Gas separation properties of polyether-based polyurethane–silica nanocomposite membranes

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ABSTRACT

In this study, the effect of silica nanoparticles on the gas permeation properties of polyether-based polyurethane membrane was investigated. Polyether-based polyurethane was synthesized by bulk two-step polymerization of polypropylene glycol/hexamethylenediisocyanate (HMDI)/1,4-butanediol (BDO) in mole ratios of 1:3:2. Silica nanoparticles were prepared through the sol–gel method by hydrolysis of tetraethoxysilane (TEOS). Polyurethane and polyurethane–silica nanocomposite membranes were prepared by solution blending and casting method. The prepared polyurethane–silica membranes were characterized using Fourier transform infrared (FTIR) spectroscopy, scanning electron microscope (SEM), thermal gravimetery analysis (TGA) and differential scanning calorimetry (DSC) analyses. These methods confirmed the homogenous and nano scale distribution of silica nanoparticles in prepared polymers. Gas permeation properties of polyurethane–silica nanocomposite membranes with silica content of 2.5, 5, 10 and 20 wt.% was studied for pure CO_2, CH_4, N_2 and O_2 gases. The obtained results indicated the reduction in permeability of all gases, but enhancement in CO_2/N_2, CO_2/CH_4 and O_2/N_2 selectivities was observed by increasing the content of non-permeable silica nanoparticles in polyurethane–silica membranes. In the case of polyurethane–silica (20 wt.%) nanocomposite membrane, the obtained CO_2/N_2 selectivity was 1.65 times of pure polyurethane, while the CO_2 permeability reduction of polyurethane–silica membranes was 35.6% in comparison with pure polyurethane. Finally, the modified Higuchi model was applied to predict the permeability of polyurethane–silica membranes and fairly good agreement was observed between experimental and predicted gas permeabilities of these membranes.

1. Introduction

As stated in literature, presence and proper distribution of silica nanoparticles in polymer matrix increase the mechanical strength and thermal stability of polymers [1–8]. Such unique properties of these materials have led to the increasing use of this material in the preparation of polymeric membranes [8–30].

Moaddeb and Koros [9] investigated the effect of silica particles on the gas separation properties of high performance polyimides. They showed that, incorporation of silica particles into the polymer matrix mainly improved the gas separation properties of polymer–silica membranes, especially in the case of O_2/N_2 separation. The main observed improvements were the attainment of high O_2/N_2 selectivity and O_2 permeability of some silica–polymer hybrids, simultaneously. Therefore, O_2/N_2 separation properties of

some silica–polymer membranes were above the Robeson's upper bound line, while that of the pure polymer was below the Robeson's upper bound line [9]. This upper bound was expressed as a line on a log–log plot of separation factor versus permeability of the more permeable gas above which virtually no data exists.

Kusakabe et al. [10] and Joly et al. [11] also studied the effect of silica particles on the CO_2 permeation of silica–polyimide composite membranes. The obtained results by Kusakabe et al. showed that, in the presence of silica in the polymer matrix, the CO_2 permeability of composite membranes can increase up to 10 times of that of the pure polymer [10]. The experimental results obtained by Joly et al. showed 50–100% increase in gas solubility of membranes composed of silica in comparison with the pure polyimide. They characterized the composite membranes and verified the reduction in polymer compaction by silica content, and thus the increase in the gas solubility of membranes in the presence of silica particles [11].

Nunes et al. [12] investigated the effect of the distribution of silica nanoparticles on the separation performance of polyether-

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imide membranes. Silica particles were prepared via in situ polymerization of organic compounds and hydrolysis of tetraethyl orthosilicate, simultaneously. Amino silicate was used as a compatible agent between organic and inorganic phases. The durability of hybrid membranes was also investigated for methane, butane and pentane gases at 80 bar. The obtained results by Nunes et al. showed that the gas permeability reduction in the presence of silica particles in the polymer matrix was only 10%, while, under the same condition, permeability of pure polymer dropped 60% during the durability test [12].

Other researchers like Smaihi et al. [13], Cornelius and Marand [14], Park et al. [15] and recently Boroglua and Gurkaynak [16] also investigated the effect of silica particles on the gas separation (permeation) properties of polyimide–silica membranes. Some other researchers studied the effect of silica particles on the separation performance of other polymers. Kim et al. [17] studied the gas transport properties of poly (amide-6-b-ethylene oxide) (PEBAX) in the presence of silica. They revealed that the presence of silica in the polymer matrix had an important influence on the membrane morphology and this effect led to favorable changes in the permeation properties of obtained membranes. Kim et al. reported that in the presence of silica, the degree of crystallinity of PA section markedly decreases. Therefore, the percentage of the amorphous phase of PEBAX increases and the permeabilities of gases also increase with silica content, as it was observed experimentally. The results of gas absorption in the composite membranes showed an increased uptake with increasing the amount of silica in the membranes. Kim et al. introduced two factors for such an increase in the absorption of gases in composite membranes containing silica:

- The obtained changes in the morphology of interface between silica and PA and PEO segments, and ultimately increase in the percentage of the amorphous region in the composite membrane.
- Interaction of additional OH groups of silica with polar molecules like CO_2.

Chen et al. [18,19] used in situ polymerization of silica nanoparticles in the preparation of polyether-based polyurethane/silica nanocomposites. First, silica nanoparticles were added to the polyether polyol by in situ polymerization and then polymerization reaction was completed by isophoronediisocyanate (IPDI). Based on the obtained FTIR spectra and TGA thermograms, it was shown that in the case of in situ polymerization method, silica and polyether segments interact more than that of simple blending method. This phenomenon further increases the glass transition temperature of hybrid polymers and also the homogeneous distribution of silica nanoparticles in the polymer. The obtained results also showed that the mechanical and physical properties of polyurethane–silica hybrids in the presence of silica particles with 28 nm size were the optimum. In addition, polyurethane–silica hybrids produced by the method of in situ polymerization had better mechanical properties than those made by simple blending method [18,19].

Chen et al. [20], also investigated the effect of silica nanoparticles on the mechanical and thermal properties of polyether based polyurethane prepared by in situ polymerization. The obtained results showed that adding silica nanoparticles into the polymer improved the hardness, glass transition temperature and adhesion between different layers of polyurethane, however, increased the resin viscosity.

