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Structural and transport properties of polydimethylsiloxane based polyurethane/silica particles mixed matrix membranes for gas separation

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Abstract−Mixed matrix membranes of synthesized polyurethane (PU) based on toluene diisocyanate (TDI), polydimethylsiloxane (PDMS) and polytetramethylene glycol (PTMG) with polyvinyl alcohol based polar silica particles were prepared by solution casting technique. The homogeneity and thermal properties of the prepared PDMS-PU/silica membranes were characterized using scanning electron microscope (SEM), differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The SEM micrographs confirmed the distribution of silica particles in the polymer matrix without agglomerations. Gas permeation properties of membranes with different silica contents were studied for pure CO_2, CH_4, O_2, He and N_2 gases. The obtained results indicated the permeability of the condensable and polar CO_2 gas was enhanced whereas permeability of other gases decreased upon increasing the silica content of the mixed matrix membranes. The permeability of CO_2 and its selectivity over N_2 was increased from 68.4 Barrer and 22 in pure PDMS-PU to 96.7 Barrer and 64.4 in the mixed matrix membranes containing 10 wt% of the silica particles.

Keywords: Gas Separation, Membrane, Silica, Polyurethane

INTRODUCTION

There has been growing attention for the use of polymer membranes in the gas separation industry, due to their potential energy saving capacity compared with more traditional separation techniques. Polymeric membranes with both high permeability and selectivity are desirable [1]. However, the currently available polymeric membranes suffer from the typical trade-off between permeability and selectivity, and fabrication of membranes with higher permeability and selectivity for gas separation is the key challenge in improving the competitiveness of membrane technology [2-4]. One of the most important methods for improving the gas permselectivity of membranes is the incorporation of silica particles into the polymer matrix forming, the so-called mixed matrix membranes (MMMs) [5]. In the past several years, inorganic particles such as silica particles were widely introduced into a polymeric matrix to improve the heat resistance, radiation resistance, and the mechanical and electrical properties of polymeric membranes; the main goal for the addition of silica particles to rubbers is to improve the gas permselectivity properties and to reduce the cost of membrane [6-8]. However, similar or even improved gas selectivities were reported compared to the corresponding pure polymer membranes. There has been a strong interest in developing and investigating mixed matrix membranes based on silica particles. Merkel et al. have shown significant deviation from expected permeation behavior of high free volume polymers, e.g., poly (4-methyl-2-pentyne) (PMP) and poly (2, 2-bis (trifluoromethyl)-4, 5-difluoro-1, 3-dioxole-co-tetrafluoroethylene), containing silica particles. They have reported an increase in permeability and selectivity by adding nano-structured fumed silica to several glassy high free volume polymers [6,7]. This increase resulted from the capacity of the silica particles to disrupt the polymer chain packing and increase the available free volume available for molecular transport [7-13].

Pinnau et al. investigated organic vapor/gas separation properties of PMP membranes containing silica particles. They have shown that addition of fumed silica particles to a high free volume polymer such as rigid chain polyacetylene, increases the absolute permeability to penetrant molecules and increases the selectivity of n-butane to methane [14,15].

In other research, investigation of the effect of silica particles on the CO_2 permeation in silica polyimide composite membranes has shown that the CO_2 permeability of these composite membranes can increase up to 10 times of that of the pure polymer [16]. The gas transport properties of poly (amide-6-b-ethyleneoxide) (PEBAX) in the presence of silica have been also studied [17]. The results indicated that the presence of silica in the polymer matrix had an important influence on the membrane morphology and consequently led to favorable changes in the permeation properties of obtained membranes. The effect of the distribution of silica nanoparticles on the separation performance of poly ether imide membranes was investigated by Nunes et al. [18]. They reported the gas permeability reduction in the presence of silica particles in the polymer. The gas transport properties of mixed matrix polymers depended on the particle size, polymer structure, surface characteristics and degree of particle dispersion. Some authors have investigated the effect of silica nanoparticles on the gas separation properties of polyurethane (PU) membranes; these results indicated reduction in gas permeabilities with enhancement selectivities of CO_2/N_2 and CO_2/CH_4

