

Pervaporative Studies Using Polyimide-Filled PDMS Membrane

P. Garg,¹ R. P. Singh,² L. K. Pandey,¹ V. Choudhary³

¹Defence Research and Development Establishment, Jhansi Road, Gwalior 474002, India

²Centre for Fire, Explosive and Environment Safety, Timarpur 110054, Delhi, India

³Centre for Polymer Science and Engineering, Indian Institute of Technology, 110016, New Delhi, India

Received 4 March 2009; accepted 25 July 2009

DOI 10.1002/app.31255

Published online 7 October 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The application of pervaporation (PV) to the removal of volatile organic from aqueous solutions has become very interesting in the last few years. It is caused by the increasing level of compounds, such as petrochemical solvents (benzene, toluene, and xylenes) or chlorinated solvents (trichloroethylene or tetrachloroethylene), which are polluting the natural environment. In this work, effects of polyimide (PI) (prepared by direct polycondensation of dihydride and diamine followed by thermal cyclization of polyamic acid) filler on PV properties of poly(dimethyl siloxane) (PDMS) have been studied. PDMS membrane filled with PI was used for the separation of benzene (Bz) and toluene (Tol) from the diluted aqueous solution and the results were compared with the neat PDMS membrane of similar thickness. The PDMS-PI membrane showed normal-

ized flux (J') upto 1.2 kg $\mu\text{m}^2/\text{h}$ for Bz and 1.48 kg $\mu\text{m}^2/\text{h}$ for Tol and selectivity of organics varies from 7.3 to 3.2 for Bz and 8.9 to 2.8 for Tol with increasing concentration of organics. Concentration of PI filler in PDMS varied 5–25% w/w. PI filler increases thermal as well as mechanical stability of filled PDMS membranes. PDMS membrane filled with 25% PI was chosen for the pervaporation studies. The membranes were characterized by FTIR, thermogravimetric analyser and scanning electron microscopy. The mechanical strength of PDMS filled with 25% w/w PI (SPI-25) membrane was found to be 2.7 MPa. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1967–1974, 2010

Key words: pervaporation; toluene; benzene; poly(dimethyl siloxane); polyimide; composite membrane

INTRODUCTION

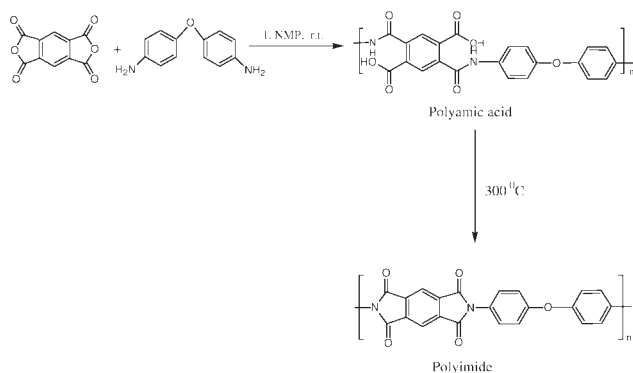
In the last few years, pervaporation (PV) has become an intensive developing separation technique.^{1–3} PV is emerging as an energy efficient alternative to distillation and other separation methods for liquid mixtures, especially for the separation of azeotropes, close boiling mixtures, isomers, and temperature sensitive products.^{4–8} Unlike distillation, the separation mechanism in PV is not only based on the relative volatility of the components alone but also on the differences in sorption and diffusion properties of the feed components towards the membrane material as well as its permselectivity.

Recently, the application of PV to volatile organic compounds (VOC) removal from water has become very interesting. It is the result of an increasing level of these substances in the natural environment. Man-made VOCs are generated by several sources, such as municipal waste, traffic or industrial, and

agricultural activity.¹ Very dangerous is the increasing amount of petrochemical solvents, especially benzene, toluene, xylenes, or chlorinated solvents, such as, trichloroethylene or tetrachloroethylene. For organic compound separation from water, many hydrophobic materials have been investigated for VOCs removal. The poly(dimethyl siloxane) (PDMS) is the most interesting and promising membranes and has been extensively studied for the separation of organics from aqueous media due to its hydrophobic nature.¹ However, their unsatisfactory selectivity of organics versus water has yet limited their applications to some extent.^{1,9,10} Research articles have indicated that despite of its strong hydrophobicity, PDMS rubbery membrane show high water permeation, which may be ascribed to higher diffusion rate of water molecules with smaller size than most of the organic molecules through soft PDMS polymer chains. Thus, the poor selectivity of organics versus water through PDMS is obtained.¹¹ To achieve high selectivity or high flux for specific compounds the modification of membranes, such as filling, grafting, or coating have been performed.¹ The most common is adding fillers, especially high aspect ratio fillers. It also improves physical properties, such as increased stiffness or reduced creep and a variety of other purposes, such as improved

Correspondence to: V. Choudhary (veenach@hotmail.com).