Recently, the authors investigated the effect of silica nanoparticles on the gas separation properties of PBI and EVA membranes [21,22]. As shown, the solubility of the CO_2, CH_4 and N_2 gases in the membranes increased by increasing the silica content in the polymer matrix, whereas diffusivity of gases decreased. The resultant effect of silica addition to PBI was CO_2/N_2 selectivity increment due to increase in CO_2 permeability and reduction in noncondensable

N_2 gas permeability [21]. The obtained results showed the enhancement in gas permeation and selectivity of CO_2/N_2 and CO_2/CH_4 pair gases in the case of EVA/silica nanocomposites. The authors have also published their studies on polyurethane membranes in literature and investigated the effects of hard segments, the chain extender length and the effects of urethane and urea content on the gas permeation properties of polyurethane and polyurethane urea membranes [31–33].

Studies in the field of adding silica particles into the polyurethanes, has mainly focused on the physical and mechanical behavior of these polymers [8,18–20,23–34]. Up to date, there are rare reports about adding silica particles into the polyurethane and its effect on gas permeation properties of these polymers in the literature [30]. Therefore, in the present study, the gas permeation properties of polyurethane–silica nanocomposite membranes were investigated. In this regard, silica nanoparticles have been prepared using tetraethoxysilane (TEOS) in the sol–gel process and applied to modify the structure of the polyurethane membranes and improve their gas permeation properties. The permeability of CH_4, CO_2, O_2 and N_2 gases were obtained at various silica contents. Also the permeation behavior of the nanocomposite membranes has been modeled by modified Higuchi model and the new coefficient for studied gases was suggested for this model.

2. Materials and methods

2.1. Materials

Polypropylene glycol (PPG, $M_w = 2000 \, \text{g mol}^{-1}$) was obtained from Sigma Aldrich and dried at 80 °C under vacuum for 48 h to remove the residual water. 1,4-Butanediol (BDO), hexamethylenediisocyanate (HMDI), and N,N-dimethylformamide (DMF) were purchased from Merck. The chain extenders (BDO) were dried over 4 Å molecular sieves before using. The dibutyltindilauryate (DBTDL) supplied by Merck was used as a catalyst. CO_2, N_2 and O_2 gases (purity 99.99) were purchased from Roham Gas Co. (Tehran, Iran) and CH_4 (purity 99.9) was bought from Air Products Co.

2.1.1. Polymer synthesis

Polyurethane was synthesized by bulk two-step polymerization method [32,33]. PPG was incubated with HMDI for 2 h at 85–90 °C under nitrogen atmosphere to obtain macrodiisocyanate prepolymer. The chain extension of prepolymer was performed by addition of BDO at room temperature. In order to obtain linear polymer, the molar ratio of NCO:OH was kept 1:1. The molar ratios of the used components were as follows: PPG:HMDI:BDO = 1:3:2.

2.2. Preparation of polyurethane membrane

Polyurethane solution was prepared by dissolving (10 wt.%) synthesized polyurethane in DMF at atmospheric pressure and 70 °C. The prepared solution was filtered and cast in a petri dish and heated at 65 °C for 24 h. Then, the prepared film located in vacuum oven at 65 °C for another 5 h for complete removal of the solvent.

2.3. Preparation of silica nanoparticles and polyurethane–silica nanocomposite membranes

Silica nanoparticles were prepared via the hydrolysis of tetraethoxysilane (TEOS) in ethanol at the presence of hydrochloric acid as a catalyst [21]. Initially, tetraethoxysilane (25 g) and 3-glycidyloxypropyltrimethoxysilane (GOTMS) (4 g) as a coupling agent were mixed together in dry ethanol (30 ml) at 70 °C for an hour. Consequently, a mixture of ethanol (30 ml), deionized water (7.5 g) and hydrochloric acid (0.83 g) was added drop-wise to the

Table 1
Silica content and T_g of polyurethane–silica nanocomposite membranes obtained by DSC analysis.

Sample	Silica content (wt.%)	T_g of soft segments (°C)
PU		−60.3
PU-S2	2.5	–
PU-S5	5	−60.23
PU-S10	10	−60.63
PU-S20	20	−61.2

reacting mixture. TEOS was hydrolyzed under continuous agitation at 80 °C for 1 h leading to the formation of a clear and transparent silica-sol. PU–silica nanocomposite membranes were prepared by the same method following the addition of the silica-sol in different weight fractions to the polymer solution. The volume fraction (Φ_s) of silica in hybrid membranes was calculated by the following equation:

$$\Phi_s = \frac{w_s/\rho_s}{w_{pu}/\rho_{pu} + w_s/\rho_s} \tag{1}$$

where w_s and w_{pu} refer to the weight of silica and polyurethane, and ρ_s and ρ_{pu} are the density of silica and polyurethane, respectively. The density of silica and polyurethane were 2.2 g/cm³ and 1.1 g/cm³, respectively. The thickness of the prepared membranes was measured using a micrometer and found to be around 100 micrometers.

The silica content and glass transition temperatures (T_g) of the nanocomposite membranes are given in Table 1.

2.4. Characterization

2.4.1. FTIR spectroscopy

A BIO-RAD FTS-7 Fourier transform infrared spectrometer was used to characterize the synthesized polyurethane and polyurethane–silica nanocomposite membranes at room temperature. The scanning frequency range was 4000–400 cm⁻¹.

2.4.2. Thermal analysis

Thermal properties of the films were measured by differential scanning calorimetry (DSC) using Metler-Toledo DSC822ᵉ at heating rate of 5 °C/min and the temperature range of −120 to 300 °C. The degradation temperature and the actual amount of the silica in the polymer have been evaluated by Thermal gravimetery analysis (TGA) using PL at heating rate of 10 °C/min and the temperature range of ambient to 800 °C.

2.4.3. Scanning electron microscopy (SEM)

The morphology of the membranes and the presence of silica nanoparticles were examined using scanning electron microscopy (SEM). All the samples were coated with gold/palladium and observed with a Philips XL30 (Philips, The Netherlands) scanning electron microscope.

