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PDMS–silica composite membranes with silane coupling for propylene separation

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ABSTRACT

Polydimethylsiloxane (PDMS) coated membranes on a polysulfone (PSf) support were fabricated for propylene recovery from off-gas stream. PDMS coated membrane, however, showed trade-off trends that permeability and selectivity are inversely proportional to each other. Addition of silica nanoparticles of 12–400 nm size into PDMS matrix enhanced both separation factor and propylene permeance from 5.2 to 7.3 from 31 to 36 GPU, respectively. Silica nanoparticles in composite membrane tended to agglomerate with each other. Coupling of silica nanoparticles with a silane coupling agent modified the silica surface to enhance the compatibility with PDMS. Several coupling agents for silica nanoparticles in the PDMS/organic solvent system were tested and mercapto silane showed the best characteristics as a coupling agent in terms of hydrophobicity and thermal stability. Successful coupling was confirmed by FT-IR, and better dispersion of coupled silica nanoparticles in PDMS matrix was attained. Composite membrane with coupled silica nanoparticles still enhanced separation factor up to 8.5 and propylene permeance up to 42 GPU. Effects of size and amount of the silica nanoparticles were examined by comparing fumed silica and sol-gel silica. Fumed silica enhanced the sorption of propylene into membrane matrix to increase the separation factor maintaining the propylene permeance. Sol-gel silica disrupted chain packing to increase the propylene permeance maintaining the selectivity. Increase of silica content enhanced the separation factor as well as propylene permeance. However, excessive silica loading in PDMS solution caused problems in coating process, and optimum silica nanoparticle content was 15 wt%. This work showed the novelty in preparation of organic–inorganic composite membranes with enhanced permeance and selectivity by properly coupling the silica particles before loading.

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1. Introduction

In petrochemical processes, unreacted organic materials such as ethylene, propylene, styrene monomer remain in an off-gas stream from a nitrogen purge bin, which are flared into the atmosphere. These materials are cost expensive and the loss of these materials causes enormous economic loss. It also causes serious environmental problems, including carbon dioxide generation affecting global warming. Therefore, it is necessary to recover the unreacted organic materials as well as the nitrogen from the off-gas for reuse [1–3]. Attempts to recover these materials from off-gas were performed by developing the novel membrane with improved performances.

Various methods for the separation of organic vapors have been developed depending on the concentration of the organic vapors and the flow rate of the stream [4]. Membrane process can be applied to the systems in a wide range of organic vapor concentrations, and can also offer specific advantages in terms of low energy

cost, simplicity of operation, and compactness of design [5]. Moreover, the membrane process can be combined with other separation techniques such as adsorption and condensation to make hybrid processes with better recovery efficiency and adaptability of the process to various situations.

Membrane Technology and Research, Inc. (MTR, Menlo Park, CA) developed a combination of compression–condensation and membrane separation called VaporSep® to recover olefin monomers and nitrogen from the purge bin. The membranes produced by MTR are composite membranes formed by coating a selective thin layer of a rubbery polymer on a microporous support that provides better mechanical strength [3,6]. Among the rubbery polymers, poly(dimethylsiloxane) (PDMS) is a solubility-selective polymer that is more permeable to vapors (condensable) than to gases (non-condensable) [7]. Accordingly, PDMS membranes have been used in the separation of vapor/gas mixtures [8–10]. However, gas separation using polymeric membranes shows distinct trade-off trends regardless of whether glassy or rubbery polymers are used. More permeable polymers are generally less selective and vice versa [11].

The separation capability of the membranes can be improved by utilizing the organic–inorganic composite membranes. Boom

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et al. [12] discussed the effect of zeolite nanoparticles incorporated in rubbery polymers on the pervaporation properties of methanol/toluene mixtures. The addition of zeolite led to an increase in methanol flux and a decrease in toluene flux through the membranes. According to Yang et al., addition of silica nanoparticles increased the PDMS crystallinity, while zeolite addition decreased the PDMS crystallinity [13]. Zeolite addition improved the separation performance of toluene and ethylacetate more than silica addition [13]. Moaddeb and Koros [14] determined that the gas transport properties of thin polymeric membranes in the presence of silicon dioxide nanoparticles were improved to the upper limit of performance. It was also reported that the incorporation of nonporous, nano-sized fumed silica fillers in the glassy polymers poly(1-trimethylsilyl-1-propyne) (PTMSP) [15,16] and poly(4-methyl-2-pentyne) (PMP) [17–19] led to an increase in permeability and vapor/gas selectivity. The addition of nonporous, fumed silica nanoparticles to high-free-volume, glassy polymers was discovered to increase both permeability and vapor/gas selectivity simultaneously. This resulted from the capacity of these fillers to disrupt polymer chain packing and to increase the system free volume [15–17].

However, silica nanoparticles have a high surface area covered by silanol groups. This hydrophilic surface is not very compatible with the polymer matrix. In addition, the silica nanoparticles on the hydrophilic surface easily adhere to each other through hydrogen bonding and form agglomerates, which cause the uneven distribution of nanoparticles into a polymer matrix. Therefore, chemical treatment of the nanoparticle surface is necessary to achieve better compatibility and the uniform dispersion of the nanoparticles into the polymer matrix [20,21].

Coupling agents improved the practical adhesive bond of polymers to minerals, which may involve an increase in adhesion, but may also involve improved wetting, rheology, and other handling properties [22]. The coupling agent may also modify the interphase region to strengthen the organic and inorganic boundary layers [21]. Silane coupling agents are often used to modify the silica surface through their unique bifunctional groups [23,24].

