

## Chemical modification/grafting of mesoporous alumina with polydimethylsiloxane (PDMS)

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### ABSTRACT

A method for polydimethylsiloxane grafting of alumina powders is described which involves chemical modification of the surface of mesoporous (5 nm)  $\gamma$ -alumina flakes with a linker (3-aminopropyltriethoxysilane: APTES), either by a solution phase (SPD) or a vapour phase (VPD) reaction, followed by PDMS grafting. The systems were analysed by FTIR, gas adsorption/desorption and TGA. Grafting is proven by FTIR for all cases, meaning that a covalent bond exists between inorganic particle and organic moiety. It is demonstrated that the way of applying APTES (by SPD or VPD) has an effect on the morphology of linker as well as of PDMS. A more controlled grafting of the APTES linker on  $\gamma$ -alumina is possible by the VPD method, resulting in efficient grafting and good infiltration of PDMS in the pores of the inorganic system. Stability tests on these PDMS grafted alumina show no degradation after 14 days soaking in a wide range of solvents. Surface modification of metal oxide particles by organic moieties via a chemical reaction can adapt its interfacial properties and renders a high chemical stability of these inorganic-organic hybrids. This validates the use of these materials under severe applications like in membranes for solvent nanofiltration or for protein immobilization and resin modification in e.g. chromatographic applications.

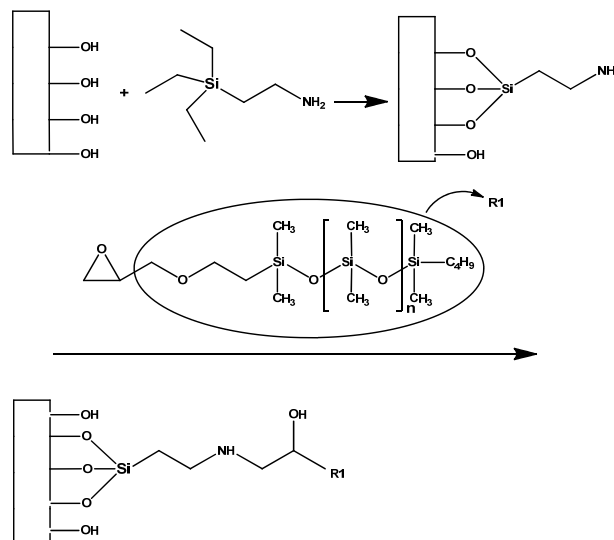
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### 1. Introduction

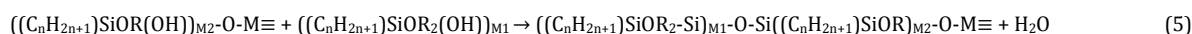
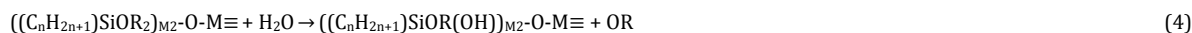
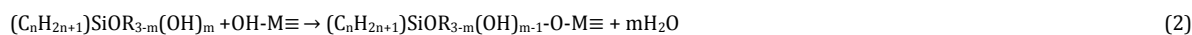
Surface modification of metal oxide particles with organic moieties is typically achieved by means of reactions between the surface hydroxyl groups of metal oxide particles (M-OH) and coupling reagents such as organosilane or organophosphorus compounds. This process is called grafting. In this process, a covalent bond is formed between the polymer matrix and the inorganic particle. For membrane applications, particularly for nanofiltration of non-aqueous systems, the use of these hybrids is a new and promising strategy. Ceramic membranes present high thermal, mechanical and chemical stability [1]. Unfortunately, their reduced selectivity and limited pore size availability, combined with their hydrophilic character, hampers their application [2,3]. Grafting polymers on ceramic membranes offers the opportunity to tailor and manipulate interfacial properties, while retaining the mechanical strength and geometry of the supported ceramic material. Several types of molecules can be used for modification of inorganic materials, for instance phosphate derivatives [4-6], chlorosilanes and alkoxy silanes [2,3,7,8], polysiloxanes [9] and Grignard reactants [10]. The strategy employed in this paper, is grafting with polydimethylsiloxanes. PDMS-based membranes have been widely used as solvent resistant nanofiltration (SRNF) membranes, due to their

hydrophobic character, thermal and chemical stability and good permeability values in non-polar solvents. However, their swelling behaviour in non-polar solvents hampers its application [11,12]. Since ceramic membranes present no swelling, grafting of polysiloxanes on the surface and pores of these ceramic membranes is expected to reduce their swelling behaviour and consequently improve membrane performance and overall stability. For covalent bonding of these polymers to the surface -OH groups, a linker/coupling agent is required. Silanes can be used as coupling agents and act as a bridge between the inorganic surface and the polymer to be grafted. In order to achieve this, the silanization agent should contain one or more hydrolysable groups (e.g. alkoxy or chloro groups) as well as a functional group (anchoring site; e.g. -NH<sub>2</sub>), which can act as a linking point for the polymer. In this work a mono-epoxy-terminated PDMS is selected as the polymer to be grafted and 3-aminopropyltriethoxysilane (APTES) is used as a linker as presented in Figure 1.

In the case of trialkoxysilanes, covalent bonding occurs through the hydrolysis of the Si-OR groups (R=CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>) forming Si-OH groups (Equation 1) and an alcohol as by product (methanol, CH<sub>3</sub>OH, or ethanol, C<sub>2</sub>H<sub>5</sub>OH). The Si-OH groups interact with the OH groups of the metal oxide surface forming M-O-Si bonds on the substrate through a condensation reaction (Equation 2).



**Figure 1.** Schematic reaction between 3-aminopropyltriethoxysilane (APTES) and the mono(2,3-epoxy) polyether-terminated polydimethylsiloxane (PDMS) on a  $\gamma$ -alumina surface.



where M is the metal (in this work aluminium) and m is the number of hydrolysed surface groups. The presence of a catalyst as water [13,14], or an amine [15] during hydrolysis is required. However, the presence of too much water causes polycondensation of the silanes resulting in a very thick silane layer, which can condense in the water phase without any covalent attachment to the surface. This leads to a low surface and pore coverage and hence to a poor quality of the layer.