2.4.4. Gas permeation tests

The pure gas (O_2, N_2, CH_4, and CO_2) permeation properties of polyurethane–silica membranes were carried out using a constant pressure method [33]. The feed side pressure of the membrane cell was kept at 10 bar. The permeate side was maintained at atmospheric pressure. The gas permeability was determined from the following equation:

$$P = \frac{q\updownarrow}{A(p_1 - p_2)} \tag{2}$$

where P is permeability expressed in barrer (1 barrer = 10^{-10} cm³(STP) cm cm⁻² s⁻¹ cmHg⁻¹), q is flow rate of the permeate gas passing through the membrane (cm³/s), l is the
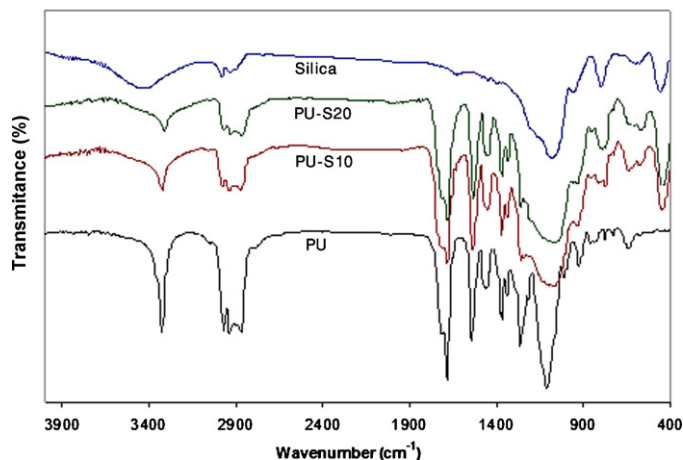

Fig. 1. FTIR spectra of polyether-based polyurethane–silica nanocomposites.

membrane thickness (cm), p_1 and p_2 are the absolute pressures of the feed side and permeate side, respectively (cmHg) and A is the effective membrane area (cm²).

The ideal selectivity (permselectivity), $\alpha_{A/B}$, of membranes was calculated from pure gas permeation experiments as follows:
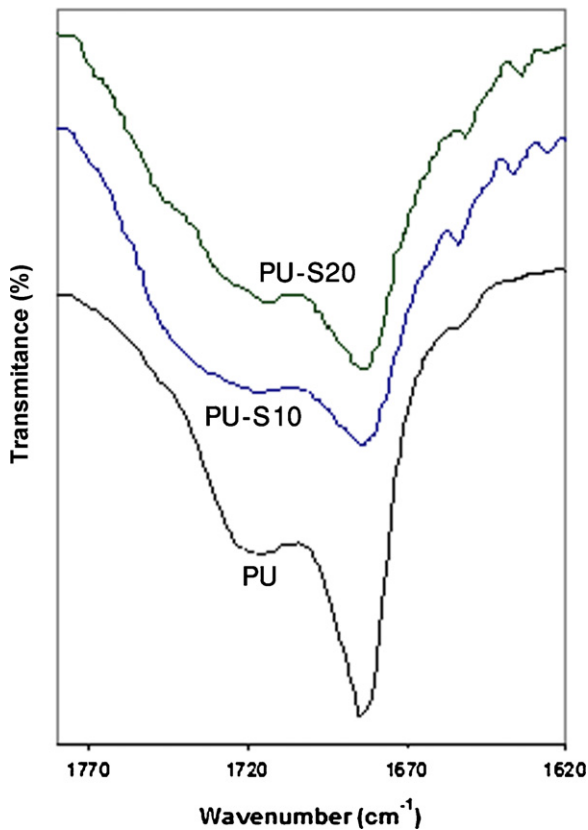
$$\alpha_{A/B} = \frac{P_A}{P_B} \tag{3}$$

3. Results and discussion

3.1. FTIR analysis

Structural characteristic of pure silicate, polyurethane and nanocomposite polyether-based polyurethane–silica hybrid membranes were carried out using FTIR analysis. The FTIR spectra of prepared composite membranes were shown in Fig. 1. As can be seen, the asymmetric vibration Si–O–Si peak at 1077 cm⁻¹ is easily observed in all nanocomposite membranes. The peaks related to the oscillatory vibrations of Si–O–Si at 453 cm⁻¹ and symmetrical vibrations of Si–O–Si at 795 cm⁻¹ in the composite membranes are also well observed.
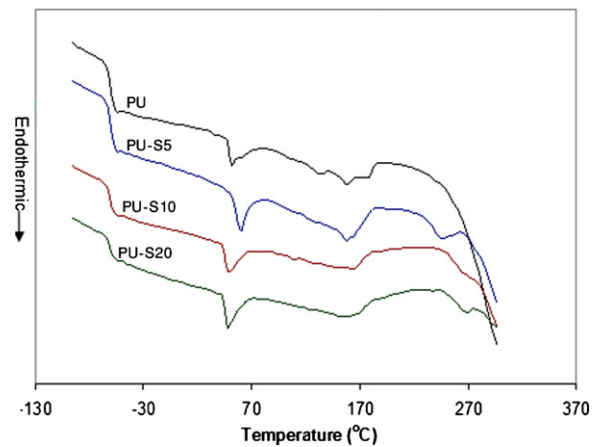
More inspection of the effects of silica nanoparticles on the phase separation of hard and soft segments of prepared membranes will follow by the presentation of the peaks related to the carbonyl groups. Fig. 2 shows the absorption of urethane carbonyl groups in pure polymer and hybrid membranes. The peak appeared in lower frequency (around 1682 cm⁻¹) refers to the bonded and the one appeared in higher frequency (around 1718 cm⁻¹) refers to the free carbonyls. As it was shown in Fig. 2, the free carbonyl peak slowly shifts toward the hydrogen-bonded carbonyl bond and finally removed by increasing silica content. This observation indicates more hydrogen bonding between urethane carbonyl groups and urethane N–H groups in hard segments. It can be deduced that a portion of the silica nanoparticles is able to distribute in soft segments of the polymer by interaction of OH groups in silica with ether groups of polyol in polyurethane. Therefore, the amount of available ethereal pieces of soft segments groups to create hydrogen bond with the N–H groups reduces and hence urethane N–H groups interact more with carbonyl groups of hard segments of urethane. So it may be concluded that the silica particles could distribute in the polymer chains by introduction of the good interaction between their OH groups and ether groups in the soft segments of urethane.

Fig. 2. FTIR spectra of polyether-based polyurethane–silica nanocomposites in the C=O stretching region.