Contract grant sponsor: Ministry of Defence, Govt. of India.



Scheme 1 Synthetic scheme of polyimide

thermal stability, high voltage resistance, electrical conductivity, radiation shielding, optical, and aesthetic effects.^{12,13} Aromatic polyimides (PI) have been widely employed in the past for various applications due to their excellent dielectric, thermal, adhesion, dimensional stability, and mechanical properties.^{14,15} However, most commercial PIs are usually insoluble in common organic solvents and infusible, which posed limitations on their extensive applications. However, PIs can be used as filler for various rubbery polymers to improve its mechanical, thermal, and separation properties. In this study, PI-filled PDMS membrane was used to investigate the separation of toluene and benzene from water and the results were compared with PDMS membrane.

EXPERIMENTAL

Materials

Pyromellitic dianhydride and 4,4'-oxydianiline were purchased from Aldrich Chemicals Co. (USA). *N*-methyl pyrrolidone (Fluka) was purified by stirring with NaOH, dried over P₂O₅ and then distilled under reduced pressure. Vinyl terminated poly(dimethyl siloxane) with mixed viscosity 3000 mPas (RTV 2/Silastic 9050/30P) from Dow Corning, (Germany) was used as such. The reagents used for PV and sorption, such as benzene and toluene in this study were of HPLC grade (Merck Germany).

Preparation of polyimides

PI was prepared using one step method reported by Sroog et al.¹⁶ The synthetic route and structure of PI is shown in scheme 1.

Procedure

4,4'-diaminodiphenyl ether (0.05 mol) in 100 mL of dry *N*-methyl pyrrolidone was taken in a 500 mL

three necked round bottom flask fitted with mechanical stirrer, nitrogen inlet, and condenser fitted with drying tube of CaCl₂. Benzene-1,2,4,5-tetracarboxylic dianhydride (0.05 mol) was added slowly to the solution with vigorous mixing. Concentration of solution was kept 10% (w/v). After complete addition, reaction mixture was stirred for 24 h at room temperature. The solution became highly viscous within half an hour. After 24 h, the temperature of reaction mixture was raised to 160°C (2 h) and 200°C (1 h). After thermal cyclization of polyamic acid, PI was precipitated by pouring the contents into distilled water. PI thus obtained was separated by filtration and then dried in vacuum oven at 100°C (4 h), 200°C (2 h), and 300°C (1 h) to ensure complete cyclization. The resulting PI was insoluble in common organic solvents and was infusible. Received PI was crushed in a pestle and mortar and finally micronized using a cryo-grinder. PI powder was sieved to get particles of 5–20 μm in diameter.

Preparation of membranes

PDMS membrane was prepared by casting solution of PDMS RTV 2/Silastic 9050/30P [Part A and part B in the ratio of 10 : 1]. Required amounts of PDMS solution (part A and part B in the ratio of 10 : 1) were mixed thoroughly using a magnetic stirrer for about 1 h. After degassing, the solution was then spread on the teflon sheet supported by a glass plate with the help of doctor's blade. It was then left overnight for curing. Resulting PDMS membrane was annealed at 150°C for 8 h under vacuum to ensure complete curing.

Similarly, PI powder filled PDMS membranes were prepared by mixing PDMS (part A: part B – 10 : 1) with varying amounts of PI ranging from 5–25% (w/w). For the preparation of filled membranes, PI filler was first homogeneously dispersed in the silicone fluid (Part A) with the help of a turbine-type impeller. The crosslinker (Part B) was then added and mixed thoroughly using magnetic stirrer for 1 h. The resulting mixture was then degassed under vacuum, spread on a teflon sheet supported by a glass plate and cured overnight. Curing of the resulting film was done by annealing it at 150°C for 8 h under vacuum. Due to low resistance of PDMS material, all the membranes were casted having thickness of 80 μm. The measurement of thickness was done by digital micrometer (Mitutoyo) and is an average of 20 points from the membrane area (100 cm²). Several samples were prepared by taking 5, 10, 15, 20, and 25% (w/w) of PI filler and the samples have been designated as SPI-5, SPI-10, SPI-15, SPI-20, and SPI-25.

