Coupled-PDMS grafted mesoporous γ-alumina membranes for solvent nanofiltration

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A B S T R A C T

In this paper grafting of mesoporous γ-alumina membranes with hydride terminated polydimethylsiloxane is described. Vinyltriethoxysilane is used as linking agent and tetrakis(vinyldimethylsiloxy)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 γ-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 γ-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 oganosilanes 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 γ-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 γ-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 γ-alumina membranes with hydride terminated polydimethylsiloxanes is described. Vinyltriethoxysilane is used as linking agent and tetrakis (vinyldimethylsiloxy)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(vinyldimethylsiloxy)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 α-Al$_2$O$_3$ supported γ-Al$_2$O$_3$ membranes with a diameter of 39 mm were purchased from Pervatech. The mean pore diameter of the 3 μm thick γ-Al$_2$O$_3$ layer and the 1.7 mm thick α-Al$_2$O$_3$ support were 5 nm and 80 nm, respectively [14,15]. The γ-Al$_2$O$_3$ powder was bought from Alfa-Aesar, having a BET surface area of 84.38 m^2/g.

The unmodified γ-Al$_2$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 γ-Al$_2$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 γ-Al$_2$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(vinyldimethylsiloxy)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(vinyldimethylsiloxy)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 γ-Al$_2$O$_3$ by means of FTIR, a γ-Al$_2$O$_3$ powder was used as starting inorganic material. The grafting procedure of the γ-Al$_2$O$_3$ powder was nearly the same as for grafting the γ-Al$_2$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 γ-Al$_2$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 γ-Al$_2$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 absorbed vinyltriethoxysilane. The powder was further dried for 2 h at 100 °C the vacuum oven. Further grafting with PDMS, coupled with tetrakis(vinyldimethylsiloxy)silane, was performed by the same SPD method as described for the γ-Al$_2$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 cm^{-1} with a resolution of 4.0 cm^{-1}. The grafted γ-Al$_2$O$_3$ powder sample is considered to have the same chemical characteristics as the actual γ-Al$_2$O$_3$ membrane and therefore can be used to describe the chemical reactions that occur between ceramic membrane and grafting agent.

Thermogravimetrical 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 μl *Millipore Q2* water was dropped at a speed of 2 μl 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

of 500 rpm to prevent concentration polarization on the membrane surface. Sudan Black B (Fluka, MW 456.54 g/mol) was used at a concentration of 8000 ppm as probe solute in pure solvents. The rejection test was performed until an equilibrium retention value was reached. All measurements were performed on three different membrane samples to ensure reproducibility and three measurements were done for each sample. UV–vis Spectrophotometer was used to analyze the Sudan Black concentrations in the feed and permeate. In order to check for the occurrence of any concentration polarization, fluxes of solvents with solutes were compared with those of pure solvents. Between each cycle, the samples were rinsed with the previous solvent and subsequently three times ultrasonically cleaned in ethanol for 10 min at room temperature. After this ultrasonic treatment the membranes were dried in a vacuum oven under nitrogen for 24 h at 30 °C. After being cooled down, membranes were soaked for 24 h in the solvent to be tested.

The solvent fluxes and the rejection results of the membranes developed in this work were compared with those of two other types of PDMS-grafted ceramic membranes as developed in previous works. These are γ-alumina membranes grafted with a mono-vinyl-terminated PDMS (n = 39), using mercaptopropylsilane as the linker, hereinafter referred to as M2 [4], and γ-alumina membranes grafted with mono-epoxy-terminated PDMS (n = 10) and aminosilane as the linker, hereinafter referred to as M3 [3]. All membranes were tested in the same equipment for flux and rejection measurements.

