



Pyrolyzed polysiloxane membranes with tailorable hydrophobicity, porosity and high specific surface area

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ABSTRACT

Polysiloxane precursors with either only methyl moieties or methyl and phenyl groups are used for the preparation of graded structures with adjustable hydrophobicity, macroporosity and specific BET surface area. We demonstrate how the membrane properties can be controlled by adjusting the precursor ratio, the applied pyrolysis temperature as well as the sieving fraction of the precursor powder. The surface characteristics are evaluated by contact angle measurements and compared with data from vapor sorption experiments. Water contact angles can be adjusted from about 100° to 140° depending on the precursor type used during pyrolysis at 630 °C, while featuring a high specific BET surface area from 419 to 534 m²/g. The contact angles can be decreased to values between about 80 and 100° by pyrolysis at 700 °C. Graded membranes are synthesized by using different precursor ratios and applying a one-step pyrolysis process. The macroporosity is controlled by the sieving fraction of the precursor powder. The obtained graded membranes have a high potential for a variety of applications in separation processes.

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1. Introduction

Membranes with gradients of their physico-chemical properties are often needed as effective materials for separation processes [1]. For instance, gradients of wettability enhance the separation of CO₂ from methanol/water in waste management devices of micro direct methanol fuel cells which use methanol and air on the feed side and produce CO₂ and H₂O as waste [2]. Gradients of surface chemistry are furthermore desired for micro fluidics applications where the transport of water droplets can be achieved along a wettability gradient [3] or for the investigation of molecular interaction in cell or biomolecule adhesion experiments [1,4]. Concerning the preparation of surface gradients, including gradients of wettability, a variety of methods are known and reviewed by Genzer et al. [5]. Gradual surface modification can for example be achieved by corona treatment and by methods using physical adsorption or chemical bonds. Grafting of polymers onto a substrate can be used as well as an approach, where polymerization initiators are gradually distributed at the substrate surface where polymeric chains start to grow in the presence of monomers [1]. Gradients can also be achieved by varying immersion time for the creation of self-assembled monolayers of alkanethiols on gold [4] or by diffusion-controlled silanization of SiO₂ surfaces [2]. These methods create a hydrophobicity gradient on surfaces, but

not within the bulk of monolithic membranes as needed for separation processes on a larger scale.

Membrane performance in separation processes is a function of selectivity and a certain degree of permeability [6]. The selectivity can be enhanced by providing suitable interaction potentials like hydrophobic interactions while macropores can be used to increase membrane permeabilities. There are different methods for the generation and control of macroporosity of ceramic membranes like partial sintering, the replica technique, the use of sacrificial templates or the direct foaming method [7–8]. Direct foaming of ceramic powder suspensions and alkanes, can for example result in graded porosity by adjusting stirring velocities for emulsification of different layers [9].

A less frequently used but easy method for the formation of macroporous monoliths with desired shape is agglomeration of hydrophobic particles in a mold [10]. Hydrophilic silica particles with silanol groups at the particle surface form solvation layers in water and therefore stable aqueous suspensions. Silica particles that are modified with hydrophobic organic moieties, however, stick together in aqueous medium due to hydrophobic forces [11]. Polysiloxanes with hydrophobic organic moieties are therefore expected to form macroporous agglomerated structures as well.

Pyrolysis of these organically modified and therefore hydrophobic polymeric organic inorganic hybrid materials can result in interesting physico-chemical properties that change as function of the pyrolysis temperature [12]. The pyrolytic conversion can be used to adjust the membrane characteristics for separation processes. Polysiloxane based hybrid materials are known to sustain a

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precursor dependent change of their surface characteristics from hydrophobic to more hydrophilic [13–15] and to develop high specific BET surface areas during pyrolytic conversion at intermediate temperatures of 500–700 °C [16]. High specific surface areas can thus be created in an easy manner, without the necessity of an etching process or similar processes to introduce porosity in e.g. VYCOR glass. During pyrolysis of phenyl and methyl group containing precursors, the phenyl groups are converted at lower temperatures (500 °C) than its methyl groups, which are mainly converted at temperatures above 600 °C [17]. A gradient from hydrophobic to hydrophilic properties can be achieved by using a temperature gradient throughout a film during pyrolysis [13]. However, the creation of hybrid ceramic membranes with a gradient of hydrophobicity should also be possible without using a gradient of the pyrolysis temperature throughout a monolithic membrane.

Polysiloxanes are promising materials for the generation of membranes with graded properties, due to the different possibilities to adjust the hydrophobicity as well as the specific surface area. This study reports a straightforward process for the preparation of gradients of hydrophobicity, macroporosity and high specific BET surface areas for monolithic membranes by agglomeration of pre-cross-linked polysiloxane powder and subsequent pyrolysis without the need of any temperature gradients. The successful tailoring of the wettability was shown by contact angle measurements of water droplets and the impact of the hydrophobicity on the wettability investigated by *n*-heptane and water vapor sorption experiments. The adjustability of the microstructure was investigated by SEM, mercury intrusion and profilometry and the specific surface area determined by nitrogen adsorption.