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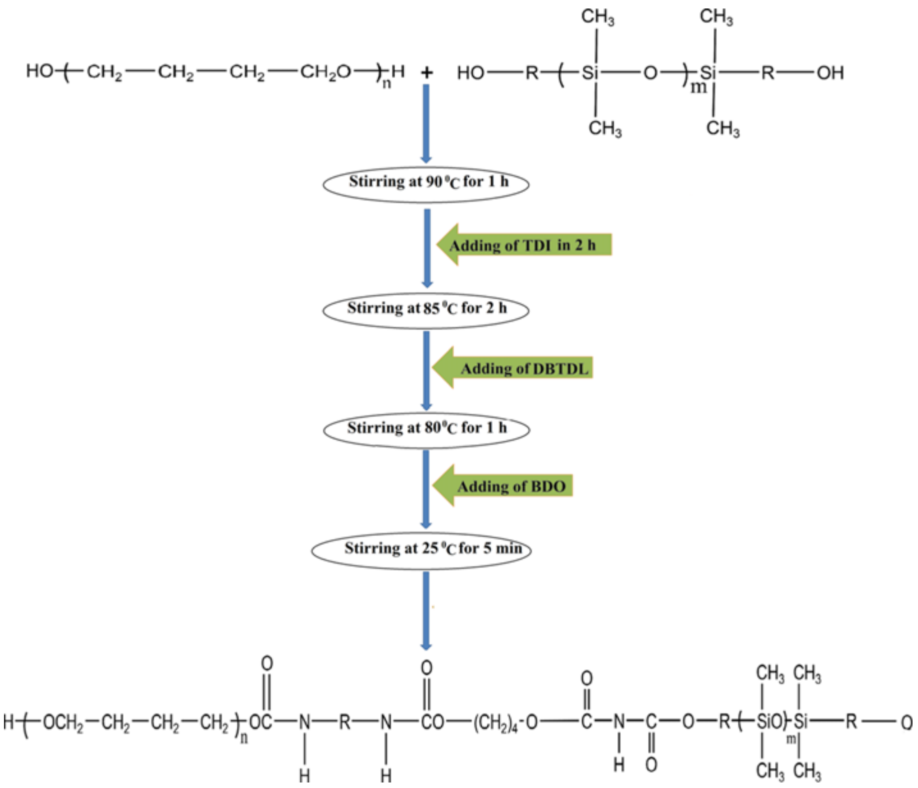

Scheme 1. Synthesis of PU-PDMS.

[17,19].

Polyurethanes (PU) are an important class of special polymers that comprise a diverse family. PU is usually used to prepare different kinds of membranes due to its excellent chemical resistance and thermal stability, good elasticity, good gas permeability and other properties such as high tensile strength, abrasion and oil resistance [20,21]. For the membrane applications, siloxane-based PU has been one of the most attractive membrane materials due to its unique properties that arise mainly from the nature of the siloxane bond and high permeability to gases and organic vapors. The modification of polyurethanes by siloxane is mostly achieved by introduction of usually linear polydimethylsiloxane into PU backbone as a part of soft segments. However, the use of siloxane-based polyurethane membranes for gas separation is limited by their low selectivity [22].

In this study, discrete silica particles synthesized by situ method in presence of polyvinyl alcohol by Semsarzadeh et al. [5] into PU-PDMS mixed matrix membranes were incorporated. These particles were used without further surface modification in PU-PDMS matrix to prepare mixed matrix membranes. Structural characteristics of these membranes were studied by FTIR, SEM and DSC. These results were correlated with gas permeation measurements. In particular, the effect of the amount of silica on permeability of gases through the membranes was investigated. The results indicate that incorporation of these ultrafine dense particles in the PU-PDMS matrix leads to an increase in CO_2 permeability as well as gas selectivity.

EXPERIMENTAL

1. Materials

Polytetramethylene glycol (PTMG, Mw=2,000 gmol^{-1}) was obtained from Arak Petrochemical Company and Poly (dimethylsiloxane) bis (hydroxyalkyl) terminated (PDMS, Mn=5,600 gmol^{-1}) were obtained from Sigma-Aldrich. 1,4-butanediol (BDO) and Toluene diisocyanate (TDI), n-butanol were purchased from Merck. The chain extender (BDO) was dried over 4 Å molecular sieves before use. PTMG was dried at 80 °C under vacuum condition for 48 h in order to remove the residual water. CO_2, N_2 , O_2, CH_4 and He gases (purity 99.99%) were purchased from Roham Gas Co. (Iran). Spherical polar silica particles were synthesized according to a previously published procedure [5].

