Hydrolytic stability of PEG-grafted γ-alumina membranes: Alkoxysilane *vs* phosphonic acid linking groups

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ABSTRACT

Small polyethylene glycol (PEG) molecules were grafted on ceramic γ-alumina membranes, by making use of organo-alkoxysilanes or organo-phosphonic acids as linking groups. It was proven by FTIR that the short PEG brushes are chemically grafted into the pores of a 5 nm γ-alumina mesoporous support, which results in a decrease of the pore diameter as measured by cyclohexane permporometry (reduction of 2.1 nm). The stability of these PEG-grafted membranes was investigated in water for 216 h. Permeability and liquid state ^{1}H NMR were used to show that PEG-modified membranes with an alkoxysilane linking group degrade rapidly during exposure to water. On the contrary, the phosphonic acid linking group remained grafted on γ-alumina supports for at least 216 h in water. In conclusion, this work shows a promising and simple method for the fabrication in a green solvent (water) of hydrophilic organically-modified ceramic membranes, which can be successfully applied for wastewater treatment.

1. Introduction

Nanofiltration (NF) processes were first introduced in the 1980s for removal of small organics and divalent ions from water, achieving a molecular weight cut-off (MWCO) in the range of 200–1000 Da [1,2]. The development of solvent stable polymeric membranes makes it possible for the chemical industry to use them as alternatives to conventional separation methods, like distillation, which are energy, material, and capital intensive [3]. To broaden the application of membranes in the chemical industry, membranes must show high stability under pressure, high temperatures, and in the presence of aggressive solvents. However, many polymeric membranes, while under high pressure (compaction) and/or in apolar solvents (swelling), suffer from performance drop.

Ceramic membranes can offer a solution, due to their high mechanical, chemical and thermal stability, which makes them applicable in organic solvent nanofiltration (OSN) [4,5], desalination and wastewater treatment [6–9]. Most pristine ceramic membranes are in general unable to remove small organic molecules (<400 Da) and dissolved salts, which makes them unsuitable for NF applications. To reduce the pore size of the respective membrane, polymers with low molecular weight can be chemically tethered via a linking group on porous

γ-alumina [4,5,10], silica [11], titania [12] or zirconia [13] supports.

Tanardi et al. [14], used alkoxysilanes as linking groups to graft polydimethylsiloxane (PDMS) on mesoporous γ-alumina supports, resulting in higher rejections of small molecular weight polyethylene glycols (PEGs) in comparison to pristine γ-alumina membranes (MWCO of 400–600 Da instead of 7500 Da). In another paper [10], γ-alumina porous supports were modified with PEG-alkoxysilane with various functional groups (e.g., bis-linking group, ureido group) and different ethylene glycol units (between 10 and 45) and it is proven, by using a combination of characterization techniques (FTIR, ^{29}Si NMR, TGA, N$_2$ sorption), that surface modification can be achieved in one step under an inert atmosphere. These membranes showed higher permeabilities for hexane than for ethanol and Sudan Black (456 Da) rejections of 54 and 89% were observed respectively for each solvent. However, in these works, no spectroscopic analysis of the modified membranes was conducted, to confirm chemical grafting of the polymer with the inorganic surface. Additionally, the stability of the layer during extended solvent permeation measurements was not studied.

The field of metal-oxides surface modification is dominated by alkoxysilane linking groups. However, several studies indicate that alkoxysilane grafted oxides are hydrolytically unstable [15,16]. Szczepanski et al. [15] assessed the hydrolytic stability of 3

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aminopropyltrimethoxysilane (APS) and 3-(2- aminoethyl)aminopropyl trimethoxysilane (AEAPS) modified anodized aluminium oxide (AAO) membranes. The primary amines, on the grafted surface, were further reacted with a succinnimidyl ester substance leading to amide bond formation. Then, the grafted membranes were treated with a phosphate buffer saline solution (pH = 7.6) and post-treatment analysis showed a decrease in the concentration of the grafted material, on the surface, over time in the buffer solution. The effect was found to be most dramatic with the AEPAS, which has a free secondary amine that according to Szczepanski affects the pH near the grafted surface where the Si–O–Al bond is located. Therefore, the authors claim that the stability of the Si–O–Al bond depends on the pH surrounding the grafted surface and thus implying that alkoxysilane grafted alumina should be relatively stable under neutral aqueous conditions.

Kujawa et al. [16] assessed the stability under hydrolytic conditions with pure and basic water (pH 12–14) of a series of hydrophobic polymer brushes (perfluoroalkyl-triethoxysilane), grafted on alumina, as well as titania and zirconia powders The authors followed the degradation of the polymeric layer via TGA analysis before and after the modified materials were treated in air or aqueous solution. Small degradation (5–8%) was observed in water after a prolonged time (1–2 years). However, significant degradation (30%) was observed under basic conditions within 2 h of immersion, demonstrating the good stability of alkoxysilane grafted oxides in pure water, as compared to their rapid degradation under extreme pH's.

Moreover, Debrassi et al. [17] compared the stability of different linking groups (hexadecyl -alkoxysilane, -phosphonic acid, -carboxylic acid, -alkyne, and -alkene) in water at pH 7. Utilizing contact angle measurements, the authors identified the alkoxysilane (and phosphonic acid) linking group as stable in water.

It must be emphasized that studies on the stability of alkoxysilane modified alumina materials in water were focussed on either reactive (e. g. primary or secondary amines) functional groups [15] or hydrophobic layers [16,17]. Up to date, no research was performed on the stability of the Si–O–Al in neutral water and in the presence of a hydrophilic inert polymeric layer.

