Journal of Membrane Science 564 (2018) 259–266

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Poly (maleic anhydride-*alt*-1-alkenes) directly grafted to γ-alumina for high-performance organic solvent nanofiltration membranes

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ARTICLE INFO

Keywords:
Alternating copolymer
Grafting
Alumina membrane
Organic solvent nanofiltration

ABSTRACT

In this study we describe a novel and simple method to couple covalently poly (maleic anhydride-*alt*-1-alkenes) to γ-alumina nanofiltration membranes for the first time. The 1-alkenes varied from 1-hexene, 1-decene, 1-hexadecane to 1-octadecene. The grafting reaction was between the reactive anhydride moieties of the polymer and surface hydroxyl groups, resulting in highly stable bonds. The modified membranes were investigated for their permeation and rejection performance of Sudan Black (SB, M_w 457 Da) in either toluene or ethyl acetate (EA) solution, and very high rejections (> 90%) and high permeation flux were observed compared to unmodified membranes. Initially, the SB in toluene solution was found to bind strongly to the surface hydroxyl groups of the unmodified membranes, an effect not observed in EA solution.

1. Introduction

Nanofiltration is a pressure-driven, membrane-based separation technique with performance properties between those of ultrafiltration (UF) and reverse osmosis (RO) membranes [1,2]. Organic solvent nanofiltration (OSN) is a young separation technique with applications ranging from the recovery of homogeneous catalysts to the purification of organic solvents [3–7]. For such applications a high chemical, mechanical and thermal membrane stability, an excellent long-time performance, and a limited pre-treatment and maintenance are often desired [8].

As polymer-based membranes have a tendency to swell or even dissolve in organic solvents, the use of ceramic membranes for OSN has therefore been growing rapidly in recent years [9–12]. Ceramic membranes show the desired high mechanical strength, are resistant to compaction and do not swell. Despite these superior properties the presence of surface hydroxyl groups makes them hydrophilic which limits their use in non-aqueous media.

A challenging strategy to overcome this limitation is by masking the surface hydroxyl groups by chemical modification with organic monolayers or polymers [3,13,14]. The resulting hybrid organic-ceramic membranes combine the best of two worlds: the superior properties of ceramics with tuned surface properties by proper organic/polymer chemistry. While the fabrication of hybrid organic-inorganic membranes with incorporated nanoparticles has been widely studied [15–20], hybrid polymeric-ceramic membranes in the area of OSN are much less explored. Such hybrid membranes can be obtained by two different methods. Firstly, by *in-situ* modification of ceramic membranes via sol-gel techniques, where the modification takes place during the selective layer preparation step. Secondly, by post modification of the ceramic membranes with polymers [11,21–26]. The grafting of organic/polymeric moieties to alumina membranes has proven to be a convenient post-modification technique to adjust and control the membrane properties [13]. The surface OH groups are first treated with a primer acting as a linker/coupling agent between the surface OH and the organic/polymer moiety [27,28]. In order to obtain this first step, various silane coupling agents have been investigated [29,30]. For instance, 3-amino propyl triethoxy silane (APTES) and 3-mercapto propyl triethoxy silane (MPTES) were used as linker for the covalent grafting of polydimethylsilane (PDMS) to γ-alumina membranes [13,31–33].

We have now explored the application of maleic anhydride-*alt*-1-alkenes alternating copolymers in the modification of inorganic membranes for the first time. The maleic anhydride unit is highly reactive towards surface OH-groups, enabling direct covalent polymer coupling, thus without the use of a linker unit. In addition, the 1-alkene unit can

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https://doi.org/10.1016/j.memsci.2018.07.042
Received 12 February 2018; Received in revised form 7 May 2018; Accepted 15 July 2018

be varied from short chain to long chain alkenes, enabling tuning of the affinity of the functionalized membranes with various organic solvents. Here, we have investigated a series of four copolymers: three tailor-made alternating copolymers using 1-hexene to 1-hexadecene and one commercially available copolymer containing a hydrophobic block based on 1-octadecene. The (physico-) chemical properties of these compounds are studied in detail, before providing a comprehensive investigation on the performance of γ-alumina membranes grafted with these copolymers.

2. Experimental section

2.1. Materials

All chemicals were purchased from Sigma-Aldrich, unless otherwise indicated. 1-Hexene (≥ 99%), 1-octene (98%), 1-decene (purum, ≥ 97%, Fluka) and 1-hexadecene (> 99%, TCI Europe N.V.) were used for the alternating copolymerization reaction. 2,2′-Azo-*bis*-iso-butyronitrile (AIBN) (purum, ≥ 98%) was recrystallized twice from methanol. Maleic anhydride (MA) (puriss, ≥ 99%) was purified before use by recrystallization from anhydrous benzene and followed by sublimation. Poly(maleic anhydride-*alt*-1-octadecene) (number-average molecular weight M_n: 30–50 kDa). Flat disc-shaped α-alumina membranes (having a diameter of 39 mm, a thickness of 2 mm, and a pore diameter of 80 nm) supporting a thin (3 µm) γ-alumina layer (mean pore diameter of 5 nm), and mesoporous γ-alumina flakes with a pore diameter of ca. 5 nm, were all purchased from Pervatech B.V., The Netherlands.