2. Polymer Synthesis

The PU-PDMS was prepared via a two-step condensation reaction [23]. The mixture of PDMS and PTMG was incubated with TDI for 2 h at 85-90 °C under nitrogen atmosphere to obtain macrodiisocyanate prepolymer. The prepolymer was examined for NCO content using the standard method of n-butyl amine titration (ASTM D2572). The chain extension of prepolymer was performed by addition of BDO at room temperature. To obtain linear polymer, the

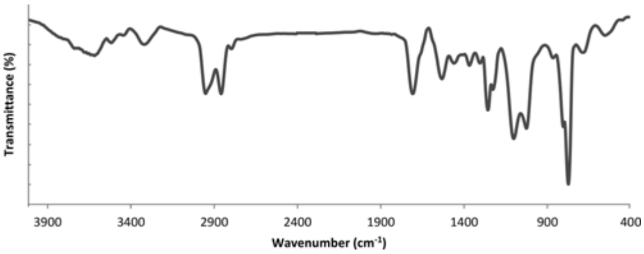

Fig. 1. FT-IR spectra of synthesized PDMS-PU in (400-4,000 cm^{-1}) spectral region.

molar ratio of NCO : OH was kept at 1 : 1. The molar ratios of the used components were as follows: PTMG/PDMS : TDI : BDO= 1 : 3 : 2 and PTMG/PDMS=2/1. The basic synthesis mechanism of PU-PDMS is schematically illustrated in Fig. 1.

3. Preparation of Mixed Matrix Membranes

Pure PU-PDMS membranes were prepared by solution casting and solvent evaporation technique. In this method 1 g of the PDMS-PU was dissolved in 10 g of n-butanol and stirred for 6 h at 65 °C leading to a clear solution. The bubble-free polymer solution was cast onto a previously teflonized glass Petri dish and left at room temperature under atmospheric pressure for three days. The resulting membranes were dried in a vacuum oven for 10 h at 70 °C. The fabrication procedure for mixed matrix membranes was identical to the pure polymer membrane preparation with the additional step of incorporating silica particles. PU-PDMS and silica particles were mixed in the following proportions: PU-PDMS/silica: 99/1, 98/2, 95/5 and 90/10 wt%. Casting solutions were prepared from the co-dissolution of PU-PDMS and silica particles at a total polymer concentration of 10 wt% (1 g polymer and silica in 10 g n-butanol). The mixture of PU-PDMS and silica particles was allowed to mix for 10 h at 65 °C. Obtained solutions were optically clear and showed neither visible separation into bilayers nor any solid precipitation upon standing. The membranes were cast on to a teflonized Petri dish. The evaporation and heat treatments for the mixed matrix membranes were identical to that of pure polymer membranes. Thickness of the membranes was around 150 mm as measured by a micrometer caliper. The average thickness of an individual membrane was calculated based on the results of five separate thickness measurements at different points on the membrane surface.

MEMBRANE CHARACTERIZATION

1. Fourier Transform Infrared (FT-IR)

A Perkin-Elmer Spectrum One FT-IR spectrophotometer was used to characterize the synthesized PDMS-PU. KBr method was used at room temperature. Meanwhile the scanning frequency range was 4,000-400 cm^{-1}. All the samples used for FT-IR measurement were prepared by casting the 2 wt% PU-PDMS solutions on a KBr discs.

2. Thermal Analysis

Thermal properties of samples were characterized in the temperature range from −100 to 190 °C by using a Netzsch DSC 204 calorimeter. Measurements, including baseline determinations were performed at the scanning rate of 10 °C/min, and the experiments were conducted by a nitrogen purge gas stream. Melting and glass-transition temperature values were obtained from cooling scan of thermograms. Samples with size of 3-5 mg were placed in aluminum DSC pans with nitrogen flowing at 50 mL/min as the blanketing gas. The degradation temperature and the actual amount of the silica in the polymer were evaluated by Thermal gravimetry analysis (TGA) using PL at heating rate of 10 °C/min and the temperature range of ambient to 800 °C.

3. Morphology

The cross-section morphology of membranes was examined using scanning electron microscopy (SEM). Cross-sections of membranes were obtained by fracturing in liquid nitrogen. All samples were coated with gold/palladium and were observed with a Philips XL30 (Netherlands) scanning electron microscope (SEM).

4. Gas Permeation Measurements

The pure gas (CO_2, N_2 ,O_2, CH_4 and He) permeation properties of PU-PDMS and PU-PDMS/silica mixed matrix membranes were measured using a constant pressure method at room temperature (25 °C) [24]. The feed side pressure of the gases ranged from 4 to 10 bar. The permeate side was maintained at atmospheric pressure. The gas permeability was determined from the Eq. (1).