3.2. Morphology of polyurethane–silica nanocomposite membranes

The presence and distribution of silica nanoparticles in the polyurethane membranes has been studied by SEM. Fig. 3 shows the SEM micrographs of the prepared polyurethane–silica hybrid
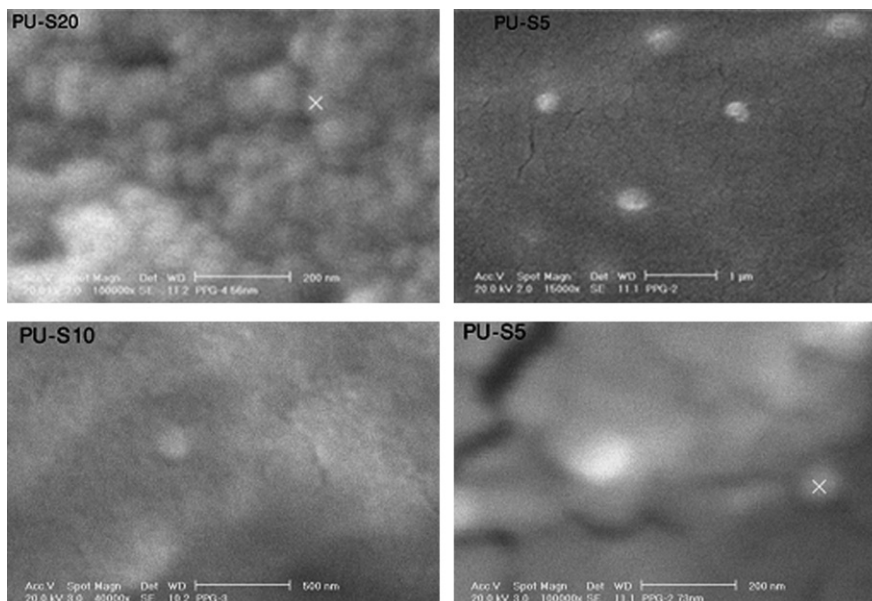

Fig. 4. DSC thermograms of polyurethane–silica membranes.

membranes. As it was shown, the presence and nanometric distribution of silica particles in prepared membranes is evident.

3.3. Thermal properties of polyurethane–silica nanocomposite membranes

The thermal properties of polyurethane membranes composed of silica nanoparticles were evaluated by DSC and TGA analyses. Fig. 4 shows the DSC thermograms of prepared samples. There is a T_g transition around $-60\,^{\circ}$C which is related to the glass transition temperature of soft segments. Also, there are two T_m peaks; a wide T_m peak in the range of 120–170 $^{\circ}$C and a small T_m peak at 50–60 $^{\circ}$C; respected to the hard segment crystallinity. Polypropylene glycol due to its vicinity on regularity could not crystalline anymore, so the crystallization peak which is appeared on the high temperature range of 120–170 $^{\circ}$C and small T_m peak at 50–60 $^{\circ}$C would only respect to crystallization of hard segments. The crystalline peak appeared in the range of 50–60 may respect to hard segments which are connected to the soft segments. Due to higher molecular mobility of the soft segments, this T_m appeared at lower temperatures. The wide endothermic peak of crystalline structure of hard segments is due to distributed nature of the hard segments

Fig. 3. SEM images of the fracture surface of polyurethane containing silica nanoparticles.
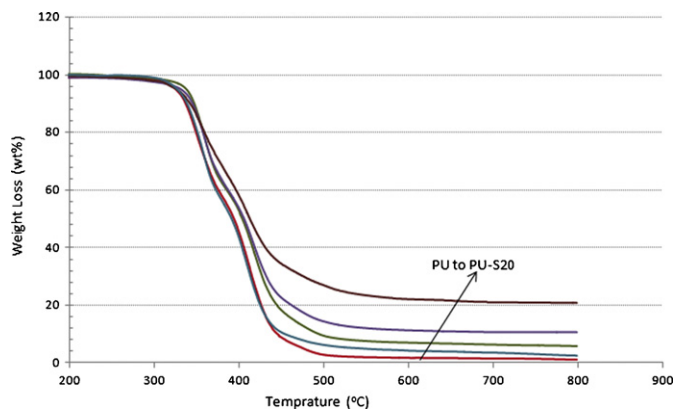
Fig. 5. TGA analysis of polyurethane and polyurethane–silica hybrid membranes.

Fig. 6. Effect of silica content in polyurethane–silica membranes on permeability of CO_2, CH_4, O_2, and N_2 gases.

in polymer. The presence of the crystalline peak of hard segments also shows the high phase separation of hard and soft segments.

As shown in Fig. 4, the glass transition temperatures of polymers are less than zero and are associated with polyol that is not changed after the arrival of silica. This phenomenon indicates no change in the dynamic of polyol chains in the presence of silica nanoparticles in polymers.

According to the abovementioned FTIR test results, and because of the hydrogen bonding between silica and polyol chains, a decrease in the mobility of chains was expected. But any changes in the mobility of polyol chains in the presence of silica have been occurred, it would respect to the reduction in the amount of hydrogen bonding between hard and soft segments of the polymer. By addition the silica particles into the polymer, the bonding between polymer chains and silica occurred and also the amount of hydrogen bonding between polyol and hard segment decreases. Based on the FTIR spectra, the amount of physical bonding between hard and soft segments of polymer in the absence of silica particles in the polymer is more than that of silica particles distribution in the polymer. Therefore, it can be concluded that in the presence of silica, hydrogen bonding between hard and soft segments of polymer is replaced by hydrogen bonding between silica particles and polyol chains and total chain mobility of polyol will not change significantly. Also it can be seen in Fig. 4 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 that lead to wide transition. Fig. 4 also shows that by increasing the silica particles the crystalline peak of hard segments do not change remarkably. It concludes that most of the silica particles distributed in soft segment domains.

