

A New Technique for Preparation of PDMS/Ceramic Nanocomposite Membrane for Gaseous Hydrocarbons Separation

E. Jannatdoust,^{1,2,3} A. A. Babaluo,^{1,2} F. Abbasi,^{1,2} M. Akhfar Ardestani,¹ M. Peyravi^{1,2}

¹Institute of Polymeric Materials, Sahand University of Technology, Tabriz, I.R. Iran

²Nanostructure Materials Research Center (NMRC), Sahand University of Technology, Tabriz, I.R. Iran

³Department of Chemical engineering, Urmia University of Technology, Urmia, I.R. Iran

Received 29 May 2010; accepted 6 January 2012

DOI 10.1002/app.36771

Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A novel composite membrane using polydimethylsiloxane (PDMS) as a top active layer and ceramic nanocomposite as the support layer was developed for the gaseous hydrocarbons separation. For the fabrication of hybrid membranes, nanocomposite technology applied for manufacturing ceramic supports with controllable microstructures. Also, a new method was used for coating a uniform and no penetrated polymeric layer. Top layer of ceramic support with nanocomposite microstructures was fabricated using 5 wt % α -Al₂O₃-SiO₂ bidispersed suspensions with optimum weight fraction of second phase (SiO₂) based on the fractional collision frequency theory. PDMS selective layer was coated on the outer surface of the porous ceramic nanocomposite support by dip-coating method. In this respect, the effect of several parameters

such as pretreatment temperature, PDMS solution concentration, and number of coated polymeric layers on prepared layers morphology and hybrid membrane performance in the separation of condensable hydrocarbons (iso and *n*-butane) from hydrogen were investigated. The results showed that the membranes fabricated at 140°C as pretreatment temperature and three polymeric layers by 7, 15, and 15 wt % PDMS concentration, respectively, had a high selectivity (>25 at 2 bar) in C₄H₁₀/H₂ separation. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: nanocomposite; hybrid membranes; PDMS; condensable hydrocarbon; hydrogen

INTRODUCTION

In recent years, membrane-based gas separation is becoming increasingly popular due to its inherent advantages over the more traditional methods. Some of their strong points are low capital and operating costs, low energy requirements, and simplicity in operation, as well as compactness and portability.^{1,2} Membrane-based separation processes have also been proposed for the recovery of higher hydrocarbons (C₂⁺) from natural gas or hydrogen-containing off-gas streams. Due to the presence of the product gas (methane or hydrogen) as major components in these feed streams, to minimize membrane area requirements (lower capital cost) and eliminate recompression cost by maintaining the product gas at feed pressure, it is highly desirable to use organic-vapor-selective membranes.³

Properties of inorganic (ceramic) substrates like high flux and high mechanical, chemical, and thermal stability make them ideal supports for gas separation applications. But, commercial ceramic membranes, having a pore diameter equal to or larger than 5 nm, are not efficient in separating of gas mixtures. Because, the controlling gas transport mechanism in the porous ceramic membranes with nanometric pore size (<10 nm) is Knudsen diffusion, providing a low selectivity for the gas mixtures separation. Therefore, other efficient transport mechanisms such as surface flow, molecular sieving, and solution-diffusion should be introduced in these membranes.^{4,5}

To introduce these mechanisms in the inorganic membranes, the membrane material has to be made more interactive with penetrates. Such shortcomings can be overcome by surface modification of the ceramic substrate with a polymeric active layer.⁶ Inorganic porous substrates have surface hydroxyl groups, which readily react with compounds such as fluorosilanes,⁷ chlorosilanes,^{8–13} vinyls,^{6,14} etc. These compounds can be used to introduce specific functionalities on the surface of the membrane, altering its properties toward sorption and diffusion of gases.⁴

Correspondence to: A. A. Babaluo (a.babaluo@sut.ac.ir).

Contract grant sponsor: Sahand University of Technology (SUT).

Typical polydimethylsiloxane (PDMS) membranes are good examples of rubbery polymeric membranes that are more permeable to condensable vapors than to permanent gases.¹⁵ Its glass transition temperature is among the lowest values recorded for polymers (-129°C) indicating a very flexible polymer backbone with long-range segmental motion active event at very low temperatures.^{16–18} As a result, PDMS-based membranes usually have a relatively higher flux for organics than glass-state membranes.^{16,19–22} Currently, PDMS elastomer is the most commonly used membrane material for the separation of organic vapors from permanent gases.³

The viability and applicability of a composite membrane, which combines the separation properties of a coating (polymeric) material and the mechanical strength of a ceramic supporting layer, in the area of vapor permeation has gained much attention lately, leading to numerous research attempts.²³ Leger et al. prepared PDMS membrane grafted onto a porous alumina support. The permeation results showed that permeate molecules are transported by solution-diffusion mechanism, as in a dense polymeric film.⁵ Hong and Hong used PDMS/ceramic composite membrane for the pervaporation of IPA (isopropanol)/water system.²⁴ Liu et al. developed a new PDMS/ Al_2O_3 composite hollow fiber membrane by coating a PDMS-oligo film on the outer surface of an Al_2O_3 hollow fiber porous substrate.²⁵ But, a few works have been published on the modification of ceramic membrane by PDMS for gas separation processes, especially separation of noncondensable molecules (H_2 and N_2) from condensable hydrocarbons. Therefore, study on the modification of ceramic supports with PDMS for the higher hydrocarbons separation is necessary.

In addition to chemical, thermal, and mechanical stability, the support layer should adhere well to the top layer and, most importantly, its porosity should be as high as possible in order to avoid additional mass transfer resistance for the permeating compounds. On the other hand, wide pores in the support may also lead—in an indirect way—to high mass transfer resistances when the top layer material intrudes such pores. This happens easily at the moment a dilute polymer solution is coated on top of the support during membrane formation.²⁶ Several techniques have already been developed to prevent this penetration. The support pores can be filled with a nonsolvent for the coating polymer,^{27–30} with a solvent,³¹ or with highly viscous materials³² before applying the coating solution. Another way to limit penetration consists in casting top layers from a concentrated solution which forms a gel as soon as the support is contacted.^{33,34} The last technique was also applied in our previous work,³⁵ but in the case of the ceramic supports, all of these techniques might

have an undesirable effect on good adhesion between PDMS layer and ceramic support.

In this work, a novel nanocomposite membrane using PDMS as the top active layer and ceramic membrane as the support layer was developed. For the fabrication of PDMS/ceramic membranes, nanocomposite technology was applied for manufacturing ceramic supports with controllable microstructures. PDMS selective layer was coated on the outer surface of the porous ceramic nanocomposite support by dip-coating method. In this respect, the effect of several parameters such as pretreatment temperature of support, PDMS solution concentration, and number of coated polymeric layers on the prepared layers morphology and PDMS/ceramic nanocomposite membrane performance in higher hydrocarbons separation were investigated. Further, dense homogeneous PDMS membrane was prepared by solution casting technique for comparing.