Grignard reagents are well-established alternatives to alkoxysilanes. Mustafa et al. [18], hydrophobized porous titania nanofiltration membranes ($\varnothing_{pore} \approx 0.9$ nm) to mitigate irreversible fouling in wastewater treatment, by using Grignard reagents. Grignard grafting results in a single bond formation between the graft and the titanium centre, resulting in a highly stable graft. The authors [18] observed that methyl and phenyl Grignard grafted membranes showed lower water permeabilities (8–9 L h^{-1} m^{-2} bar^{-1}) compared to pristine membranes (20 L h^{-1} m^{-2} bar^{-1}) but higher resistance to irreversible fouling. Even though, Grignard grafting on the titania surface offers a good and stable alternative to alkoxysilanes, the strict conditions (i.e., multiple reaction steps, oxygen and water-free) can be troublesome for large scale applications [12].

Organo-phosphonic acids were successfully used for surface modification of a wide range of ceramics providing a stable and easy-to-synthesize graft [17–19]. The phosphonic acid (PA) linking group can react even under aqueous conditions by condensation (P–OH) and/or coordination (P=O) with the support surface to form up to three P–O–M bonds per molecule [20]. Mustafa et al. [18], used methyl and phenyl phosphonic acid grafts to modify titania membranes with a pore size of 0.9 nm. The resulted membranes exhibited slightly lower permeabilities compared to the pristine ceramic support (15 instead of 20 L h^{-1} m^{-2} bar^{-1}) and a similar PEG MWCO (≈ 500 Da). However, a smaller degree of irreversible fouling was found compared to the unmodified titania membrane. Up to date, the surface modification of micro or mesoporous ceramic supports with phosphonic acid linking groups was reported using small molecules (e.g., ethyl, phenyl, etc.) [18,21–24].

The preparation of hydrolytic-stable polymeric/ceramic hybrid membranes requires a precise selection of the linking group and the composition of the graft. In this work, we explore the hydrolytic stability

of modified polyethylene glycol (PEG)/γ-Al$_2$O$_3$ membranes and the influence on the chemical nature of the linking group. Two types of linking groups were selected, namely the trimethoxysilane and phosphonic acid linking groups, with various short chains (between 7 and 11 units) of polyethylene glycols (PEGs). A PEG layer, grafted on a porous ceramic support in order to reduce its pore size, has the potential to improve the membrane performance in water, due to its hydrophilic nature. Furthermore, the PEG polymers used have no reactive functional groups and thus cannot promote any Si–O–Al bond activation, contrary to previous findings [15]. This, allows us to observe the stability of the Si–O–Al bond in pure water for the first time. Details and sample codes of the precursor materials used are given in Fig. 1. The phosphonic acid-grafted membranes are prepared in water under ambient atmosphere, while for the alkoxysilane grafted-membranes toluene was used as a solvent and a water-free environment (nitrogen flow) is necessary. The chemisorption of the linking groups is investigated using a set of characterization techniques, such as FTIR, permporometry, and water contact angle. Finally, the stability of the chemical bond between the precursor and the ceramic is tested at room temperature in water and evidenced by water permeation measurements and ^{1}H liquid NMR.

2. Experimental

2.1. Materials

The alpha-alumina (α-Al$_2$O$_3$) substrates (disc: 21 mm of diameter, 2 mm of thickness, 80 nm pore diameter) were supplied from Pervatech B. V., the Netherlands. These ceramic substrates comprise primarily of macroporous α-alumina (>99%), which ensures mechanical stability under pressure. The polished side of these supports were dip-coated with a boehmite sol and subsequently calcined at 650 °C for 3 h. The procedure was performed twice to eliminate any defects on the surface of the inorganic membrane, yielding a thin inorganic layer of 3 µm in total thickness and an average pore diameter of 5 nm (as determined by cyclohexane permporometry). Further details for the fabrication and the characteristics of the γ-Al$_2$O$_3$ layer can be found elsewhere [25,26]. Mesoporous γ-Al$_2$O$_3$ flakes were prepared using 30 mL of the same boehmite sol as used for dip-coating and obtained the same calcination procedure as described above.

MethoxyPEG10-phosphonic acid ethyl ester (MePEG10PE, 650 g/mol), PEG10-phosphonic acid ethyl ester (PEG10PE, 588.1 g/mol), MethoxyPEG11-triethoxysilane (MePEG11Si, 720.96 g/mol), MethoxyPEG7-triethoxysilane (MePEG7Si, 544.75 g/mol) starting materials were purchased from Specific Polymers and used as received. Anhydrous toluene (99.8%), anhydrous dichloromethane (99.8%), ethanol (absolute), sodium hydroxide (0.1 M) and the
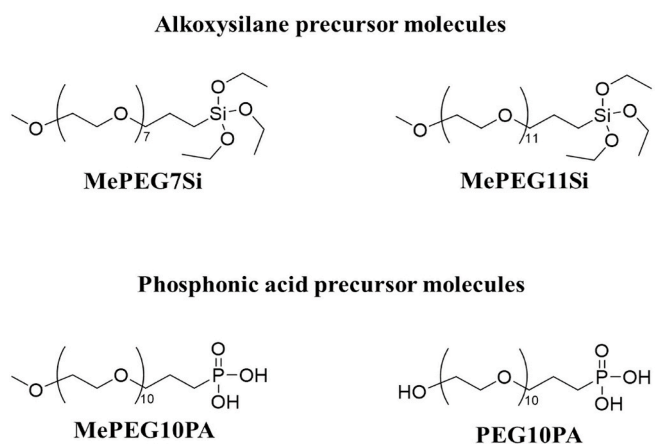
Alkoxysilane precursor molecules

MePEG7Si   **MePEG11Si**

Phosphonic acid precursor molecules

MePEG10PA   **PEG10PA**

Fig. 1. Chemical structures of precursor materials used for the fabrication of membranes and code names of the fabricated membranes.

bromotrimethylsilane (TMSBr 97%) were supplied by Sigma-Aldrich and used without further purification. Ultrapure MilliQ water was used in all reactions.