In this work, PDMS–silica composite membranes were prepared for the separation of propylene from simulated off-gas of same composition as produced in polypropylene plants. Silica nanoparticles were introduced into the PDMS matrix, in order to improve both permeability and separation factor of the membrane. Silane coupling agents are known to modify the silica particles to induce the uniform dispersion of silica nanoparticles in the PDMS matrix. Silane coupling process was investigated in terms of types and conditions of silane coupling agents. Effect of silica contents on membrane performance was also examined. Furthermore, effects of the size of silica particles were examined and interpreted by comparing two kinds of silica: fumed and sol–gel silica. Enhancement of both permeance and separation factor was attempted by novel composite membranes made of PDMS and silane-coupled silica in this study.

2. Experimental

2.1. Materials

In this study, PDMS membranes and PDMS–silica composite membranes were prepared by coating PDMS solution on a polysulfone (PSf) support according to the conventional solvent casting method on non-woven fabric. Dope solution was composed of PSf (Udel P-1700, Amoco Co.), *n*-methyl-2-pyrrolidone (NMP, Aldrich Co., HPLC grade) as solvent, and polyvinylpyrrolidone (PVP, GAF Chemical Co., K-15) as an additive at the composition of PSf:PVP:NMP = 18:15:67. Distilled water was used as a nonsolvent. PSf support was pre-wetted with *n*-hexane to minimize the intrusion

Table 1

Characteristics of silica nanoparticles.

Characteristics	Fumed silica	Sol–gel silica
Average particle size (nm)	12	300–400
BET surface area (m ² /g)	200 ± 25	10–15
pH	3.7–4.7	10–11

of the PDMS solution keeping it over the support. It was also reported that a higher viscosity of PDMS solution clearly limited its intrusion into the support [25]. PDMS (RTV 655, General Electric) was selected, which is composed of the PDMS prepolymer and a cross-linking agent. Air bubbles were removed from PDMS solution by leaving it over night in a sealed flask at room temperature.

For the preparation of PDMS–silica composite membranes, two different silica nanoparticles were used. Hydrophilic fumed silica (Aerosil 200) was provided by Degussa, Korea and the other silica nanoparticles were prepared by sol–gel method, the details are described elsewhere [26]. Table 1 shows the physical properties of both silica nanoparticles, which were supplied by manufacturer for fumed silica and by the group who prepared them for sol–gel silica.

For the silane coupling of silica nanoparticles, three kinds of silane coupling agents were used such as 3-mercaptopropyl-trimethoxysilane (MrPS), 3-aminopropyl-trimethoxysilane (AmPS) and 3-methacryloxypropyl-trimethoxysilane (MtPS). Characteristics of silane coupling agents used in this work were listed in Table 2. Toluene, *n*-hexane, and methanol were purchased from Aldrich Co., and used as received.

2.2. Membrane preparation

The PDMS coating solution was prepared by dissolving PDMS prepolymer and cross-linking agent with a weight ratio of 10:1 in *n*-hexane. Silica nanoparticles were added into the PDMS coating solution and stirred for 12 h before coating. For better dispersion of silica nanoparticles in the PDMS matrix, the silica nanoparticle surface was modified with silane coupling agents in toluene for 6 h at 70 °C prior to addition into PDMS coating solution. Unreacted silane coupling agents were washed in a stirred methanol bath for 2 h and coupled silica nanoparticles were dried in a vacuum oven (BMDV-30, Balmann, Korea) at 100 °C for 6 h. PDMS coating solution was poured on to the PSf support inclined by 45° to make uniform coating. Then it was cured at 150 °C for 90 min to complete the cross-linking reaction to make PDMS–silica composite membrane.

2.3. Characterizations

The influences of silane concentration and type on the effectiveness of the silane coupling of silica nanoparticles were investigated using the thermal gravimetric analyzer (TGA, TGA-7, Perkin-Elmer, Waltham, MA). The weight loss of silane-coupled silica nanoparticles indicated the adsorption of silane coupling agents on the silica surface as a result of silane coupling. The thermal stability of the membranes was also analyzed using TGA.

Fourier transform infrared (FT-IR) spectroscopy (System 2000, Perkin-Elmer, Waltham, MA) analysis was performed to investigate the chemical bonding between silica nanoparticles and silane coupling agents. A silica powder sample ground with KBr was prepared and FT-IR spectra were obtained at transmission mode in the wavelength range from 400 to 4000 cm⁻¹. Chemical structure analysis of the membranes was also performed using FT-IR in the reflectance mode (attenuated total reflection, ATR).

Surface and cross-section morphology of the membranes were observed with a scanning electron microscope (SEM, Stereoscan 440, Leica, Wetzlar, Germany). Distribution of elements along the cross-section of the membranes was recorded in an energy disper-

Table 2
Characteristics of silane coupling agents used in the experiments.