EXPERIMENTAL

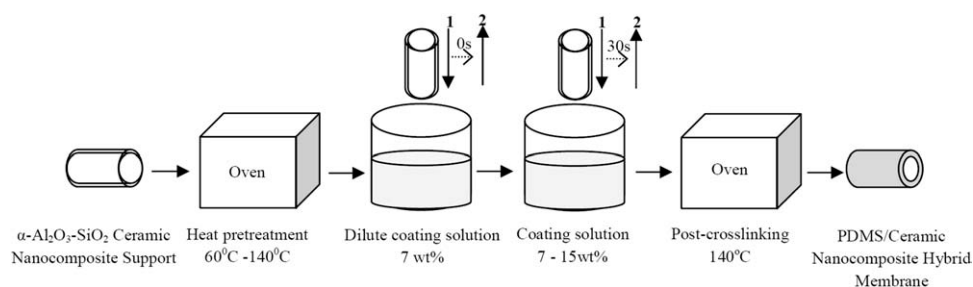
Materials

In this work, alumina tubular porous substrates were used as support systems. Submicron (240 nm) and nano alumina (50 nm) and nano silica (40 nm) powders were synthesized according to the procedures described in Refs. ^{36–38} and used for preparation of intermediate and top layers of nanocomposite ceramic supports. Polyacrylic acid ammonium salt (Darvan 821-A, R.T. Vanderbilt, Morwalk, United States) and polyethylene glycol with molecular weight of 6000 g/mol (PEG6000, Merck Co., Germany) were used as stabilizer and polymeric binder, respectively. Dense homogeneous silicone rubber membrane and selective top layer of the composite membranes were LSR 40-10:1, V 40082 type (Rhodia, French). The silicone kit was a two-component system, consisting of a vinyl-terminated prepolymer with high molecular weight (Part A) and a crosslinker containing several hydride groups on shorter PDMS chains (Part B). The chloroform (BDH, England) were used as solvent, without further purification.

Membrane preparation

Dense homogeneous PDMS membrane

A casting solution was prepared by dissolving Part A and Part B with a weight ratio of 10 : 1, in a 10 wt % PDMS/chloroform solution. The casting solution was poured into a glass petri dish and then allowed to dry in room temperature. After drying and pre-curing at room temperature overnight, the membranes were placed in an oven at 100°C for 24 h to ensure complete crosslinking.



Scheme 1 Multistep dip-coating procedure of the tubular type PDMS/ceramic nanocomposite membranes.

PDMS/ceramic nanocomposite membrane

Ceramic nanocomposite support. Tubular multilayer alumina supports with controllable microstructures for PDMS/ceramic composite membranes were prepared by applying nanocomposite technology. These supports consist of three layers: (a) a high-quality macroporous support system providing mechanical strength to the system, (b) mesoporous intermediate layers whose roles are to reduce any inherent defects of the support and to prevent the infiltration of the top layer nanoparticles into the pores of the support and (c) a nanoporous top layer with controllable microstructure in nanometric scale. Tubular alumina porous support systems were prepared by gel-casting method and then, nanostructure intermediate and top layers were coated on the porous supports systems by dip-coating method. Intermediate layers were fabricated by applying an optimum routine method: this technique was twice coating of 5 wt % submicron slurry without applying vacuum followed by vacuum dip coating of 5 wt % submicron and 1 wt % nano alumina slurry.³⁹ Top layer of ceramic support with nanocomposite microstructures was fabricated using alumina and silica bidispersed suspensions. The optimum weight fraction of the second phase (SiO₂) was determined based on the fractional collision frequency theory.⁴⁰ Silica nanoparticles cause good adhesion between PDMS polymer layer and ceramic support. Stable nano alumina and silica bidispersed suspension has been prepared using 5 wt % of α -Al₂O₃-(22.3 wt %)SiO₂, 0.3 mL (per 100 g of ceramic powder) of polyacrylic acid ammonium salt as stabilizer and 5 wt % (based on ceramic powder) of PEG as polymeric binder.^{40,41} Nanocomposite top layer was obtained by dipping the multilayer support in the prepared suspension and allowing to stand 30 s and raised up with velocity of 40 mm/min.⁴² The support systems were dried for 24 h at ambient temperature and sintered at 1450°C for 5 h and 1350°C for 2 h, for macroporous supports and coated layers, respectively.

PDMS/ceramic composite membrane. Coating solutions were prepared with different weight percents of PDMS in chloroform. The tubular type PDMS/ceramic nanocomposite membranes were prepared in a multistep dip-coating procedure (Scheme 1):

ramic nanocomposite membranes were prepared in a multistep dip-coating procedure (Scheme 1):

- Step 1. Heat pretreatment of α -Al₂O₃-SiO₂ nanocomposite supports.
- Step 2. Dip coating of the hot ceramic supports with dilute coating solutions without dipping time.
- Step 3. Dip coating of the pretreated supports (in Step 2) with different concentration of coating solutions for 30 s, and then drying at room temperature for 20 min.
- Step 4. Postcrosslinking at 140°C for 20 min.

Membrane characterization

Morphology and surface topology

Morphology and surface topology of the manufactured composite membranes were investigated by optical microscopy (Olympus PMG3, Japan) and scanning electron microscopy (SEM, CamScan MV2300, England). Also, SEM micrographs were used to analyze the top-layer thickness and penetration of the coating solution into the ceramic supports pores.

Gas permeation experiments

Only pure gas permeation measurements were run in this study. The tubular membrane was held in a cylindrical module with feed and retentate openings

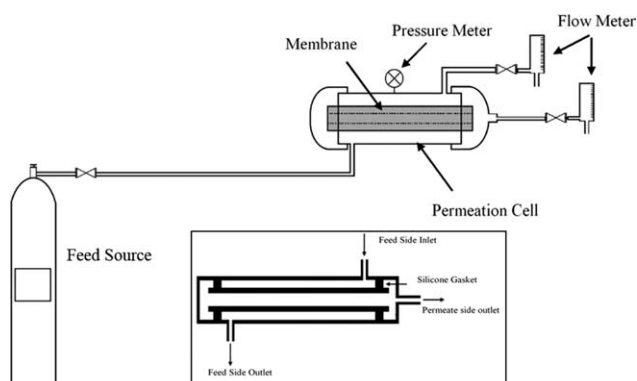


Figure 1 Schematic of tubular permeator.

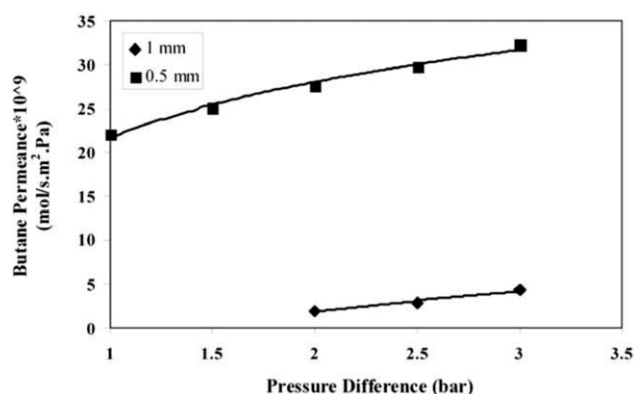


Figure 2 Butane permeance versus pressure difference for dense homogeneous PDMS membranes with different thickness: (■) 0.5 mm and (◆) 1 mm thickness.

at either end of the module and a permeate opening on the tube side. At each ends, rubber orings were held tight on the tube side by screw caps to ensure

