Supporting Information

PDMS mixed matrix membranes filled with novel PSS-2 nanoparticles for ethanol / water separation by pervaporation

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Experimental

Preparation of mixed matrix membranes

To form the mixed matrix membranes, two components of the PDMS (RTV-615 A and B, prepolymer and cross-linker respectively) were dissolved separately in anhydrous toluene. The PSS-2 particles were dispersed ultrasonically in toluene for 1h to disaggregate clusters. The prepolymer and cross-linker solutions were mixed with the PSS-2 dispersion and stirred at 60^{o} C for 4 h in order to partially crosslink the solution to obtain a reasonable viscosity. The filler fraction was expressed as :

$$Filler\ fraction = \frac{(weight\ of\ \ sphere)}{(weight\ of\ sphere) + (weight\ of\ polymer)} \times 100\ (wt\ \%)$$

The resulting pre-polymerized PDMS solution was poured into a glass Petri dish and covered with a funnel in order to achieve slow evaporation of the solvent. The petri dish was subsequently kept at 110 ^{o}C for at least 1h in order to complete the crosslinking. After crosslinking, the membrane was detached from the petri dish and stored in a dust-free environment. Membranes with different PDMS:filler ratios were prepared, while PDMS membranes without PSS-2 particles were prepared for comparison. The thickness of each membrane was measured using a Mitutoyo disk micrometer (series 369) at 6 points across the surface and averaged. Thickness of all membranes were in the range of 120 to 200 µm.

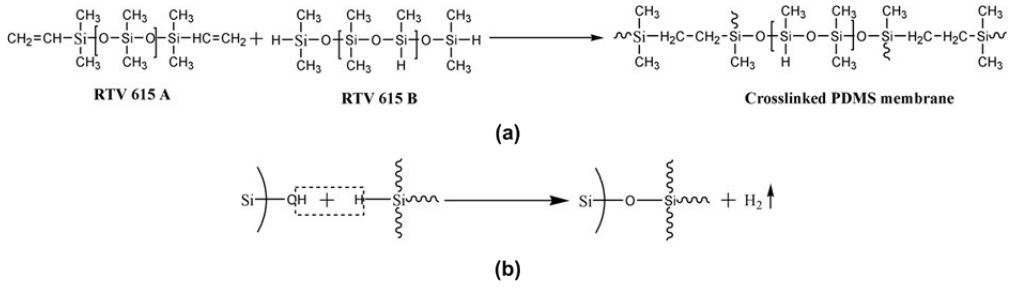


Fig. S1. (a) Assumed chemical composition of the RTV 615 compounds and their reaction; (b) assumed chemical crosslinking between surface silanols of PSS-2 and PDMS.

Pervaporation

A cross-flow pervaporation module was used, as represented in figure 3. A feed pump was used to circulate the feed through the cells at a speed of 1L/min to avoid concentration polarization and it was confirmed by the Reynolds number of 5780 calculated for the system by using equation (1).

$$Re = \frac{\rho v d_h}{\mu} \quad (1)$$

where, Re is Reynolds number, ρ is density of the fluid (kg/m^3), υ is the kinematic velocity (m^2/s), d_h is the hydraulic diameter of the pipe (m) and μ dynamic viscosity of the fluid (Pa.s). The temperature was kept constant at 40 ^{o}C. During pervaporation, a vacuum (< 1 mbar) was applied on the permeate side to ensure a constant driving force for the separation. The active membrane area was 0.001589 m^2. Membranes were left to reach a steady state for at least 12 h. The samples were then collected for 3 h. Experiments were carried out with 6 wt% aqueous ethanol. This concentration was found to be a good representation of ethanol concentration in the feed used by other researchers in similar separations alcohol/water mixtures. Obtained permeates were collected as a function of time in round bottom glass containers using liquid nitrogen in a dewar flask as a cooling trap. The concentration of ethanol in the permeate samples was determined using a refractometer (ATAGO RX-7000α). Three replicates of each MMM were prepared and measured in parallel. The permeate samples were collected twice after overnight equilibration for each membrane. An average value with standard deviation was calculated out of these 6 observations.