Multilayer reactions can also be expected under certain experimental conditions e.g. by an excess of water molecules. These multilayer reactions proceed through the hydrolysis of the alkoxy group of the free silane (molecule 1,  $M_1$ ; equation 3) and a surface silane (molecule 2,  $M_2$ ; equation 4) followed by a condensation reaction (equation 5).

Control over the amount of water/moisture is required in order to prevent the formation of a multilayer. For silanes, containing non-hydrolysable groups such as amino groups ( $-\text{NH}_2$ ), equations 3-5 may not apply, while other reactions can occur as well. The electron-rich amino group catalyses the condensation of the silicon side of the molecule with the surface OH group, forming a covalent bond. Besides this hydrogen bonding or ionic interaction with surface OH groups, a reaction with other silane molecules is also a possible path [16]. Consequently, the morphology and structure of the aminosilane-modified surface strongly depends on (1) reaction conditions [16-26] (e.g. concentration, reaction temperature, type of solvent, reaction time, phase of reaction, surface water or humidity) (2) silane nature (number of reactive groups, size) [23,24,27], (3) curing conditions [16,28] and (4) the properties of the inorganic support (pore size, [OH]). Surface-saturated layers of aminosilanes can be deposited under dry conditions, meaning in a dried organic solvent, or in the gas phase. However, an organic solvent still contains small amounts of water, which easily results in cross

polymerization and multilayer formation. Because no solvents are used in the gas or vapour phase deposition method, the presence of water can be excluded. Still modification of metal oxides with different kinds of organosilanes is mostly performed by solution phase methods [4-7,16-23,27,28]. In literature some studies are reported on gas-solid reactions of silanes onto metal oxide surfaces [22,24,25]. Controlled hydrolysis of alkoxy silanes, solvent removal, washing procedures and others can be avoided when using gas-phase techniques. Furthermore, silane overlayers deposited by a gas phase are better ordered, more uniform and more reproducible than layers deposited from solutions.

In this work, the influence of the phase of the deposition method (solution phase: SPD or vapour phase: VPD) on the structure of the aminosilane (APTES) layer and the impact on subsequent PDMS grafting is studied. In order to validate the applicability of these systems for solvent filtration, the thermal and chemical stability of these two systems were tested. A combination of techniques, like FTIR spectroscopy, gas adsorption/desorption, thermogravimetric analysis, are used to provide detailed information about the chemical nature of the incorporated organic moieties and their effect on the mesoporous structure of the alumina flakes. This work gives insight into the phenomenon of post-modification of mesoporous inorganic powders by grafting both surface and pores of these powders.

## 2. Materials and Methods

### 2.1. Materials

3-Aminopropyltriethoxysilane (APTES) is obtained from Aldrich and used as received. The solvents (toluene, *n*-hexane, isopropanol, tetrahydrofuran, chloroform, methanol, dimethyl

formamide, 1-methyl-2-pyrrolidone and butanol) are obtained from Aldrich and used as received. All solvents referred before are anhydrous. Acetone and ethanol are purchased from Aldrich and used as received. Mesoporous  $\gamma$ -alumina flakes are prepared from a boehmite sol. These flakes are dried and subsequently calcined at 625 °C for 1 hour at a heating rate of 1 °C/min, as described in detail in reference [29]. The polysiloxane (mono(2,3-epoxy)polyether-terminated polydimethylsiloxane: PDMS) is obtained from ABCR. The polymer has a molecular weight of 1000 g/mol and a viscosity of 10-15 mPa.s. Prior to grafting, the  $\gamma$ -alumina flakes are pre-treated by soaking in an ethanol:water (2:1, v:v) solution for 24 hours at ambient temperature, dried in a vacuum oven at 100 °C for 24 hours and stored under nitrogen atmosphere until further use. This pre-treatment is done to remove dust and to promote a suitable degree of hydroxylation.

## 2.2. Grafting of $\gamma$ -alumina flakes with APTES by solution phase deposition (SPD)

The introduction of amino groups onto the alumina surface, i.e. the preparation of an "initiator site", is achieved by the reaction of the surface OH groups with APTES. A typical example is as follows:

(1) In a glove box under nitrogen atmosphere a 100 mL 25 mM APTES-toluene solution is added to 600 mg of  $\gamma$ -alumina flakes in a 250 mL 4-necked round flask,

(2) The mixture is then removed from the glove box, refluxed for 4 hours at 80 °C under a nitrogen flow. After this reaction the mixture is cooled to room temperature and centrifuged at 7500 rpm for 20 min. A washing/centrifuging procedure is repeated 3 times with fresh toluene to remove any non-reacted silane. Subsequently the modified flakes are washed in a mixture of 2:1 ethanol:water and centrifuged at 7500 rpm for 10 min. This procedure is again repeated 2 times with a fresh solution. The solvent is removed and the modified flakes are dried at 100 °C under vacuum for 24 hours.

## 2.3. Grafting of $\gamma$ -alumina flakes with APTES by vapour phase deposition (VPD)

This method implies that inside a glove box, under nitrogen atmosphere, a 100 mL toluene-silane solution, using an APTES concentration of 25 mM, is added to a 250 mL 2-necked round flask. In a second 250 mL 2-necked round flask 600 mg of alumina flakes are placed. Magnetic stirrers are added to both flasks. The flasks are then connected with a glass tube ("bridge") and the system is removed from the glove box, flushed with nitrogen and heated to 80 °C. After 4 hours both flasks are allowed to cool down and the modified flakes are washed and dried using the same procedure as described for the  $\gamma$ -alumina, modified by the SPD method.