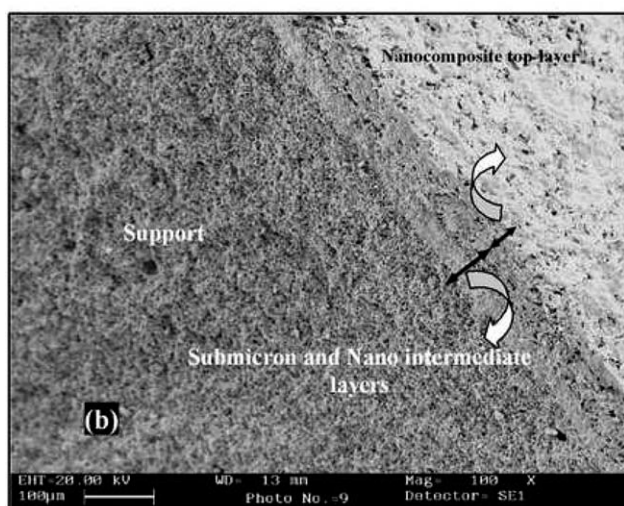
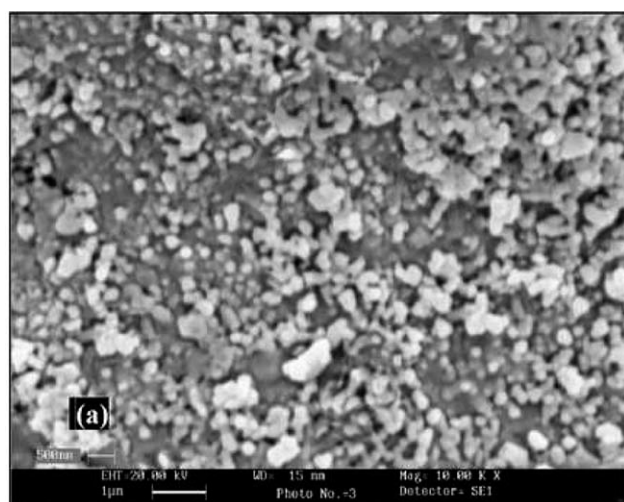


Figure 3 SEM micrographs of the coated (a) surface and (b) cross-section of ceramic nanocomposite support.

sealing. During the experiment, gas was provided to the feed inlet and the retentate exit was held in the dead-ended position. The permeate outlet was connected to a bubble flow meter and the permeate pressure was atmospheric (see Fig. 1).

The membrane performances were characterized in terms of permeance and selectivity. The pure-gas permeation properties of dense homogeneous PDMS membrane and PDMS/ceramic composite membrane were determined with hydrogen and higher hydrocarbons (butane) at different feed pressure and ambient temperature. The values of ambient temperature and pressure measured during experiments were used to convert volumetric flow rate to molar flow rate assuming ideal gas behavior. Thus, the gas permeance was calculated by:

$$P = \frac{273dV}{22.4A(P_{\text{feed}} - P_{\text{perm}})T dt} \quad (1)$$

where A is the membrane flow area (m²), P_{feed} and P_{perm} are the feed and permeate pressures (Pa), respectively, and dV/dt is the volumetric flow rate (L/s). Membrane permselectivity (α_i ; ideal selectivity)

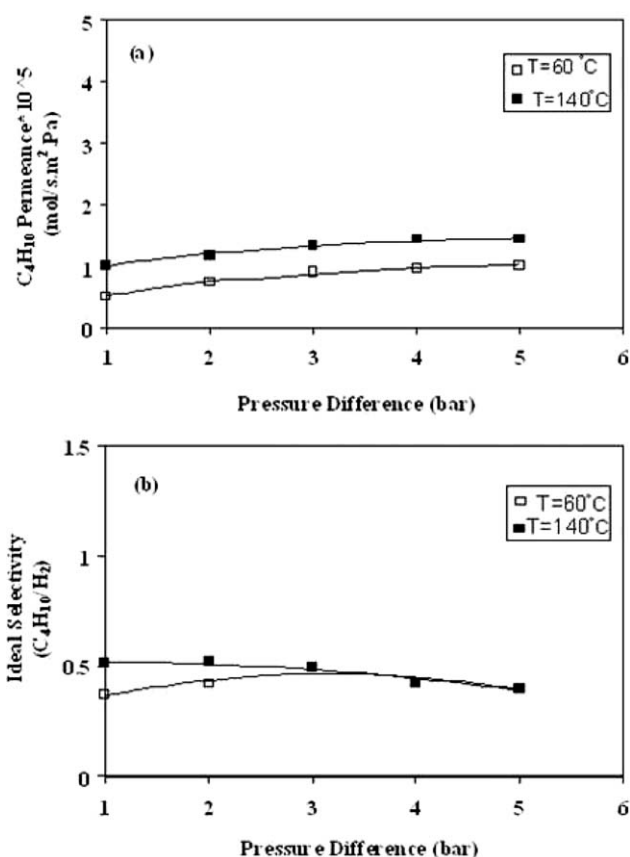


Figure 4 (a) Butane permeance and (b) C₄H₁₀/H₂ ideal selectivity vs. the pressure difference for PDMS/ceramic nanocomposite membranes pretreated at 60°C and 140°C and dip coated in a 7 wt % PDMS solution.

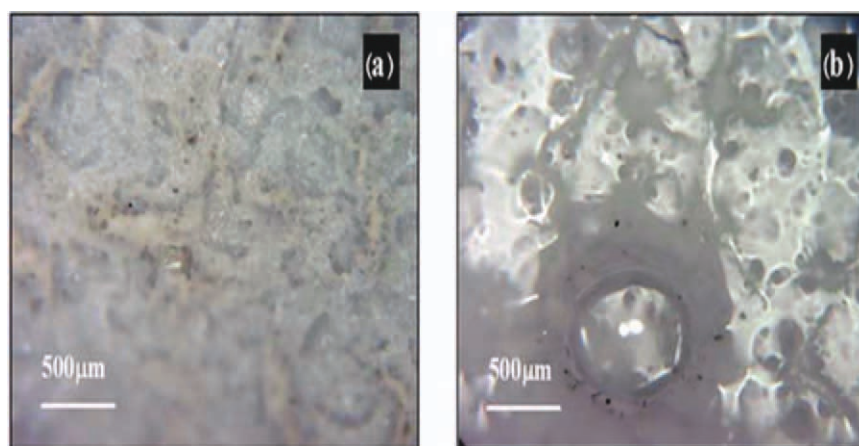


Figure 5 Optical microscopy images of the coated surface of PDMS/ceramic nanocomposite membranes pretreated at 140°C and dip coated by: (a) 7 wt % and (b) 15 wt % PDMS solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was calculated for pure hydrocarbon over hydrogen by dividing the gases permeance as following:

$$\alpha_1 = \frac{P_{\text{hydrocarbon}}}{P_{\text{hydrogen}}} \quad (2)$$

RESULTS AND DISCUSSION

Dense homogeneous PDMS membrane

Figure 2 shows the butane permeance versus pressure difference at ambient temperature for dense homogeneous membranes with different thickness. It can be seen that the butane permeance increases with increasing the pressure difference. In addition, the results indicated that the gas permeance increases significantly with decreasing membrane thickness. However, mechanical strength of polymeric membranes decreases considerably with decreasing membrane thickness, so that we could

not take permeation data for PDMS membranes with thickness of 0.5 mm at higher pressures (>3 bar). Also, permselectivity of PDMS membranes with 0.5 mm thickness was measured for a binary gas mixture ($\text{C}_4\text{H}_{10}/\text{H}_2$) at ambient temperature and feed pressure of 1.5 bar. The obtained selectivity result ($\alpha_{I,(\text{C}_4\text{H}_{10}/\text{H}_2)} = 78$) showed a desirable performance of PDMS membranes in the separation of hydrogen (noncondensable gas) from condensable hydrocarbons. But, due to their low mechanical strength and permeability, it is important to use ceramic supports as hybrid structures.