3. Results and discussion

3.1. Grafting performance

In this work chemical grafting was carried out using two consecutive reaction steps as shown in Fig. 1. The first step is the grafting of vinyltriethoxysilane to the ceramic pore wall as depicted in step 1 of Fig. 1. Grafting proceeds according to the reaction between a surface hydroxyl group with an ethoxysilane group resulting in a vinyl-terminated surface with a covalent Si—O—Al bond to the ceramic. In the second reaction step, the hydride terminated PDMS is reacted with the available vinyl group of the linker and of the tetrakis(vinyldimethylsiloxy)silane through a hydrosilylation reaction using a Pt catalyst, which is the addition of the H—Si bond across the C double bond (Fig. 1, step 2). The two step reaction as shown in Fig. 1 is aimed to create a random network structure grafted inside the membrane pores.

Fig. 2 shows the possible structures formed during the grafting reaction. The morphologies (a) and (b) are the result of respectively grafting the organic moiety parallel or perpendicular to the membrane pore wall. Morphology (c) is a result when "free" polymers are formed without reaction with the inorganic surface. It is expected that the latter morphology will be removed from the grafted system by washing (see experimental).

In Fig. 3 FTIR spectra are given of the unmodified, vinyl-grafted and coupled-PDMS-grafted γ-Al₂O₃ powders. Fig. 3b gives the FTIR spectrum after the grafting reaction of the linker (vinyltriethoxysi-
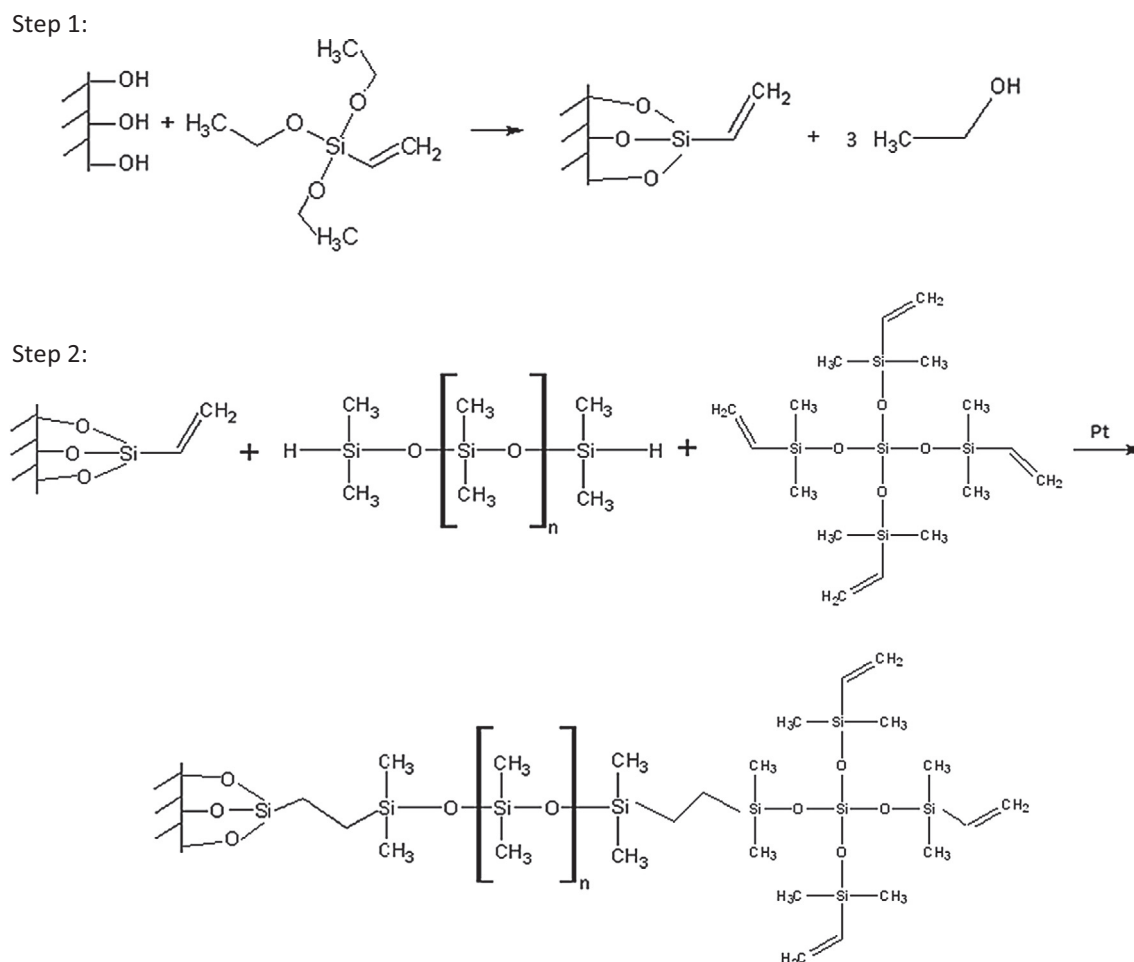