$$p=\frac{ql}{A(p_1-p_2)} \tag{1}$$

where P is permeability expressed in Barrer (1 Barrer=10^{-10} cm^3 (STP) cm/(cm^2 s cm-Hg), q the flow rate of the permeate gas passing through the membrane (cm^3(STP)/s), l the membrane thickness (cm), p_1 and p_2 the absolute pressures of feed side and permeate side, respectively (cm-Hg), and A the effective membrane area (cm^2). The ideal selectivity, $\alpha_{A/B}$ (the ratio of single gas permeabilities) of membranes was calculated from pure gas permeation experiments:

$$\alpha_{A/B}=\frac{P_A}{P_B} \tag{2}$$

RESULTS AND DISCUSSION

1. FT-IR Characterization

The FT-IR spectrum of synthesized PU-PDMS is depicted in Fig. 2. The absorption peaks due to the urethane hard segments are at around 3,320 cm^{-1} (-NH stretching) and 1,750 cm^{-1} (-CO contracting) [25]. Other absorption peaks due to the soft segments are at about 2,920 and 2,850 cm^{-1} (-CH_2 symmetric and asymmetric stretching), 1,260 cm^{-1} (-CH_3 bending), 1,020, 1,100 cm^{-1} (-Si-O-Si- and -C-O-C- bending) and 803 cm^{-1} (-CH_3 rocking of -Si$(CH_3)_2$-O-) attributable to the PDMS and PTMG. Several characteristic absorption peaks of PTMG and PDMS are overlapped, but the absorption peaks of the urethane hard segment resulting from the reaction between isocyanate (-NCO) and hydroxyl (-OH) groups verified the synthesis of PDMS/PTMG based PU. The disappearance of NCO stretching vibration at 2,270 cm^{-1} is used to show the completion of the reaction as shown [25,26].

2. Thermal Analysis

The thermal properties of PU-PDMS membranes composed of silica nanoparticles were evaluated by DSC and TGA analyses. DSC thermograms of PU-PDMS and PDMS-PU/silica mixed matrix membranes with different silica content are presented in Fig. 3. The synthesized PU-PDMS exhibits only a glass transition temperature at

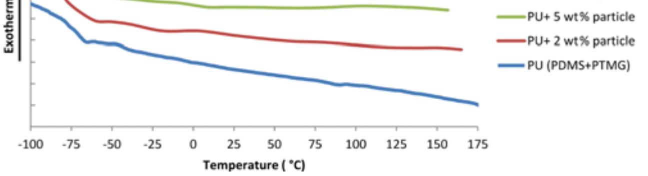

Fig. 2. DSC curves of synthesized PU-PDMS and PU-PDMS/silica composite membranes with different silica content.

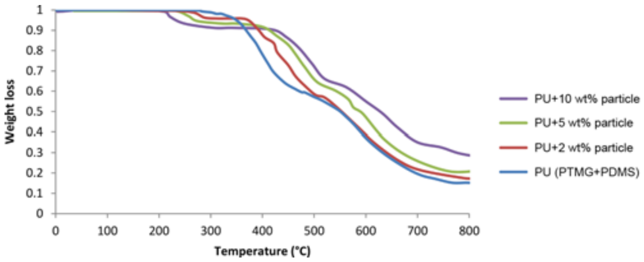

Fig. 3. TGA analysis of PDMS-PU and PDMS-PU/silica hybrid membranes with different silica content from 2 to 10 wt%.

−79 °C. There were no observations of melting transitions of the soft and hard segment regions. These are desirable for preparing highly permeable polymers, since crystallinity reduces gas permeability [27]. Since the silica has the -OH groups on its surface, it should readily interact with PDMS-PU macro-molecular chains via hydrogen bonding between -OH groups of silanol and -NH-CO- or C-OO groups from PDMS-PU, but these weak electrostatic interactions cannot significantly influence the segmental motion of soft PTMG molecular chains upon addition of silica particles. Thus the PDMS-PU/silica mixed matrix membranes have similar values of Tgs [28]. Also in Fig. 3, by increasing the silica particles in the polymer, the slope of the glass transition state decreases. Slope decrease of the glass transition state indicates silica particles and polyol interact together, which makes the chain mobility more difficult and therefore the process covers a wider temperature range [29].

The thermal stability of the PU-PDMS/silica mixed matrix membranes was investigated using TGA. Fig. 4 shows the weight reduction of the prepared mixed matrix membranes with temperature.

The decomposition of PU-PDMS based membranes starts from 340 °C. Two different slopes of weight reduction were observed in these membranes. The first one is related to the breakage in urethane bonds, because the thermally weakest link is the urethane bond, while the second step is related to the thermal decomposition of polyol [30]. In all composite membranes, the first degradation temperatures (T1), i.e., the temperatures at 5% weight loss of the composites are in the range of 230-300 °C.

As shown in Fig. 4, in the case of mixed matrix membranes, the slope of weight reduction decreases by increasing the amount of silica in the polymer. Based on this phenomenon it can be concluded that the thermal stability of the polymer increases by addition of silica nanoparticles into the polymer; this might be due to adsorption of the decomposition vapor by silica particles. Fig. 4 also shows that the remaining membrane weight after applying heating up to 800 °C is consistent with the theoretical silica weight percentage of mixed matrix membranes. This could be a good reason for full entrance of silica particles into the polymer during membrane preparation.