## 2.4. Grafting of the APTES-grafted alumina flakes with PDMS

The introduction of the siloxane-based polymer is achieved by the reaction between the grafted amino groups and the epoxy groups of the siloxane polymer (PDMS). A typical procedure is as follows:

(1) In a glove box, under nitrogen atmosphere, a 100 mL 2-isopropanol-PDMS solution, using a PDMS concentration of 25 mM, is added to 300 mg of APTES-grafted alumina flakes,

(2) The mixture is removed from the glove box, refluxed for 24 hours at 75 °C under a nitrogen flow. After 3 hours the reaction vessel is cooled to room temperature and the solvent is removed by centrifuging at 7500 rpm for 20 min, washed with anhydrous 2-isopropanol and dried in the same way as described before.

## 2.5. Characterization methods

Fourier-Transform Infrared spectra (FTIR) of grafted powders are obtained with a TGA-IR Tensor 27 system spectrometer (Bruker Optick GmbH) in the range 400-4000  $\text{cm}^{-1}$ , using a resolution of 4  $\text{cm}^{-1}$  and 16 scans. An FT-IR spectrum of unmodified pre-treated  $\gamma$ -alumina flakes is used for background correction. Nitrogen adsorption/desorption isotherms are collected at 77 K using a Gemini system, VII version (Micromeritics Instruments Corp.) Specific surface areas are calculated by using the multi-point Brunauer-Emmett-Teller (BET) method in the relative pressure range of  $P/P_0 = 0.05-0.2$ . Pore size distributions are evaluated from the desorption branches of the  $\text{N}_2$  isotherms by means of the Barrett-Halenda-Joyner (BJH) model between relative pressures  $P/P_0 = 0.35-0.9$  and the average pore sizes are estimated from the peak positions of the BJH pore size distribution curves [30]. This method is based on Kelvin's equation, stating that condensation occurs in pores with radius  $r_K$  at  $p/p_0$  which for cylindrical pores is represented by:

$$\left( \ln \left( \frac{p}{p_0} \right) = -2\gamma_s V_{\text{mol}} / RT r_K \right) \quad (6)$$

with  $\gamma_s$  the surface tension of the liquid-vapour interface (8.85 MJ/m<sup>2</sup> for  $\text{N}_2$ ),  $V_{\text{mol}}$  is the molar volume of the condensed  $\text{N}_2$  (34.7  $\text{cm}^3$ ),  $R$  the gas constant and  $T$  the temperature. The pore volume of these mesopores are obtained from the amount of nitrogen adsorbed at  $P/P_0 = 0.95$ . Before measurement each sample is vacuum-degassed at 200 °C for 12 hours.

Thermogravimetric analyses are conducted on a Netzsch TG 449 F3 Jupiter® equipment at a heating rate of 10 °C/min under  $\text{N}_2$  atmosphere. In all cases a run from room temperature till 1000 °C is performed and around 20 mg of sample is used. Before the measurement, each sample is heated from room temperature till 150 °C at a heating rate of 10 °C/min to remove any adsorbed water.

In order to assess the stability, PDMS-grafted  $\gamma$ -alumina flakes are soaked in various solvents: toluene, n-hexane, isopropanol, tetrahydrofuran, dichloromethane, acetone, chloroform, n-butanol, methanol, N,N'-dimethylformamide and 1-methyl-2-pyrrolidone. Approximately 0.1 g of grafted  $\gamma$ -alumina flakes is soaked in 10 g of solvent and stirred for 14 days at room temperature. The powders are centrifuged at a speed of 7500 rpm for 5 minutes, 3-times washed with fresh solvent, centrifuged and air-dried overnight. The stability of the grafted flakes is analysed by FTIR.

## 3. Results and discussion

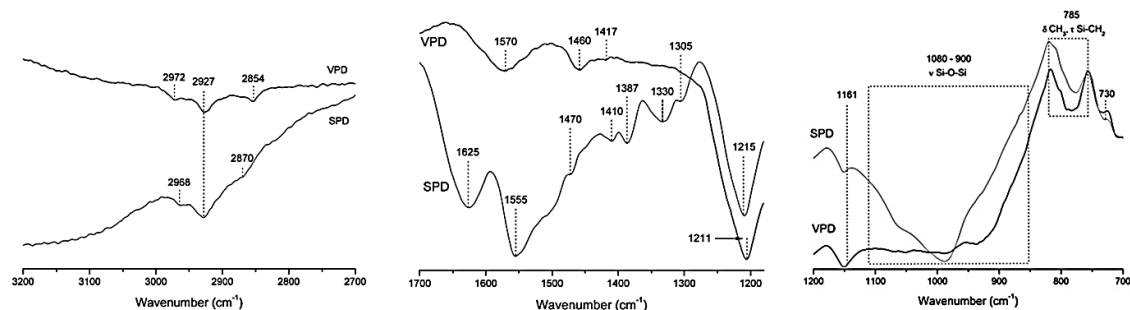
### 3.1. FTIR analysis

#### 3.1.1. Influence of the APTES deposition method

Figure 2 shows the IR spectra of alumina flakes grafted with 3-aminopropyltriethoxysilane (APTES) by solution phase deposition (SPD) and vapour phase deposition (VPD). The frequencies and assignments of each vibrational mode are listed in Table 1. For the unmodified alumina flakes the broad peak between 3600-3000  $\text{cm}^{-1}$  can be assigned to the stretching modes of the various types of surface hydroxyl groups (M-OH) of alumina, while the peak at 1640  $\text{cm}^{-1}$  can be attributed to the bending mode of residual intra-molecular water ( $\delta$  OH). After APTES grafting new characteristic peaks, consistent with the incorporation of APTES, were formed. The peaks in the range 3000-2700  $\text{cm}^{-1}$ , ascribed to the methyl and methylene stretches (Table 1), confirms the presence of the propyl chain of APTES. However, for the SPD method the presence of the weak peaks at 2968, 2870, 1387  $\text{cm}^{-1}$ , due to the different vibrations modes of the methyl group present in the ethoxy group, indicate that not all ethoxy groups were efficiently hydrolysed.

**Table 1.** FT-IR wavenumber ( $\text{cm}^{-1}$ ) assignments of the main bands for APTES as grafted on  $\gamma$ -alumina flakes by SPD or VPD.