Thermal stability of polyurethane–silica composite membranes was studied using TGA. Fig. 5 shows the weight reduction of prepared composite membranes with temperature. As seen, the decomposition of polyether-based polyurethane membranes starts from 350 °C, and up to 450 °C, 90 to 95% of the weight of polymer in each sample decreases. Two different slopes of reduction were observed in this region. These two different slopes show that there are two different weight reductions in prepared polymers. First one is related to the breakage in urethane bonds, while the second step is related to the thermal decomposition of polyol [35]. As shown in Fig. 5, in the case of nanocomposite 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. Presented results in Fig. 5 also show that the remaining membrane weight after applying heating up to 800 °C is consistent with the theoretical silica weight percentage of nanocomposite membranes. This could be a good reason for
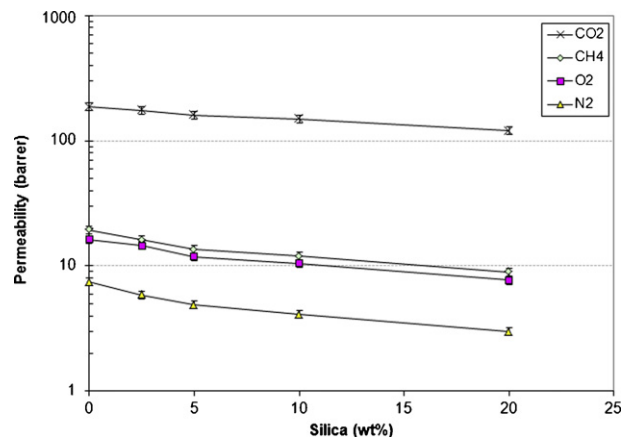
fully entrance of silica nanoparticles into the polymer during membrane preparation. It should be noted that the remaining weights after heating up to 800 °C were 1.11%, 2.9%, 5.81%, 11% and 21.5% for pure polymer, and nanocomposite membranes containing 2.5, 5, 10 and 20 wt.% of silica, respectively.

3.4. Gas permeation properties of polyurethane–silica membranes

Fig. 6 shows the effect of silica nanoparticles on the gas permeability of polyurethane–silica membranes. As shown in this figure, the permeability of CO_2 is significantly higher than those of other gases in all pure and composite membranes. As described before, the high permeation rate of CO_2 in comparison with other studied gases is due to its low kinetic diameter, high condensability and more interaction of this polar gas with polar groups in polymer [32,34]. As shown in Fig. 6, the permeability of methane is higher than those of oxygen and nitrogen in spite of its higher molecular size. The higher permeability of methane in comparison with oxygen and nitrogen could be acceptable because of its higher condensability. As known, the solution mechanism is dominant in permeation of gases through rubbery polymers. Therefore, the obtained results would show the high rubbery properties of pure and composite membranes.

Fig. 6 also shows the gas permeability of membranes reduces by increasing the amount of silica nanoparticles in polymer. It is suggested in polyurethane membranes that soft segment domains are formed as a result of a microphase separation and permeable to molecules, whereas the hard segment domains act as an impermeable barrier. Although the hard segment domains are not expected to be accessible to permeating molecules, they can influence the overall gas transport properties of a polymer due to their ability to serve physical crosslinks and change the dynamics of the soft segments [32].

In the case of polyurethane–silica composite membrane, there are two hard and soft segment regions for distribution of silica nanoparticles. From entropic point of view it appears that silica nanoparticles prefer to distribute in the hard segment of polyurethane [36,37]. The presence of silica particles in the hard phase can help the formation of crystals in the polymer [36]. It can also prevent the formation of crystals by disturbing the regularity and density of the nearby chains and reduce the amount of crystallinity of the polymer [24]. As shown in the DSC results, no significant difference between the crystallinity of polyurethane before and after addition of silica nanoparticles was observed. However, FTIR results showed that the probability of distribution of

particles in the soft phase exists. The gas permeability test results (Fig. 6) also showed that gas permeability in all prepared composite membranes decreased with increasing the amount of silica nanoparticles.

Therefore, based on the abovementioned results, it would be concluded that the most population of silica nanoparticles is distributed in the soft phase. As mentioned above, the soft segments are permeable domains in polyurethane membranes. Though, distribution of these particles in the soft phase due to the impermeability properties of silica particles reduces the permeation of gases in polymer. So, gas permeability reduction can be attributed to the presence of silica particles in the soft segment regions and restriction of molecular passing direction and creation a meander path to pass through. Soft and flexible polyol segments of polyurethane, alone have the necessary flexibility and movement to create space for movement of gas molecules. The presence of additional substances such as nonpermeable silica particles reduces the free volume of soft segments and reduces the passage areas of gas molecules. It should be noted that in the case of glassy polymers, the presence of spherical particles sometimes causes the extra voids between polymer chains and prevent the chain compression [18].

Comparison of gas permeability in polyurethane and polyurethane–silica composites (as shown in Fig. 6) shows that the gas permeabilities of carbon dioxide, methane, oxygen and nitrogen in the pure polymer decrease from 186.47, 19.5, 16.26 and 7.47 barrer to the amount of 120, 8.632, 7.69 and 2.98 barrer in the polyurethane–silica (20 wt.%) composite membrane, respectively. Calculated reduction values of gas permeability of prepared nanocomposite membranes in respect to pure polyurethane are in the following order:

$$CO_2\,(35.6\%) < O_2\,(52.7\%) < CH_4\,(54.19\%) < N_2\,(60.1\%)$$

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 [32]. Therefore, higher reduction of N_2 permeability in comparison with CO_2 and O_2 is due to its large molecular size and because of the presence of silica nanoparticles, is acceptable. In contrary to that of N_2, less reduction in permeability of methane gas, with larger molecular size than nitrogen, was observed. The main reason attributes to more condensability of methane in the membrane.

The presence of silica nanoparticles due to its non-organic nature would create some special spaces in the interface of organic polymer and non-organic particles which are suitable for dissolution of condensable gases. Also, FTIR spectra of polyurethane–silica samples showed that in addition to introduction of SiO_2 groups, some OH groups will enter the membrane. The presences of these groups in polymer structure provide appropriate positions for the dissolution of gases. Thus, by increasing the content of silica in polymer, solution of condensable methane gas will increase, and in spite of its larger molecular size than N_2, its permeability decreases slower.

In the case of carbon dioxide, its lower permeability reduction with increasing silica compared to other gases is due to both its small molecular size and also it's more dissolution in the membrane due to the increased polar OH groups in the polymer with increasing silica content. Good interaction between polar carbon dioxide and polar OH groups in silica increases the dissolution of CO_2 in the polymer.