3. Morphology

The presence and distribution of silica particles in the PU-PDMS membranes have been investigated by SEM. Fig. 5 shows the SEM micrographs of the prepared PU-PDMS/silica hybrid membranes. The presence and homogeneous distribution of the prepared membranes are evident from the SEM micrographs. It is also observed that the embedded filler particles exhibited excellent interfacial bonding with the polymer without any apparent defect at the polymer-particle interface (Fig. 5).

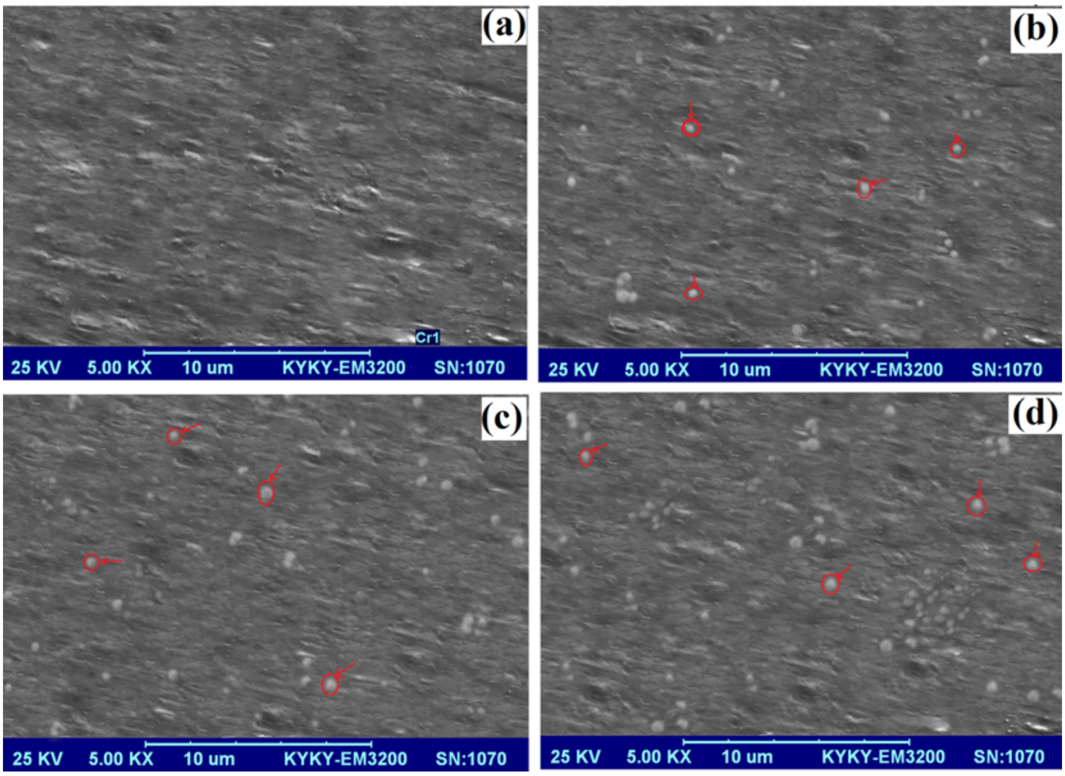

Fig. 4. SEM photographs of cross section of PU-PDMS and PU-PDMS/silica membranes: (a) cross section of PU-PDMS, (b) cross section of PU-PDMS/silica 98/ wt%, (c) cross section of PU-PDMS/silica 95/5 wt% and (d) cross section of PU-PDMS/silica 90/10 wt%.