Ceramic nanocomposite supports

In Figure 3 SEM micrographs of coated surface and cross-section of the ceramic nanocomposite support are presented. As can be seen, by applying the mentioned modification method procedure, the multi-layer membrane was fabricated successfully and no

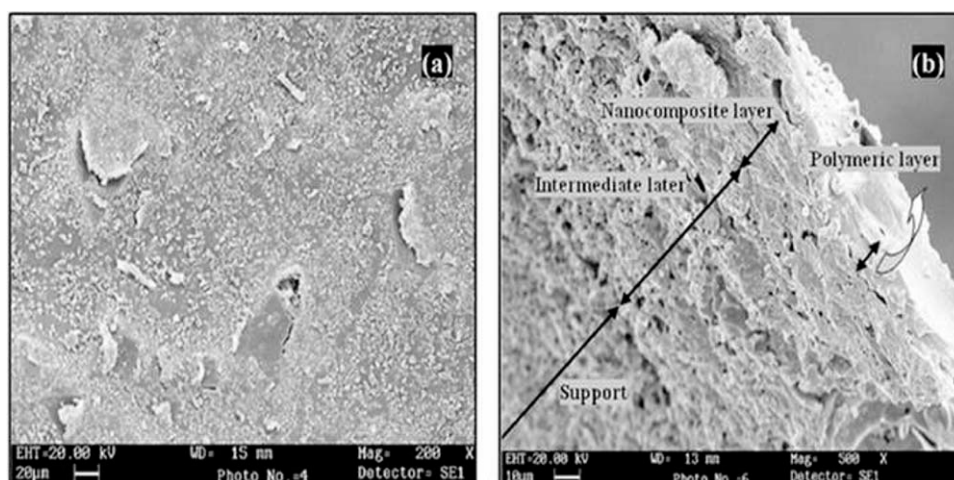


Figure 6 SEM micrographs of the coated (a) surface and (b) cross-section of PDMS/ceramic nanocomposite membrane pretreated at 140°C and dip coated by 7 wt % PDMS solution.

defect could be observed. With regards of the SEM images, the fabricated ceramic nanocomposite support promotes a high performance in membrane separation processes due to its defect-free surface and its multilayer structure with no penetration.

PDMS/ceramic nanocomposite membranes

Effect of pretreatment temperature

The effects of two different heat pretreatment temperatures, i.e., 60°C and 140°C were studied. Ceramic nanocomposite supports were pretreated in these temperatures and then immediately dip coated by 7 wt % PDMS solution. Figure 4 displays butane permeance and C_4H_{10}/H_2 selectivity versus the pressure difference for these PDMS/ceramic nanocomposite membranes. As can be seen in this figure, the C_4H_{10} permeance of membrane pretreated at 140°C is higher than membrane pretreated at 60°C. However, there is no visible difference among the two membranes selectivities. The higher permeance of butane in the membranes pretreated at high temperatures indicated that the intrusion of polymer solution in the support decreases by increasing pretreatment temperature which can be due to the more initial crosslinking in the surface of the hot support.

Effect of PDMS solution concentration in the first layer (pretreatment step)

To investigate the effect of PDMS solution concentration in the first polymer coating layer, two different concentrations, 7 and 15 wt %, were studied. Ceramic nanocomposite supports heat pretreated at 140°C and then immediately dip coated by different concentrations of PDMS solution. Figure 5 shows the optical microscopy images of the coated membranes. It can be seen that there were many bubbles in the surface of membrane coated by 15 wt % PDMS solution. While, there is no bubble in the surface of membrane coated by 7 wt % PDMS solution.

SEM micrographs of the coated surface and cross-section of PDMS/ceramic nanocomposite membrane pretreated at 140°C and dip coated by 7 wt % PDMS solution are given in Figure 6. It can be observed that polymer could be able to cover the surface of ceramic completely, but PDMS top layer was not defect-free [Fig. 6(a)]. In addition, intrusion of polymer layer into pores of the support was not considerable and the boundary between the top layer and support was clear [Fig. 6(b)]. Thus, 7 wt % PDMS solution was selected as optimum polymer solution concentration for the first polymer layer preparation on the ceramic support.

Effect of PDMS solution concentration in the second layer

The effects of two different PDMS solution concentrations, 7 and 15 wt %, to prepare the second poly-

meric layer on the pretreated membranes were studied. PDMS/ceramic nanocomposite membranes pretreated at 140°C and dip coated by 7 wt % PDMS solution, in this step was coated by different concentrations of PDMS solution. To compare performance of membrane layers in different cases (two times coating in PDMS solution with low concentration instead of one time coating in solution with high concentration), the third and fourth layers were also

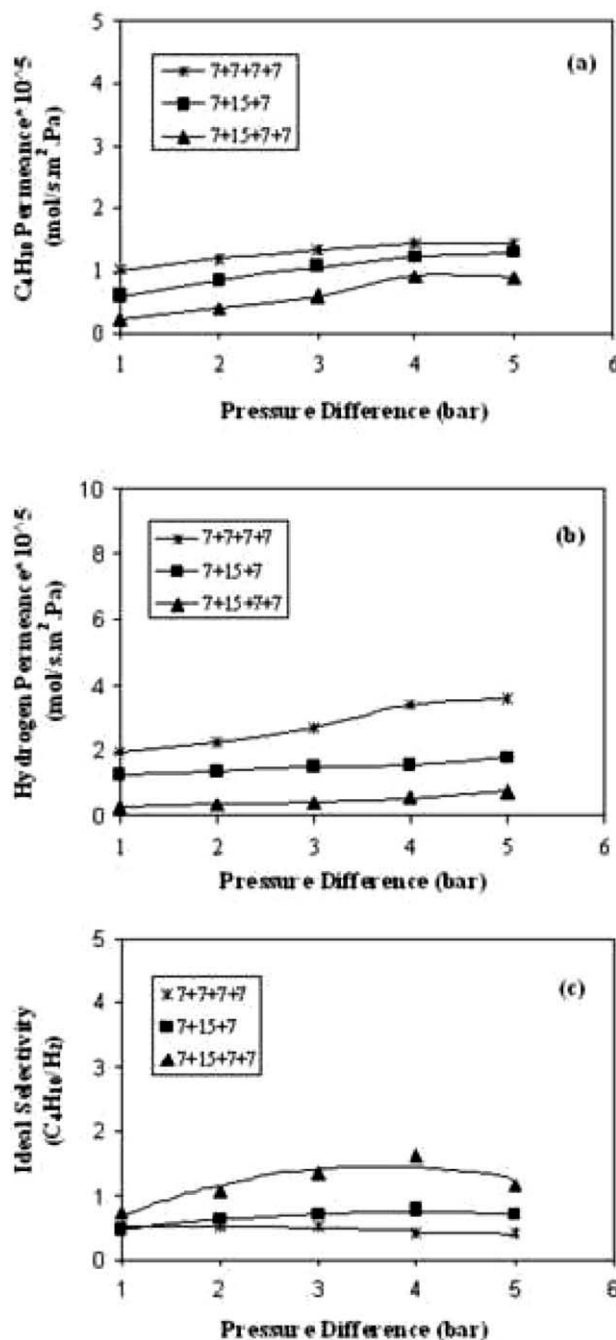


Figure 7 Permeation properties of PDMS/ceramic nanocomposite membranes vs. pressure difference: (a) butane permeance, (b) hydrogen permeance, and (c) C_4H_{10}/H_2 ideal selectivity.