2.2. Synthesis of the PEG phosphonic acids

The MethoxyPEG10-phosphonic acid (MePEG10PA) and the PEG10-phosphonic acid (PEG10PA) were synthesized by the method as described by McKenna et al. [27]. The (under anhydrous condition) reaction between bromotrimethylsilane (TMSBr) and phosphonate esters (MePEG10PE or PEG10PE) results in the formation of the corresponding trimethylsilyl phosphonate esters. Hydrolysis of these trimethylsilyl phosphonate esters afforded the desired phosphonic acids in the form of brown viscous liquids with 98% yield. The detailed experimental procedure and the spectroscopic analysis (FTIR, ^{1}H and ^{13}C NMR) are provided in the supporting information and are in good agreement with literature data.

2.3. Grafting procedure

Prior to grafting, the γ-alumina mesoporous supports or flakes were soaked in an ethanol/water (2:1) mixture, to ensure a clean surface and to provide additional hydroxyl groups on the pore surface. Then, the solution was decanted for the membranes, whereas the flakes were centrifuged. The materials were then dried at 50 °C under vacuum for 12 h.

2.3.1. Preparation of the PEG-alkoxysilane grafted γ-alumina membranes and flakes

The PEG-alkoxysilane modified membranes were prepared by adapting the grafting procedure from Tanardi and co-workers [10], using similar γ-alumina discs. Under an inert atmosphere, 0.1 mmol of either MePEG7Si or MePEG11Si was placed in a reaction flask and dissolved in 100 mL of anhydrous toluene. Subsequently, the γ-alumina mesoporous support was immersed in the solution and stirred for 24 h at 110 °C. After this time, the solution was cooled to room temperature and the resulting PEG-alkoxysilane/γ-alumina grafted membranes were washed in a sonicated bath with 5 mL of toluene (1x) and subsequently with 5 mL of ethanol (3x) for the total duration of 2 h. The samples, denoted MePEG7Si or MePEG11Si reflecting the polymer used, were dried under vacuum for 12 h at 50 °C. For the preparation of the PEG-alkoxysilane grafted γ-alumina flakes, the same procedure was employed except that 500 mg of powder were immersed in 50 mL 4.8 mM PEG-alkoxysilane solution.

2.3.2. Preparation of the PEG-phosphonic acid grafted γ-alumina membranes and flakes

Here 0.1 mmol of the PEG phosphonic acid (either MePEG10PA or PEG10PA) was added in a reaction flask and dissolved in 100 mL water. The pH of the solution, which was initially ~3, was adjusted to 4 by dropwise addition of 0.1 M NaOH solution. The pH of the reaction solution was adjusted to 4 in order to avoid any possible degradation of the γ-alumina surface, during the grafting reaction. Subsequently, the γ-alumina mesoporous support was placed in the solution and it was refluxed for 24 h at 100 °C. The resulting PEG-phosphonic acid grafted γ-alumina membranes were washed with 5 mL water (1x) and 5 mL ethanol (3x) in a sonicated bath for 2 h. Finally, the modified ceramics, denoted MePEG10PA or PEG10PA, were dried 12 h under vacuum at 50 °C. For the preparation of the PEG-phosphonic acid grafted γ-alumina flakes the same procedure was employed, except that 500 mg of powder were immersed in 50 mL of a PEG-alkoxysilane solution at 4.8 mM.

2.4. Characterization

FTIR analyses on pristine and grafted γ-alumina membranes were conducted using a PerkinElmer Spectrum 100 spectrometer. Spectra

were recorded in the 4000-600 cm^{-1} range using 10 scans at a resolution of 4 cm^{-1} (γ-alumina spectrum was used as background).

TGA analyses on grafted and non-grafted γ-alumina flakes were conducted by a coupled TGA-MS 2960 from TA Instruments. γ-Alumina flakes were used instead of membrane samples, due to the low relative amount of γ-alumina, compared to the whole ceramic support, leading to low concentrations of grafted material in the membrane. As a result, the low weight of the polymer in the membrane sample can significantly affect the quality of the measurements. In all cases, a two-step program was utilized; room temperature to 150 °C at a heating rate of 10 °C/min under nitrogen and dwell 1 h (drying step), subsequently heated to 1000 °C at a heating rate of 2 °C/min under nitrogen and dwell for 1 h in air to remove any remaining organic material. Each test was performed with approximately 40 mg of material.

Water contact angle data, using the sessile drop method, were collected on grafted γ-Al$_2$O$_3$ membranes by a QCM Optical Contact Angle instrument. For individual samples, six spots on the surface were measured and averaged. Three samples were tested for each reaction condition, i.e. 18 data points were used to calculate the average contact angle and the standard deviation.

Cyclohexane permporometry measurements were performed on pristine and grafted γ-alumina membranes to evaluate the pore size distribution, before and after grafting. In this test first, the filling of the pores takes place via capillary condensation of a volatile substance (cyclohexane). During a stepwise decrease of the cyclohexane partial pressure, the pores open in order of decreasing diameter. Simultaneously, the pore size distribution is calculated from flux measurements of non-condensable gases (oxygen and nitrogen) through the free pores, using the Kelvin equation. Dead-end pores are excluded from this measurement. Further details are given in Ref. [28].