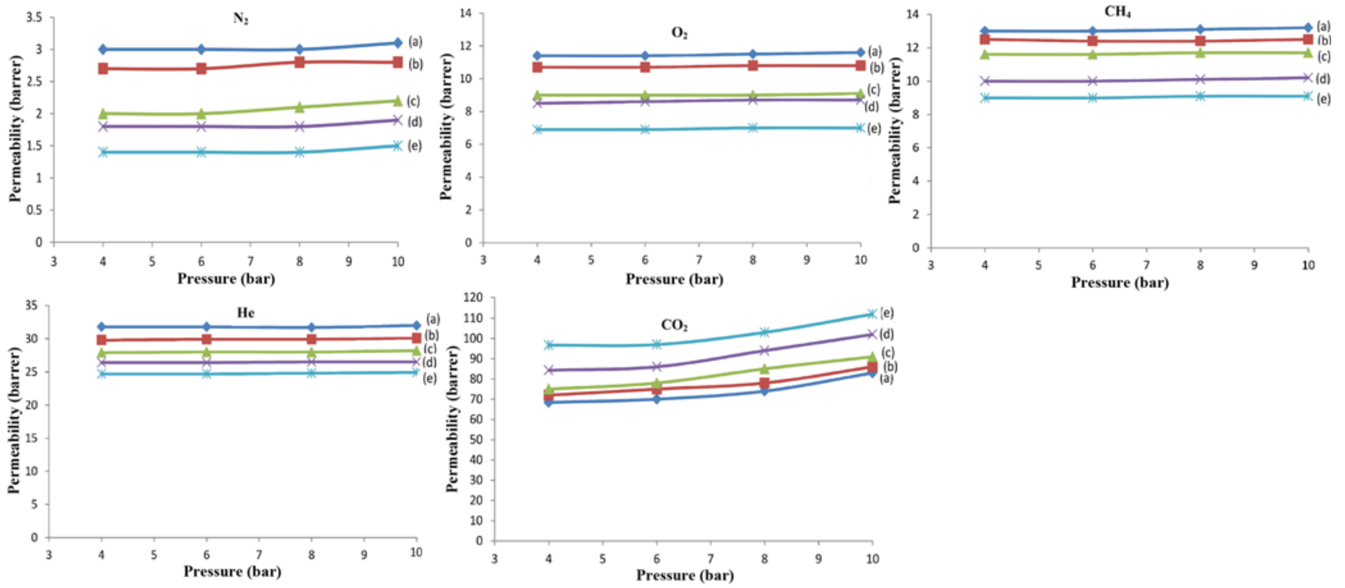

Fig. 5. Pure gas permeabilities of membranes as a function of upstream pressure at 25 °C: (a) PDMS-PU, (b) PDMS-PU/silica 99/1 wt% (c) PDMS-PU /silica98/2wt%, (d) PDMS-PU/silica 95/5 wt%, (e) PDMS-PU/silica 90/10 wt%.

4. Gas Permeation Properties

The solution-diffusion transport model was applied for discussing the gas permeation properties of PU-PDMS/silica mixed matrix membranes [31]. Membrane permeability for PU-PDMS and PU-PDMS/silica mixed matrix membranes with 1, 2, 5 and 10 wt% silica particles were determined by exposure to CO_2, CH_4, O_2, N_2 and He. The upstream pressure was varied between 4 and 10 bar, whereas the downstream pressure was atmospheric pressure.

For all PU-PDMS/silica mixed matrix membranes, the permeability values are in the following order: $P\ (CO_2)>P\ (He)>P\ (CH_4)>P\ (O_2)>P\ (N_2)$.

This permeability order is related to the kinetic diameter, solubility and the critical temperature for the gas molecules [32]. CO_2 has small molecular size and high condensation temperature in comparison to the other gases (Table 1).

CO_2 is a polar gas that can interact with polar chain polymers. Hence, the permeability of CO_2 in comparison with other gases in PU that contain polar groups in the main chain of the polymer is considerably higher [33]. The higher permeability of helium in comparison with methane, oxygen and nitrogen is due to its lower molecular size (Table 1). As reported in Table 2, the permeability of CH_4 is higher than N_2 in all of the prepared mix matrix membranes. Although CH_4 has a higher molecular size, its higher permeation relative to N_2 confirms the domination of the solubility mechanism in the transport of gases through the prepared hybrid membranes. Therefore, it can be concluded that the PU-PDMS and PU-PDMS/silica hybrid membranes have a rubbery property in gas permeation.

Table 1. Gases critical temperature, kinetic diameter and critical volume at 25 °C

Gas	Critical temperature[a] (K)	Kinetic diameter[a] (A)	Critical volume[a], V_c (cm^3/mol)
He	33.2	2.89	57.5
N_2	126.2	3.6	89.3
O_2	154.6	3.5	73.5
CH_4	190.6	3.8	98.6
CO_2	304.2	3.3	91.9

[a] Ref. [31]

The results of gas permeation tests (Table 2) also show that the CH_4, O_2, He and N_2 permeabilitities of composite membranes decrease as the amount of silica particles increase, while the permeability of CO_2 increases. Generally, dispersing impermeable particles in polymer matrices decreases gas permeability [34]. The reduction in gas permeability in the studied mixed matrix membrane may refer to several effects in polymer matrices: (a) the reduction in free volumes, (b) the reduction in chain mobility of soft segments, and (c)

Table 2. Pure gas permeation properties of PU-PDMS and PU-PDMS/silica hybrid membranes at 25 °C and 10 bar