Coupling agents	3-Mercaptopropyl-trimethoxysilane	3-Aminopropyl-trimethoxysilane	3-Methacryloxypropyl-trimethoxysilane
Abbreviation	MrPS	AmPS	MtPS
Source	Aldrich Co.	Aldrich Co.	Acros Organics
Purity	95%	97%	98%
Chemical structure			
Molecular weight	196.34	179.29	248.35
Specific gravity	1.057	1.027	1.04

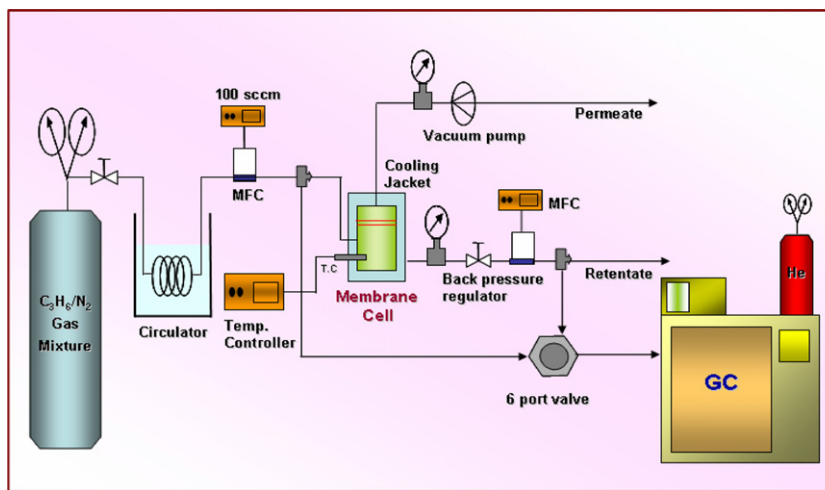


Fig. 1. A schematic diagram of membrane performance test apparatus.

sive X-ray spectrometer (EDX, Link ISS, Oxford, Oxfordshire, UK) system attached to the SEM. Intensity of X-ray generated from the specimen bombarded with accelerated electron beam was detected in terms of X-ray energy for element analysis. EDX scanning of the cross-section of the membrane provided the elementary composition in terms of coating depth. Atomic force microscope (AFM, Autoprobe CP research system, Thermo Microscope Inc., Plainview, NY) was used to obtain surface image of the membrane. Small squares (2 cm × 2 cm) of the sample were cut from the membranes and attached to a stainless steel sample puck. AFM images were obtained with a specimen (10 μm × 10 μm) by using a silicone probe in non-contact mode, and three images were taken from each sample.

2.4. Performance test

The performance tests were carried out with the permeation apparatus illustrated in Fig. 1. The vapor/gas mixture consisted of 15 vol.% propylene, and 85 vol.% nitrogen was used as feed, which was confirmed as a common composition for real processes. The feed rate was maintained at 100 cm³/min by a mass flow controller (MFC). The feed gas was cooled to about 0 °C by being passed through a refrigerating bath circulator before entering the membrane cell to make the propylene more condensable. The effective membrane area in the membrane cell was 32.15 cm². The driving force for permeation was supported by using a vacuum pump in the permeate side. The compositions of feed and retentate streams were measured by a gas chromatograph (HP 5890 Series II) equipped with a thermal conductivity detector (TCD).

The permeability and separation factor were calculated from flux and composition data obtained. Permeability was expressed as permeance in GPU units, where 1 GPU is 10⁻⁶ cm³/cm² s cmHg.

It should be noted that membrane thickness was not accounted to calculate the permeability. The separation factor was given by the ratio of concentration of two components in the permeate stream over that in the feed stream.

3. Results and discussion

3.1. PDMS membranes

PDMS prepolymer composition in casting solution affected the performance of the membrane, as shown in Fig. 2. As PDMS prepoly-

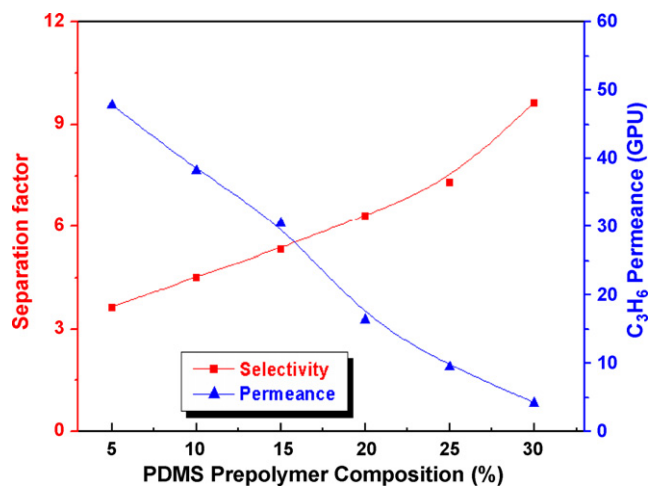


Fig. 2. Effect of PDMS prepolymer composition on performance of PDMS membranes.

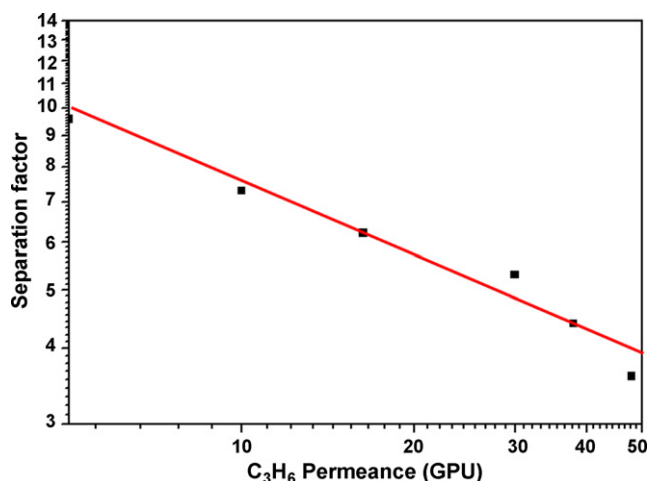


Fig. 3. The trade-off relationship of PDMS membranes.

mer composition increased, the coating solution viscosity increased to result in the increase of the thickness of the coating layer, which increased the diffusion resistance through the membrane. Therefore, permeability dramatically decreased with increasing PDMS prepolymer composition. However, an increase of PDMS prepolymer composition enhanced the separation factor, since PDMS has a greater affinity with propylene than nitrogen. Moreover, propylene could be more condensed in cooled test cells than nitrogen, which enhanced the solubility of propylene into the membrane matrix [27].

