stability towards organic solvents [25]. Upon successful grafting, the grafted polydimethylsiloxane will act as a hydrophobic pillow that will enhance the permeation of nonpolar organic solvents through the membrane pores. The reaction between the MPTES-grafted $\gamma\text{-Al}_2\text{O}_3$ membrane and monovinyl terminated PDMS is represented in step 2 of Fig. 1. It is a thiol-ene reaction which involves the reaction of a S–H with a double bond. Thiol-ene reactions are efficient since it produces high yields and the resulting chemical bond is stable in various solvents [26].

3.2. FTIR

Fig. 2 shows the FTIR absorbance spectra of unmodified, silane-grafted and polymer-grafted $\gamma\text{-Al}_2\text{O}_3$ powders. Fig. 2a shows the spectrum of the unmodified $\gamma\text{-Al}_2\text{O}_3$ powder. For the silane-grafted powder spectrum (Fig. 2b), the characteristic absorption peaks at 1060 and 700 cm^{-1} are attributed to the covalent Si–O–Al bonds [27,28] confirming that grafting of the linker, MPTES, on the $\gamma\text{-Al}_2\text{O}_3$ powder has occurred. The peaks at 2335 and 2362 cm^{-1} in Fig. 2b are ascribed to S–H stretching of the thiol (SH–) groups from the MPTES-grafted $\gamma\text{-Al}_2\text{O}_3$ powder [29]. During the grafting reaction not all three functional alkoxy groups from the MPTES might react with the surface –OH groups. One or more hydrolysable groups out of total three functional alkoxy groups that are present at MPTES may also react with one of the silanols from the adjacent MPTES forming a siloxane network. The reaction of silanols with the surface hydroxyl groups on the ceramic surface and the adjacent silanols can happen at the same time, creating Si–O–Si bonds that are apparent by the peak at 1092 cm^{-1} [30]. The polycondensation reaction between two silanols occurs through the reaction:



The peak at 2935 cm^{-1} is ascribed to the asymmetric stretching of CH_2 from the propyl groups of the grafted silanes [31]. The peak at 1246 cm^{-1} is assigned to the CH_2 wagging of the $\text{Si}(\text{CH}_2)$ groups of the grafted silanes [31]. During the grafting reaction between the MPTES-grafted $\gamma\text{-Al}_2\text{O}_3$ powder and the MVPDMS polymer, the S–H bond should be broken by forming a covalent S–C bond through a thiol-ene reaction. Clearly the S–H bands at 2335 and 2362 cm^{-1} disappeared after reaction of the linker with MVPDMS as can be seen from Fig. 2c, confirming the thiol-ene reaction between MPTES and MVPDMS. In the FTIR spectrum of polymer-grafted $\gamma\text{-Al}_2\text{O}_3$ powder (Fig. 2c), the peaks at 2965 cm^{-1} and 2874 cm^{-1} are ascribed to C–H asymmetric stretching and symmetric stretching of methyl (CH_3 –) groups of PDMS [31]. A strong peak at 1260 cm^{-1} is caused by symmetric C–H bending and peaks at 860 and 793 cm^{-1} are caused by Si–C vibration and CH_3 rocking from the SiCH_3 group [30]. The two peaks at 1092 and 1017 cm^{-1} are ascribed to the Si–O–Si bond [30,31]. These peaks