Membrane PU-PDMS (wt%)/silica (wt%)	Permeability (barrer)				
	N_2	O_2	CH_4	CO_2	He
100/0	3.1±.1	11.6±.6	13.2±.7	68.4±4.1	32.0±2.5
99/1	2.8±.2	10.8±.6	12.5±.6	72.0±5.1	30.1±1.8
98/2	2.2±.1	9.1±.7	11.7±.6	75.0±5.2	28.2±1.8
95/5	1.9±.1	8.7±.5	10.2±.6	84.3±5.6	26.5±1.2
90/10	1.5±.1	7.0±.4	9.1±.6	96.7±5.9	24.9±1.0

creation of tortuous paths in diffusion of gases through mixed matrix membranes. However, this trend is not always obeyed in particle-filled polymers. In the case of glassy polymers, the presence of spherical particles sometimes causes extra voids between polymer chains and prevents chain compression, thereby increasing the free volume in the polymer phase, which then may act to increase permeability [35,36]. In heterogeneous rubbery systems, change in solubility (e.g., from adsorption of light gases on a particle surface) at the polymer-particle interface may cause permeability to be greater in composites than in the unfilled polymers [37,38].

The influence of particle content on gas permeability can only partially be attributed to the effect of particles on gas solubility and diffusivity [9]. Increasing the silica content in the membranes can reduce the diffusivity for all of the gases applied in this study. The diffusivity reduction is actually related to the restricted motion of the gas molecules in the PU-PDMS soft segment and formation of pathways with more tortuosity in the polymer matrix. Incorporation of silica particles by PVA content increases the density of polar OH groups in the matrix and forming polar sites at the polymer-silica interface, which aids the solution of the condensable gases in the membrane [33]. So, the decrease in N_2, O_2, He and CH_4 permeabilities can be attributed to the reduction of the diffusivity. Increased permeability of the condensable CO_2 gas is mainly related to the enhancement of gas solubility due to increasing of the active sites for gas solution in polymer matrix. In this case, the increment in the gas solubility is more than the reduction in the gas diffusivity [5,39].

Calculated reduction values of the gas permeability of the prepared mixed matrix membrane containing 10 wt% silica with respect to the pure PU-PDMS are in the following order: He (22%)<CH_4 (31%)<O_2 (39%)<N_2 (51%).

By reducing the amount of free volume of the polymer, the gas molecules with larger size are more restricted for crossing the polymer thickness than smaller ones and thus their permeabilities will decrease more [19]. Therefore, the higher reduction of N_2 permeability in comparison with other gases is due to its large molecular size.

Table 3 also presents the CO_2/N_2, CO_2/CH_4, CO_2/He, CO_2/O_2 and O_2/N_2 permselectivity of PU-PDMS and PU-PDMS/silica mixed matrix membranes. According to Table 3, increasing the amount of silica particles in membranes to 10 wt% increases selectivity of CO_2/N_2, CO_2/CH_4 and CO_2/O_2 gases from 22 to 64.4, 5.1 to 10.6 and 5.9 to 13.8, respectively. It is evident that an increase in the amount of silica particles in the membranes results in the increase of selectivity of all of the gases.

Comparative increase in permselectivity of pair gases showed that the increase in CO_2/N_2, CO_2/CH_4 and CO_2/O_2 (in the membrane with 10 wt% silica particles) is 293, 207 and 233%%, respectively. The highest selectivity was observed for the CO_2/N_2 pair. This is mainly due to the higher solubility of CO_2 and lower solubility of N_2 than other light gases for both the PU-PDMS and mixed matrix membranes.

Considering the solution-diffusion mechanism, the selectivity of gases in polymers is specified by diffusivity and solubility-selectivity which enables the polymer chains to separate small molecules from large ones, condensable molecules from non-condensable ones and polar molecules from non-polar ones. The selectivity of pairs O_2/N_2 does not change significantly with mixed matrix composition because the solubility selectivity of O_2/N_2 is almost the same [40].

The more increasing of CO_2/N_2 selectivity in comparison with CO_2/CH_4, is attributed to the very low condensability of N_2 in comparison with CH_4. Therefore, in spite of higher molecular size of the CH_4 that could result in higher diffusivity-selectivity of CO_2/CH_4 in comparison with CO_2/N_2, domination of solution mechanism causes the high solubility of CH_4 and low solubility-selectivity [24].