The relationship between the permeability and selectivity of PDMS membranes for the separation of propylene and nitrogen is plotted in Fig. 3. Selectivity was inversely proportional to permeability. It showed the typical trade-off relation as Robeson's line, whose upper bound could not be reached by PDMS membranes [28]. In order to overcome the trade-off trend of polymeric membranes, composite membranes were prepared by adding silica nanoparticles into the PDMS coating solution.

3.2. PDMS–silica composite membranes

PDMS–silica composite membranes were prepared by adding silica into the PDMS solution for both fumed silica and sol–gel silica. Effects of silica content in the PDMS solution on the membrane

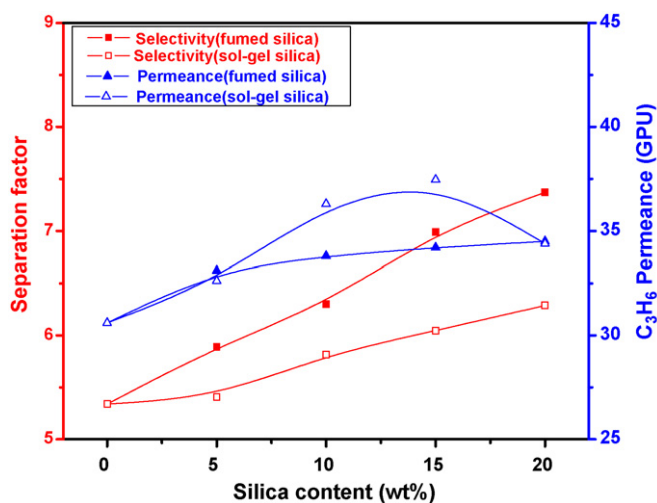


Fig. 4. Effect of silica content on the performance of composite membranes made of PDMS and uncoupled silica nanoparticles.

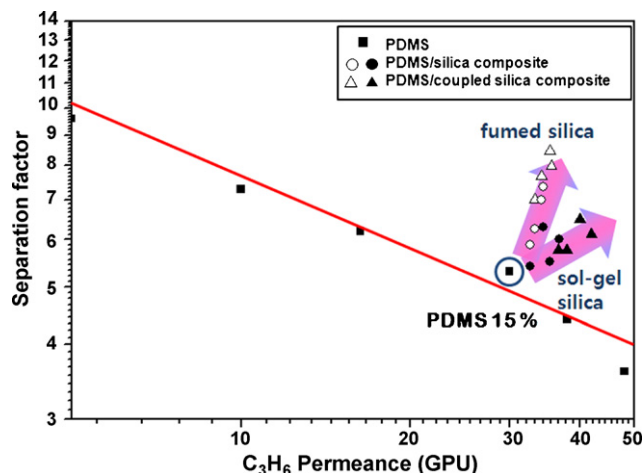


Fig. 5. Performance variation of composite membranes made of PDMS/silica nanoparticles, coupled and uncoupled.

performance were investigated. As silica content increased, both permeability and selectivity increased as shown in Fig. 4 for both fumed silica and sol–gel silica, which discords with the trade-off trend.

Silica nanoparticles are known to have a higher affinity with organic vapor [16,17]. Incorporation of silica nanoparticles into the PDMS matrix could increase sorption of propylene into the membrane matrix. Moreover, it also increased the surface roughness and area of the composite membranes to increase the sorption. Therefore, both propylene permeability and separation factor were improved by increasing the silica content for both fumed silica and sol–gel silica. Therefore, the addition of silica nanoparticles into the PDMS matrix overcame the trade-off trend, as shown in Fig. 5.

Regarding increased permeability, it has been reported in the literature that fumed silica incorporated in the glassy polymer matrix might disrupt polymer chain packing and then caused an increase of polymer free volume [18]. For sol–gel silica, the incorporation increased permeability to reach the maximum value at 15% of silica

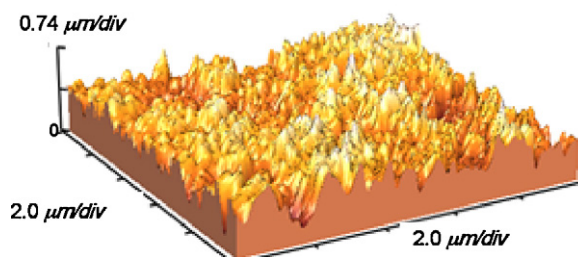
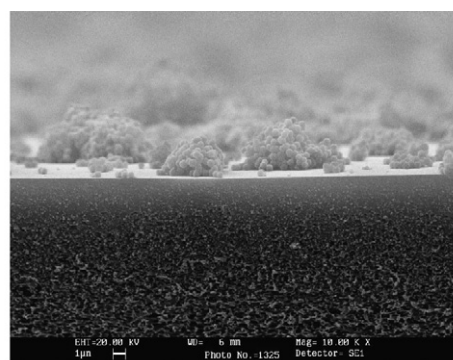


Fig. 6. SEM photograph and AFM 3D-image of PDMS–fumed silica particle composite membrane (silica content = 15%).