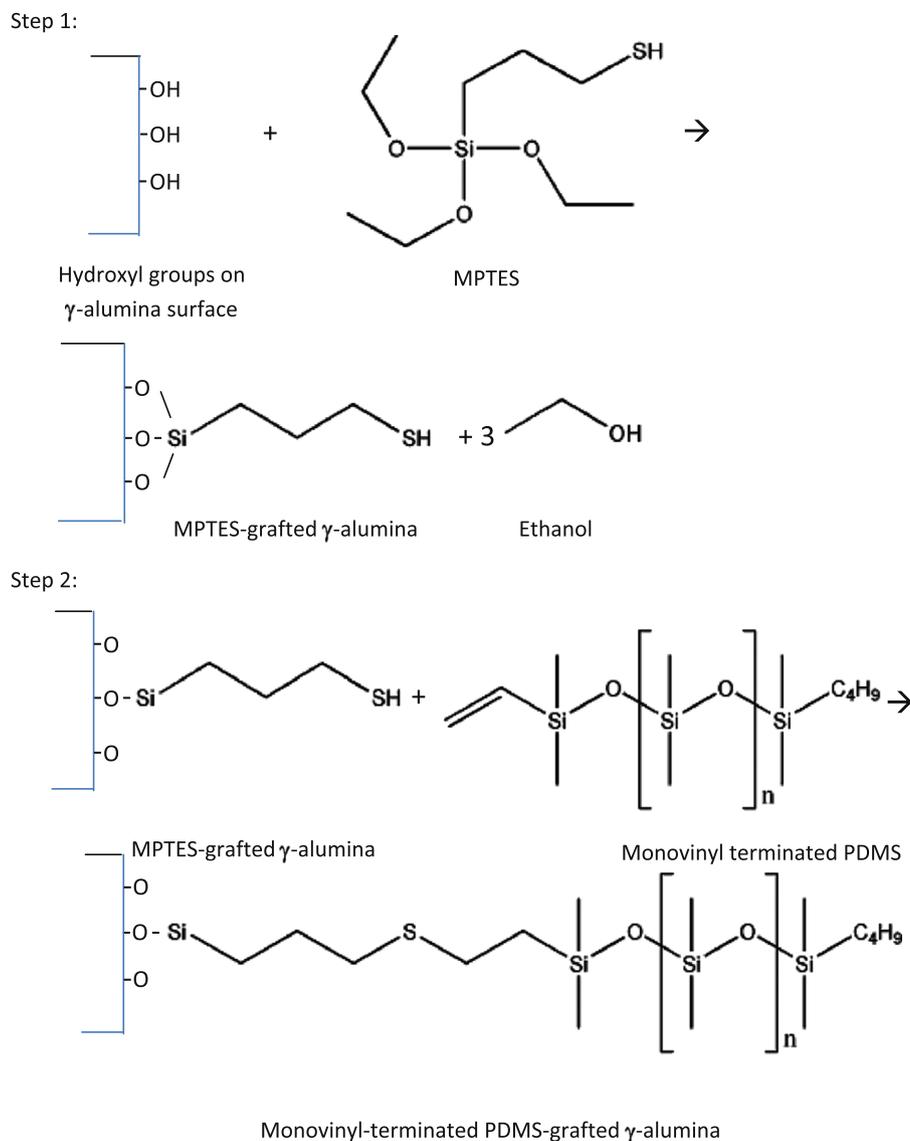


Fig. 1. Proposed grafting reactions; step 1 grafting of the linker MPTES; step 2: grafting of PDMS.

at 793, 1017, 1092, 1260 cm^{-1} and 2965 cm^{-1} confirm the presence of polydimethylsiloxane groups on the PDMS-grafted γ - Al_2O_3 powder [23,30,31].

Fig. 3 shows a schematic illustration of the possible structure resulted from the overall reaction between linker and alumina and respectively between linker and PDMS.

It can be concluded from these FTIR analysis that the grafting reaction between γ -alumina and MPTES and subsequently with a monovinyl terminated PDMS is successfully performed.

3.3. Contact angle

Table 1 shows the measured contact angles of the unmodified, silane-grafted, and PDMS-grafted γ - Al_2O_3 membranes. The observed change in the contact angles represents the change of the surface properties of the modified membrane relative to those of the unmodified substrate. The contact angle measurements were taken from 5 different points on the flat membrane surface and averaged. The negligible standard deviation shows that grafting reaction has occurred homogeneously over the membrane surface.

For the unmodified γ -alumina membrane, the water droplet immediately wetted the membrane surface. A corresponding water contact angle of 0° is therefore assumed, indicating the hydrophilic characteristic of the γ - Al_2O_3 membrane due to natural presence of hydroxyl (OH^-) groups on the ceramic surface. In general, an increase in contact angle was observed after modification of γ - Al_2O_3 membranes with MPTES and PDMS.

A higher contact angle observed after modification with MPTES might be attributed to the presence of the thiol group and the hydrophobic propyl group after modification of γ - Al_2O_3 with MPTES. Thiol (SH^-) groups are less polar than hydroxyl (OH^-) groups, causing a weaker attraction between the water droplet and the MPTES-grafted γ - Al_2O_3 membrane, and thus a comparatively higher contact angle.