Fig. 7 shows the CO_2/N_2, CO_2/CH_4 and O_2/N_2 permselectivities of polyurethane–silica nanocomposite membranes. As it can be seen, by increasing the silica content in nanocomposites, all permselectivities increased.
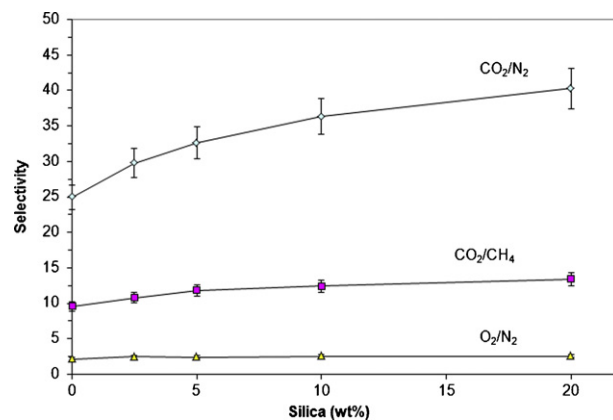

Fig. 7. CO_2/N_2, CO_2/CH_4 and O_2/N_2 permselectivities versus silica content of polyurethane–silica nanocomposite membranes.
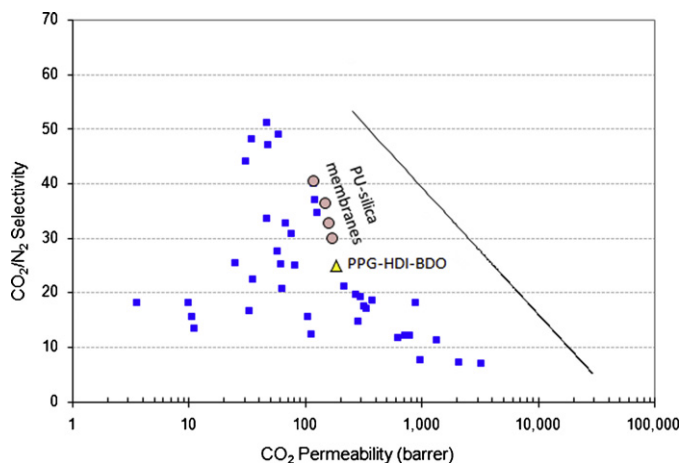

Fig. 8. Comparison of CO_2/N_2 separation performance of polyurethane–silica nanocomposite membranes with Robeson's upper bound line.

Fig. 7 shows that CO_2/N_2, CO_2/CH_4 and O_2/N_2 permselectivities increase from 24.96, 9.56 and 2.17 for pure polyurethane to 41.26, 13.43 and 2.58 for polyurethane–silica (20 wt.%). Comparative increase in permselectivity of pair gases shows that the increase in CO_2/N_2, CO_2/CH_4, O_2/N_2 permselectivities are 65.3%, 40.5% and 18.9%, respectively.

As known in solution-diffusion mechanism of permeation of gases through polymeric membranes, the permselectivity of a pair gas is composed of solubility selectivity and diffusivity selectivity of the gases in membrane. By addition of the silica nanoparticles into the membranes, as mentioned, the permeation of larger molecular size gases restricted more than that of smaller one [32]. It offers the more molecular sieve property of composite membranes by increasing the silica in them. Though, the better molecular sieve property of composite membranes offers the enhancement in permselectivity of CO_2/N_2, CO_2/CH_4 and O_2/N_2 gases in nanocomposite membranes.

In the case of O_2/N_2, because the condensabilities of these two gases are very low and not very different, the molecular size difference in this pair of gases plays an important role. Therefore, the improvement of diffusivity selectivity due to better molecular sieve property of nanocomposite membranes, only cause the selectivity increment and finally the total selectivity increment is not very high. But in the case of CO_2/N_2 and CO_2/CH_4 gases because of more condensable property and also more interaction of CO_2 in comparison with methane and nitrogen, the solubility selectivity also has effective role on enhancement of permselectivity of pair gases.
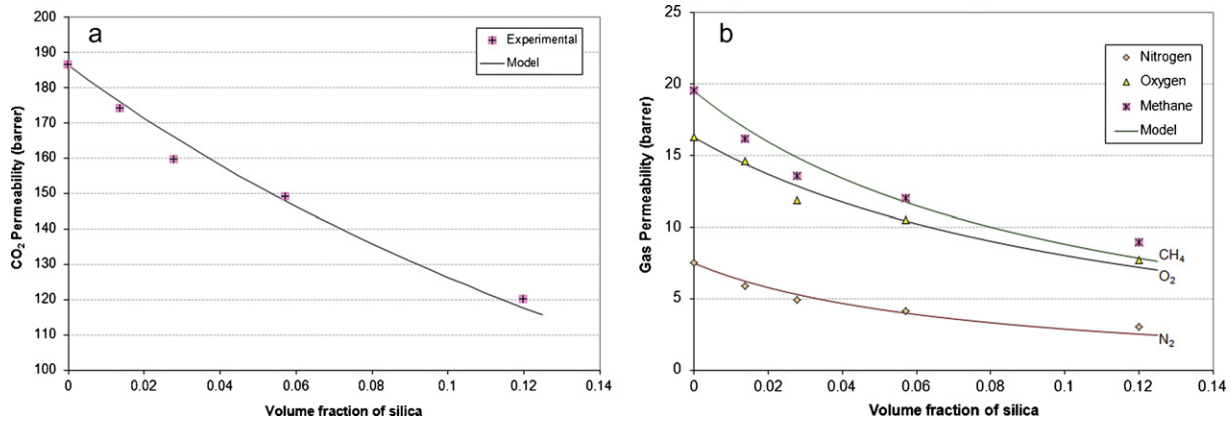
Fig. 9. Experimental and predicted permeability of polyurethane–silica membranes for (a) CO_2 and (b) N_2, CH_4 and O_2 gases.

Therefore, the enhancements in CO_2/N_2 and CO_2/CH_4 selectivities are significantly more than that of O_2/N_2 selectivity. Finally, the more increasing of CO_2/N_2 selectivity in comparison with CO_2/CH_4, is attributed to very low condensability of nitrogen in comparison with methane. As mentioned, the suitable sorption sites on polymer–silica interface offer more solubility of condensable gases and solution of methane due to its condensable nature which is significantly more than that of nitrogen. Therefore, in spite of higher molecular size of the methane which could offer higher diffusivity selectivity of CO_2/CH_4 in comparison with CO_2/N_2, domination of solution mechanism causes the high solution of methane and lowers the solubility selectivity.