CHARACTERIZATION

FTIR studies

IR spectra of PI and PDMS/PDMS-PI membranes were recorded using a Thermo Nicolet 6700 spectrophotometer at a resolution of 4cm^{-1} .

Thermal characterization

Thermogravimetric analysis was done using TA thermogravimetric analyzer, Model TGA-2950. A heating rate of $10^\circ\text{C}/\text{min}$ and a sample size of 5 ± 2 mg was used in each experiment. Thermogravimetric traces were recorded in nitrogen atmosphere (flow rate $60\text{ mL}/\text{min}$).

Morphological characterization

The morphology of cross-section of membranes was studied using scanning electron microscope (SEM) (JEOL JSM 840, magnification 200,000X at 5 kV and 6×10^{-10} A) after coating with gold using an ion sputter (JFC-1100) (Fig. 3). Distribution of PI particles in PDMS solution is uniform [Fig 3(a,b)]. Figure 3(c,d) indicated that PI filler particles were completely wetted by PDMS as no air gap is visible at the interface of PDMS and PI filler.

Determination of sorption

For sorption studies, dry membranes of predetermined weight (W_d) were immersed in benzene, toluene, and water, separately at $30 \pm 1^\circ\text{C}$ for 72 h to allow them to attain an equilibrium sorption. The specimens were removed from the container and quickly wiped with tissue paper to remove superfluous liquid. The weight of swelled membrane (W_s) was recorded on a Shimadzu balance with an accuracy of 1×10^{-4} g. The average of three measurements was taken to determine the extent of sorption also called swelling index (Q) as per the equation given below.¹⁷

$$Q = (W_s - W_d)/W_d \times 100 \quad (1)$$

where W_s is the weight of membrane after immersion in benzene, toluene, or water and W_d is the dry weight of membrane.

Sorption isotherms

The sorption isotherms for benzene, toluene, and water vapor were determined using an automated sorption analyzer termed Intelligent Gravimetric Analyzer (IGA) procured from M/s Hiden Analytical, (England). The measurement was done on the basis of mass relaxation in the polymer accompany-

ing vapor sorption. The concentration of vapors was increased in 14–16 equal steps at constant temperature of $30 \pm 1^\circ\text{C}$ and the corresponding increase in weight of the samples was monitored to obtain the sorption, which were fitted into appropriate sorption models and converted to the isotherms by software. The change in weight of polymer with time was recorded and the isotherm was approximated from the kinetic data by auto fitting into the appropriate sorption models.¹⁸

Pervaporation studies

The PV experiments were carried out at $30 \pm 1^\circ\text{C}$ using a batch stirred reactor described by Netke et al.¹⁸ The effective membrane area was 29.40 cm^2 . The membrane was supported on a filter paper over a porous sintered steel disk having 6.4 cm dia. Before PV experiments, membrane was allowed to equilibrate with the feed solution for 24 h. After the attainment of steady state, the permeate was condensed in cold traps immersed in liquid nitrogen. The permeate composition was determined by gas chromatography equipped with thermal conductivity detector maintained at a temperature of 90°C and OV-17(3 wt %, 100–120 mesh) stainless steel column 1.8288 m (6ft.) \times 0.3175 mm (1/8 in. \times 2 mm) at a temperature of 300°C . The injector was kept at 90°C . The downstream pressure was maintained at 1 mm Hg in all the experiments. The flux (J) was determined by measuring the weight of permeate and using the eq. (2).¹⁷

$$J = w/Ah \quad (2)$$

where A is the effective membrane area and h is the time for the PV. The normalized flux (J') was obtained from the product of flux and thickness (μm) of the membrane.

The permeation selectivity (γ_p) was calculated using the following eq. (3).¹⁷

$$\gamma_p = \frac{Y_{\text{organics}}/Y_{\text{water}}}{X_{\text{organics}}/X_{\text{water}}} \quad (3)$$

where Y and X are the weight fractions of water and organic species in the feed and permeate, respectively.

