Gas Separation Performance of Polyvinylchloride - Silica Nanocoposite Polymeric Membrane

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Abstract

In the last decades improving the performance of polymeric membranes, for example adding inorganic nanoparticles in polymer matrix is one of the predominant concerns of the researchers. In the present work, the separation of oxygen, nitrogen, methane and carbon dioxide gases by PVC/silica nanocomposite membranes were investigated. Silica nanoparticles were prepared via sol-gel method. Membranes were prepared by thermal phase inversion method. The prepared nanocomposite membranes were characterized using FTIR, SEM and TGA methods. The results demonstrate a nano-scale and good distribution of silica particles in the polymer matrix. This confirms the desirable mixing of the silica in polymer and also a good compatibility between the two phases. The thermal properties of PVC membranes were also improved by adding silica particles. The performances of prepared membranes in gas separation were measured at pressure of 10 barg and temperature of 25 ∘C. The obtained results showed that the permeability of all gases increased. Also by entering silica nanoparticles in PVC matrix, the performances of separation of CO_2 from CH_4 and separation of CO_2 from N_2 were increased.

Keyword: Gas separation, Nanocomposite membrane, Silica, Polyvinylchloride (PVC)

Introduction

Poly (vinyl chloride) (PVC) is one of the commodity polymers of highest worldwide consumption. The utilization of PVC in a wide variety of applications derives from the good properties of this polymer, especially high compatibility with additives, easy processability and recyclability. Although the low cost and the good properties of PVC have contributed to extend the use of this material to different applications of commercial importance, studies on the performance of PVC films in gas separation are scarce. Earlier work carried out in our laboratories showed that PVC membranes exhibit low permeability to gases accompanied of rather high selectivity [1-3].

Polymer–inorganic nanocomposite materials, herein defined as inorganic nanofillers dispersed at a nanometer level in a polymer matrix, have been investigated for gas separation, and have the potential to provide a solution to the trade-off problem of polymeric membranes [4-5]. For example, many polymer–inorganic nanocomposite membranes show much higher gas permeabilities but similar or even improved gas selectivities compared to the corresponding pure polymer membranes [6]. The nanocomposite materials may combine the advantages of each material: for instance, the flexibility and processability of polymers, and the selectivity and thermal stability of the inorganic fillers. Additionally, the gas separation performance of nanocomposite membranes can be further enhanced by chemical modification [7].

Exprimental

1. Material

PVC polymer purchased from Vinythai Co (THAI), Dimethylformamid (DMF) as a solvent, Tetraethoxysilane (TEOS), 3-glycidyloxypropylterimethoxy silane (GOTMS), hydrochloric acid (HCl) and ethanol required for preparation of silica particles were provided from Merck (GERMANY).

2. Dense Membrane Formation

A solution casting method was used to prepare the dense film [8]. The average thickness of the films was 35 microns.

3. Preparation of silica nanoparticles and PVC–silica composite membrane

Silica nanoparticles were prepared via the hydrolysis of tetraethoxysilane (TEOS) in ethanol at the presence of hydrochloric acid as a catalyst. Initially, tetraethoxysilane (25 g) and a coupling agent 3-glycidyloxy propylterimethoxysilane (GOTMS) (4 g) were mixed together in dry ethanol (30 ml) at a temperature of 70 ∘C for 1 h. Consequently, a mixture of ethanol (30 ml), deionized water (7.5 g) and hydrochloric acid (0.83 g) was added drop-wise to the 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. PVC–silica nanocomposite membranes were prepared by the same method following the addition of the silica-sol in different weight fractions to the polymer solution.

Result and discussion

1. FTIR spectra

The analysis of PVC-silica showed peak at 435 cm^{-1} (attributed Si-O-Si Rocking), 1077 cm^{-1} (attributed Si-O-Si asymmetric Stretching) and 3438 cm^{-1} (attributed Si-OH Stretching). Fig 1 shows the FTIR spectra of prepared structures. The obtained results show that the peaks related to nanosilica increased by increasing the nanoparticles content in membranes.

2. TGA analysis

The thermal properties of PVC-silica membranes were determined by DSC and TGA analyses. Fig 2 showed that T_g and T_d increased with adding nanoparticle.