Fig. 1. The reaction steps of grafting γ-alumina with the vinyltriethoxysilane linker (step 1) and subsequently with hydride terminated polydimethylsiloxane (PDMS) plus the coupling agent tetrakis(vinyldimethylsiloxy)silane (step 2).
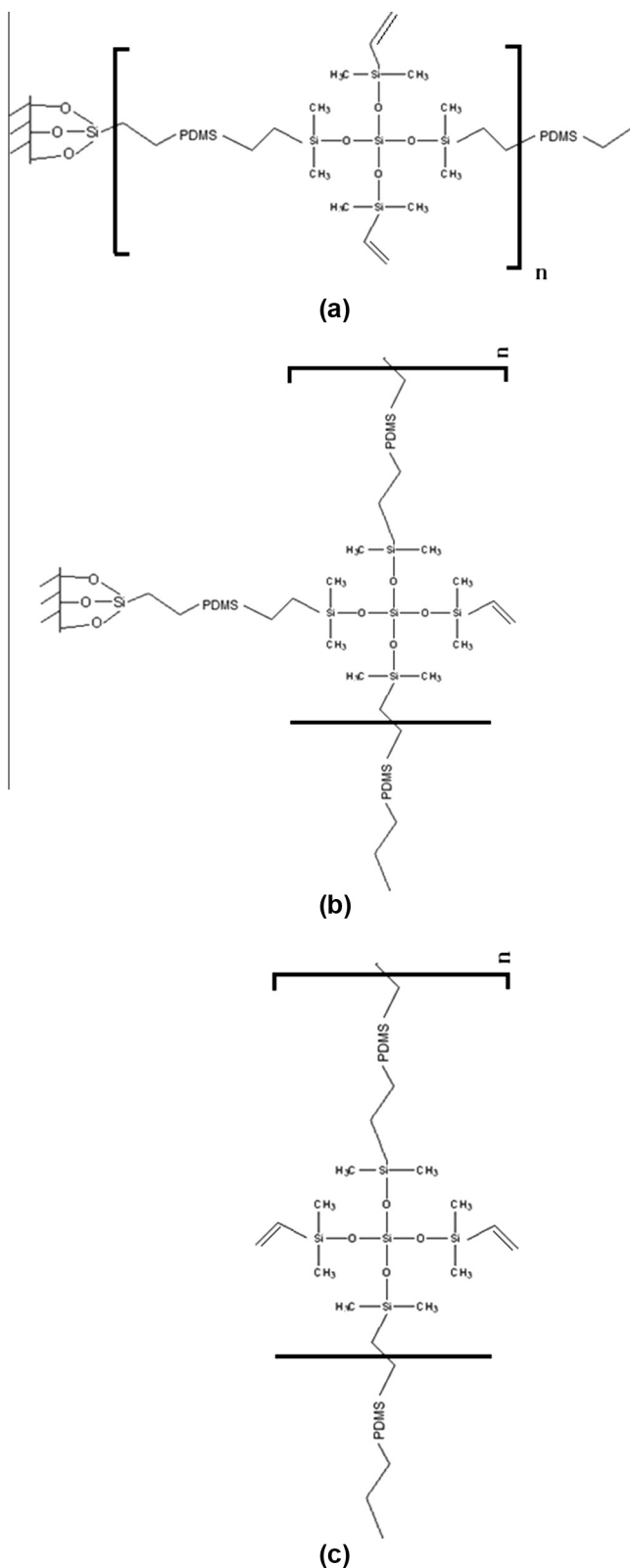
(a)

(b)

(c)

Fig. 2. Several possible structures resulted during random grafting: (a) and (b) possible morphologies of grafting on the inorganic surface; (c) "free" polymer, formed without reaction with the inorganic surface.