A further increase in contact angle was observed after modification with PDMS. The higher contact angle might be attributed to the nonpolarity of the dimethylsiloxane groups. There are more potential sources contributing to the actual contact angle value, such as the nanotextures of the grafted moieties depending on the molecule orientation and grafting density of the grafted moieties, in combination with the presence of the pores. For a comparison, the modification of γ -alumina membranes with a mono-epoxy-

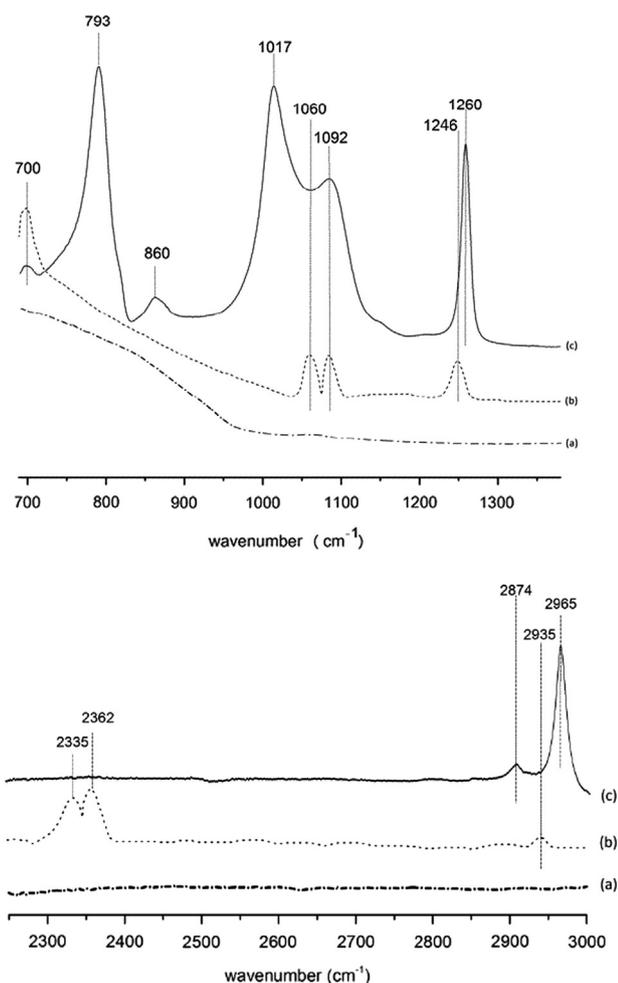


Fig. 2. FTIR absorbance spectra of (a) unmodified γ - Al_2O_3 powder (b) MPTES-grafted γ - Al_2O_3 powder and (c) PDMS-MPTES-grafted γ - Al_2O_3 powder.

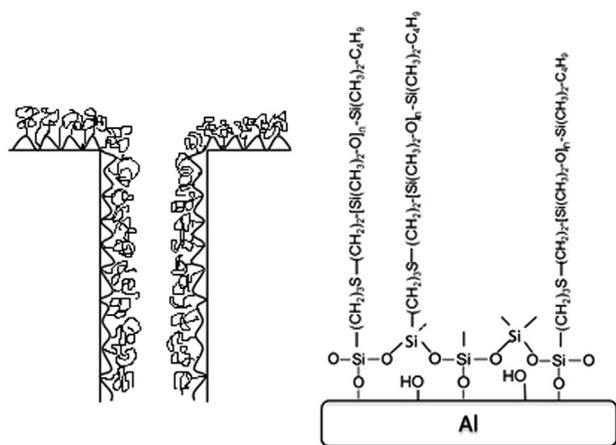


Fig. 3. Possible pore structure resulting from the grafting process (for illustration only, without any scaling purpose intended).

terminated PDMS ($n=10$), using an aminosilane as the linker, resulted in contact angle values ranging from 91° to 97° [19].

3.4. Permeation

Permeation tests were conducted on the unmodified and modified membranes, using toluene as a probe solvent to assess

Table 1

Water contact angles (deg) of unmodified, MPTES and MPTES-PDMS grafted γ - Al_2O_3 membranes.

	Unmodified (γ - Al_2O_3 membrane)	After silylation with MPTES	After PDMS grafting
Contact angle (deg)		44 ± 2	95 ± 1

Table 2

Toluene permeability of unmodified, MPTES and MPTES-PDMS grafted γ - Al_2O_3 membranes. Average values and standard deviations are given for measurements on three different membranes.