3. SEM analysis

Figure 3 shows the SEM micrographs PVC-silica membranes. The figure shows that PVC-silica led to a homogeneous structure. The uniform dense membrane without any defects makes these membranes acceptable for our gas permeation studies. The nano scale distribution of particles have been appeared in the figures.
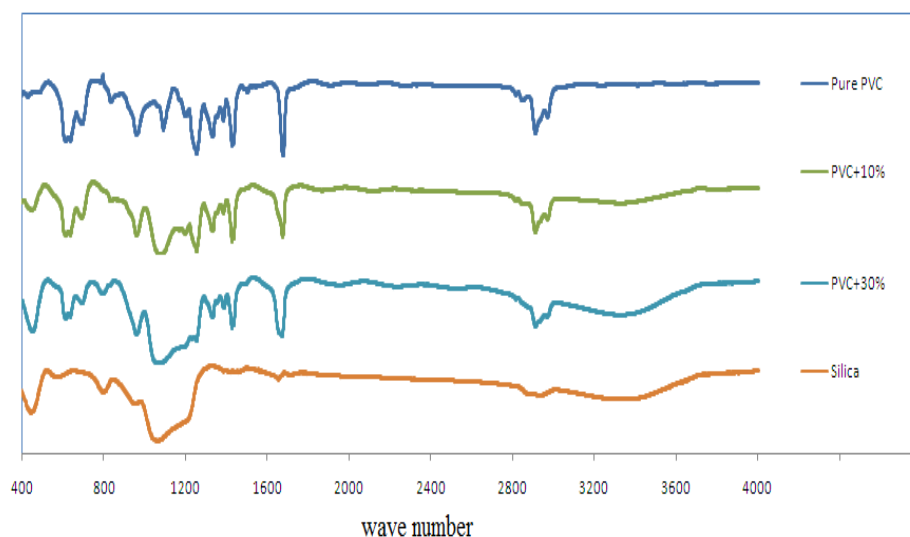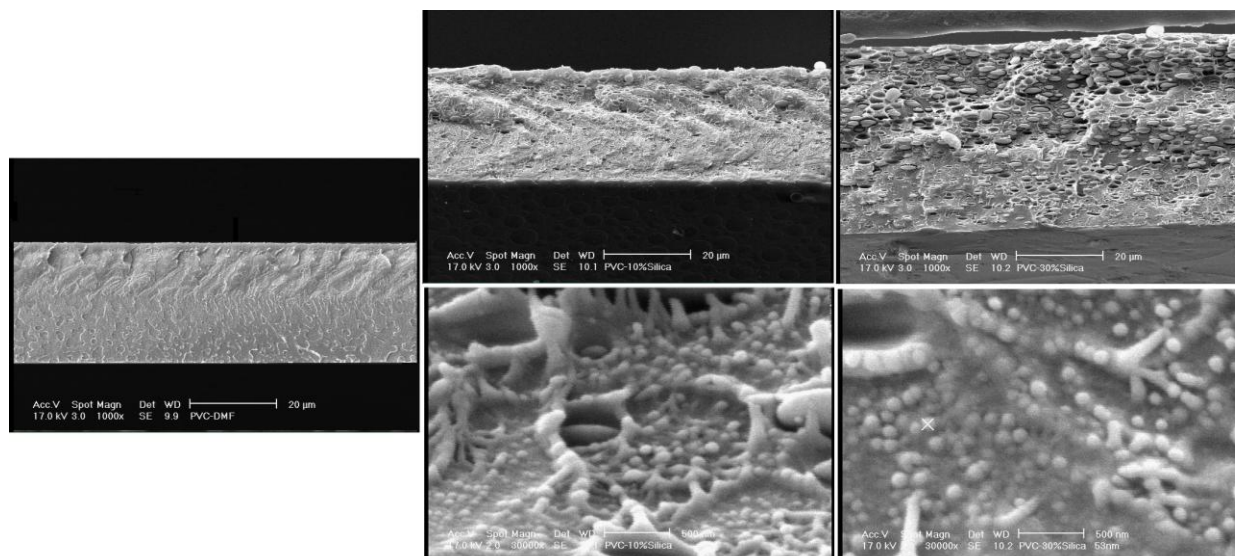

Fig.1- FTIR spectra of membrane
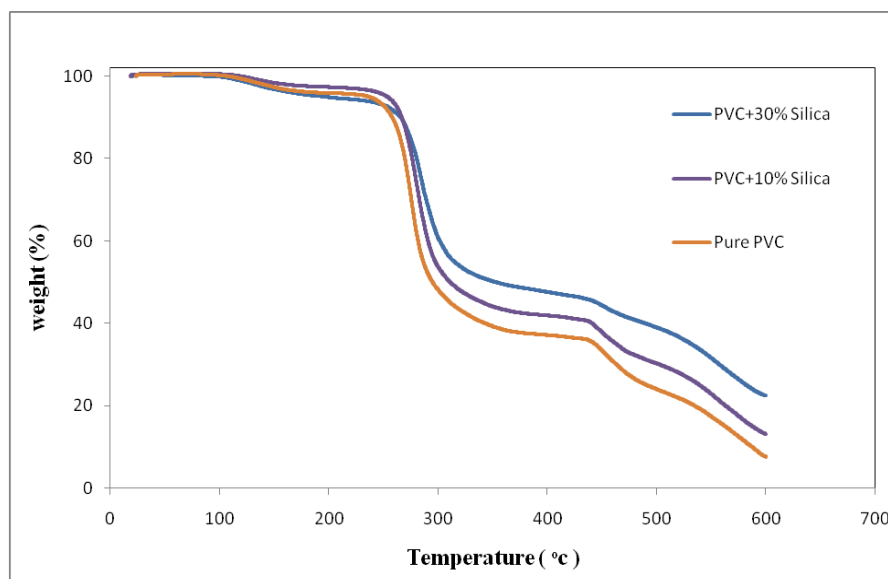
Fig.2- SEM of pure PVC and PVC-silica