Fig. 3. FTIR absorbance spectra of (a) unmodified γ-Al$_2$O$_3$; (b) vinyl grafted γ-Al$_2$O$_3$; (c) coupled-PDMS grafted γ-Al$_2$O$_3$.

means that one or more hydrolysable groups out of total three functional alkoxy groups that are present at the vinyltriethoxysilane linking agent can react with the surface hydroxyl groups of γ-Al$_2$O$_3$ forming a covalent Si—O—Al bond between linker and alumina membrane surface, or a hydrolyzed alkoxy group reacts with an adjacent silanol through the reaction of —Si—OH + Si—OH → —Si—O—Si— + H$_2$O, forming a covalent Si—O—Si bond. In Fig. 3b, the peak at 1399 cm^{-1} is ascribed to the bending of CH$_2$ of the vinyl groups (—CH=CH$_2$), while the peak at 1635 cm^{-1} is a characteristic absorption peak for the bending of the vinyl C=C groups [22]. The peaks at 2845 and 2912 cm^{-1} can respectively be attributed to the asymmetric and symmetric stretching of CH$_2$ and furthermore the peak at 2980 cm^{-1} is attributed to the symmetric stretching of C=C of the vinylsilanes [23]. These FTIR results, combined with the fact that none of these peaks are present in the FTIR spectrum of the unmodified γ-Al$_2$O$_3$ (Fig. 3a), clearly demonstrate that the grafting reaction in step 1 of Fig. 1 has occurred.

FTIR data, measured after the grafting reaction, indicated in Fig. 1 (step 2), are given in Fig. 3c. During this reaction step the hydrides (—H) of the hydride-terminated PDMS will react with the vinyl groups (—CH=CH$_2$) of the vinylsilanes, grafted on the γ-Al$_2$O$_3$ surface, as well as with the vinyl groups of the tetrakis-(vinyldimethylsiloxy)silane coupling agent. This hydrosilylation reaction will form a stable covalent (—Si—C—C—Si—) bond (see Fig. 1, step 2). The peaks at 1399 cm^{-1} and 1635 cm^{-1}, ascribed to resp. CH$_2$ and C=C bending of the vinyl groups (—CH=CH$_2$), as present in the silane grafted γ-Al$_2$O$_3$ system (indicated in Fig. 3b), are no longer observed after the reaction with PDMS plus coupling agent (see Fig. 3c). From these results it can be concluded that the amount of vinyl groups, if they are present after reaction step 2 (Fig. 1), is below the detection limit. This confirms that a complete hydrosilylation reaction has occurred of hydride PDMS with the vinyl groups of the linking agents and/or the vinyl groups of the coupling agent. In the FTIR spectrum of the PDMS grafted powder, the peak at 793 cm^{-1} is attributed to the stretching of Si—C from the SiCH$_3$ group of PDMS [21]. The two peaks at 1017 and 1092 cm^{-1} can be ascribed to the Si—O—Si group of dimethylsiloxanes [21,23]. A characteristic peak at 1260 cm^{-1} is attributed to