	Unmodified	After PDMS Grafting
Toluene permeability ($\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$)	5.80 ± 0.11	2.09 ± 0.13

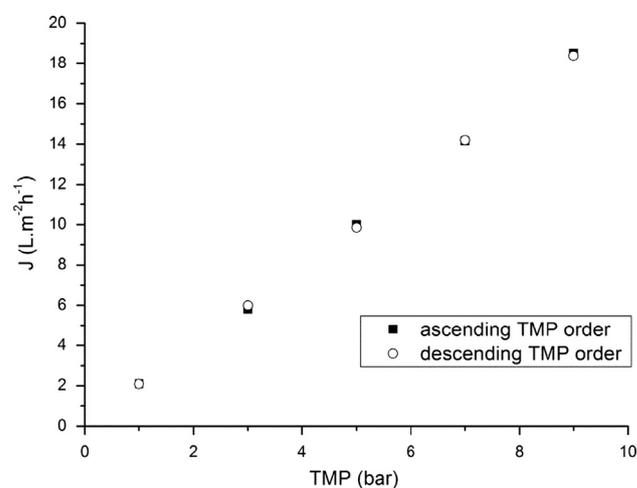


Fig. 4. Flux (J) as a function of Trans-Membrane Pressure (TMP) at room temperature.

the membrane permeability after grafting with PDMS. The toluene permeability of the unmodified and modified γ -alumina membranes are shown in Table 2. From Table 2, it can be seen that the toluene permeability is lower after grafting with PDMS. The improvement of wettability properties should have led to higher fluxes of toluene if it is assumed that the membrane pore size is constant before and after grafting. However, lower toluene permeability was observed after grafting with PDMS. The lower permeability observed is attributed to the membrane pore size reduction due to the presence of the grafted molecules. In such cases, overall reduction of fluxes may be the result when the flux decrease due to the pore size reduction is more significant than the flux improvements due to better surface wettability. In this work, three membranes were grafted separately using the same grafting procedure. The standard deviations, given in Table 2, were calculated from the average values of the toluene permeability of three membranes. It was demonstrated that this method of grafting results in membranes with high reproducibility.

In order to examine whether the way of applying subsequent trans-membrane pressures (TMP) affects the flux, permeation tests were performed in two different orders, starting from the lowest and going to the highest TMP and subsequently from the highest to the lowest TMP (see Fig. 4). No significant differences in fluxes were observed for ascending or descending TMP permeation tests. Thus no irreversible effects towards pressure are present in the tested transmembrane pressure range.

An estimation of the pore radius of the modified membrane can be obtained by using the simple pore capillary model [32]. For a steady-state system, where the solvent is incompressible, a simple capillary model for the pore geometry can be derived:

$$\frac{r_{\text{modified}}}{r_{\text{unmodified}}} = \sqrt{\frac{(L\eta)_{\text{modified}}}{(L\eta)_{\text{unmodified}}}} \quad (1)$$

where r_{modified} and $r_{\text{unmodified}}$ are the mean pore radii of the modified and unmodified $\gamma\text{-Al}_2\text{O}_3$ membranes, L_{modified} and $L_{\text{unmodified}}$ are the permeabilities of toluene for the modified and unmodified membranes in $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$, and η_{modified} and $\eta_{\text{unmodified}}$ are the toluene viscosity.

The mean pore radius of the unmodified $\gamma\text{-Al}_2\text{O}_3$ membrane is 2.5 nm, as determined by permporometry [13]. The values of L_{modified} and $L_{\text{unmodified}}$ are respectively 2.1 and $5.8 \text{ L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$. By applying these data in Eq. (1) a pore radius of 1.5 nm is calculated for the PDMS modified membrane. In this model any possible interactions between solvent and the respective membranes are not taken into account. This implies that in the case of negligible interfacial tension differences between the reference and the system in question, the estimated pore radius value of 1.5 nm might hold. However, the PDMS-modified membrane is much more hydrophobic than the pure $\gamma\text{-Al}_2\text{O}_3$ and it is therefore expected that there is less interfacial tension between the toluene and the grafted PDMS. So, the estimation method as used over here is expected to give a maximum value of the pore radius for the PDMS-modified membrane. The same calculation for the γ -alumina membranes grafted with a mono-epoxy-terminated PDMS ($n=10$), using an aminosilane as the linker from Pinheiro et al. work [23] gave a maximum pore radius of 1.83 nm, with L_{modified} and $L_{\text{unmodified}}$ of 3.1 and $5.9 \text{ L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$.