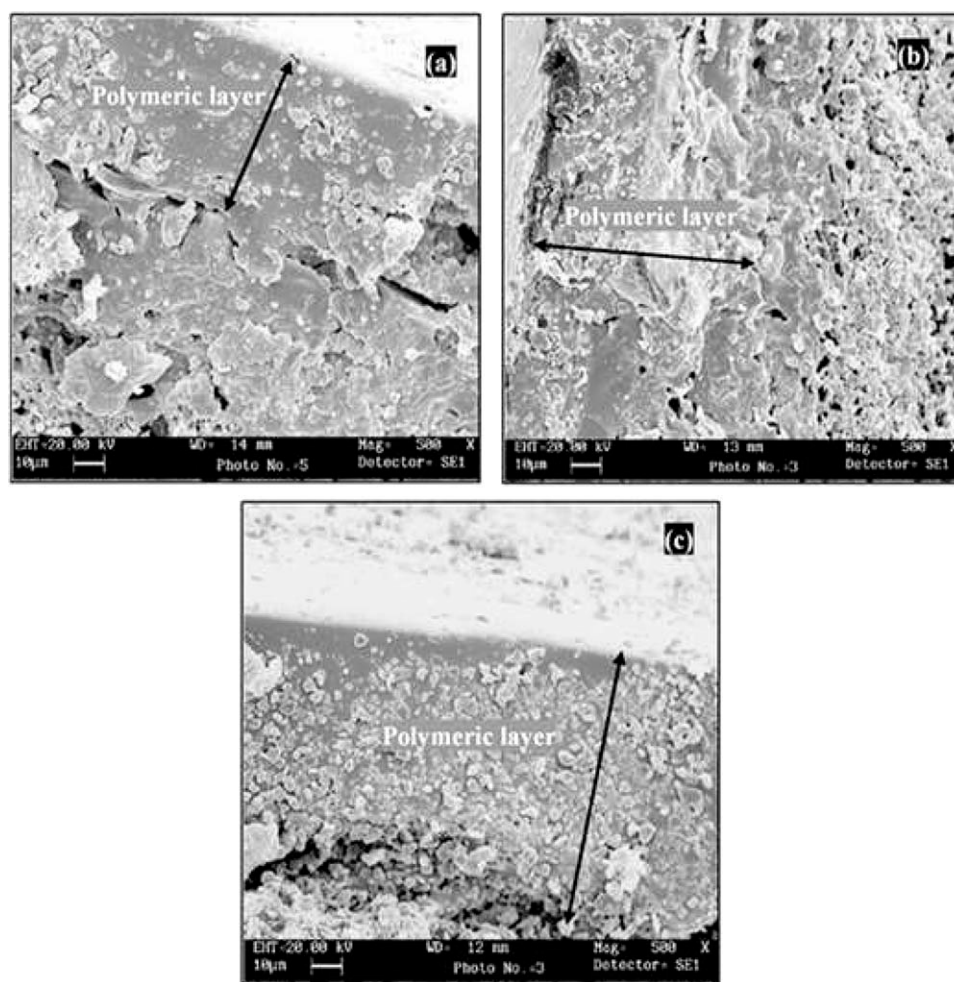


Figure 8 SEM micrographs of cross-section of the PDMS/ceramic nanocomposite membranes: (a) without, (b) with two times, and (c) with four times coating by 7 wt % PDMS solution after the second layer.

coated in PDMS solution with low concentration (7 wt %). Figure 7 displays permeance and selectivity versus the pressure difference for PDMS/ceramic nanocomposite membranes dip coated by PDMS solutions with different concentrations in the second layer. The permeance of gases decreases with increasing PDMS solution concentration. In addition, as shown in Figure 7(c), C_4H_{10}/H_2 selectivity in the composite membranes increases with increasing PDMS solution concentration. Thus, 15 wt % PDMS solution can be selected as a suitable polymer solution concentration for the second polymer layer in the preparation of PDMS/ceramic nanocomposite membranes.

Effect of number of coated polymeric layers with dilute polymer solution

To eliminate any defects of the membranes and to form a dense and uniform polymer layer, coated membranes with two polymeric layers were dip coated by a 7 wt % PDMS solution for different times. SEM micrographs of cross-section of the prepared PDMS/ceramic nanocomposite membranes

with and without two and with four polymeric layers after the second layer are illustrated in Figure 8. As shown, thickness of PDMS layer increases with increasing number of coated polymeric layers.

In Figure 9, SEM micrographs of coated surface of the prepared PDMS/ceramic nanocomposite membranes, with different coating layers are presented. As can be seen, there are many defects on the surface of the membranes and by increasing the number of polymeric layers, the cracks size decrease significantly and more uniform surface is achieved.

Figure 10(a,b) show permeance of single gases (H_2 , C_4H_{10}) through PDMS/ceramic nanocomposite membranes with different numbers of polymeric layers. The permeance of gases decreases with increasing the number of coated layers. In addition, as shown in Figure 10(c) and Table I, C_4H_{10}/H_2 selectivity of composite membranes increases with increasing number of coated layers. The obtained results revealed that the solution-diffusion mechanism can be a dominant transport mechanism in these types of composite membranes. The low C_4H_{10}/H_2 selectivity of these membranes can be confirmed by SEM micrographs,