lane) with γ-Al$_2$O$_3$, as indicated in step 1 of Fig. 1. The broad peak in the region 1000–1100 cm^{-1} consists of a peak at 1060 cm^{-1} and a peak at 1090 cm^{-1} which can be attributed to the formation of covalent Si—O—Al and Si—O—Si bonds respectively [19–21]. This
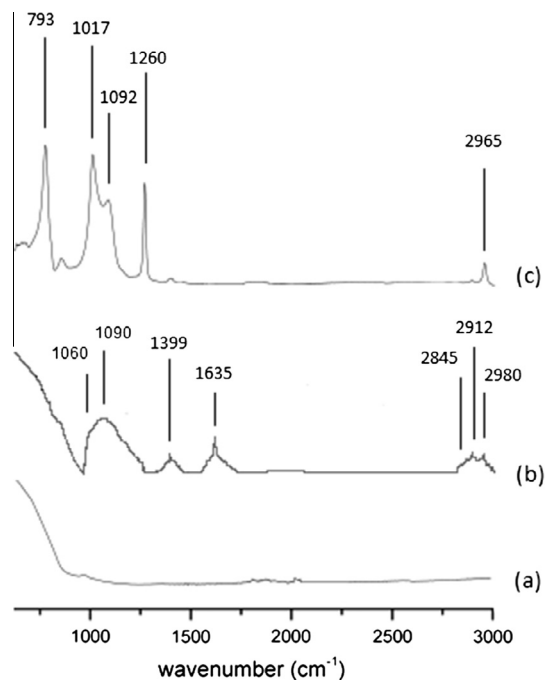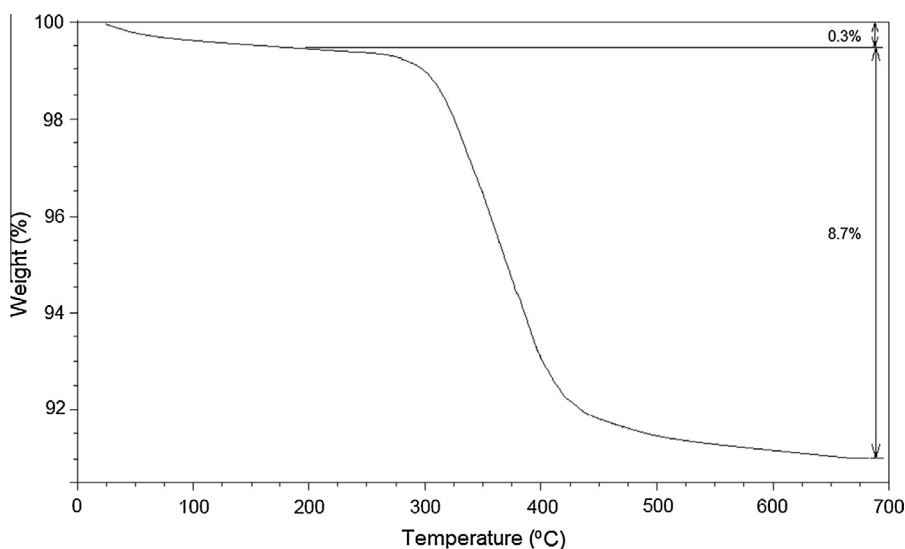
Fig. 4. TGA results of the PDMS grafted γ-Al$_2$O$_3$ powder.

Table 1
Water contact angle of unmodified γ-Al$_2$O$_3$, vinyl grafted γ-Al$_2$O$_3$, and PDMS grafted γ-Al$_2$O$_3$.

	Unmodified (γ-Al$_2$O$_3$ membrane)	After silanization with vinyltriethoxysilane	After reaction with PDMS and tetrakis (vinyldimethylsiloxy) silane
Contact angle (°)	0	63 ± 2	108 ± 1

symmetric C—H bending from the SiCH$_3$ group. The peak at 2965 cm^{-1} can be assigned to the asymmetric stretching of C—H of the methyl groups of the PDMS [23]. The presence of all these IR peaks indicates the presence of PDMS on the grafted powder and that the reactions, as given in Fig. 1, have occurred [3,18,21,23].

Fig. 4 shows the TGA results of PDMS grafted γ-Al$_2$O$_3$ powder. A first stage of weight loss (around 0.3%) was observed up to 200 °C. This initial weight loss can be attributed to the evaporation of adsorbed solvents from the samples. A second stage in weight loss of 8.7% was found at higher temperatures with a maximum loss observed in the temperature range between 300 °C and 400 °C. This significant weight loss can be attributed to the decomposition of the organic groups from the grafted samples. The decomposition temperature of the organic groups is higher than the boiling point of the individual grafting agents which are 205 °C, 160 °C, and 130 °C, respectively for the hydride PDMS, vinyltriethoxysilane, and tetrakis(vinyldimethylsiloxy)silane. Thus, the TGA analysis suggests that due to grafting an increase in the thermal stability of the organic moieties is achieved.