For study of the hydrolytic stability of the grafted materials, ^{1}H liquid-state NMR spectra were acquired using a Bruker Ascend 400 MHz NMR spectrometer at frequencies of 400 MHz. Prior to the analysis, the grafted flakes were placed overnight in an oven at 150 °C under a nitrogen atmosphere to obtain well-dried materials. Typically, 10 mg of grafted powder were added in a borosilicate 5 mm NMR tube with 2–3 mL of deuterium dioxide NMR solvent. Finally, the tube was sealed with a polypropylene cap, and spectra were recorded as a function of time. Between measurements, the samples were shaken at 1500 rpm on an IKA™ VXR Basic Vibrax™ Vortex Shaker. For the purpose of this test, the samples were kept sealed from the initial addition of reagents to the last recorded spectrum.

2.5. Water permeability

Water permeability experiments were performed on a dead-end high throughput setup incorporating 8 units in a single measurement. Prior to the experiment, membranes were soaked in water for- 1 h to hydrate the active layer. The stainless steel cell was filled with the feed solution and nitrogen was used to pressurize the cell. Permeate fluxes were obtained by measuring the permeate weight as a function of time. All measurements were conducted on three samples for each type of membrane. At every pressure point, 3 data sets were recorded every 0.5 – 1 h and averaged to find the water flux of the membrane.

3. Results and discussion

With the aim to develop hybrid ceramic membranes for aqueous waste treatments, polyethylene glycol (PEG) brushes were grafted on the pore surface of γ-alumina mesoporous substrates with a native pore diameter of 5 nm. According to Ref. [29], the radius of gyration of PEG polymers in solution, having similar Mw as the ones used in our study, is approximately 0.5 nm for MePEG7Si and between 0.6 and 0.7 nm for the other PEG polymers used. The alkoxysilane linking group is calculated to have a radius of approximately 0.3–0.4 nm, whereas the phosphonic acid is a more compacted group and has a calculated radius of 0.1–0.2

nm. Thus, it is expected that in the reaction mixture the molecules exhibit a minimum length of 1.6 nm and a maximum of 2.2 nm. This means that the molecules can infiltrate from the bulk solution into the 5 nm pores of the γ-alumina layer and graft the pore surface. Nevertheless, the grafting reaction was performed for 24 h under reflux, to allow for higher grafting densities inside the ceramic pores.

Water contact angle results of both the unmodified γ-alumina substrate and the grafted membranes are shown in Table 1. For each set of membranes, identical water contact angle values were obtained at different locations on the membranes, suggesting a homogeneous grafting over the entire surface. Independently of the linking function used, the water contact angles increased after grafting from 0° for γ-alumina to values around 35–50° for the grafted membranes. An increase in water contact angle is correlated with change in surface properties of the membranes. According to Tanardi et al., PEG-alkoxysilane modified membranes exhibit water contact angles of about 40°, which is in accordance with the results provided here. It must be noted that values lower than 90° correspond to surfaces with high wettability. Thus, PEG grafted membranes show hydrophilic properties [30].

To study the pore size of the hybrid membranes, cyclohexane permporometry measurements were conducted (Table 1). Independently of the type of PEG used (either 7 or 11 units), the alkoxysilane-modified membranes show a pore shrinkage, compared to the bare γ-alumina membrane, of approximately 2 nm. On the other hand, the phosphonic acid-modified membranes show a smaller decrease in pore size varying between 1.1 and 1.5 nm. For identical PEG unit lengths (compare MePEG10PA and MePEG11Si) a large difference in pore size is observed. This can be explained by homocondensation reactions occurring between trifunctional alkoxysilanes, which does not occur with phosphonic acid linking groups [31]. This homocondensation means that the relatively reactive alkoxysilane group can condense with other alkoxysilanes on the ceramic surface forming a multilayer. Besides, alkoxysilane homocondensation can lead to denser monolayers, resulting in the polymer chains extended away from the inorganic surface [32]. Both cases can result in significant pore shrinkage. In addition, Tanardi et al. [10], showed by means of solid-state NMR that polymeric chains can hinder homocondensation reactions between alkoxysilanes and thus hinder multilayer formation, suggesting that under our grafting conditions monolayer formation is promoted.

The phosphonic acid, on the other hand, exhibits two distinctive reaction pathways [20]. The first reaction pathway involves the hydroxyl groups (Al–OH) on the ceramic surface which act as nucleophiles and attack on the electrophilic phosphorus atom of the phosphoryl group (P=O). As a result, a P–OH group can acquire a free proton (H^+) and expel a water molecule leading to the consumption of the P–OH groups under grafting conditions. The second reaction pathway involves the coordination of the electron-rich oxygen atom of the phosphoryl group (P=O) to a Lewis acid centre. Thus, the activation occurs via the formation of a phosphoryl-aluminium complex, which can react with neighbouring hydroxyl groups, yielding a stable Al–O–P bond [33]. The difference in reactivity between phosphonic acid and alkoxysilane linking groups could potentially explain the pore size differences.

TGA analysis was performed on PEG-modified γ-alumina flakes to assess the amount of grafted species on the ceramic support (or reaction yield). For TGA analyses γ-alumina flakes were used (see experimental section 2.4). The TGA curves of unmodified and modified γ-alumina flakes are shown in Fig. S8 of the supporting information (Section C), while the resulting weight losses are given in Table 1. At temperatures above 200 °C the PEG-modified flakes show a more significant drop in weight, compared to the unmodified γ-alumina flakes, which is attributed to the presence of PEG on the ceramic surface. Alkoxysilane-modified flakes show a 10% weight loss whereas phosphonic acid-modified flakes show a loss of~ 5% organics by weight, compared to unmodified γ-alumina. Tanardi et al. [10], showed similar weight losses (10%) for PEG-alkoxysilane-modified flakes. From the weight loss data, a qualitative analysis of the reaction yield (grafting density) is made and the results are provided in Table 1. The alkoxysilane grafted flakes show higher reaction yields than the phosphonic acid PEG derivatives (50–60% difference). As mentioned before, this is attributed to the higher reactivity of the alkoxysilane linking group in toluene compared to the reactivity of the phosphonic acid in water and in agreement with the smaller pore shrinkage observed for the phosphonic acid derivatives.