APTES SPD, $\text{cm}^{-1}$	APTES VPD, $\text{cm}^{-1}$	Assignment	Reference
2968	2972	$\text{CH}_3$ asymmetric stretching ( $\nu_s \text{CH}_3$ )	[18,20,24]
2927	2927	$\text{CH}_2$ asymmetric stretching ( $\nu_{as} \text{CH}_2$ )	[18,20,24]
-	2854	$\text{CH}_2$ symmetric stretching ( $\nu_s \text{CH}_2$ )	[18,20,24]
2870	-	$\text{CH}_3$ symmetric stretching ( $\nu_s \text{CH}_3$ )	[20,24]
1625	-	Al-OH..... $\text{NH}_2$ bending ( $\delta \text{NH}_2$ hydrogen bonded)	[17,31]
1555	1570	$\text{NH}_2$ bending (scissoring) ( $\delta \text{NH}_2$ )	[16,20,32]
1470	1460	$\text{CH}_2$ bending (scissoring) ( $\delta \text{CH}_2$ ) and $\text{CH}_3$ (ethoxy) bending ( $\text{CH}_3$ , only for SPD)	[18,24,32]
1410	1417	Bending mode of $\text{CH}_2$ directly attached to Si ( $\delta \text{CH}_2$ )	[18,24,32]
1387	-	$\text{CH}_3$ (ethoxy) symmetric deformation ( $\delta \text{CH}_3$ )	[18,24]
1330	-	C( $\text{CH}_2$ ) deformation (wagging) ( $\delta \text{CH}_2$ )	[33]
1305	-	$\text{CH}_2$ twist-rock deformation ( $\tau \text{CH}_2$ )	[18]
1215	1211	Si( $\text{CH}_2$ ) wagging ( $\omega \text{CH}_2$ )	[32]
1161	1161	$\text{CH}_2$ twisting ( $\tau \text{CH}_2$ )	[32]
1070-990	1080-990	Si-O in-plane stretching ( $\nu \text{Si-O-Si}$ )	[18,24]
775	775	Si-C stretch ( $\nu \text{Si-C}$ )	
730	730	$\text{CH}_2$ rock-twist ( $\tau \text{CH}_2$ )	[33]

**Figure 2.** FT-IR spectra for  $\gamma$ -alumina flakes modified with 3-aminopropyltriethoxysilane (APTES) by solution phase deposition (SPD) or by vapour phase deposition (VPD).

This means that either incomplete siloxane hydrolysis has occurred or physically adsorbed non-hydrolysed APTES was not effectively removed. For the VPD method only one of these bands, with lower intensity, can be observed ( $2972 \text{ cm}^{-1}$ ), indicating that for VPD the majority of the alkoxy groups have reacted with the Al-OH surface groups by hydrolysis and condensation reactions. The presence of the propyl side chain of APTES is also confirmed by the peaks between  $1500\text{-}1200 \text{ cm}^{-1}$  and  $800\text{-}700 \text{ cm}^{-1}$ . These regions are characterized by the bending, twisting, rocking and wagging vibration modes of the methylene group, as assigned in Table 1. The presence of a broad band centred at  $1560\text{-}1550 \text{ cm}^{-1}$  due to the bending of  $\text{NH}_2$  groups is a clear evidence for the presence of amine groups, proving the incorporation of the APTES onto the alumina flakes. In the case of SPD grafting another peak at  $1625 \text{ cm}^{-1}$  is present as well. Several authors have attributed this peak to the oxidation of the amine to form a bicarbonate salt in a reaction with atmospheric  $\text{CO}_2$ , particularly when the samples were reacted and dried in air. However, in our case the reactions were performed under nitrogen and subsequently dried under nitrogen. Culler *et al.* [17] have attributed this peak to the formation of a hydrogen-bonded coupling structure, formed between the Al-OH groups of the surface and/or with free silanol groups (Si-OH) and the amine groups of the coupling agent. Therefore, the presence of this band might indicate the presence of hydrogen bonded species. Another possible explanation is the presence of impurities in the siloxane network such as water molecules, capable of hydrogen bonding with OH surface groups which have not reacted with APTES, and/or with amino group of the APTES molecules. This can lead to a band around  $1630 \text{ cm}^{-1}$ . However given the intensity of this band and the absence in the FTIR spectra for the APTES VPD grafted flakes (Figure 2) this does not seem to be a plausible explanation.

For the VPD system less intense bands are observed, especially the ones attributed to the methylene and amino groups. This is most probably due to a lower loading of the linker, since a thin (mono)layer is expected in this case, whereas for the SPD a thick multilayer is expected. This is also confirmed by the broad and intense band observed in the SPD IR spectrum between  $1100\text{-}900 \text{ cm}^{-1}$ , due to the Si-O-Si stretching modes (symmetric and asymmetric), which is much less pronounced in the VPD spectra ( $1080\text{-}1022 \text{ cm}^{-1}$ ).

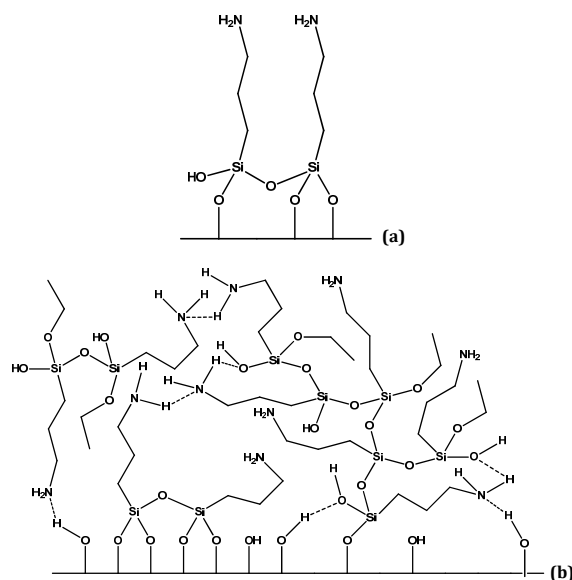
An explanation for the stronger appearance of Si-O-Si stretching modes is that the deposition of silane from the liquid phase suffers from the deposition of aggregated alkylsilane molecules while in the vapour-phase method aggregate formation is prevented. Vertical polymerization (Figure 3b) is avoided in the VPD case, since oligomeric precursors in solution have a low vapour pressure and rarely vaporize [34]. For VPD only condensation reactions between adjacent silanes, bound to the surface, are possible (horizontal polymerization) resulting in a thin layer. In solution-phase reactions APTES molecules can either covalently bond to the surface OH and/or with adjacent silanol groups, but the amino groups can also form hydrogen bonds with other amino or silanol groups of adjacent silanes as illustrated in Figure 3b. In conclusion, the presence of all the characteristic bands described above allows us to conclude that modified amino silylated  $\gamma$ -alumina flakes were successfully obtained.