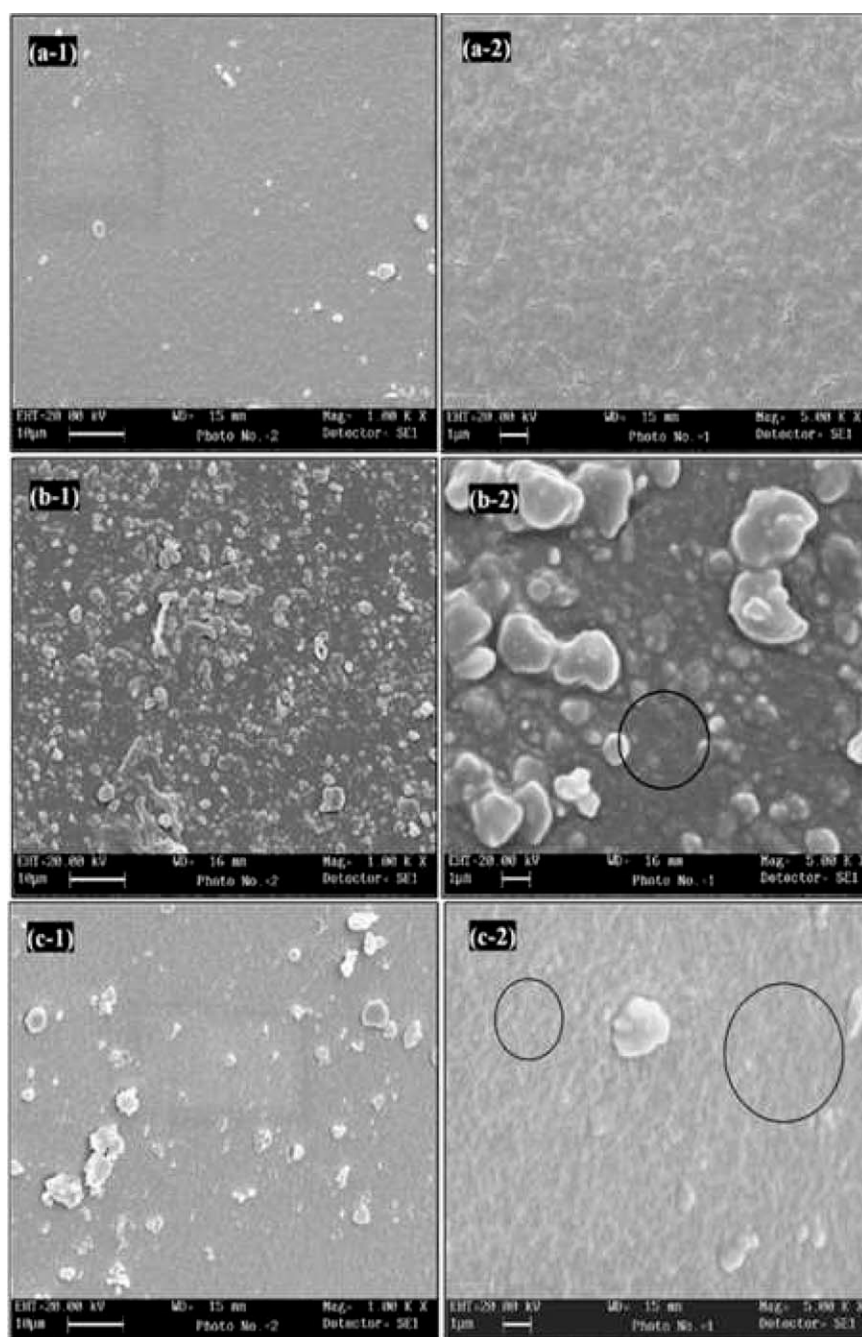


Figure 9 SEM micrographs of coated surface of PDMS/ceramic nanocomposite membranes: (a) without, (b) with two times, and (c) with four times coating by 7 wt % PDMS solution after the second layer with different magnifications.

illustrating no defect-free polymer layers on the membranes surface. Thus it can be concluded that coatings by low concentration PDMS solution do not have desirable effect on the PDMS/ceramic nanocomposite membranes performance.

Effect of PDMS solution concentration in the third layer

To investigate the effect of PDMS solution concentration in the third polymer coating layer, three different concentrations; 7, 10, and 15 wt % were studied.

In the previous section, PDMS/ceramic membrane prepared with 7 wt % PDMS solution in the third layer did not show good performance in the separation of condensable hydrocarbons. This membrane showed a very high butane permeance [8.41×10^{-6} mol/(m² s Pa)] and very low selectivity (0.62) at ambient temperature and feed pressure of 2 bar. The obtained permeation results confirmed that the polymeric layer is not dense and uniform.

Figure 11 shows permeance of single gases (H₂, C₄H₁₀) through PDMS/ceramic nanocomposite membranes dip coated by 10 and 15 wt% PDMS

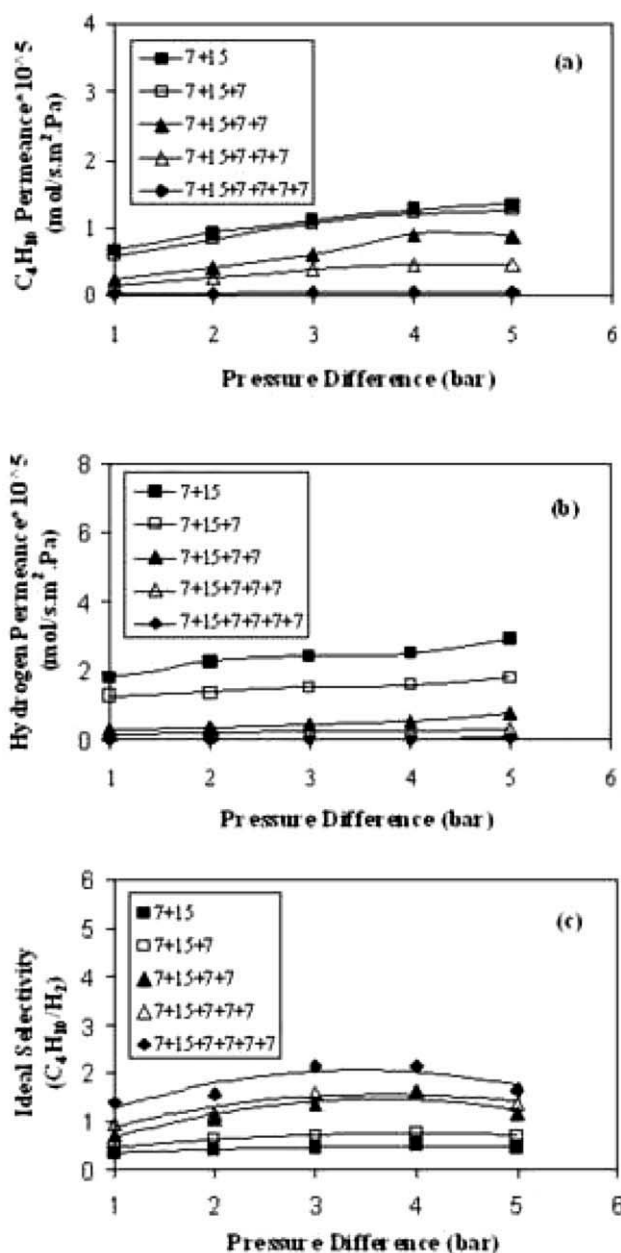


Figure 10 Permeation properties of PDMS/ceramic nano-composite membranes with different polymeric layers vs. pressure difference; (a) butane permeance, (b) hydrogen permeance, and (c) C₄H₁₀/H₂ ideal selectivity.

solutions in the third layer. As shown in this figure, the permeance of *n*-butane was highly nonlinear with pressure drop. It increased then became constant with an increase in the pressure difference across the membrane. The permeance of hydrogen was constant with the pressure difference. These results show good agreement with previous lectures.^{4,16} The zero slope of the permeance of hydrogen versus pressure difference indicates that Knudsen diffusion dominates the transport of light gases through these membranes.⁴³ Also, the permeance of gases decreases with increasing PDMS solution con-

TABLE I
C₄H₁₀/H₂ Ideal Selectivity of PDMS/Ceramic Nanocomposite Membranes with Different Numbers of Polymeric Layers After the Second Layer

Pressure difference (bar)	Ideal selectivity				
	Number of polymeric layers after the second layer				
	7+15	7+15+7	7+15+7+7	7+15+7+7+7	7+15+7+7+7+7
1	0.372	0.465	0.728	0.952	1.379
2	0.409	0.620	1.062	1.183	1.554
3	0.465	0.707	1.363	1.576	2.143
4	0.507	0.770	1.611	1.634	2.127
5	0.465	0.707	1.169	1.375	1.670

centration. This trend can be due to increasing the thickness of polymeric top layer with increasing PDMS solution concentration. Contrary to the composite membrane prepared in low concentration of