A large difference in reaction yields is also observed between the two alkoxysilane grafted flakes. The MePEG7Si graft has approximately 50% more yield than the MePEG11Si, while for both alkoxysilane derivatives a pore shrinkage of about 2 nm was observed by cyclohexane permporometry (see Table 1). According to well-established polymer chemistry rules, the polymer chain height, H, which correlates with layer thickness and thus pore-size reduction, depends on the nature of the medium, i.e. the solvent. In "good" solvents the height of the brush is linearly correlated to the polymer length, n, and the grafting density, σ. In "poor" solvents the height relates linearly with the length, n, but shows a lower dependency with the grafting density, $\sigma^{0.33}$ [33]. Thus, in cyclohexane (a "poor" solvent used for permporometry) the polymer length, rather than grafting density, will have a large effect on the brush height and thus to the pore size measured by cyclohexane permporometry. Therefore, from permporometry and TGA results we can assume that alkoxysilanes are forming monolayers under the grafting conditions used herein.

FTIR analyses provide insight in the reactions of the linking groups with the inorganic surface. The high resolution of the ATR-FTIR equipment used allows us to perform detailed measurements on the grafted membranes, as given in Fig. 2. Reports in literature show that grafting can result in the formation of different grafted states with varying stabilities. Brodard-Severac et al. [34] found, by means of ^{17}O MAS NMR, that phosphonic acid-grafted titania contained approximately 5% of unreacted acidic sites (P–OH), implying the presence of multiple species. In addition, FTIR analyses can be used to evidence the presence of physiosorbed species, which remain on the surface after thoroughly washing, and affect the stability of the polymeric layer and the performance of the membrane. Fig. 2A shows the FTIR spectra in the range of 700 and 1500 cm^{-1} for the pure molecules. In each spectrum, a high-intensity band at 1095 cm^{-1} is visible and is attributed to the etheric unit (–C–O–C–) of the polymer [35]. The same band is visible for all the grafted ceramic membranes (Fig. 2B), which confirms the
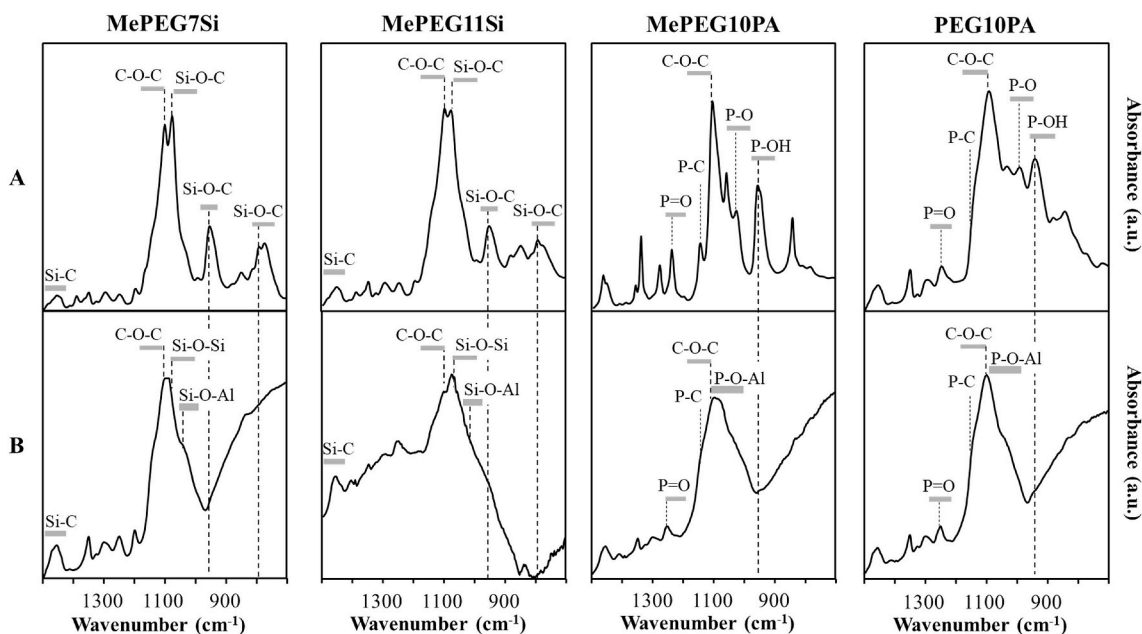
Table 1

Water contact angle and pore diameter of the γ-alumina unmodified substrate and the grafted membranes as well as grafting performance (= reaction yield). The standard deviation is determined from the results obtained from three samples prepared under similar conditions. The pore shrinkage was obtained using the average pore diameter of the γ-alumina and the grafted membranes.