### 3.1.2. Polydimethylsiloxane grafting

Anchoring amine groups ( $\text{NH}_2$ ) are introduced on the surface and pore walls of the alumina flakes by means of the successful grafting of APTES. A PDMS grafted alumina flake can be obtained through a nucleophilic substitution reaction between these amine groups and the epoxy groups present on the polysiloxane polymer. This is achieved by epoxy ring opening.

**Table 2.** FT-IR wavenumber ( $\text{cm}^{-1}$ ) assignments of the main bands for PDMS as grafted on  $\gamma$ -alumina flakes modified with APTES by SPD or VPD.

PDMS SPD, $\text{cm}^{-1}$	PDMS VPD, $\text{cm}^{-1}$	Assignment	Reference
2962	2960	$\text{CH}_3$ asymmetric stretching ( $\nu_{\text{as}} \text{CH}_3$ )	[35,36]
2927	2925	C-H stretch ( $\nu \text{C-H}$ )	[35,36]
2873	2874	$\text{CH}_2$ asymmetric stretching ( $\delta \text{CH}_2$ )	[37]
1562	1562	NH bending (scissoring) ( $\delta \text{NH}$ )	[36]
1460-1450	1470-1440	$\text{CH}_2$ bending (scissoring) ( $\delta \text{CH}_2$ )	[38]
1410	1410	$\text{CH}_3$ asymmetric bending mode of the $\text{Si-CH}_3$ ( $\delta \text{C-H}_3$ )	[35,38]
1342	1344	$\text{C}(\text{CH}_2)$ wagging mode ( $\omega \text{CH}_2$ )	
1260	1259	$\text{CH}_3$ symmetric bending of the $\text{Si-CH}_3$ ( $\delta \text{C-H}_3$ )	[35,38]
1080	1080	Si-O-Si symmetric stretching ( $\nu_{\text{s}}, \nu_{\text{s}} \text{Si-O-Si}$ )	[36]
1018	1028	Si-O-Si asymmetric stretching ( $\nu_{\text{as}}, \nu_{\text{as}} \text{Si-O-Si}$ )	
838	840	$\text{CH}_3$ rocking of the $\text{Si-CH}_3$ ( $\delta \text{C-H}_3$ )	[38]
787	791	Si-C stretch ( $\nu \text{Si-C}$ )	
740	740	$\text{CH}_3$ rocking ( $\delta \text{CH}_3$ ) + $\text{CH}_2$ rock-twist ( $\tau \text{CH}_2$ )	[36]
683	674	Si-C stretch ( $\nu \text{Si-C}$ )	[36]

**Figure 3.** Possible types of bonding/interaction between APTES molecules and alumina substrates (a) horizontal polymerization (b) horizontal and vertical polymerization combined with hydrogen bonding between adjacent amino groups and with surface OH groups.

The polysiloxane (mono(2,3-epoxy)polyether-terminated polydimethylsiloxane) was chosen because of its low viscosity. A low viscosity polymer is preferable for a more efficient pore infiltration since the diffusion into the pore will be easier for such a system. The use of a monofunctional PDMS results in only one bond formation to the surface through the amino anchoring groups allowing the chain to stretch far from the surface, as desired.

Figure 4a and b display the FT-IR results of PDMS grafted on alumina modified with APTES by SPD and VPD respectively. The wavenumbers and assignments of each vibrational mode are listed in Table 2. Due to PDMS grafting, new peaks appear between  $3000\text{-}2800 \text{ cm}^{-1}$ , which confirms the presence of  $(\text{Si-CH}_3)_2$  and  $\text{CH}_2$  and  $(\text{CH}_2)_3$  groups. In the region between  $1500\text{-}800 \text{ cm}^{-1}$  more intense bands are observed when compared with the linker IR spectra (Figure 2). This IR region corresponds to vibration modes for both methyl and methylene groups including a band at  $1470\text{-}1440 \text{ cm}^{-1}$  due to the  $\text{CH}_2$  scissoring mode and a peak at  $1410 \text{ cm}^{-1}$  due to the asymmetric bending mode of the methyl group ( $\delta \text{CH}_3$ ), a band at  $1340\text{-}1330 \text{ cm}^{-1}$  due to the twisting deformation mode of the methylene group ( $\tau \text{CH}_2$ ) and finally three new peaks at  $1260\text{-}1259 \text{ cm}^{-1}$ ,  $840\text{-}838 \text{ cm}^{-1}$  and  $790 \text{ cm}^{-1}$  due to the symmetric bending of the methyl groups, connected to the silicon atom ( $\delta_{\text{s}} \text{Si-CH}_3$ ). The presence of all these bands proves the incorporation of the polymer on the flakes. As discussed before the VPD process results in the formation of an APTES

monolayer. Less PDMS is expected to be grafted and therefore less intense bands were observed in the PDMS-VPD IR spectra when compared with the PDMS-SPD IR spectra as is confirmed by a more intense band at around  $1200\text{-}1000 \text{ cm}^{-1}$ , due to the Si-O-Si stretch, for SPD when compared with VPD. Due to the presence of this broad band, a peak corresponding to the C-O stretching band of the  $\text{CH}_2\text{-O-CH}_2$  bond in the polymer structure, expected at  $1113 \text{ cm}^{-1}$ , cannot be observed. The chemical modification through the reaction with the epoxy ring results in the formation of a secondary amine (Figure 1), which is confirmed by FTIR through the deformation mode of the N-H group at around  $1570\text{-}1560 \text{ cm}^{-1}$  (Table 2). The PDMS grafting is proven by the absence of the anti-symmetric stretching vibration of the cyclic ether at around  $910 \text{ cm}^{-1}$  and the peak at  $1289 \text{ cm}^{-1}$  due to the symmetric stretching vibration of the cyclic ether. From these FT-IR data it can be concluded that all epoxy rings of PDMS have reacted completely with the amine group of the APTES via a covalent bonding, resulting in a successful grafting of PDMS on APTES modified  $\gamma$ -alumina flakes.