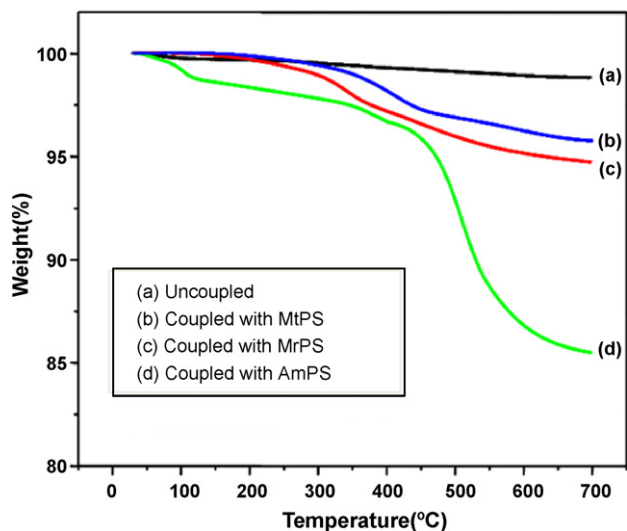


Fig. 7. TGA analyses for fumed silica nanoparticles coupled with various silane coupling agents at 5 wt% of concentration.

content and then decreased beyond this point due to the increased density of the PDMS layer. Fumed silica could also increase the permeability due to the same reason though absolute value and increasing rate were not as high as those of sol-gel silica case. Fumed silica showed a better separation factor than sol-gel silica because the former had a smaller particle size and greater surface area than the latter as shown in Table 1.

PDMS-silica composite membranes prepared by the mixing of uncoupled silica nanoparticles with PDMS solution were examined by SEM and AFM. As shown in SEM images given in Fig. 6, silica nanoparticles were agglomerated on top of the PDMS selective layer instead of uniform dispersion into the PDMS matrix. It was considered that silica nanoparticles might have hydrophilic surface properties, resulting in low compatibility with PDMS, due to the presence of silanol groups on the surface [29,30]. From AFM imaging, it was also confirmed that the roughness and surface area of the membrane increased due to the incorporation of silica nanoparticles. RMS roughness was increased up to 180 nm and surface area

was doubled for sample of 20 wt% of silica content compared with the sample without silica. However, the silica nanoparticles were not uniformly distributed due to agglomeration, and they could be removed by swabbing because they were not properly bound to the surface. Even though the addition of silica nanoparticles enhanced membrane performance, the membranes should have had a firmer structure for stable performance. PDMS-silica composite membranes should secure the uniform dispersion and proper binding of silica nanoparticles into the PDMS matrix.

3.3. Silane coupling of silica nanoparticles

Silica nanoparticles were not uniformly dispersed in the PDMS matrix when they were used without pretreatment. Chemical treatment of silica nanoparticle surface with the silane coupling agent was attempted for better dispersion of the silica nanoparticles into the PDMS matrix. TGA analyses were performed for silica nanoparticles coupled with three different silane coupling agents. The weight loss was originated from the decomposition of the silane functional group grafted on the silica surface after silane coupling [20,29]. Coupled silica showed a weight loss of 5%, 15%, and 4% for MrPS, AmPS and MtPS, respectively, as shown in Fig. 7. Results indicated that the reactivity of AmPS with silica nanoparticles was the best among three silane coupling agents. However, AmPS-coupled silica had a hydrophilic amino group [30], and was not well dispersed due to its hydrophilicity. MrPS and MtPS had less hydrophilic mercapto and carbonyl groups [31,32], and better dispersion could be attained by silane coupling with those. TGA weight loss data showed that MrPS could be slightly more reactive with silanol groups than MtPS.

The chemical bonding between silica nanoparticles and silane coupling agents was characterized by FT-IR as shown in Fig. 8. Silane-coupled silica showed the characteristic peaks at 2940 cm^{-1} (C-H₂ stretching) and 1470 cm^{-1} (C-H₂ bending), which are common for all three silane coupling agents. Each silane coupling agent showed its own characteristic peak related to its functional group. It was considered that the mercapto group was relatively less polar than the amino and carbonyl groups, and thus had a low intensity in the spectra. Since silanol groups on the silica surface reacted with the silane coupling agents through a condensation reaction [33], the intensity of the silanol group at 3450 cm^{-1} decreased. From the