2. Experimental

Prior to membrane preparation commercial methyl–phenyl polysiloxane powder with a melting range of 50–90 °C (Silres[®] H44, Wacker Chemie AG) and pure methyl polysiloxane powder with a melting range of 35–55 °C (Silres[®] MK, Wacker Chemie AG) were pre-cross-linked by heat treatment in air at 80 °C, 140 °C and 200 °C with a heating rate of 60 °C/h and a dwell time of 2 h, respectively. The dwell time at 200 °C was increased to 10 h for the methyl–phenyl polysiloxane in order to obtain similar softening/melting temperatures and therefore the same processing temperature as for the methyl polysiloxane. The pre-cross-linked polysiloxane was ground to fine powder with a planetary ball mill (Retsch, PM 400). Different sieving fractions were obtained by using analytical sieves with mesh sizes of 25, 40, 50, 75, 90, 100 and 125 µm.

2.1. Membrane preparation

For preparation of non-graded monoliths a chosen sieving fraction of pre-cross-linked polysiloxane was filled into polypropylene/polyethylene tubes prepared from a syringe (B. Braun Melsungen AG) and agglomeration of the powder occurred in tempered water at 88 °C after sealing the tube with filter paper on both ends (Fig. 1a). The obtained monoliths have to be aged in ammonia (25%) for 5 days in order to increase the degree of cross-linking and therefore to obtain membranes, which maintain their shape and microstructure during pyrolysis. The aged membranes were dried at room temperature and pyrolyzed under flowing nitrogen at temperatures between 450 and 700 °C. The temperature was increased with 120 °C/h to 100 °C below the final temperature and with 30 °C/h to the final temperature, using a dwelling time of 4 h. The structure of the precursors and a general scheme of com-

positional changes during the pyrolytic conversion are shown in Fig. 1b. For obtaining membranes that exhibit a gradient of wettability separately pre-cross-linked methyl–phenyl and methyl polysiloxane powder with different ratios (1:0, 0.8:0.2, 0.6:0.4, 0.4:0.6, 0.2:0.8 and 0:1) were mixed and stacked in the polypropylene/polyethylene tubes. Membranes with a gradient of the macropore size were obtained by stacking different sieving fractions of the pre-cross-linked polysiloxane powder.

2.1.1. Specimen denotation

Membranes were either prepared with methyl polysiloxane powder (Silres[®] MK, Wacker Chemie AG), methyl–phenyl polysiloxane powder (Silres[®] H44, Wacker Chemie AG) or mixtures of these. The prepared specimens were denoted with MK or H44 for specimens with one precursor or with the content of MK for membranes prepared from mixtures of both precursors. Moreover, the used sieving fractions are listed as well as the pyrolysis temperature. As an example 0.2MK 50–100p630 is prepared with 20 wt.% MK and 80 wt.% H44 of sieving fractions obtained with mesh sizes of 50 and 100 µm, respectively and the membrane was pyrolyzed at 630 °C after aging and drying. The samples used within this study are listed in the [Supplementary information \(Table S1\)](#).

2.2. Characterization

For contact angle measurements the outer section of the membrane was removed by polishing in order to determine the wettability within the bulk of the membrane material and the membrane cross-sections were used for analysis. The average surface roughness (*S_a*) of the cross-sections of the membranes was adjusted to 9.5 ± 1.3 µm, using SiC paper to diminish the effect of the microstructure on the wettability. The surface roughness was determined with an optical profilometer (Plµ2300, Sensofar) according to ISO25178, resulting in *S_a* and the maximum height of the surfaces (*S_z*), being measured from the highest peak to the lowest valley. Photographs of sessile drops (10 µL) of double deionized water were recorded for the determination of contact angles. The photographs were recorded with a digital microscope (Keyence, VHX 600 dso, objective: VH-Z20R/Z20 W). Contact angle measurements were performed with the open-source software ImageJ (version 1.43 u, National Institutes of Health, USA), averaging measurements for 5 drops on each specimen. The microstructure was analyzed from SEM images, which were recorded with 20 kV (Camscan Series 2, Obducat CamScan Ltd.) after embedding with two component epoxy resin, polishing with SiC paper and sputtering the specimens with gold (K550, Emitech, Judges Scientific plc.). Mercury intrusion was used to determine the macroporosity (Pascal 140/440 POROTEC GmbH) of the membranes. The specific BET surface area was determined by nitrogen adsorption at –196 °C (Belsorp-Mini, Bel Japan Inc.) after grinding and sieving the membrane material (mesh size 300 µm) to diminish limitation of nitrogen diffusion within the timeframe of the experiment. Moreover, the surface characteristics of these powder sieving fractions were investigated by isothermal water and *n*-heptane vapor sorption experiments at 22 °C, recording adsorption desorption isotherms (Belsorp18-3, Bel Japan Inc.).

3. Results

Monolithic membranes were prepared from different ratios of H44, a polysiloxane with methyl and phenyl moieties and MK, exhibiting methyl groups only. The membranes were pyrolyzed in nitrogen atmosphere at 450–700 °C. A scheme of the general change of the composition of the precursor and the polarity of the resulting material during the pyrolysis process is depicted in

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