As stated by other researchers, for commercial and industrial use of membranes in gas separation processes, membranes must have a maximum amount of permeability and selectivity. The obtained results from prepared polyurethane–silica membranes were compared with Robeson's upper bound line [38] in Fig. 8. As shown, the prepared polyurethane–silica membranes lay close to Robeson's upper bound line and this means prepared nanocomposite membranes present better CO_2/N_2 separation performance than other PU membranes. The variation of nanocomposite membranes, in spite of their lower permeability, shows better performance because of their better selectivity.

3.5. Membrane permeability prediction using modified Higuchi model

The permeability behavior of polyurethane–silica membranes has been modeled using modified Higuchi model. As it was stated in our previous publication [21], Eq. (4) predicts the gas permeability of hybrid membranes in the presence of impermeable material like silica particles:

$$\frac{P_{eff}}{P_c} = 1 \frac{6\Phi}{4 + 2\Phi - K_H(1 - \Phi)} \tag{4}$$

The Higuchi constant, K_H, was selected 0.78 by Higuchi for the best fit of the experimental data to model [39]. In our previous work we tried to fit the Higuchi model for predicting the gas permeability of PBI–silica hybrid membranes. As evaluated in PBI–silica nanocomposite membranes the Higuchi constant should change to higher values to fit the Higuchi model to experimental data. The K_H constant establishes the effect of filler in membrane. We suggested by decreasing the size of the particles to nanoscale size the impression of particles would increase and the Higuchi constant would be modified. We established that $K_H = 3.7$ shows the best fit of N_2 permeation data to Higuchi model [21].

In the case of PU–silica nanocomposite membranes, the Higuchi model fitted to experimental data and the appropriate K_H constants

Table 2
The obtained values of K_H parameter for different gases in the polyurethane–silica nanocomposite membranes by curve fitting.

Component	K_H
CO_2	2.6
O_2	3.35
CH_4	3.45
N_2	3.58

extracted for CO_2, N_2, CH_4 and O_2 gases (Table 2). As presented in Table 2, K_H increases as the molecular size of the gases increase, except in the case of nitrogen and methane which may refer to the higher condensability of methane. The order of K_H is in good agreement with the order of reduction values of gas permeability of prepared nanocomposite membranes in respect to pure polyurethane.

Higuchi constant:

$$CO_2 (2.6) < O_2 (3.35) < CH_4 (3.45) < N_2 (3.58)$$

Reduction value of gas permeability:

$$CO_2 (35.6\%) < O_2 (52.7\%) < CH_4 (54.19\%) < N_2 (60.1\%)$$

It would be concluded that by increasing the effect of nanoparticles in membranes, the Higuchi constant would increase. Fig. 9 also shows the experimental data and predicted data obtained from Higuchi model applying K_H parameter from Table 2. As shown in Fig. 9, experimental data are consistent with predicted permeabilities by Higuchi model for prepared polyurethane–silica membranes.

4. Conclusions

In this study, the effect of silica nanoparticles on the gas permeation properties of polyether-based polyurethane–silica membranes was investigated. In this regard, polyurethane was synthesized by bulk two-step polymerization method. Polypropylene glycol was incubated with HMDI under nitrogen atmosphere to obtain macrodiisocyanate prepolymer. The chain extension of prepolymers was performed by addition of BDO at room temperature.

Silica nanoparticles were prepared through the sol–gel method by hydrolysis of tetraethoxysilane (TEOS). Therefore, polyurethane–silica nanocomposite membranes were prepared by solution blending and casting method. The prepared

polyurethane–silica membranes were characterized using FTIR, SEM and DSC methods.

FTIR and SEM results verified the presence of silica nanoparticles in the prepared samples. The gas permeation properties of prepared nanocomposite membranes also showed the decrease in gas permeability of membranes with silica content, but increase in CO_2/N_2 and CO_2/CH_4 selectivities. The permeation of gases also modeled by modified Higuchi model. The new constants for Higuchi model obtained for studied gases. The experimental data and modified model showed good agreement.

References

[1] M. Garci, G. van Vliet, S. Jain, B.A.G. Schrauwen, A. Sarkissov, W.E. van Zyl, B. Boukamp, Polypropylene/SiO_2 nanocomposites with improved mechanical properties, Rev. Adv. Mater. Sci. 6 (2004) 169.

[2] P. Yang, G. Wang, X. Xia, Y. Takezawa, H. Wang, S. Yamada, Q. Du, W. Zhong, Preparation and thermo-mechanical properties of heat-resistant epoxy/silica hybrid materials, Polym. Eng. Sci. 48 (2008) 1214.

[3] B.-K. Chen, C.-T. Su, M.-C. Tseng, S.-Y. Tsay, Preparation of polyetherimide nanocomposites with improved thermal, mechanical and dielectric properties, Polym. Bull. 57 (2006) 671.

[4] M.I. Sarwar, S. Zulfiqar, Z. Ahmad, Polyamide–silica nanocomposites: mechanical, morphological and thermomechanical investigations, Polym. Int. 57 (2008) 292.

[5] E. Kontou, M. Niaounakis, Thermo-mechanical properties of LLDPE/SiO_2 nanocomposites, Polymer 47 (2006) 1267.

[6] A. Bansal, H. Yang, C. Li, B.C. Benicewicz, S.K. Kumar, L.S. Schadler, Controlling the thermomechanical properties of polymer nanocomposites by tailoring the polymer–particle interface, J. Polym. Sci. B: Polym. Phys. 44 (2006) 2944.

[7] Y. Zheng, Y. Zheng, R. Ning, Effects of nanoparticles SiO_2 on the performance of nanocomposites, Mater. Lett. 57 (2003) 2940.

[8] H. Zhou, Y. Chen, H. Fan, H. Shi, Z. Luo, B. Shi, The polyurethane/SiO_2 nano-hybrid membrane with temperature sensitivity for water vapor permeation, J. Membr. Sci. 318 (2008) 71.

[9] M. Moaddeb, W.J. Koros, Gas transport properties of thin polymeric membranes in the presence of silicon dioxide particles, J. Membr. Sci. 125 (1997) 143.

