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Development of a PDMS-grafted alumina membrane and its evaluation as solvent resistant nanofiltration membrane



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ABSTRACT

A new solvent resistant nanofiltration (SRNF) membrane is developed by grafting a PDMS polymer into the pores of a 5 nm γ -alumina ceramic membrane. These PDMS-grafted γ -alumina membranes were attained through a two-step synthesis. The linking agent, 3-aminopropyltriethoxysilane (APTES), was first applied on a ceramic membrane either by a vapor phase or a solution phase method, followed by grafting of an epoxy-terminated PDMS. Through this route it was possible to tune the pore size and to engineer the surface chemistry (e.g. hydrophobicity) of ceramic membranes in favor of non-polar organic solvent permeation. Reproducible results were obtained for filtration experiments with hexane, toluene and isopropanol (IPA). As expected, higher permeabilities were found for non-polar solvents than for more polar solvents (resp. $4.8 \pm 0.1 \text{ l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for hexane, $3.1 \pm 0.5 \text{ l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for toluene and $0.54 \pm 0.04 \text{ l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for IPA). A Molecular Weight Cut Off (MWCO) of $500 \pm 10 \text{ Da}$ was determined. Stability tests in hexane, toluene and IPA have shown that these newly developed membranes were stable in all these solvents during testing periods of up to 170 days.

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1. Introduction

Solvent resistant nanofiltration (SRNF) has gained increasing interest, as it is an effective and energy-saving technology in several strategic fields, such as pharmaceutical industry, fine chemistry and petrochemistry [1]. For these applications state-of-the-art nanofiltration membranes, as used in an aqueous environment, are not suitable and therefore there is a need for developing robust nanofiltration membranes, which are stable and highly selective in an aggressive environment such as a continuous exposure towards organic solvents.

In general, nanofiltration membranes can be divided into two major groups according to their material properties: organic (polymeric) membranes and inorganic (ceramic) membranes. Today polymeric membranes are commercially available and have found multiple applications in fields like recovery of organometallic catalysts from organic solutions [2], for the recovery of dewaxing solvents from dewaxed lube oil filtrates in petrochemistry [3] and in the recovery and purification stages in the biodiesel production process [4]. However, these membranes tend to swell in solvents like toluene, hexane, acetone, methanol, isopropanol, ethyl acetate, which reduces their potential for separation because of a decrease in selectivity, in particular when non-polar solvents

are involved [5–10]. Van der Bruggen et al. [11] found lower solute rejection when hexane was used as solvent if compared with separations involving alcohols and water as solvent and they proposed that this was due to the interaction between membrane and solvent. Another drawback is the limited chemical stability with respect to aggressive solvents like NMP and DMF [12].

In contrast to polymeric membranes, ceramic membranes are characterized by a non-swelling behavior and a high chemical and thermal stability in all types of polar and non-polar organic solvents [13–20]. In addition ceramic membranes are mechanically stable under operational pressures of up to 20 bar, under which most polymers will severely suffer from compaction [19]. Despite these superior characteristics ceramic membranes are not compatible for application with organic solvents due to their hydrophilic character, which leads to low fluxes for non-polar solvents [13,15–18].

Therefore, much focus is on developing new classes of membranes for improving the filtration performance under SRNF conditions, i.e. enhancing chemical and mechanical stability, reducing swelling effects of polymeric membranes and enhancing solvent affinity. Polysiloxane-based polymers, like PDMS, are often used as polymeric SRNF membranes. PDMS displays a unique combination of characteristics which include high free volume, flexibility of the siloxane backbone, thermal and chemical stability, hydrophobicity and solubility in non-polar solvents. However, their swelling behavior, particularly in non-polar solvents hampers its application. The use of strongly swelling

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solvents like hexane will result in an increase in free space between the polymer chains and consequently in a less selective convective solute transport. For non-polar solvents Tarleton et al. [6] observed ~80% swelling of the initial thickness at ambient pressure for a 2 μm thick PDMS separating layer coated on a PAN support. In literature several solutions are proposed to overcome or to reduce this swelling effect like the use of halogen-substituted silicon rubbers [20], crosslinking via a plasma treatment [21] or via an irradiation technique [6,22,23], or the introduction of fillers in silicon rubber [24,25]. Robinson et al. [22] and Tarleton et al. [6,23] studied PDMS/PAN membranes, which were crosslinked to various degrees by means of electron beam irradiation. As a consequence solute rejection increased with increasing degree of crosslinking, but solvent permeability decreased. It is also shown that the addition of fillers in silicon rubber reduces swelling. Vankelecom et al. [24] and Gevers et al. [25] prepared filled PDMS membranes using three different fillers (silica, carbon and zeolites). Incorporation of zeolites (silicates) resulted in an increased solute rejection in non-polar solvents (e.g. toluene, hexane, etc.) even at high temperatures (up to 80 °C) [25]. However, these membranes still showed low effective permeabilities due to their large top layer thickness (> 20 μm). More recently, Zwijnenberg et al. [26] prepared a SRNF α -Alumina/PDMS hollow fiber composite membrane by coating a pre-crosslinked PDMS/toluene solution of viscosity of 175 mPa on the outside wall of the hollow fiber. Pre-crosslinking was carried out in order to prevent pore intrusion of the PDMS in the supports, which can result in pore blocking and in a decrease of solvent permeation [27].