Membrane	N° PEG units	Contact angle (°)	Pore diameter (nm)	Pore shrinkage (nm)	Weight loss PEG (%)	Reaction yield[a] (%)
γ-Al$_2$O$_3$	-	0	5.5 ± 0.1	-	-	-
MePEG7Si	7	51 ± 1.6	3.7 ± 0.2	1.8	10	62
MePEG11Si	11	52 ± 5.0	3.4 ± 0.2	2.1	10	42
MePEG10PA	10	34 ± 9.0	4.4 ± 0.0	1.1	6	26
PEG10PA	10	42 ± 4.0	4 ± 0.1	1.5	5	22

[a] The yields were calculated using the TGA results and by assuming that the weight loss is only related to the decomposition of the organic part. Details on the calculation can be found in the Supplementary Information.

Fig. 2. FTIR spectra of the pure molecules (A) and the grafted membranes (B). The complete spectra from 4000 to 650 cm^{-1} can be found in SI.

integrity of the PEG-polymer after grafting.

Concerning the bands related to the linking group, the pure alkoxysilane (MePEG7/11Si) molecules exhibit two characteristic peaks at 1080 and 815 cm^{-1} which correspond to the stretching vibrations of the unhydrolyzed Si–O–C bonds [36,37]. Moreover, the band at 952 cm^{-1} is attributed to the asymmetrical stretching of the three ethoxy leaving groups (Si–OC$_2$H$_5$), appended on the alkoxysilane functional group [38]. Grafting of the PEG-alkoxysilane on alumina surfaces leads to significant changes for both cases (MePEG7/11Si) observed via FTIR. Accordingly, the broad band centred at 1090 cm^{-1} is ascribed to the formation of a Si–O–Al bond after grafting [39,40]. This is further confirmed by the disappearance of the Si–O–C (1080 and 815 cm^{-1}) bands and the absence of the ethoxy leaving groups at 952 cm^{-1} after grafting [32–35].

The FTIR spectra of the pure phosphonic acid (PA) molecules, as displayed in Fig. 2A, show a band at 1250 cm^{-1}, which is attributed to the stretching vibration of the phosphoryl group (P=O) whereas the stretching of the acidic groups (P–OH) is visible at ~980 cm^{-1} [24,31]. The modified PA membranes (Fig. 2B) exhibit a broad band centred at ~1100 cm^{-1} which is ascribed to the formation of the desired P–O–Al bond [24,41,42]. The P=O bond seems unchanged for the grafted materials, however the disappearance of the P–OH band after grafting indicates bidentate attachment with the surface [41,42]. In conclusion, FTIR analysis suggests that in both cases grafting has been successfully performed with no or no significant amounts of physiosorbed material on the surface of the ceramic support.

3.1. Membrane behaviour in water

The stability in water of the chemical bonding between the PEG molecule and alumina surface was investigated by ^{1}H NMR and water flux experiments as a function of time.

Liquid ^{1}H NMR was used to identify the potential products of the hydrolysis reaction between the modified γ-alumina support and deuterated water (D$_2$O). For this experiment, it was not possible to use directly the grafted membranes, due to the low amount of grafted species compared to the bulk (see also TGA discussion). Therefore, γ-alumina flakes, modified in the same way as was done for the membranes, were used instead. The flakes were immersed in D$_2$O at room temperature, and ^{1}H NMR spectra were recorded in D$_2$O on each sample

at specific times (1 h, 96 h, 288 h for the alkoxysilane and 1 h, 96 h, 408 h for phosphonic acid-modified alumina flakes). During the liquid NMR experiments, only the hydrolysed species which diffuse in the solvent are detected. Because the NMR analyses were conducted in the same tube for each condition, the peak of the etheric unit at 3.69 ppm was used as a reference to follow the appearance of hydrolysed species in the D$_2$O solvent, and for this reason the spectra were plotted from 3 to 4 ppm. The ^{1}H NMR spectra of the pure molecules and the hydrolysed products of grafted alumina flakes are provided in Fig. 3. ^{1}H NMR spectra of the pristine alkoxysilane and phosphonic acid PEG present a very intense peak at 3.69 ppm ascribed to the repetitive etheric unit (–CH$_2$OCH$_2$–). The methoxy end-group of the PEG chain is visible with low intensity at 3.36 ppm. For the PEG-phosphonic acid with the hydroxyl end-group (PEG10PA) this peak at 3.36 ppm is not observed. PEG-polymers are known as hydrolytically stable materials and thus it is expected that hydrolytic stability tests will affect only the linking groups [43]. After a short exposure to D$_2$O (≤1 h) both types of alkoxysilane-grafted flakes (MePEG7/11Si) exhibit two distinctive chemical shifts at 3.69 and 3.36 ppm which can be respectively attributed to the etheric unit of the polymeric chain and the methoxy end-group as a result of the hydrolysis reaction. Moreover, the intensities of these peaks are increasing over time which is due to a higher concentration of hydrolysed species in solution. Thus, the ^{1}H NMR analysis indicates a fast hydrolytic degradation at room temperature of the alkoxysilane graft on γ-alumina materials. Similarly, ^{1}H NMR spectra were recorded for phosphonic acid PEG-modified flakes. The ^{1}H NMR study clearly shows that the phosphonic acid-modified flakes are not affected by the presence of water even after 408 h. Hence, we have clear indications that phosphonic acid PEG-modified materials do not exhibit hydrolysis after a long period in water, at room temperature.