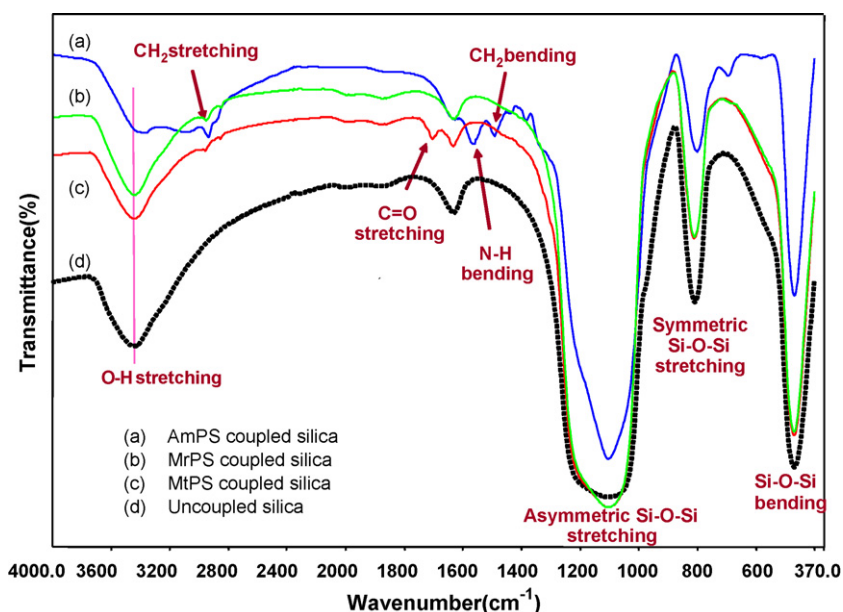


Fig. 8. FT-IR spectra of fumed silica nanoparticles coupled with various silane coupling agents at 5 wt% of concentration.

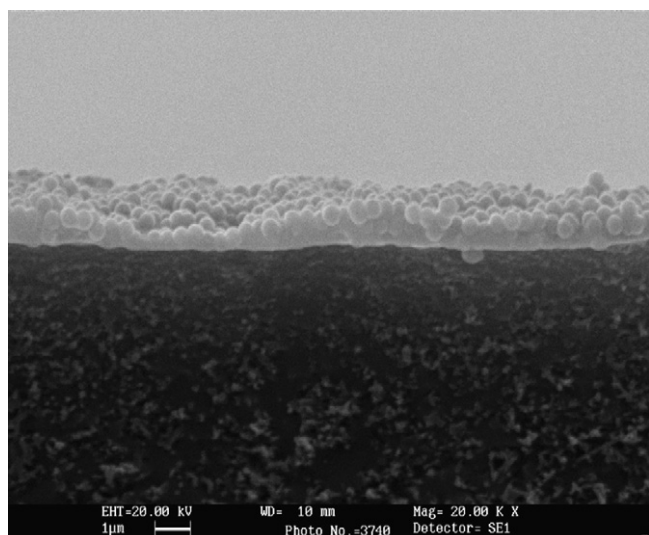


Fig. 9. SEM photograph of PDMS-fumed silica nanoparticle composite membrane coupled with mercapto silane (silica content = 15 wt%).

FT-IR analysis, it was safe to conclude that the functional groups of silane coupling agents were successfully introduced onto the silica surface. MrPS was the most effective coupling agent than the others and it was used for further study.

3.4. PDMS–silica composite membranes with silane coupling

The surface and cross-section morphology of PDMS–silica composite membranes were characterized by SEM and AFM. In PDMS–silica composite membranes with silane coupling, silica nanoparticles were well dispersed in the PDMS matrix, as can be seen in Fig. 9. Silica nanoparticles coupled with MrPS had hydrophobic surfaces due to the hydrophobicity of MrPS, and the interfacial interaction between silica nanoparticles and the PDMS matrix increased [21]. The effect of MrPS-coupled silica content in PDMS–silica composite membranes was examined. Fig. 10 shows the surface morphology of the membranes characterized by AFM. Silica nanoparticles were piled up at the top of the membrane, resulting in the increase in thickness of the silica-filled PDMS selective layer. Fig. 11 shows the distribution of surface asperity height obtained by bearing ratio analysis. When the silica content

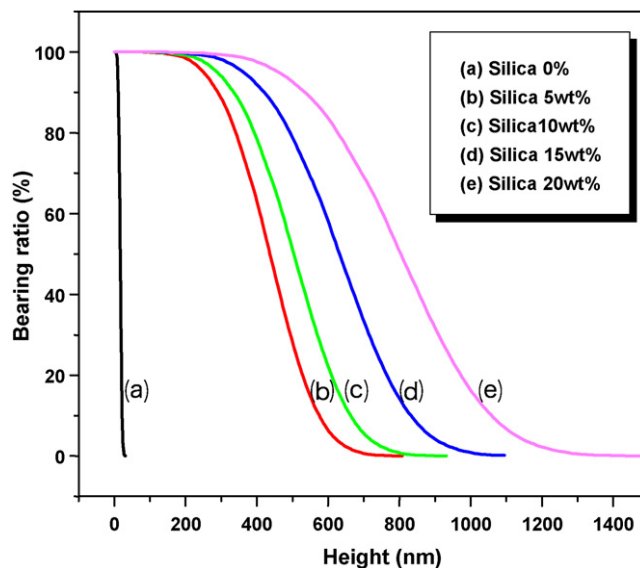


Fig. 11. Surface asperity of PDMS-fumed silica nanoparticle composite membrane coupled with mercapto silane.

in the PDMS matrix increased, the surface height tended to increase due to the charged silica [34]. This caused the increase of RMS (root mean square) average roughness and surface area (Fig. 12) in the PDMS–silica composite membranes. Therefore, the sorption of organic vapors into the membrane increased as inferred from the separation factor data in Fig. 13. RMS of average roughness was calculated from the roughness data measured three times for each sample with standard deviations less than 2.0. From these results, it was concluded that this variation of surface morphology affected membrane performance as shown in Fig. 13.