An alternative approach is the introduction of a covalent bond between a polymer and a ceramic surface which can provide a solution to overcome several problems, occurring with each independent type of membrane. This can be achieved by polymer grafting, which implies the reaction of OH groups from the metal oxide ceramic surface with hydrolysable groups from an organic moiety resulting in a covalent bond. This is expected to reduce

polymer swelling, since the polymer is immobilized inside the pores of the ceramic membrane. Besides, the ceramic pore will act as a rigid frame, which will restrain the grafted polymer from compaction when high pressures are applied to the membrane. An increase in membrane performance is also expected through a reduction in pore size and through an enhancement of specific interactions/affinities between membrane and permeating molecules. A suitable polymeric material, e.g. PDMS, grafted on the ceramic pore walls can render the hydrophobic character of the porous ceramic. This enables us to engineer the solvent affinity of ceramic membranes, which are initially hydrophilic.

To our knowledge the only reported PDMS (as silicon oil) grafted membrane by using a ceramic as support was by Leger et al. [28]. They evaluated this system for both gas permeation and pervaporation of pure organic solvents. This membrane was chemically and thermally stable, unaffected by organic solvents as toluene, THF and acetone, but it degraded in high and low pH media.

In this paper a new fabrication method was designed for grafting PDMS on a supported γ -alumina membrane (pore size 5 nm) using polysiloxane mono(2,3-epoxy)polyetherterminated polydimethylsiloxane:(PDMS) as presented in Fig. 1. The surface modification strategy employed is based on the formation of an aminosilane monolayer on a hydroxyl-terminated inorganic substrate, followed by the reaction of the amino group with the epoxy-terminated PDMS, having a low molecular weight and viscosity, enabling the formation of a PDMS grafted layer in the pores of the γ -alumina membrane. Two different linker deposition methods (solution or vapor phase) were used in order to evaluate the effect of linker deposition on PDMS grafting. Contact angle and permporometry measurements were used to access the extension of the modification and to determine membrane properties. In order to evaluate the effect of the PDMS grafting on the long-term membrane performance, toluene, hexane and IPA permeabilities were measured. To further characterize the membrane the Molecular Weight Cut Off (MWCO) was determined as well.

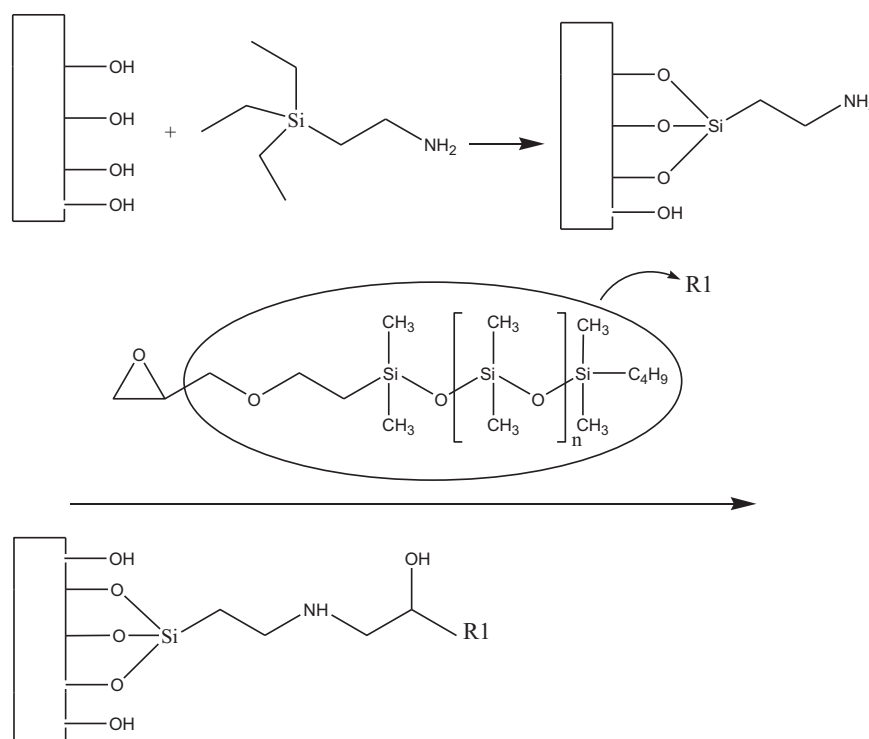


Fig. 1. Schematic reaction between of 3-aminopropyltriethoxysilane (APTES) and the mono(2,3-epoxy) polyetherterminated polydimethylsiloxane (PDMS) on a γ -alumina surface.

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