The behaviour of the γ-alumina membranes, in pristine and grafted form, was investigated by water flux measurements at 5 different pressures, as shown in Fig. 4. The data were recorded after the flux reached equilibrium, which was achieved between 0.5 and 1 h after starting the experiment. The pristine γ-alumina supports, tested under similar conditions, show permeabilities of 8–9 L m^{-2} h^{-1} bar^{-1} (Fig. S9), whereas grafted membranes exhibit an almost 10-fold drop in permeability. Tanardi et al. [10] studied the permeability of PEG grafted membranes with apolar (hexane) and polar (ethanol) solvents. The pristine γ-alumina support showed hexane and ethanol permeabilities of 8.4 and
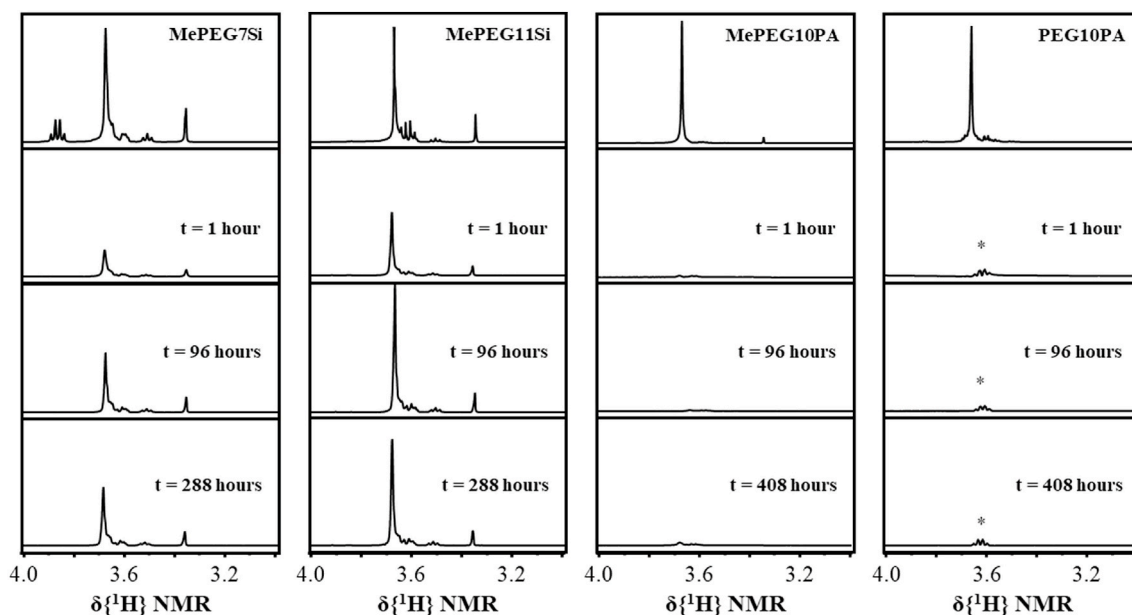
Fig. 3. Liquid ^{1}H NMR of the precursor molecules (top spectra) and the hydrolysed products of the modified γ-alumina flakes after a specified time in deuterated water. The asterisk (*) denotes solvent contamination. The complete spectra from 0 to 5 ppm can be found in SI.
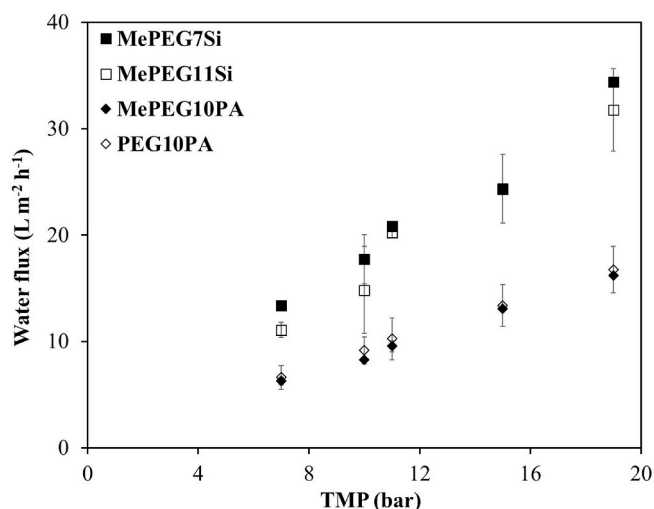

Fig. 4. Water flux as a function of pressure for grafted membranes. Error bars indicate standard deviation between three membranes prepared under similar conditions.

3.4 L m^{-2} h^{-1} bar^{-1}. PEG grafting on the support resulted in lower permeabilities (hexane = 3.4 L m^{-2} h^{-1} bar^{-1}, ethanol = 0.8 L m^{-2} h^{-1} bar^{-1}), showing higher resistance to the polar solvent and thus larger drop in permeability compared with the γ-alumina support (factor 4 drop for ethanol, while a factor 2.5 for hexane). The authors related this permeability trend of the PEG membranes with the swelling degree of the PEG brushes in each solvent. The more polar ethanol swells significantly more the polymers resulting in lower permeabilities. For the same reason the water permeability of the PEG grafted membranes is expected to be significantly lower than the pristine support. Thus, the 10-fold drop in water permeability observed in our study is probably related to a strong swelling degree of the grafted PEG brushes in the pores of the support.

According to permporometry results (Table 1), the PEG-alkoxysilane grafted membranes have smaller pore diameters than the PEG-phosphonic acid membranes and should result in lower water

permeabilities [44], which seems to be in contradiction with the results in Fig. 4. However, as seen from the behaviour of the grafted materials in water by ^{1}H NMR, we can assume that the alkoxysilane graft degrades fast. Even after 1 h some of the grafted species are hydrolysed (see Fig. 3). As we used an equilibrium time of 0.5–1 h for determining the water flux prior to the first measurement, it is expected that within that period already a reasonable amount of the alkoxysilane graft is hydrolysed. Therefore, the difference between the permporometry and permeability results can be attributed to the fast hydrolysis of the grafted PEG-alkoxysilane species in water. Further investigation on the behaviour of the alumina modified membranes is needed to assess the assumptions of the hydrolysis of alkoxysilane grafts in water.