3.5. Chemical stability

The chemical stability of the membrane material in toluene was analyzed on $\gamma\text{-Al}_2\text{O}_3$ flakes grafted with only MPTES and flakes grafted with MPTES and PDMS. If the chemical bond between the grafting agents and the $\gamma\text{-Al}_2\text{O}_3$, was not stable then toluene, used as solvent for grafting the membranes, would likely wash away the grafting agents. The FTIR spectra of the MPTES grafted $\gamma\text{-Al}_2\text{O}_3$ powder immersed in toluene at different temperatures (30–90 °C) are shown in Fig. 5. From these chemical stability tests, it was observed that the MPTES grafted $\gamma\text{-Al}_2\text{O}_3$ powder immersed in toluene at all temperatures showed no changes in FTIR spectra. The characteristic bands of S–H at 2335 and 2362 cm^{-1} were still present with no change in intensity. It was demonstrated that continuous stirring for 6 days cannot dissolve the MPTES that has

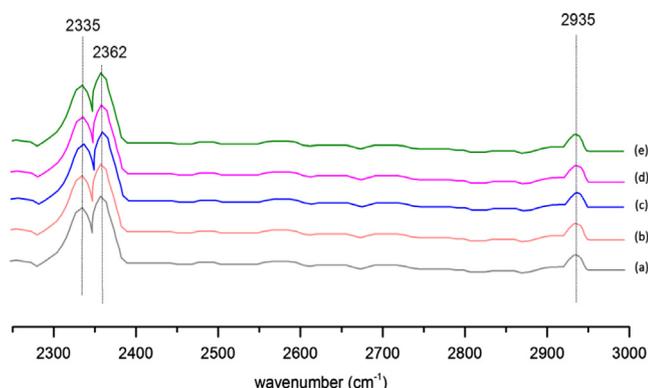


Fig. 5. FTIR Absorbance Spectra of MPTES-grafted $\gamma\text{-Al}_2\text{O}_3$ powders soaked in toluene at different temperatures for 6 days: (a) no immersion, (b) 30 °C, (c) 60 °C, (d) 80 °C, (e) 90 °C.

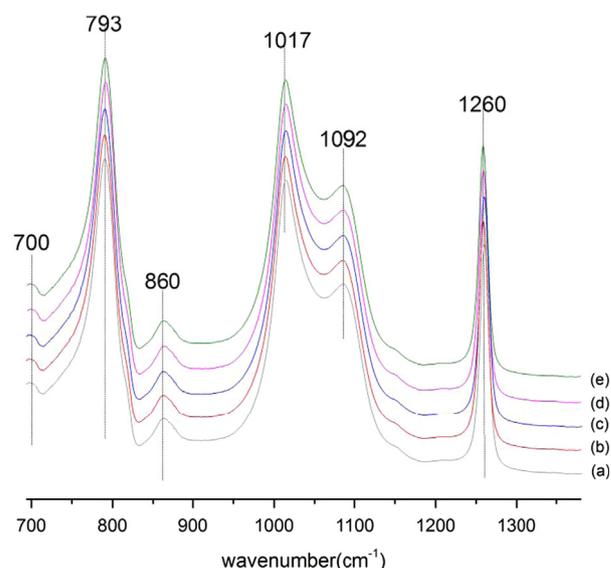


Fig. 6. FTIR Absorbance Spectra of PDMS-MPTES-grafted $\gamma\text{-Al}_2\text{O}_3$ powders soaked in toluene at different temperatures for 6 days: a) no immersion, b) 30 °C, c) 60 °C, d) 80 °C, e) 90 °C.

been grafted onto the $\gamma\text{-Al}_2\text{O}_3$ powder. This is only possible if a stable covalent bond is present between the grafted moiety and the $\gamma\text{-Al}_2\text{O}_3$ surface.