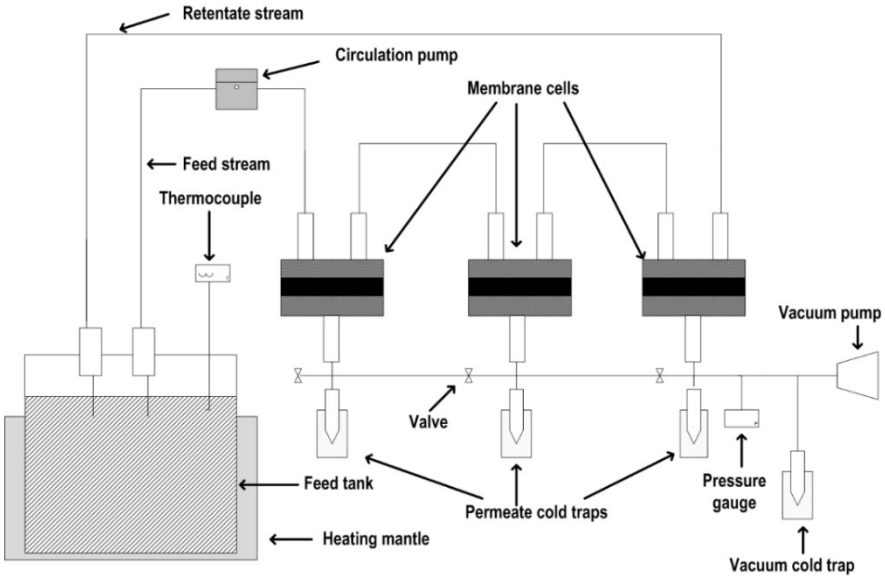


Fig. S2. Pervaporation cross-flow set-up with 3 membrane cells in series.

Thickness normalized flux (J) was calculated (kg/m^{2}h) using equation (1):

$$J = \frac{m}{A.t} \tag{1}$$

where, m (kg) mass of the sample, A (m^2) active membrane area, and t (h) collection time.

The separation factors of the membranes were calculated as follows (2):

$$\beta = \frac{\left(\frac{x_A}{x_B}\right)_{permeate}}{\left(\frac{x_A}{x_B}\right)_{feed}} \tag{2}$$

where x is the weight fraction, x_A represents the preferential component (ethanol) and x_B stands for water.

Scanning electron microscopy (SEM) of PSS-2 particles

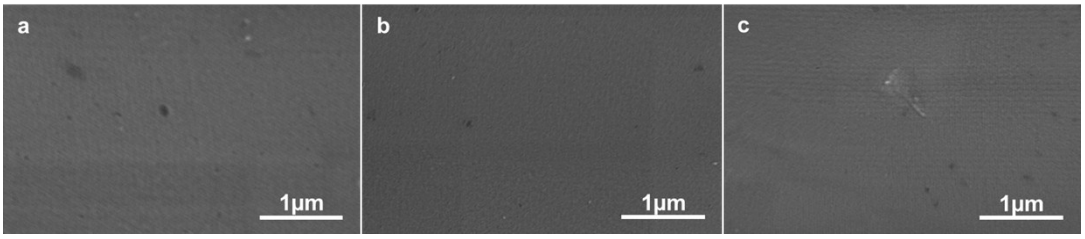
Scanning electron microscopy (SEM) micrographs of PSS-2 were obtained with a Nova NanoSEM 450 (FEI) at 2kV.

N_2 physisorption of PSS-2 particles

N_2 physisorption isotherms were obtained using a Micromeritics TriStar II (Micromeritics instrument Corporation, Norcross, Georgia). The measurements were performed at –196 °C and in order to remove any adsorbed species the PSS-2 sample was outgassed at 300 °C for 2 h prior to the measurement. The total surface area was calculated using the Brunauer, Emmet and Teller model (BET model). The micro pore volume was derived using the t-plot method.

Thermo gravimetrical (TGA) analysis of PSS-2 particles.

TGA was performed on a TGA-Q500 TA instrument using an nitrogen flow and a heating rate of 20 °C min^{-1}.

Fig. 

S3. Thermogravimetric analysis (TGA and DTGA) of PSS-2 particles.

Membrane characterization

SEM

Scanning electron microscopy (SEM) was used to take images of the surfaces and cross-sections of the MMMs (obtained by breaking membranes submerged in liquid nitrogen). Pictures were acquired at 10.0 kV on a Philips XL 30 FEG-SEM. Samples were mounted onto SEM sample holders and coated with a 1.5-2 nm thick gold layer to reduce sample charging under the electron beam.

Fig. S4. Surface SEM

micrographs of MMMs filled with PSS-2 nanoparticles (a) 10 wt%, (b) 15 wt%, and (c) 20 wt% loading.

Contact angle measurement

The water contact angles (CA) on the surface of MMMs were measured using the sessile drop method with a contact angle goniometer (Krüss DSA 10 Mk2). All CA measurements were taken at room temperature using DI water. Multiple measurements (at least 6) at different locations of the membrane sample were taken to obtain representative data.

Sorption measurements

Sorption of liquids in the membranes was determined on membrane strips at room temperature. The membrane strips were dried in the oven at 120 ^{o}C before measuring the sorption by immersion in the liquids for at least 24h. The amount adsorbed was determined by weight. The membrane surface was wiped quickly before weighing.