In Fig. 14, FT-IR (ATR) spectra changes were illustrated from the PSf support, PDMS membrane, and PDMS–silica composite membranes with and without coupling. PDMS coating on PSf formed additional peaks located at 800 cm^{-1} (symmetric Si–O–Si stretching) and $1000\text{--}1100\text{ cm}^{-1}$ (asymmetric Si–O–Si stretching), while the intensity of the PSf peaks decreased. PDMS–silica composite membranes had a similar tendency to that of PDMS membranes. PDMS–silica composite membranes with no coupling mainly had peaks related to silica and PDMS because silica nanoparticles were concentrated at the top of the membranes. The characteristic peaks

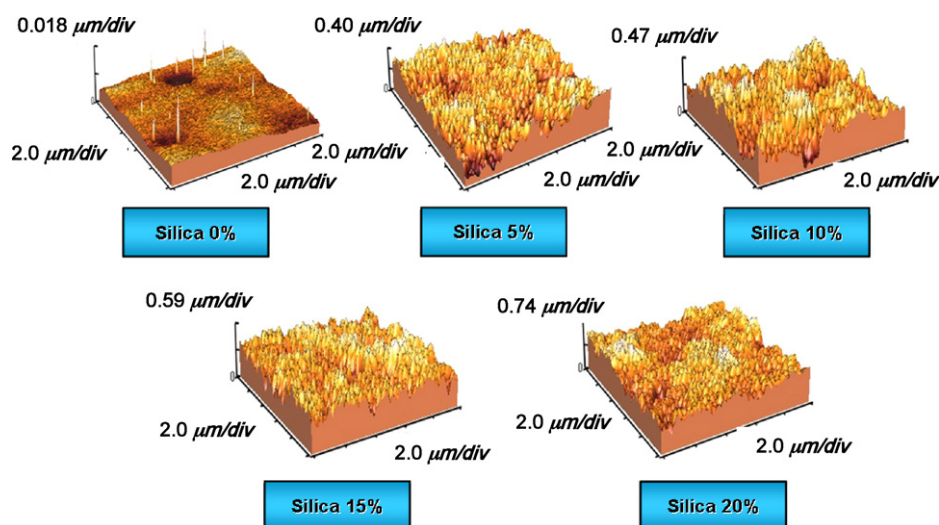


Fig. 10. AFM 3D images of PDMS-fumed silica nanoparticle composite membrane coupled with mercapto silane.

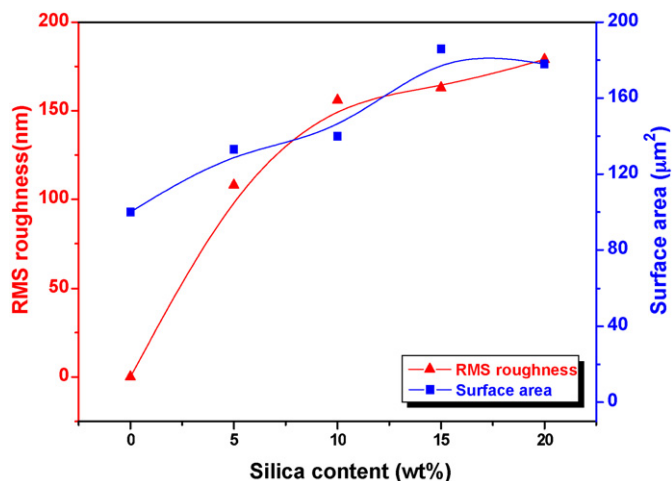


Fig. 12. Surface roughness and area variations of PDMS-fumed silica nanoparticle composite membrane coupled with mercapto silane.

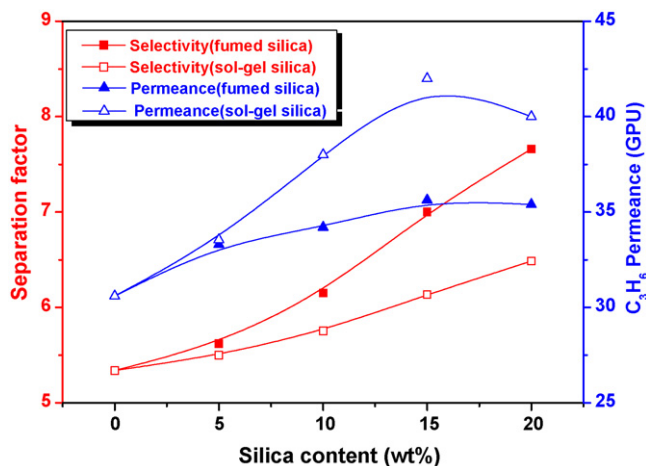


Fig. 13. Effect of silica content on performance of composite membranes made of PDMS-silica nanoparticles coupled with mercapto silane.

of PSf support almost disappeared as the thickness of the silica-filled PDMS selective layer increased. On the other hand, in the case of the membranes prepared by adding coupled silica, the peaks related to the functional group were also detected with very low intensity.

The effects of MrPS-coupled silica content on membrane performance were examined. As silica content increased, both permeability and selectivity increased, as shown in Fig. 13. When these results were compared with those for uncoupled silica as shown in Fig. 4, both separation factor and propylene permeance were increased. It was proved that the coupling of silica nanoparticles with the silane coupling agent enhanced membrane performance. Uniform dispersion of silane-coupled silica nanoparticles in PDMS matrix was very important factor to make membrane for propylene separation. The incorporation of silica nanoparticles into the PDMS matrix improved the membrane regardless of silica size for both fumed and sol-gel silica.