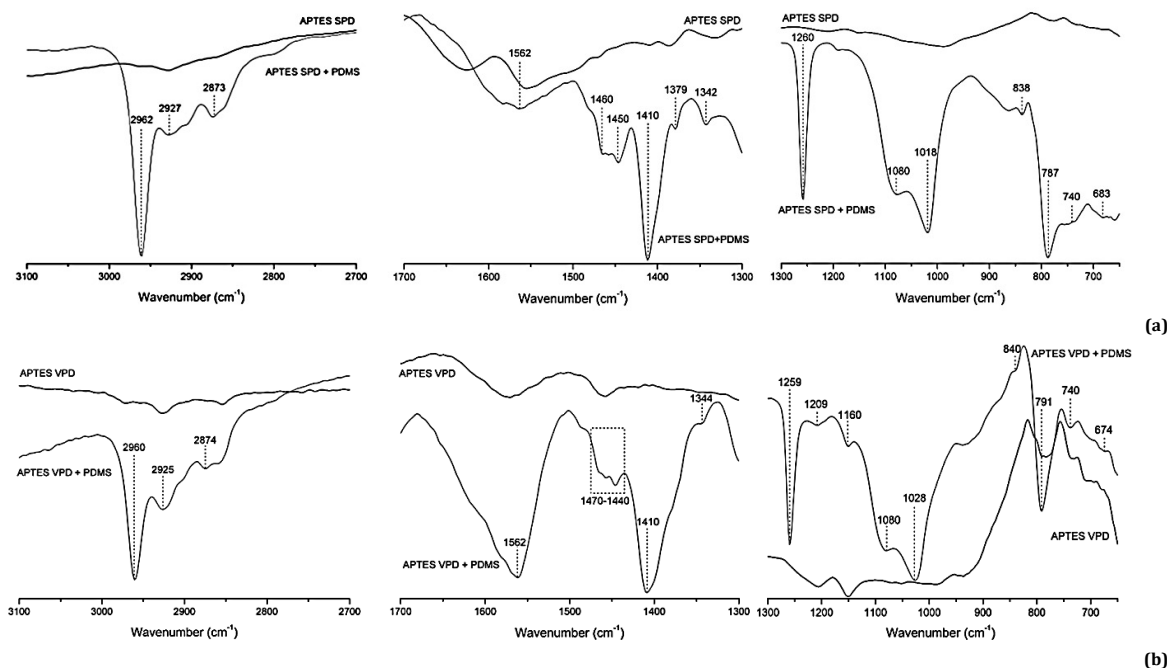
### 3.2. Pore microstructure of grafted alumina flakes

In order to evaluate the effect of different grafting moieties and deposition methods on the morphology and structure of pores of the  $\gamma$ -alumina flakes, nitrogen adsorption/desorption measurements were performed.



**Table 3.** Mean mesopore diameter (Mean  $d_p$ ) from BJH fit ( $d_p$  BJH), pore volume ( $V_p$ ) and surface area ( $A(N_2)$ ) for pure  $\gamma$ -alumina flakes (AF) and flakes modified with APTES via SPD and VPD and subsequently with PDMS.

Sample ID	Mean $d_p$ , (nm)	$V_p$ , ( $\text{cm}^3 \text{g}^{-1}$ )	$A(N_2)$ , ( $\text{m}^2 \text{g}^{-1}$ )
AF	4.8	0.39	256
AF+APTES SPD	3.8	0.28	211
AF+APTES SPD +PDMS	3.5	0.18	120
AF+APTES VPD	4.2	0.37	252
AF+APTES VPD +PDMS	2.2	0.12	106

**Figure 4.** FT-IR spectra of  $\gamma$ -alumina flakes modified with APTES and subsequently with PDMS; APTES grafted by (a) SPD and (b) VPD method.

### 3.2.1. APTES grafting

The  $N_2$  adsorption-desorption isotherms of  $\gamma$ -alumina flakes grafted with 3-aminopropyltriethoxysilane (APTES) via solution phase deposition and vapour phase deposition are presented in Figure 5a and 6a, respectively.

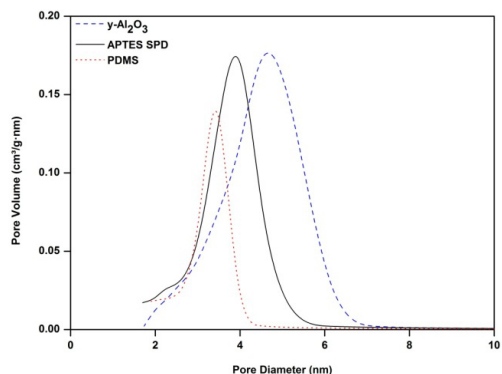
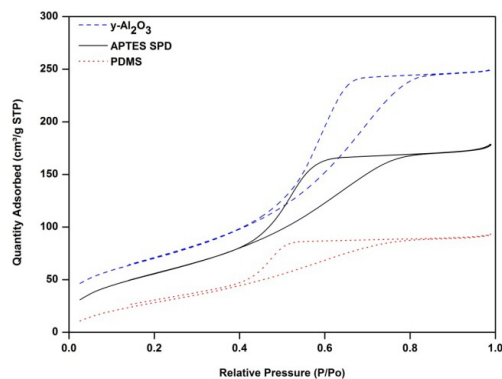
For both methods the isotherms are characteristic for monolayer-multilayer adsorption followed by capillary condensation. This is typically for a type IV isotherm with an H1 hysteresis loop, associated with mesoporous materials with narrow necks and a relative low level of pore connectivity [30]. The pore size distributions, calculated by the BJH method, based on the desorption branch, are given in Figure 5b and Figure 6b. For both grafting methods a monodisperse pore-size distribution is observed. The BET surface area ( $S_{\text{BET}}$ ), mesopore volume ( $V_p$ ) and mean pore size ( $d_p$ ) values are given in Table 3.