3.2. Membrane characteristics

The results of the contact angle measurements on unmodified, silane-grafted, and polymer-grafted γ-Al$_2$O$_3$ membranes are given in Table 1. The contact angle values are the average of contact angles taken from 5 different points on the membrane surface. The almost negligible standard deviation indicates that the grafting reaction has occurred homogeneously over the membrane surface.

For the unmodified gamma-alumina membrane, the water droplet immediately wetted the membrane surface. A corresponding water contact angle of 0° is therefore assumed, indicating the hydrophilic character of the γ-Al$_2$O$_3$ membrane due to natural

occurrence of hydroxyl (OH—) groups on the ceramic surface. A relatively higher contact angle was observed after modification of γ-Al$_2$O$_3$ with vinyl triethoxysilane. The higher contact angle might be attributed to the presence of the vinyl groups. Vinyl (C=C) groups are less polar than hydroxyl (OH—) groups, causing a weaker attraction between the water droplet and the vinyl-grafted γ-Al$_2$O$_3$ membrane, and thus a relatively higher contact angle. Other factors such as the nanotextures of the grafted moieties as a result of the molecule orientation, the grafting density of the grafted moieties, as well as the presence of the pores can contribute to the actual contact angle value [24].

After grafting with PDMS and coupling agent an increase in contact angle was observed. A higher contact angle for the PDMS-grafted membranes relative towards the vinyl grafted γ-Al$_2$O$_3$ membranes might be attributed to the nonpolarity of dimethylsiloxane groups. The contact angle measurement suggests that a change in the membrane surface wettability has occurred after grafting. For a comparison, a contact angle in the range of 91–97° was observed for γ-alumina membranes grafted with a mono-epoxy-terminated PDMS (n = 10), using an aminosilane as the linker [3], and a contact angle of 95° was observed for γ-alumina membranes grafted with a mono-vinyl-terminated PDMS (n = 39), using mercaptopropylsilane as the linker [4]. The slightly larger contact angle observed in this work, when compared to the previously reported results, might be attributed to the more dense structure realized due to the use of a coupling agent.

3.3. Membrane performance

Fig. 5 shows the flux of toluene, ethyl acetate and isopropanol through the modified membranes at different trans membrane pressures (TMPs) at 20 °C.

A linear relationship of flux versus pressure was observed for increasing as well as decreasing trans membrane pressure (TMP). The linearity of flux versus TMP suggests that the membrane structure does not deform under the applied TMP.

In Table 2, the fluxes of toluene, ethyl acetate, and isopropanol and the rejection results of Sudan Black in different types of solvents at 20 °C and TMP of 10 bar for the three types of membranes are given. No significant differences were observed between the flux of the solvent with solutes and that of the pure solvents suggesting that no concentration polarization occurred during the rejection measurements at 50% recovery.

A membrane permeability constant (k) is determined from the Hagen-Poiseuille relation $\left(J_i = \frac{k_i}{\mu_i}\Delta P\right)$ (Table 2). This viscosity-corrected membrane permeability constant is a function of the parameters representing the membrane pore geometry as given by: $k_i = \frac{\varepsilon_i r_{p,i}^2}{8\tau l}$, where ε_i is the membrane porosity, $r_{p,i}$ the pore diameter, τ the membrane tortuosity, and L the membrane thickness.

The results in Table 2 indicate that there is an increase in flux and permeability constant and a decrease in retention from M1 to M2 to M3. A trade-off is seen between the flux and rejection in which a higher flux accompanied by a lower rejection.