However, the type of silica had influence on aspects of performance improvement. When fumed silica was used, the improved performance was mainly explained by separation factor rather than permeance. Fumed silica has smaller particle size (12 nm) and much greater surface area (200 m²/g) than sol-gel silica (300–400 nm and 10–15 m²/g). Therefore, it enhanced the sorption of propylene on silica surface to increase the separation factor, while it slightly increased propylene permeance despite more sorption as shown in Fig. 5 due to the increase of mass transfer resistance build up by fume silica particles. On the contrary, the permeance of propylene was much improved when sol-gel silica was used. Separation factor increase was not as much as that for fumed silica due to the less surface area. Sol-gel silica has relatively larger particle size than fumed silica to disrupt chain packing of the membrane to increase the propylene permeance [35].

This can be explained in two different ways. First, as silica content increased, the thickness of the silica-filled PDMS layer increased, and the permeation path could be distorted by the silica nanoparticles, which indicated the increase of mass transfer resistance [35]. Second, silica nanoparticles were filled into the PDMS polymer chain and might disrupt chain packing of PDMS. Therefore, an optimum silica content for a greater improvement of membrane performance is required, and this depends on silica nanoparticle

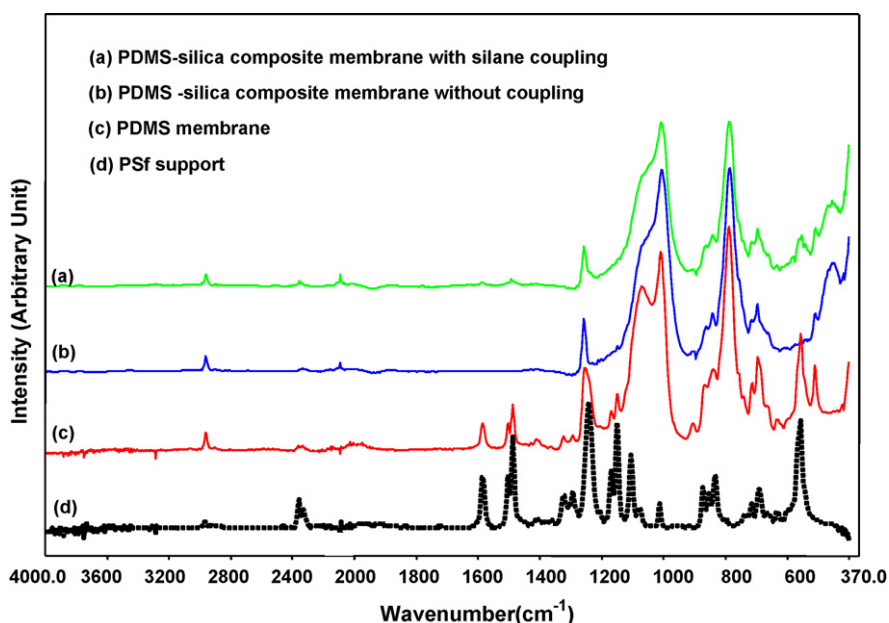


Fig. 14. FT-IR (ATR) spectra of PDMS and PDMS-silica nanoparticle composite membranes (silica content: 15 wt%, silane coupling agent: mercapto silane).

size [16]. This showed good agreement with AFM analysis, which reported that the surface area of the membrane decreased at a higher silica content.

Fig. 5 shows the inverse trade-off relationship of the separation of propylene and nitrogen in PDMS–silica composite membranes. This was attributed to the improvement in both permeability and selectivity by the incorporation of inorganic nanoparticles into the polymer matrix. These results can probably be considered as competitive effects; the nanoparticles can increase the mass transfer resistance in a polymer matrix or they can disrupt chain packing depending on the particle size. The final results in organic–inorganic composite membranes may be a balance of both of these effects [16].

4. Conclusion

PDMS coating on a Psf support enabled the separation of propylene from off-gas due to the affinity between propylene and PDMS. Increase of PDMS content, however, decreased the permeance of propylene in spite of the high separation factor, which was called as trade-off trends depicted as Robeson's line. PDMS–silica composite membranes overcame the limit of typical trade-off trend by increasing both separation factor and permeance. Silica nanoparticles in composite membrane were agglomerated with each other and caused uneven dispersion in PDMS matrix.

Coupling of silica nanoparticles with a silane coupling agent modified the surface of the nanoparticles to be evenly distributed in the PDMS matrix. Coupling agent for silica nanoparticles in the PDMS/organic solvent system was selected as mercapto silane in terms of hydrophobicity and thermal stability by TGA analyses. Chemical bonding between silica nanoparticles and silane coupling agents was confirmed by FT-IR analyses. Composite membrane with coupled silica nanoparticles still enhanced separation factor up to 7.5 and propylene permeance up to 42 GPU. Size and amount of the silica nanoparticles were important factor in terms of composite membrane performance.

Fumed silica has smaller particle size and much greater surface area than sol–gel silica. Therefore, it enhanced the sorption of propylene on silica surface to increase the separation factor, while it increased the mass transfer resistance of the membrane to result in little increase of propylene permeance despite more sorption. Sol–gel silica has relatively larger particle size than fumed silica to disrupt chain packing to increase the propylene permeance, while maintaining the separation factor. Optimum amount of coupled silica nanoparticles was around 15 wt% in terms of performance and solution coating process. Novel composite membranes made of PDMS and silane–coupled silica in this study overcame the trade-off trend of the gas separation membrane by enhancing both permeance and separation factor. It should be promising performance enhancement compared with those of the other membranes.

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