For the alumina flakes, grafted with APTES by the SPD and VPD method, a decrease in pore size of 1.0 nm and 0.6 nm respectively is observed if compared with the unmodified flakes. A reduction in pore volume and surface area of around 28 % and 18 % is respectively obtained in the case of SPD, whereas for VPD a less pronounced reduction of 5 % in pore volume and 2 % in surface area is obtained. All these results are an indication that the pores within the alumina flakes become more densely filled with APTES by using SPD, due to the possible formation of a multilayer system, whereas with VPD a thinner layer (maybe even a monolayer) is formed. The presence of an APTES multilayer on the SPD-derived powder is also confirmed by the SPD FTIR spectra (see Figure 2), showing a broad Si-O-Si stretching band, due to

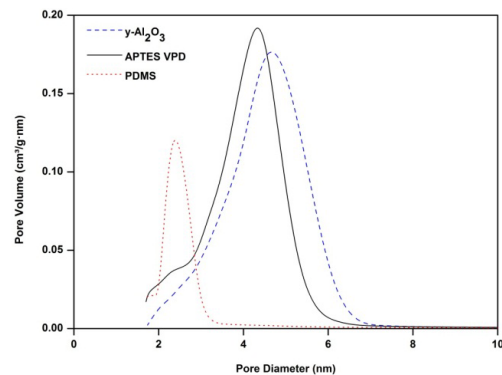
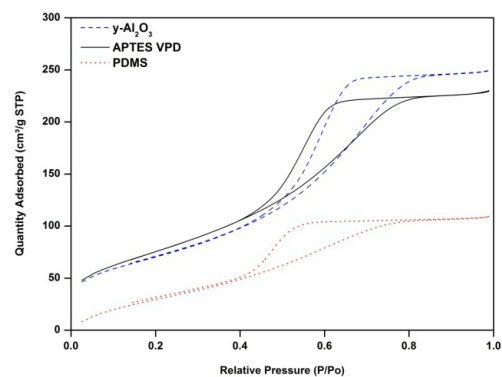
polycondensation reactions between adjacent silanes. Here the three hydrolysable ethoxy groups can react in the presence of traces of water either with the surface hydroxyl groups and/or with adjacent silanes, forming a thick polymeric network and thus a strong reduction in pore size and pore volume. Ritter *et al.* [22] have shown that, while the water content has no effect on surface silane loading, a strong pore blocking is promoted in the presence of water due to cross-linking of silane molecules. On the other hand, the tendency towards aggregation (island formation) is expected to be less pronounced in the vapour phase deposition, as discussed before, resulting in a lower decrease in pore volume, pore size and surface area for VPD if compared with the SPD method.

### 3.2.2. Polydimethylsiloxane grafting

The adsorption/desorption isotherms for PDMS grafted on alumina flakes, modified by APTES with VPD and SPD, are presented in Figure 5a and 6a, respectively. For both methods a type IV isotherm is still obtained. A clear reduction in pore volume is observed when the polymer is grafted onto the linker-modified surface, 36 % for SPD and 68 % for VPD, indicating that modification has indeed occurred inside the pores and that the modification was uniform in a sense that the pore structure remained intact and no micro porosity was observed. In addition, for both cases, a decrease in pore size was achieved (see Table 3 and Figures 5b and 6b), also confirming the presence of PDMS inside the pores. For the VPD system a stronger reduction in pore size, surface area and pore volume is achieved than for the SPD system.



**Figure 5.** (a)  $N_2$  physisorption isotherms and (b) Pore size distribution curves for pure  $\gamma$ -alumina flakes and for materials modified with APTES via SPD and subsequently with PDMS.

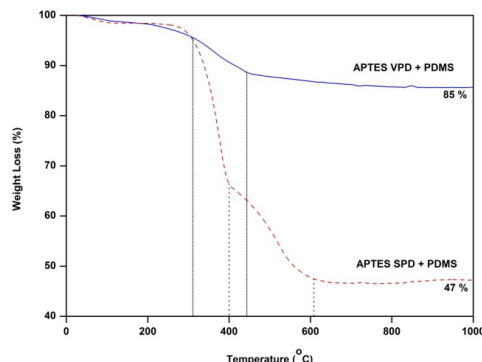


**Figure 6.** (a)  $N_2$  physisorption isotherms (b) Pore size distribution for pure  $\gamma$ -alumina flakes and for materials modified with APTES via VPD and subsequently with PDMS.

Due the formation of a thinner APTES layer during VPD more space is available for the diffusion of the polymer inside the pores, while the multilayer deposition of APTES by SPD hampers diffusion of PDMS into the pores. In conclusion, the gas adsorption/ desorption results on PDMS grafted membranes show that a deposition of the linker through a VPD method is preferable for obtaining well-grafted PDMS systems.