Fig.3- TGA analyses of membranes

4. Gas separation properties

The permeability of gases was determined using constant pressure/variable volume method. The performances of prepared membranes in gas separation were measured at pressure of 10 barg and temperature of 25 °C. The obtained results showed that the permeability of carbon dioxide, oxygen, nitrogen and methane gases increased from 0.105, 0.023, 0.0066 and 0.005 barrer in pure PVC to 0.1908, 0.048, 0.0105 and 0.007 barrer in the composite membrane containing 30%wt silica particles respectively. The permeability values increased about 82%, 108%, 59% and 40% for carbon dioxide, oxygen, nitrogen and methane gases respectively.

Also by entering silica nonoparticles in PVC matrix, the performances of separation of CO_2 from CH_4 and separation of CO_2 from N_2 were increased. Furthermore, the obtained results revealed the fact that incorporation of silica particles in the polymer matrix, i.e. increasing the number of polar OH groups as well as morphological changes induced at the silica–PVC interface, leads to the enhancement of the gas solubility in such membranes. The smaller the penetrant kinetic diameter, the higher should be the penetrant mobility through the polymer gaps should

be, to reach a new site. The results show an adequate correlation between the permeation coefficients $P_{CO2} > P_{O2} > P_{N2} > P_{CH4}$ and their kinetic diameters $\sigma_{kCO2} < \sigma_{kO2} < \sigma_{kN2} < \sigma_{kCH4}$.

Table1. Permeability coefficients and permselectivities at P = 10 barg and T = 25 °C

Structure	permeability coefficient (Barrer)[a]				permselectivity	
	CH_4	CO_2	N_2	O_2	CO_2/N_2	CO_2/CH_4
Pure PVC	0.0050	0.1050	0.0066	0.0230	15.9	21.0
PVC-10S	0.0052	0.1295	0.0092	0.0361	14.1	22.5
PVC-30S	0.0070	0.1908	0.0105	0.0480	18.2	27.3

[a] 1 Barrer = 1×10^{-10} cm^3(STP)cm/cm^2 s cmHg

Conclusion

In this study, the effect of incorporation of silica particles on the permeability of CO2, CH4 and N2 in Polyvinylchloride (PVC) membranes has been investigated. The permeability of all gases enhanced as nanocontentes increased. Furthermore, the obtained results revealed the fact that incorporation of silica particles in the polymer matrix, i.e. increasing the number of polar OH groups as well as morphological changes induced at the silica–PVC interface, leads to the enhancement of the gas solubility in such membranes, while the diffusivity of the gases in the nano-composite membrane is reduced due to the obstructions made by the particles.

References

[1] P. Tiemblo, J. Guzmán, E. Riande, C. Mijangos, H. Reinecke, Effect of physical aging on the gas transport properties of PVC and PVC modified with pyridine groups, Polymer 42 (2001) 4817–4823; (b) P. Tiemblo, J. Guzmán, E. Riande, C. Mijangos, H. Reinecke, Polymer 42 (2001) 8321 (corrigendum).

[2] P. Tiemblo, J. Guzmán, E. Riande, C. Mijangos, H. Reinecke, The gas transport properties of PVC functionalized with mercapto pyridine groups, Macromolecules 35 (2002) 420–424.

[3] P. Tiemblo, J. Guzmán, E. Riande, C. Mijangos, M. Herrero, J. Espeso, H. Reinecke, Diffusion of small molecules through modified Poly(vinyl chloride) membranes, J. Polym. Sci. Part B: Polym. Phys. 40 (2002) 964-971.

[4] F. Peng, L. Lu, H. Sun, Y. Wang, H. Wu, Z. Jiang, Correlations between free volume characteristics and pervaporation permeability of novel PVAGPTMS hybrid membranes, J. Membr. Sci. 275 (2006) 97–104.

[5] F. Peng, L. Lu, H. Sun, Y.Wang, J. Liu, Z. Jiang, Hybrid organic–inorganic membrane: solving the tradeoff between permeability and selectivity, Chem. Mater. 17 (2005) 6790–6796.

[6] T.C. Merkel, B.D. Freeman, R.J. Spontak, Z. He, I. Pinnau, P. Meakin, A.J. Hill, Ultrapermeable, reverse-selective nanocomposite membranes, Science 296 (2002) 519–522.

[7] N.P. Patel, J.M. Zielinski, J. Samseth, R.J. Spontak, Effects of pressure and nanoparticle functionality on CO2-selective nanocomposites derived from crosslinked poly(ethylene glycol), Macromol. Chem. Phys. 205 (2004) 2409–2419.

[8] M.Sadeghi, M.A.Semsarzadeh, H.Moadel, " Enhancement of the gas separation properties of polybenzimidazole (PBI) membrane by incorporation of silica nano particles ", journal of membrane science, 331 (2009) 21-30.