To further assess the stability of the grafted membranes under hydrolytic conditions, membranes were immersed at room temperature in MilliQ water for a certain period (24–216 h), dried at 70 °C under vacuum and reused to repeat the water permeability measurements. Fig. 5 presents the water permeability of the grafted membranes, including an equilibrium time in water of 0.5–1 h (= 0 h in Fig. 5) and after 24, 72 and 216 h of immersion in water. The two types of membranes (alkoxysilane and phosphonic acid-modified) show significant differences in water permeability. Namely, alkoxysilane modified membranes show an increase of 28% for MePEG7Si and 59% for MePEG11Si in water permeability after 24 h. After three days (72 h) in water, the permeability of both alkoxysilane modified membranes show a further increase of 41% for MePEG7Si and 69% for MePEG11Si which can be correlated to the degradation of the polymeric layer. On the other hand, the phosphonic acid-modified membranes show almost no change in permeability, even after 216 h of immersion in water. The increasing permeability observed solely with alkoxysilane membranes can be correlated with the degradation of the polymeric layer. Degradation of the polymeric layer could also occur due to the presence of physiosorbed species at the ceramic pore surface. However, FTIR analysis confirmed the absence of unreacted Si–OCH$_2$CH$_3$ and Si–OH groups on the grafted alumina membrane (see Fig. 2B). This, along with the permeability results, suggests that the alkoxysilane modified membranes exhibit very low hydrolytic stability. In contrast, the phosphonic acid-modified membranes seem to present good hydrolytic stability, which is in agreement with the ^{1}H NMR results indicating a stable grafted species even after 408 h (Fig. 3). Furthermore, our findings are confirmed by studies on the poisoning of zeolitic materials (high concentration of
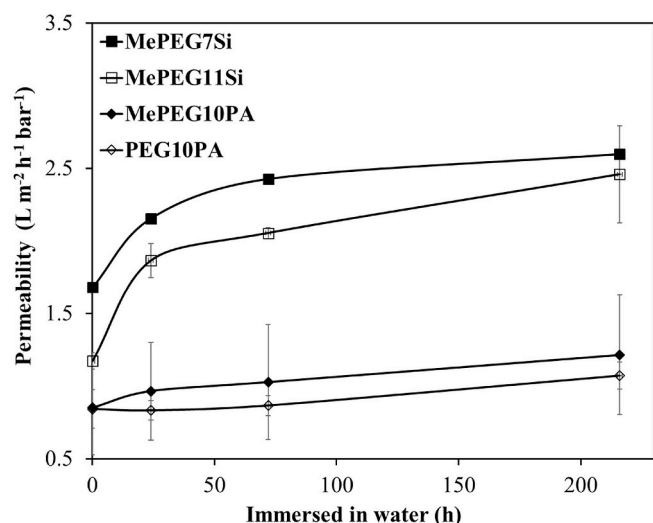
Fig. 5. Water permeability results of the PEG-grafted membranes after grafting (0 h) and after hydrolytic treatments for 216 h. Error bars indicate standard deviation, obtained over three samples prepared under the same conditions and immersed in water for the same time.

Si–O–Al bonds) with phosphoric acid (H$_3$PO$_4$) [45]. In that work it is shown that the P–O–Al bond in the presence of water is not only stable but is also favoured over the Si–O–Al bond (hydrolysed to form P–O–Al). This indicates that the grafting reaction in a green solvent, such as water, is favoured when phosphonic acid is used and additionally the grafted species formed is hydrolytically stable under process conditions involving aqueous streams. .

4. Conclusions

In this work the pore diameter of γ-alumina membranes with a size of 5.5 nm were reduced by 1–2 nm, through grafting with small PEG molecules, having either trimethoxysilane or phosphonic acid as linking groups. The phosphonic acid graft, in contrast to the alkoxysilane graft, showed stable behaviour in water even after 216 h in water, and no hydrolysis was observed with liquid NMR analysis. In contrast, it was shown that γ-alumina, covalently-grafted with PEG-alkoxysilanes, easily hydrolysed after contact with water. This shows that Szczepanski's [15] claims on alkoxysilane-modified oxides degradation being depended on the organic layer and its functionality is not entirely true and it should be expanded to hydrophilic layers in pure water, in general. So, even under neutral aqueous conditions, use of alkoxysilanes should be avoided when the modified surface is hydrophilic. In addition, liquid-state NMR, in combination with other techniques, was utilized to assess the physical interaction between liquid and solid. We showed that NMR has the potential use for an easy qualitative evaluation on the effects of a solvent in contact with a solid material, such as hydrolysis reactions on the surface of a membrane.

Finally, a promising and simple method for the fabrication of hydrophilic, phosphonic acid PEG-modified ceramic nanofiltration membranes is shown in this work, for use in industrial wastewater treatment for the removal of small organic solutes. Due to the materials involved in the fabrication step, these PEG-membranes are suitable for industrial fabrication and use.

Credit author contribution statement

Nikos Kyriakou: Initiated the work and performed most of the experiments, Wrote a first draft, which was intensively discussed and commented by all authors. **Marie-Alix Pizzoccaro-Zilamy:** Responsible for FTIR measurements and discussion/interpretation of a/o FTIR and

NMR results. **Arian Nijmeijer:** head of the group: Gave general input to this research: Mainly on interpreting transport properties. **Mieke Luiten-Olieman:** Assisted on the synthesis of the PEG grafted membranes. **Louis Winnubst:** Daily supervisor of PhD student Nikos Kyriakou: Weekly discussion with the PhD student on progress; Gave detailed scientific input during the progress of this research.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.micromeso.2020.110516.

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