Fig. 6 shows the FTIR Spectra of the PDMS-grafted $\gamma\text{-Al}_2\text{O}_3$ powder after being immersed in toluene at different temperatures (30–90 °C) for 6 days. Pure PDMS easily dissolves in toluene [33]. If PDMS is only physically adsorbed on the ceramic powder, the grafted material will easily be washed away by toluene. The characteristic absorption peaks at 793, 1092, 1017, 1260 cm^{-1} of the PDMS-grafted $\gamma\text{-Al}_2\text{O}_3$ powders were still present without any decrease in intensity, demonstrating that the grafted material can maintain its integrity even after long term exposure of toluene at elevated temperatures. From the chemical stability tests it can be concluded, that no degradation of the membrane material was found, demonstrating the potential use of these membranes in solvents like toluene at elevated temperatures.

4. Conclusion

A method of grafting a mesoporous γ -alumina layer, supported on macro porous α -alumina, with 3-mercaptopropyltriethoxysilane (MPTES) as linking agent and subsequently with Monovinyl terminated polydimethylsiloxane (PDMS) as polymer grafted to this linker was presented. It was shown that this method of grafting resulted in stable covalent bonds between the PDMS, MPTES, and γ -alumina. Contact angle measurements have shown that this method of grafting renders the $\gamma\text{-Al}_2\text{O}_3$ substrate into hydrophobic properties. The grafting method described in this paper resulted in a hydrophobic and chemically stable membrane for potential use as chemical and thermal stable organic solvent nanofiltration membranes.

Acknowledgment

The authors acknowledge the financial support from the European Union, Education, Audiovisual and Culture Executive Agency under the Program “Erasmus Mundus Doctorate in Membrane Engineering” – EUDIME (FPA 2011–2014).