The effect of feed pressure on the PU-PDMS and PU-PDMS/silica mixed matrix membranes gas permeability was studied at 25 °C. As evident in Fig. 6, the permeability coefficient change versus the upstream pressure is similar to that in the rubbery polymers [41]. The permeability coefficients of permanent gases, such as N_2, O_2, He and CH_4, are either independent of pressure or increase slightly with increasing silica contents. This behavior is typical for non-plasticizing gases in rubbery polymers and is consistent with the pressure dependence of permeability reported for these penetrants

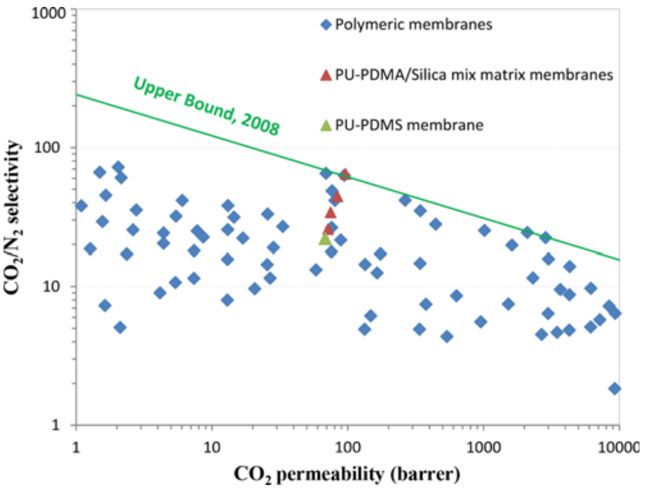

Fig. 6. Robeson trade-off line between selectivity CO_2/N_2 and CO_2 permeability [36].

Table 3. Ideal permselectivities of PU-PDMS and PU-PDMS/silica hybrid membranes at 25 °C and 10 bar

Membrane PDMS-PU (wt%)/silica (wt%)	Selectivity				
	O_2/N_2	CO_2/N_2	CO_2/O_2	CO_2/CH_4	CO_2/He
100/0	3.7±.3	22.0±2.2	5.9±.6	5.1±.7	2.1±.3
99/1	3.8±.5	25.7±4	6.7±.8	5.8±.7	2.4±.3
98/2	4.1±.5	34.0±4.2	8.2±1.3	6.4±.8	2.6±.4
95/5	4.6±.5	44.3±5.6	9.7±1.3	8.3±1.1	3.2±.4
90/10	4.7±.6	64.4±8.9	13.8±1.7	10.6±1.6	3.9±.5

in PU membranes. Also, this shows the close packing of particles in the polymeric materials, but the permeability of CO_2 increases somewhat with increasing the upstream pressure [33]. The presence of strong sorbing penetrants (such as CO_2) can plasticize the polymer matrix and increase polymer local segmental motion, resulting in an increase in diffusivity. By increasing the pressure, the CO_2 solubility and diffusivity and consequently permeability can increase in the polymer [33]. Loading particles into PU-PDMS may intensify the increase in CO_2 permeability with increasing pressure, because the particles increase the concentration of CO_2 in the film.

The obtained results from the prepared PU-PDMS/silica mixed matrix membranes were compared with Robeson's upper bound line [42] in Fig. 6. As depicted, the PU-PDMS/silica membranes lay close to Robeson's upper bound line, indicating that the prepared membranes present good CO_2/N_2 gases pair selectivity compared to the other polymeric membranes.

CONCLUSIONS

The effect of incorporation of silica particles on the gas separation properties of PU-PDMS membranes was investigated. PU-PDMS was synthesized by bulk two-step polymerization method. Polydimethylsiloxane and Polytetramethylene glycol were incubated with TDI under nitrogen atmosphere to obtain macrodiisocyanate prepolymer. The chain extension of prepolymers was performed by addition of BDO at room temperature.

PDMS-PU and PU/silica mixed matrix membranes were successfully prepared from n-butanol as solvents. The prepared membranes were characterized using FT-IR, SEM, DSC and TGA methods. TGA and SEM results verified the presence and the nanoscale dispersion of silica particles in polymer matrix. Gas permeation of PDMS-PU and PU/silica mixed matrix membranes with silica contents of 1, 2, 5 and 10 wt% was studied for N_2, He, O_2, CO_2 and CH_4 single gases under the pressures of 4, 6, 8 and 10 bar. The gas permeation properties of composite membranes showed an increase in CO_2 permeability and a decrease in N_2, O_2, He and CH_4 permeabilities, with increasing amount of silica in polymer matrix.

Comparative increase in permselectivity of pair gases showed an increase in CO_2/N_2 and CO_2/CH_4 (in the mixed matrix membranes with 10% (wt) silica) by up to 293% and 207%, respectively while O_2/N_2 did not change much because solubility selectivity of O_2/N_2 is almost the same.

Thermal results with DSC indicated that by increasing the silica particles in the polymer, the slope of the glass transition state decreases. Decrease in slope of the glass transition state indicates that silica particles and polyol interact with each other and that leads to wide transition.

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