### 3.3. Thermal stability of the grafted alumina systems

In Figure 7 thermogravimetric analysis (TGA) results are presented for alumina flakes grafted with APTES and subsequently PDMS. It is expected that the non-grafted  $\gamma$ -alumina flakes are thermally stable and will not show any degradation during these TGA temperature treatments; at least not until the calcination temperature of  $650\text{ }^\circ\text{C}$ , as applied to obtain these flakes (see experimental section). For both types of grafted powders (VPD and SPD) a small weight loss of 4 % up to  $340\text{ }^\circ\text{C}$  is observed that can be related to adsorbed water of the modified  $\gamma$ -alumina surface, trapped ethanol and partial decomposition of unreacted APTES and/or PDMS. These TGA results indicate that the  $\gamma$ -alumina flakes modified by VPD and SPD are thermally stable up till  $340\text{ }^\circ\text{C}$ . The decomposition temperatures as observed in this work (around  $340\text{ }^\circ\text{C}$ ) is higher than the boiling points of the individual liquids (APTES, b.p. =  $217\text{ }^\circ\text{C}$  and PDMS, b.p. =  $205\text{ }^\circ\text{C}$ ). Therefore, an increase in thermal stability is observed after modification. This supports the results that the aminopropyl and siloxane groups are chemically bonded to the alumina flakes. For alumina flakes, modified with APTES by VPD and subsequently with PDMS, a second stage of mass loss is observed between  $340$  and  $500\text{ }^\circ\text{C}$ . This weight loss represents the degradation of the organic groups. After heating up to  $1000\text{ }^\circ\text{C}$  an overall weight loss of 15 % for VPD is observed, though most of the weight loss occurs up till  $600\text{ }^\circ\text{C}$ . For flakes modified by SPD two distinct stages of significant weight loss can be seen above  $340\text{ }^\circ\text{C}$ . The first one is around  $400\text{ }^\circ\text{C}$  with a total weight loss of 34 %. After heating up to about  $600\text{ }^\circ\text{C}$ , the overall weight loss is 43 % for SPD, while for VPD only 15 % is observed. The much stronger decrease in weight for SPD modified flakes compared to the VPD ones cannot be explained by the decomposition of the polymer as grafted in the mesopores. It is assumed that the  $\gamma$ -alumina flakes are agglomerated in such a way that they enclose the mesopores as observed by  $N_2$  adsorption/desorption. During the grafting procedure not only the internal pores are grafted but also the outer surface of the agglomerates. For the SPD-derived flakes it is obvious that multilayer formation of APTES on the outer surface is much more pronounced than for VPD-derived flakes, which explains the much stronger weight decrease for the SPD-derived systems. As is shown by FTIR (Figure 3a) a more intense band is obtained for the Si-O-Si stretching mode due to polycondensation reactions.

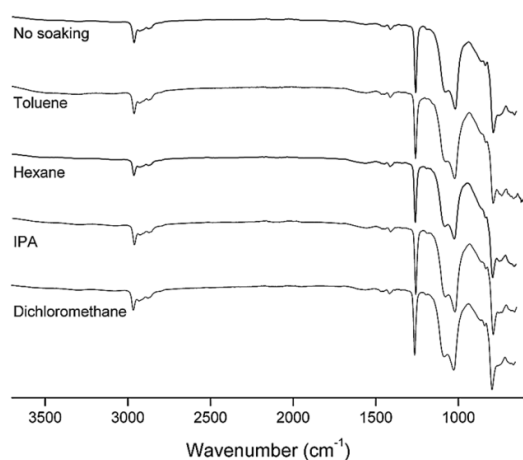


**Figure 7.** TGA of  $\gamma$ -alumina flakes modified with APTES by SPD and VPD followed by grafting with PDMS.

### 3.4. Chemical Stability

The grafted materials were soaked in different solvents for seven days in order to assess if the systems are stable under harsh conditions. FT-IR was performed and the possible disappearance of the main characteristic bands for the grafted systems or the presence of new bands was assigned as a possible degradation of the grafted flakes. FT-IR spectra before and after soaking of the PDMS grafted  $\gamma$ -alumina powders in different solvents are presented in Figure 8, which include hexane, toluene, isopropanol and dichloromethane.

For all solvents, the characteristic bands attributed to the successful incorporation of both APTES and PDMS are present. This was also observed for other solvents tested, like THF, acetone, chloroform, methanol, butanol and DMF. In the case of NMP only some small degree of degradation was observed. Therefore, this PDMS surface modification presents a promising grafting route for the preparation of solvent resistance nanofiltration membranes [39].



**Figure 8.** FT-IR spectra for  $\gamma$ -alumina dense powders modified with PDMS by using APTES as the linker before and after 7 days soaking in several organic solvents: toluene, hexane, isopropanol, dichloromethane.

Finally, it can be stated that the grafting methodology, described in this paper, is a promising route for the fabrication of solvent resistant nanofiltration membranes, where hydrophobic surfaces and solvent resistant systems are required. Preliminary experiments on  $\gamma$ -alumina supported membranes have shown that reproducible, stable membranes with good fluxes for non-polar solvents could be obtained by using a VPD method for the linker grafting step [39]. It opens new directions for solvent purification in a harsh environment and for recovery of precious substances from non-aqueous solvents in an effective and energy-saving way. In this way, more sustainable processes are achieved in e.g. the petrochemical, biochemical, fine chemical and pharmaceutical industry. Moreover, the VPD method developed in this work represents an easy and promising chemical route for the controlled modification of inorganic surfaces and particularly of nanosized pores, which can be used for applications beyond membranes, such as protective coatings, sensor modification, protein immobilization and resin modification for chromatographic applications.

### 4. Conclusions

In this study grafting through silylation of alumina flakes, having a pore size of 5 nm, has proven to be a suitable approach for engineering both surface chemistry and pore size of porous inorganic materials. PDMS grafted  $\gamma$ -alumina flakes are prepared through a two-step grafting method using APTES

(3-aminopropyltriethoxysilane as linker), applied by either vapour phase deposition or solution phase deposition and subsequent with a mono-epoxy PDMS (mono(2,3-epoxy)polyether-terminated polydimethylsiloxane). By means of these methods PDMS was grafted on both the external surface and the internal pore wall of porous alumina. Through the use of a vapour phase (VPD) technique for linker deposition a more controlled grafting can be achieved when compared with the solution phase (SPD) method. The VPD method resulted in a thinner layer of the linker and thus more free space is available for efficient diffusion of the PDMS polymer into the pores. Alumina flakes grafted with PDMS, by either applying the SPD or VPD method for the linker, were stable at temperatures up to 380 °C. Chemical stability tests showed that the PDMS grafted alumina powders were stable in a wide range of solvents, even though for a harsh solvent like NMP some small degradation could be observed.

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