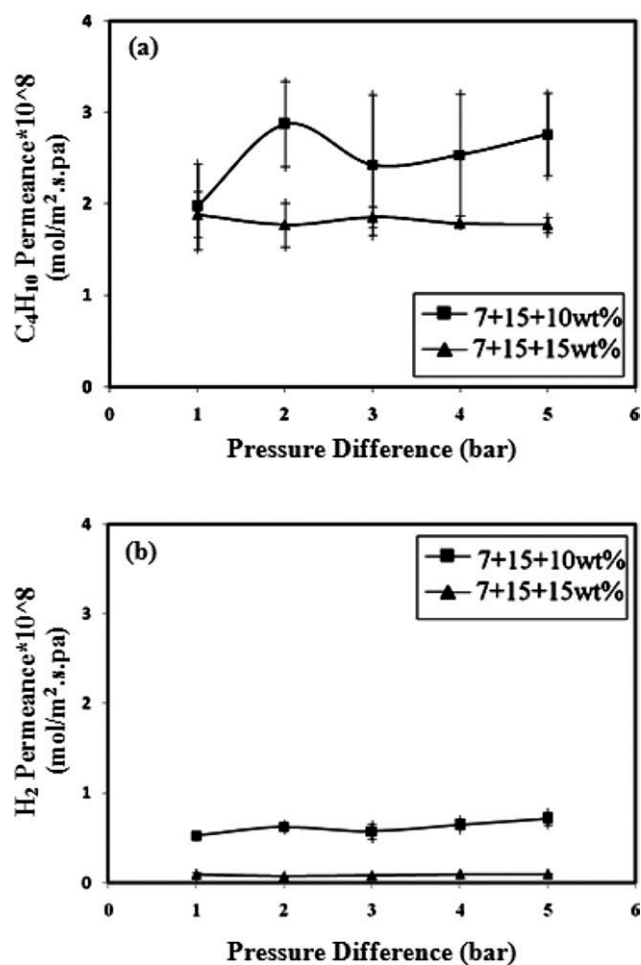


Figure 11 Permeation properties of PDMS/ceramic nano-composite membranes with different PDMS solution concentrations in the third layer: (a) butane permeance and (b) hydrogen permeance.

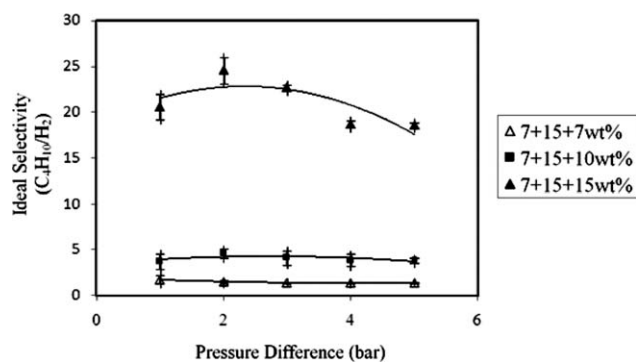


Figure 12 C_4H_{10}/H_2 ideal selectivity of PDMS/ceramic nanocomposite membranes with different PDMS solution concentrations in the third layer.

PDMS solution in the third layer, butane permeance through these membranes is higher than that of hydrogen.

Figure 12 and Table II display C_4H_{10}/H_2 selectivity versus the pressure difference for PDMS/ceramic nanocomposite membranes dip coated by 7, 10, and 15 wt % PDMS solutions in the third layer. The obtained results show that C_4H_{10}/H_2 selectivity increases significantly with increasing PDMS solu-

TABLE II
 C_4H_{10}/H_2 Selectivity of PDMS/Ceramic Nanocomposite Membranes Dip-Coated by 7, 10, and 15 wt % PDMS Solutions in the Third Layer

Pressure difference (bar)	Ideal selectivity		
	PDMS Concentration in the three polymeric layers		
	7+15+7	7+15+10	7+15+15
1	0.465	4.564	21.976
2	0.620	5.091	25.995
3	0.707	4.884	22.308
4	0.770	4.528	19.087
5	0.707	4.065	18.852

tion concentration. The obtained selectivity for PDMS/ceramic nanocomposite membranes consisting of three polymeric layers with 7, 15, and 15 wt % PDMS concentration respectively at ambient temperature and feed pressure of 2 bar is higher than 25. These results show good agreement with previous lectures that they reported the C_4H_{10}/H_2 selectivity in the unfilled, isotropic PDMS films.³

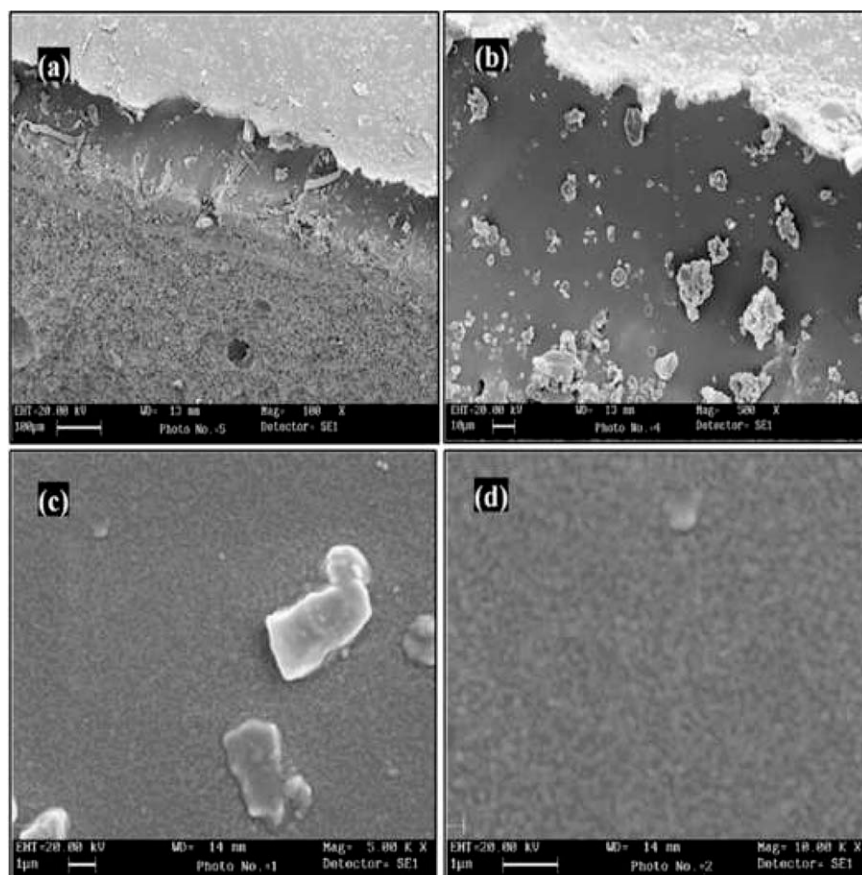


Figure 13 SEM micrographs of PDMS/ceramic nanocomposite membrane dip coated by 7, 15, and 15 wt % PDMS concentration, respectively: (a) and (b) cross-section and (c) and (d) surface of membrane with different magnifications.

The obtained results revealed that the membrane after modification no longer remained porous and the solution-diffusion mechanism is the dominant gas transport mechanism in these types of membranes.¹

The microstructure of the final PDMS/ceramic nanocomposite membrane is also shown in Figure 13. As can be seen in Figure 13(a,b), which illustrate the cross-section of the composite membrane, a perfect uniform layer of PDMS with a thickness of approximately 100 μm has been formed on the ceramic nanocomposite substrate. Figure 13(c,d) show the surface morphology of the membrane with different magnifications, confirming that the membrane surface was perfectly smooth and no defects were observed throughout the prepared PDMS top layer.