If for all solvents the membrane-solvent interaction is identical, k should be independent of the type of the permeating solvent. However, the results in Table 2 indicate that for all three membranes (M1, M2, and M3) different k values were observed for each solvent and each membrane types. The ratio of k in one solvent towards that in a reference solvent can be used to indicate the effect of the membrane-solvent interaction between the membrane and the permeating solvent on the membrane pore geometry as described in [25]. In mathematical form, it is given by

$$k_i' = \frac{k_i}{k_{ref}} = \frac{\frac{\varepsilon_i r_{p,i}^2}{8\tau l}}{\left(\frac{\varepsilon_i r_{p,i}^2}{8\tau l}\right)_{ref}} = f(V_{s,i}') = A - BV_{s,i}' \qquad (1)$$
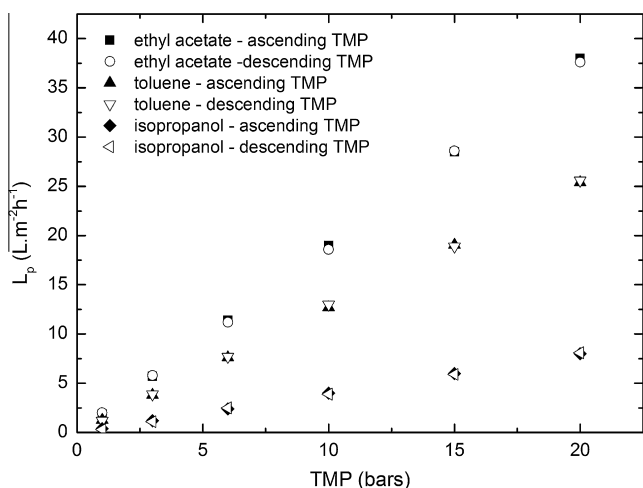

Fig. 5. Flux of toluene, ethyl acetate, and isopropanol through the modified membranes as a function of trans membrane pressure (TMP) at 20 °C.

with k_i the membrane permeability constant for solvent i, k_i' the membrane permeability constant for solvent i normalized for the k value of a reference solvent k_{ref}, $V_{s,i}'$ the sorption volume of sorbed solvent i per mass of the grafted material, normalized towards solvent of reference, and A the intercept and B the slope of a plot of k_i' versus $V_{s,i}'$. By making this correction for the sorbed volume, identical values (thus independent of solvent) of the permeability constant were observed as discussed in detail in [25].

Toluene has the strongest interaction with PDMS, followed by ethyl acetate and finally by isopropanol. Buekenhoudt et al. observed that not only solvent viscosity is important in determining the solvent transport through non-swollen ceramic membranes, but also the polarity difference between membrane and solvent influences solvent transport [26]. Further on, Marchetti et al. studied the role of preferential solvation on the non-aqueous transport through titania membranes [27]. According to the model, as proposed in the work of Marchetti et al., the membrane should be more permeable when the solvent-membrane affinity is strong, if compared to those solvents with a weaker affinity to the membranes. However this is in contrast to our results, (see Table 2), because here the permeability of toluene (having stronger affinity with PDMS) is much lower than that of isopropanol (having lower affinity with PDMS). The lower permeability of toluene (as compared to that of isopropanol) through the grafted membranes is attributed to the presence of the grafted organic moiety in the pores. For grafted membranes, the swelling of the grafted moiety (sorption of solvents by the grafted moiety) in the presence of a strongly swelling solvent (such as toluene) results in a more closed membrane structure than that in the presence of a less stronger swelling solvent [25]. According to Eq. (1), the membrane permeable volume reduces if the solvent is strongly swelling the membrane material. The Hagen-Poiseuille pore flow model, corrected for solvent sorption, can be applied for all three membranes. For the M1 (the coupled PDMS grafted membrane) the strongest interaction of toluene with the grafted PDMS results in the smallest membrane permeable volume if compared with the solvents ethyl acetate and isopropanol.

The more closed membrane structure in the presence of toluene, as a result of a stronger membrane-solvent interaction, is therefore the cause of the higher Sudan Black rejection observed in toluene as compared to those in other solvents. As a similar ceramic porous ceramic substrate is used for all types of grafted membranes, the higher Sudan Black rejection of M2 compared to that of M3 might be explained by the difference in the chain length of the

Table 2
Solvent fluxes (J), Hagen-Poiseuille membrane permeability constants (k) and Sudan Black rejections (R) in different solvents at 20 °C and TMP of 10 bar for different PDMS-grafted alumina membranes.