[10] K. Kusakabe, K. Ichiki, J. Hayashi, H. Maeda, S. Morooka, Preparation and characterization of silica–polyimide composite membranes coated on porous tubes for CO_2 separation, J. Membr. Sci. 115 (1996) 65.

[11] C. Joly, S. Goizet, J.C. Schrotter, J. Sanchez, M. Escoubes, Sol–gel polyimide–silica composite membrane: gas transport properties, J. Membr. Sci. 130 (1997) 63.

[12] S.P. Nunes, K.V. Peinemann, K. Ohlrogge, A. Alpers, M. Keller, A.T.N. Pires, Membranes of poly(ether imide) and nanodispersed silica, J. Membr. Sci. 157 (1999) 219.

[13] M. Smaihi, J.C. Schrotter, C. Lesimple, I. Prevost, C. Guizard, Gas separation properties of hybrid imide–siloxane copolymers with various silica contents, J. Membr. Sci. 161 (1999) 157.

[14] C.J. Cornelius, E. Marand, Hybrid silica–polyimide composite membranes: gas transport properties, J. Membr. Sci. 202 (2002) 97.

[15] H.B. Park, J.K. Kim, S.Y. Nam, Y.M. Lee, Imide–siloxane block copolymer/silica hybrid membranes: preparation, characterization and gas separation properties, J. Membr. Sci. 220 (2003) 59.

[16] M.S. Boroglua, M.A. Gurkaynak, The preparation of novel silica modified polyimide membranes: synthesis, characterization, and gas separation properties, Polym. Adv. Technol. (2009), doi:10.1002/pat.1543.

[17] J.H. Kim, Y.M. Lee, Gas permeation properties of poly(amide-6-b-ethyleneoxide)–silica hybrid membranes, J. Membr. Sci. 193 (2001) 209.

[18] Y. Chen, S. Zhou, H. Yang, L. Wu, Structure and properties of polyurethane/nanosilica composites, J. Appl. Polym. Sci. 95 (2005) 1032.

[19] X. Chen, L. Wu, S. Zhou, B. You, In-situ polymerization and characterization of polyester-based polyurethane/nano-silica composites, Polym. Int. 52 (2003) 993.

[20] X. Chen, B. You, S. Zhou, L. Wu, Surface and interface characterization of polyester-based polyurethane/nano-silica composites, Surf. Interface Anal. 35 (2003) 369.

[21] M. Sadeghi, M.A. Semsarzadeh, H. Moadel, Enhancement of gas separation properties of polybenzimidazole membrane by incorporation of silica nano particles, J. Membr. Sci. 331 (2009) 21.

[22] M. Sadeghi, G. Khanbabaei, A.H. Saeedi Dehghani, M. Sadeghi, M.A. Aravand, M. Akbarzade, S. Khatti, Gas permeation properties of ethylene vinyl acetate-silica nanocomposite membranes, J. Membr. Sci. 322 (2008) 423.

[23] G. Arthanareeswaran, T.K. Sriyamuna Devi, M. Raajenthiren, Effect of silica particles on cellulose acetate blend ultrafiltration membranes. Part I, Sep. Purif. Technol. 64 (2008) 38.

[24] W. Chen, Y. Su, L. Zhang, Q. Shi, J. Peng, Z. Jiang, In situ generated silica nanoparticles as pore-forming agent for enhanced permeability of cellulose acetate membranes, J. Membr. Sci. 348 (2010) 75.

[25] J. Ahn, W.-J. Chung, I. Pinnau, J. Song, N. Du, G.P. Robertson, M.D. Guiver, Gas transport behavior of mixed-matrix membranes composed of silica nanoparticles in a polymer of intrinsic microporosity (PIM-1), J. Membr. Sci. 346 (2010) 280.

[26] J. Ahn, W.-J. Chung, I. Pinnau, M.D. Guiver, Polysulfone/silica nanoparticle mixed-matrix membranes for gas separation, J. Membr. Sci. 314 (2008) 123.

[27] M. Moaddeb, W.J. Koros, Effects of colloidal silica incorporation on oxygen/nitrogen separation properties of ceramic-supported 6FDA-IPDA thin films, J. Membr. Sci. 111 (1996) 283.

[28] V.N. Banon, J.V. Bandrit, P. Vasquez, J.M.M. Martinz, Interactions in nanosilica–polyurethane composites evidenced by plate–plate rheology and DMTA, Macromol. Symp. 221 (2005) 1.

[29] M.A. Liminana, A.T. Paulu, A.C.O. Barcelo, J.M.M. Martinez, Modification of the rheological properties of polyurethanes by adding fumed silica: influence of the preparation procedure, Macromol. Symp. 194 (2003) 161.

[30] K. Kusakabe, S. Yoneshige, S. Morooka, Separation of benzene/cyclohexane mixtures using polyurethane–silica hybrid membranes, J. Membr. Sci. 149 (1998) 29.

[31] M. Sadeghi, M.A. Semsarzadeh, M. Barikani, B. Ghalei, The effect of urethane and urea content on the gas permeation properties of poly (urethane-urea) membranes, J. Membr. Sci. 354 (2010) 40.

[32] M.A. Semsarzadea, M. Sadeghi, M. Barikani, H. Moadel, The effect of hard segments on the gas separation properties of polyurethane membranes, Iranian Polym. J. 16 (2007) 819.

[33] M.A. Semsarzadeh, M. Sadeghi, M. Barikani, The effect of chain extender length on the gas permeation properties of polyurethanes, Iranian Polym. J. 17 (2008) 431.

[34] I.V. Khudyakov, R.D. Zopf, N.J. Turro, Polyurethane nanocomposites, Des. Monomers Polym. 12 (2009) 279.

[35] S.L. Huang, J.Y. Lai, Gas permeability of crosslinked HTPB-H12MDI-based polyurethane membrane, J. Appl. Polym. Sci. 58 (1995) 1913.

[36] L.H. Sperling, Introduction to Physical Polymer Science, 4th ed., John Wiley & Sons, USA, 2006.

[37] F.W. Billmeyer Jr., Textbook of Polymer Science, John Wiley & Sons, Singapore, 2000.

[38] L.M. Robeson, The upper bound revisited, J. Membr. Sci. 320 (2008) 340–390.

[39] W.I. Higuchi, A new relationship for the dielectric properties of two phase mixtures, J. Phys. Chem. 62 (1958) 649.