CONCLUSIONS

In this work, PDMS/ceramic nanocomposite membranes were successfully prepared. For the fabrication of PDMS/ceramic membranes, nanocomposite technology was applied for manufacturing ceramic supports with controllable microstructures. PDMS selective layer was coated on the outer surface of the porous ceramic nanocomposite support in a multistep dip coating procedure. Performance of these membranes was evaluated for condensable hydrocarbons separation. Based on the work done in this research the following general conclusions can be presented.

- Although dense homogeneous PDMS membranes have high selectivity for condensable hydrocarbons, the PDMS/ceramic nanocomposite membranes are known to have high permeability and mechanical strength.
- Experimental results clearly indicate that the intrusion of polymer solution in the support decreases by increasing pretreatment temperature which can be due to the more initial cross-linking in the surface of the hot support.
- The results showed that the membranes fabricated in 140°C as pretreatment temperature and three polymeric layer by 7, 15, and 15 wt% PDMS concentration respectively have a high selectivity (>25 at 2bar)) in $\text{C}_4\text{H}_{10}/\text{H}_2$ separation.
- The results of PDMS/ceramic hybrid membrane performance for higher hydrocarbons and hydrogen separation showed appropriate permeability and permselectivity which were governed by solution-diffusion mechanisms.

The authors wish to thank co-workers and technical staff of Departments of Chemical and Polymer Engineering, Institute of Polymeric Materials and Nanostructured Materials Research Center of SUT for their help during various stages of this work.

References

1. Javaid, A. *Chem Eng J* 2005, 112, 219.
2. Shao, L.; Low, B. T.; Chung, T. S.; Greenberg, A. R. *J Membr Sci* 2009, 327, 18.
3. Pinnau, I.; He, Z. *J Membr Sci* 2004, 244, 227.
4. Singh, R. P.; Way, J. D.; Dec, S. F. *J Membr Sci* 2005, 259, 34.
5. Leger, C.; Lira, H. D. L.; Paterson, R. *J Membr Sci* 1996, 120, 135.
6. Jou, J. D.; Yoshida, W.; Cohen, Y. *J Membr Sci* 1999, 162, 269.
7. Abidi, N.; Sivade, A.; Bourret, D.; Larbot, A.; Boutevin, B.; Guida-Pietrasanta, F.; Ratsimihety, A. *J Membr Sci* 2006, 270, 101.
8. Javaid, A.; Hughey, M. P.; Varutbangkul, V.; Ford, M. *J Membr Sci* 2001, 187, 141.
9. Castricum, H. L.; Sah, A.; Mittelmeijer-Hazeleger, M. C.; ten Elshof, J. E. *Microporous Mesoporous Mater* 2005, 83, 1.
10. Javaid, A.; Ford, D. M. *J Membr Sci* 2003, 215, 157.
11. Kuraoka, K.; Chujo, Y.; Yazawa, T. *J Membr Sci* 2001, 182, 139.
12. Javaid, A.; Gonzalez, S. O.; Simanek, E. E.; Ford, D. M. *J Membr Sci* 2005, 275, 255.
13. Javaid, A.; Krapchetov, D. A.; Ford, D. M. *J Membr Sci* 2005, 246, 181.
14. Yoshida, W.; Cohen, Y. *J Membr Sci* 2003, 213, 145.
15. Choi, S. H.; Kim, J. H.; Lee, S. B. *J Membr Sci* 2007, 299, 54.
16. Jiang, X.; Kumar, A. *J Membr Sci* 2005, 254, 179.
17. Chandak, M. V.; Lin, Y. S.; Ji, W.; Higgins, R. J. *J Appl Polym Sci* 1998, 67, 165.
18. Sun, Y. M.; Chen, J. *J Appl Polym Sci* 2003, 51, 1797.
19. Wu, H.; Liu, L.; Pan, F.; Hu, C.; Jiang, Z. *Sep Purif Technol* 2006, 51, 352.
20. Gevers, L. E. M.; Aldea, S.; Vankelecom, I. F. J.; Jacobs, P. A. *J Membr Sci* 281, 2006, 741.
21. Mishima, S.; Nakagawa, T. *J Appl Polym Sci* 2000, 78, 1304.
22. Bakhshi, A.; Mohammadi, T.; Aroujalian, A. *J Appl Polym Sci* 2007, 107, 1777.
23. Yeowa, M. L.; Field, R.W.; Lia, K.; Teo, W. K. *J Membr Sci* 2002, 203, 137.
24. Hong, Y. K.; Hong, W. H. *J Membr Sci* 1999, 159, 29.
25. Liu, S.; Teo, W. K.; Tan, X.; Li, K. *Sep Purif Technol* 2005, 46, 110.
26. Vankelecom, I. F. J.; Moermans, B.; Verschuere, G.; Jacobs, P.A. *J Membr Sci* 1999, 158, 289.
27. Bikson, B.; Nelson, J. K. *AP* 4,826,599 (1989).
28. Williams, S. C.; Bikson, B.; Nelson, J. K.; Burchesky, R. D. *AP* 4,840,819 (1989).
29. Williams, S.E.; Bikson, B.; Nelson, J.K.; Burchesky, R. D. *EP* 0,286,091 B1 (1994).
30. Ebert, K.; Bezzak, A.; Nijmeijer, K.; Mulder, M. H. V.; Strathmann, H. In *Euro membrane (Bath, UK) Proceedings*, 1995, I, p 237.
31. Tsai, F. J.; Kang, D.; Anand, M. *Sep Sci Technol* 1995, 30, 1639.
32. Kafchinski, E. R.; Chung, T. S. *AP* 5,213,689 (1993).
33. Blume, I.; Pinnau, I. *AP* 4,963,165 (1990).
34. Shi, E.; Huang, W.; Xiao, Z.; Li, D.; Tang, M. *J Appl Polym Sci* 2007, 104, 2468.
35. Jannatdoust, E.; Babaluo, A. A.; Abbasi, F.; Akhfar Ardestani, M.; Peyravi, M. *Desalination* 2010, 250, 1136.
36. Ahmadian Namini, P.; Babaluo, A. A.; Jannatdoust, E.; Peyravi, M.; Akhfar, M. *Iran J Chem Chem Eng* 2011, 30, 63.
37. Tahmasebpour, M.; Babaluo, A. A.; Shafiei, S.; Pipelzadeh, E. *Powder Technol* 2009, 191, 91.
38. Dabbaghian, M. A.; Babaluo, A. A.; Hadi, P.; Jannatdoust, E. *Int J Nanosci Nanotechnol* 2010, 6, 104.
39. Ahmadian Namini, P.; Babaluo, A. A.; Peyravi, M.; Akhfar, M.; Jannatdoust, E. *The 5th Int Chem Eng Congress (ICHec 2008)* 2008, Kish Island, Iran.
40. Hirata, Y.; Numaguchi, N.; Shih, W. H. *Key Eng Mater* 1999, 159-160, 127.
41. Karimian, H.; Babaluo, A. A. *Iran Polym J* 2006, 15, 879.
42. Babaluo, A. A.; Kokabi, M.; Manteghian, M.; Sarraf-Mamoory, R. *J Eur Ceram Soc* 2004, 24, 3779.
43. Higgins, S.; Kennard, R.; Hill, N.; DiCarlo, J.; DeSisto, W. J. *J Membr Sci* 2006, 279, 669.