			M1	M2[b]	M3[b]
Flux J (L m^{-2} h^{-1})	Toluene	Pure	12.7 ± 0.4	23.8 ± 1.0	30.6 ± 1.2
		Plus dye[c]	12.7 ± 0.3	23.7 ± 1.0	30.6 ± 1.2
	Ethyl acetate	Pure	19.0 ± 0.7	35.7 ± 1.4	44.8 ± 1.8
		Plus dye[c]	19.0 ± 0.7	35.8 ± 1.0	44.7 ± 1.7
	Isopropanol	Pure	4.0 ± 0.1	7.5 ± 0.3	9.0 ± 0.4
		Plus dye[c]	4.0 ± 0.1	7.6 ± 0.2	9.0 ± 0.3
k[a] (L m^{-2})	Toluene		0.21 ± 0.02	0.40 ± 0.02	0.51 ± 0.02
	Ethyl acetate		0.24 ± 0.02	0.46 ± 0.02	0.57 ± 0.02
	Isopropanol		0.27 ± 0.02	0.50 ± 0.02	0.60 ± 0.02
R at 50% recovery (%)	Toluene		95 ± 1	65 ± 1	45 ± 1
	Ethyl acetate		88 ± 1	47 ± 1	30 ± 1
	Isopropanol		80 ± 1	35 ± 1	20 ± 1

[a] k for pure solvent: The viscosity corrected membrane permeability constants according to the Hagen-Poiseuille equation, $k = J\frac{\mu}{\Delta P}$, with J solvent flux, μ the solvent viscosity, and ΔP the applied pressure.
[b] Details on fabrication of M2 and M3 membranes can respectively be found in Refs. [3,4].
[c] Flux of solvent containing 8000 ppm Sudan Black B dye.

PDMS used for grafting. When the flux data of grafted membranes with identical PDMS chain length (n = 10) with (M1) and without the use of a coupling agent (M3), then it can be seen that M1 showed 2.3–2.4 times lower flux than M3. A higher Sudan Black B rejection is achieved for M1 if compared with M3. This is an indication that the pore size of M1 is smaller than of M3. This may be a result of the thicker grafted material in the pores due to the use of a coupling agent.

It is worth to mention that the increase in rejection for the membrane, when using a coupling agent during grafting, is associated with a decrease in permeability, as indicated by the low permeability of M1 compared to M3. Comparing M1 with M2, and assuming a similar transport model, it can be seen that a stronger pore size reduction is realized for M1 by using a coupling agent, than that of M2 in which a longer chain length of PDMS was used. This indicates that from M1 to M3, there is a trend in an increase in pore size or, in other words, a decrease in thickness of the grafted organic moiety layer in the γ-alumina pores.

4. Conclusion

A method was presented of grafting a mesoporous γ-alumina layer, supported on a macro porous α-alumina membrane, with hydride terminated polydimethylsiloxane coupled with tetrakis-(vinyldimethylsiloxy)silane, by using vinyltriethoxysilane as linking agent in order to create a coupled grafted PDMS network in the ceramic pores for solvent nanofiltration. Grafting performance of the organic moieties on γ-alumina powders was analyzed by FTIR and TGA indicating that grafting of vinyltriethoxysilane and hydrosilylation between the hydride group of PDMS and the vinyl group of the linking and/or coupling agent were successfully carried out. Contact angle analysis on the grafted ceramic membranes showed that the resulting membrane surface rendered hydrophobic with a water contact angle of 108°. From pure solvent permeability and rejection tests in toluene, ethyl acetate, and isopropanol using Sudan Black as probe solute, an increased Sudan Black B rejection was found for membranes grafted with the use of coupling agent than those without the use of coupling agent. The use of a coupling agent increases the grafted organic layer thickness in the gamma alumina pores and thus a higher rejection for nanofiltration of a Sudan Black dye is observed, but with the cost of lower permeability, if compared with PDMS-grafted alumina membranes where no PDMS-coupling agent was applied.

Acknowledgement

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