2.2. Copolymerization procedure

MA (50 mmol), AIBN (0.5 mmol) and the respective 1-alkene (C_6, C_{10} and C_{16}) (50 mmol) were dissolved in anhydrous 1,4-dioxane (10 ml). The reaction mixture was then deaerated by a freeze-thaw method (3×) and sealed under argon atmosphere. Typically, the reaction proceeded for 4 h at 70 °C after which the reaction solution was added dropwise to methanol (100 ml, 5 °C). The precipitated polymers were collected by filtration, and reprecipitated from a tetrahydrofuran (THF) solution by pouring into methanol (5 °C). The solid material was dried for 24 h at 30 °C under vacuum. The obtained alternating copolymers of MA and 1-alkenes are further referred as P(MA-*alt*-C_X) where X indicates the number of carbon atoms of the used alkene.

2.3. Grafting to γ-alumina flakes and supported γ-alumina membranes

The unmodified γ-alumina membranes were washed with water and soaked in ethanol/water (2:1, vol) mixture for 24 h at room temperature to clean the surface. Then, the membranes were dried at 100 °C for 12 h under vacuum and subsequently dipped into a stirred 0.2 wt% solution of the different alternating copolymers in acetone for 12 h. Any contact between the membrane and the magnet stirrer bar was prevented. The samples were washed with pure acetone (3 times). Each membrane sample was subsequently treated at a temperature of 10 °C above their respective glass transition temperature (T_g; see Fig. S6) for 3 h. To remove any non-grafted alternating copolymers, the membranes were washed with acetone for 12 h in a Soxhlet apparatus. The same grafting procedure of the P(MA-*alt*-C_X) copolymers was performed for grafting to the unmodified γ-alumina flakes. A schematic diagram of the whole modification procedure is shown in Fig. 1. As shown, nucleophilic attack by the surface hydroxyl groups promotes ring opening of maleic anhydride and esterification reaction, resulting in carboxyl group formation. The membranes grafted with different copolymers are further referred to as γ-alumina-*g*-C_X, where X has the meaning as indicated before.

2.4. Characterization

2.4.1. Materials characterization

The number average molecular weight (M_n) of the different synthesized alternating copolymers was determined by gel permeation chromatography (GPC) in a mixture of THF: acetic acid (9:1, vol.) as eluent (flow rate: 1 ml min^{-1}, at 40 °C). The molecular weight and polydispersity index (PDI = M_w/M_n) were calibrated with polystyrene (PS) standards. Proton nuclear magnetic resonance (^{1}H-NMR) spectra of the different alternating copolymers in $CDCl_3$ were recorded at room temperature using a 400 MHz pulsed Fourier Transform NMR spectrometer (Agilent 400-MR DD2). Fourier transform infrared (FTIR) spectra of the different alternating copolymers in KBr tablets were measured using a Nicolet iS50 FTIR (Thermo Fisher Scientific Co., Madison, USA) spectrophotometer in the range of 4000–500 cm^{-1}. Each spectrum was captured by 128 scans at a resolution of 4 cm^{-1}. The thermogravimetric properties of the modified γ-alumina flakes were determined by a thermogravimetric analyzer (TGA; Mettler Toledo, TGA/SDTA 851e). The samples were heated under a N_2 atmosphere from 25 to 850 °C at a heating rate of 10 °C min^{-1}. The glass transition temperatures (T_g) of the different alternating copolymers were determined under an N_2 atmosphere using a Perkin Elmer 6000 differential scanning calorimeter (DSC). The samples were first heated to 250 °C and then cooled to 25 °C, before the DSC recordings started by heating to 250 °C at a heating rate of 10 °C min^{-1}. N_2 adsorption-desorption experiments were performed at − 196 °C for both the unmodified and copolymers grafted γ-alumina flakes, using a Gemini System VII apparatus. The surface areas were determined by using the Brunauer-Emmet-Teller (BET) method, while the pore size distributions were determined from the desorption branch of the isotherm by the Barret-Joyner-Halenda (BJH) method. The effects of surface modification on the morphology and surface roughness was studied by analyzing the membrane surface topology using an atomic force microscope (AFM, NT-MDT, Ntegra). The roughness average (Sa) in a 500 nm × 500 nm area of the membrane surface was determined from three-dimensional AFM images. Energy dispersive X-ray (EDX) analysis was conducted in the low-vacuum mode at 10 kV using JEOL 6010 LA scanning electron microscopy (SEM). The surface wetting properties (hydrophilicity/hydrophobicity) of the differently modified membranes were determined by their static water contact angle using a Krüss FM40 Easy Drop Standard instrument. According to the standard sessile drop method, a drop of water was put on the top surface of the membrane and the contact angle was measured optically using a camera from the initial contact of the water drop. At least two measurements per membrane and three different samples of each membrane were analysed and the average values are reported.

2.4.2. OSN experimental procedure

Freshly grafted membranes were used for our permeation experiments. These experiments were carried out at a transmembrane pressure (TMP) of 8 bar at room temperature using a dead-end pressure cell made from stainless steel (purchased from Pervatech B.V.). The system is pressurised using inert argon. Prior to each experiment, the membranes were preconditioned with the organic solvent for 12 h. The effective area of each membrane was 8.9 cm^2 and at least three different samples of each membrane type were tested to study the reproducibility. The model solution to be separated was composed of 20 mg L^{-1} of Sudan Black (SB) in either ethyl acetate (EA) or toluene. During the permeation, the feed solution was stirred at 400 rpm to minimize concentration polarization. The membrane cell was filled with 50 ml of feed solution per membrane and 20 ml (*i.e.*, 40% recovery) of the permeate was collected for each membrane at the permeate side. In between the separation experiments, the membrane cell was thoroughly cleaned and the membranes were rinsed with the solvent used before, dipped in absolute ethanol for 8 h and then cleaned in an ultrasonic bath of absolute ethanol for 5 min. Finally, the cleaned membranes were dried in a vacuum oven at 60 °C for 24 h before the next