References

- [1] M. Mulder, *Basic Principles of Membrane Technology*, 2nd ed., Kluwer Academic Publisher, Netherlands, 1996.
- [2] D. Bhanushali, S. Kloos, C. Kurth, D. Bhattacharyya, Performance of solvent-resistant membranes for non-aqueous systems: solvent permeation results and modeling, *J. Membr. Sci.* 189 (2001) 1–21.
- [3] P. Vandezande, L.E.M. Gevers, I.F.J. Vankelecom, Solvent resistant nanofiltration: separating on a molecular level, *Chem. Soc. Rev.* 37 (2008) 365–405.
- [4] B. Van der Bruggen, J. Geens, C. Vandecasteele, Influence of organic solvents on the performance of polymeric nanofiltration membranes, *Sep. Sci. Technol.* 37 (2002) 783–797.
- [5] S. Darvishmanesh, J.C. Jansen, F. Tasselli, E. Tocci, P. Luis, J. Degrève, E. Drioli, B. Van der Bruggen, Novel polyphenylsulfone membrane for potential use in solvent nanofiltration, *J. Membr. Sci.* 379 (2011) 60–68.
- [6] D.A. Musale, A. Kumar, Solvent and pH resistance of surface crosslinked chitosan/poly(acrylonitrile) composite nanofiltration membranes, *J. Appl. Polym. Sci.* 77 (2000) 1782–1793.
- [7] S. Darvishmanesh, J. Degrève, B.V.D. Bruggen, Performance of solvent-pretreated polyimide nanofiltration membranes for separation of dissolved dyes from toluene, *Ind. Eng. Chem. Res.* 49 (2010) 9330–9338.
- [8] E.S. Tarleton, J.P. Robinson, M. Salman, Solvent-induced swelling of membranes – measurements and influence in nanofiltration, *J. Membr. Sci.* 280 (2006) 442–451.
- [9] B. Van der Bruggen, J. Geens, C. Vandecasteele, Fluxes and rejections for nanofiltration with solvent stable polymeric membranes in water, ethanol and n-hexane, *Chem. Eng. Sci.* 57 (2002) 2511–2518.
- [10] A. Buekenhoudt, *Stability of Porous Ceramic Membranes*, Elsevier B.V, Belgium, 2008.
- [11] T. Van Gestel, C. Vandecasteele, A. Buekenhoudt, C. Dotremont, J. Luyten, B. Van Der Bruggen, G. Maes, Corrosion properties of alumina and titania NF membranes, *J. Membr. Sci.* 214 (2003) 21–29.
- [12] T. Tsuru, T. Sudou, S.I. Kawahara, T. Yoshioka, M. Asaeda, Permeation of liquids through inorganic nanofiltration membranes, *J. Colloid. Interface Sci.* 228 (2000) 292–296.
- [13] C. Leger, H.L. De Lira, R. Paterson, Preparation and properties of surface modified ceramic membranes. Part II. Gas and liquid permeabilities of 5 nm alumina membranes modified by a monolayer of bound polydimethylsiloxane (PDMS) silicone oil, *J. Membr. Sci.* 120 (1996) 135–146.
- [14] R.S. Faibish, Y. Cohen, Fouling-resistant ceramic-supported polymer membranes for ultrafiltration of oil-in-water microemulsions, *J. Membr. Sci.* 185 (2001) 129–143.
- [15] W. Yoshida, Y. Cohen, Ceramic-supported polymer membranes for pervaporation of binary organic/organic mixtures, *J. Membr. Sci.* 213 (2003) 145–157.
- [16] W. Yoshida, Y. Cohen, Removal of methyl tert-butyl ether from water by pervaporation using ceramic-supported polymer membranes, *J. Membr. Sci.* 229 (2004) 27–32.
- [17] K.C. Papat, G. Mor, C.A. Grimes, T.A. Desai, Surface modification of nanoporous alumina surfaces with poly(ethylene glycol), *Langmuir* 20 (2004) 8035–8041.
- [18] S.W. Lee, H. Shang, R.T. Haasch, V. Petrova, G.U. Lee, Transport and functional behaviour of poly(ethylene glycol)-modified nanoporous alumina membranes, *Nanotechnology* 16 (2005) 1335.
- [19] A.F.M. Pinheiro, D. Hoogendoorn, A. Nijmeijer, L. Winnubst, Development of a PDMS-grafted alumina membrane and its evaluation as solvent resistant nanofiltration membrane, *J. Membr. Sci.* 463 (2014) 24–32.
- [20] A. Nijmeijer, B.J. Bladergroen, H. Verweij, CVI Low-temperature, modification of γ -alumina membranes, *Microporous Mesoporous Mater.* 25 (1998) 179–184.
- [21] F.P. Cuperus, D. Bargeman, C.A. Smolders, Permporometry: the determination of the size distribution of active pores in UF membranes, *J. Membr. Sci.* 71 (1992) 57–67.
- [22] V.G.P. Sripathi, B.L. Mojet, A. Nijmeijer, N.E. Benes, Vapor phase versus liquid phase grafting of meso-porous alumina, *Microporous Mesoporous Mater.* 172 (2013) 1–6.
- [23] A.F.M. Pinheiro, *Development and Characterization of Polymer-grafted Ceramic Membranes for Solvent Nanofiltration* (Ph.D. thesis), University of Twente, Enschede, 2013.
- [24] W. Yoshida, R.P. Castro, J.-D. Jou, Y. Cohen, Multilayer alkoxysilane silylation of oxide surfaces, *Langmuir* 17 (2001) 5882–5888.
- [25] A.V. Volkov, G.A. Korneeva, G.F. Tereshchenko, Organic solvent nanofiltration: prospects and application, *Russ. Chem. Rev.* 77 (2008) 983–993.
- [26] C. Rissing, D.Y. Son, Thiol-ene reaction for the synthesis of multifunctional branched organosilanes, *Organometallics* 27 (2008) 5394–5397.
- [27] S. Jakobsson, Determination of Si/Al ratios in semicrystalline aluminosilicates by FT-IR spectroscopy, *Spectrosc. Tech.* 56 (2002) 797–799.
- [28] M.R. Sinko, K. Rohonczy, J. Frazl, P. Gel, Structures Containing Al(III), *Langmuir* 15 (1999) 6631–6636.
- [29] *The Chemistry of the Thiol Group*, in: S. Patai (Ed.), Ed. Wiley, London, 1974.
- [30] D.R. Anderson, *Analysis of Silicones*, Wiley-Interscience, New York, 1974.
- [31] L.J. Bellamy, *The Infra-red Spectra of Complex Molecules*, 3rd ed., Chapman and Hall, London, 1975.
- [32] F.A.L. Dullien, *Porous Media: Fluid Transport and Pore Structure* (in), Academic Press, New York (1992) 8–9.
- [33] A.F.M. Barton, *CRC Handbook of Polymer-Liquid Interaction Parameters and Solubility Parameters*, CRC Press, US, 1990.