RESULTS AND DISCUSSION

The transport phenomenon of PV separation through nonporous polymer membrane is described by solution-diffusion theory, which occurs in three steps i.e. sorption, diffusion, and desorption.¹⁹ The desorption step of vapor at the permeate side is very

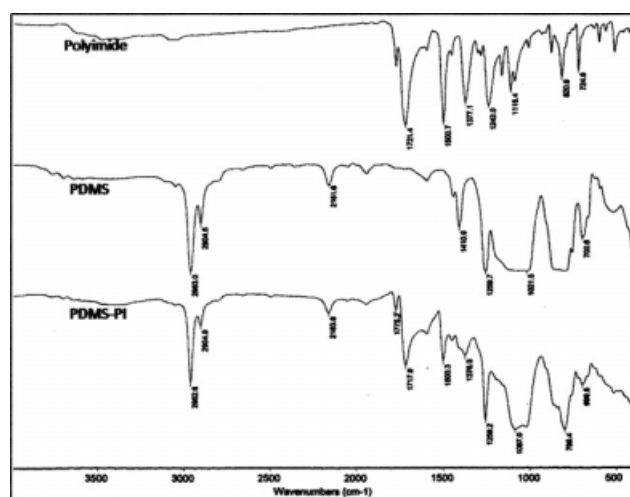


Figure 1 FTIR Spectra of PDMS, polyimide, and SPI-25 membrane.

rapid and nonselective due to low pressure at the downstream side. The characteristics of sorption and the diffusion depend on (a) the difference between the affinities of the components towards the polymer, (b) mutual interaction of the components, and (c) the way interactions with the polymer of one component affect the interactions of the other penetrant with the polymer. These interactions are affected by temperature and the feed concentration. Thus, to evaluate the overall permselective properties, the temperature was varied between 30–75°C and the feed concentration in the range of 0–100 wt % [benzene or toluene].

Characterisation of polyimide and membranes

Figure 1 shows the FTIR spectrum of PI synthesized in this work. In the FTIR spectrum of PI, sharp bands observed around 1775 cm^{-1} (C=O asymmetric stretching), 1721 cm^{-1} (C=O asymmetric stretching), 1377 cm^{-1} (C–N stretching), and 721 cm^{-1} (C=O bending) are the characteristic absorption bands of a PI. On the other hand, no characteristic band of a polyamic acid around 3363 cm^{-1} (N–H stretching) and 1650 cm^{-1} (amide C=O strength) were found

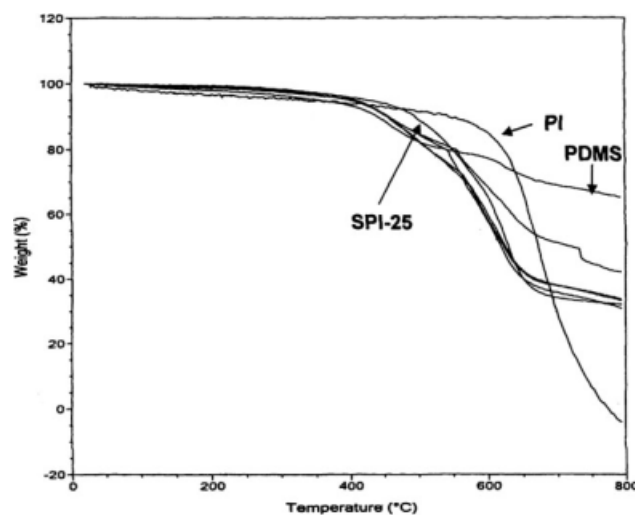


Figure 2 TG traces of Polyimide, PDMS, SPI-5, SPI-10, SPI-15, SPI-20, and SPI-25.

thus indicating complete cyclization of polyamic acid to form PI.²⁰

In the FTIR spectrum of PDMS (Fig. 1), a strong peak 1087 cm^{-1} corresponding to symmetrical Si–O–Si stretching was present. Asymmetric C–Si–O stretching for linear polymer was seen in PDMS and PDMS-PI polymers at 1259 cm^{-1} . Characteristic asymmetric and symmetric methyl stretching was also present at 2962 cm^{-1} and 2905 cm^{-1} . The FTIR spectra of PDMS and PI filled PDMS showed only a marginal shift in absorption frequencies; indicating the absence of any chemical interaction between PDMS and PI (Fig. 1).

Figure 2 shows the TG traces of PI, PDMS, and PDMS having varying amounts of PI filler. In all the samples, single step degradation was observed. The relative thermal stability of the samples was compared by comparing the initial decomposition temperature, and the decomposition temperature at various percent mass losses. The results are summarized in Table I. TG curves of PDMS and PDMS-PI membranes indicated that the addition of PI improves the thermal stability of PDMS. It is evident that decomposition temperature increased from

TABLE I
Thermal and Mechanical Properties of Membrane SPI-25

Membrane	T ₁₀	Tensile strength (MPa)	Elongation at break (%)	Modulus at 100% elongation (MPa)
PDMS	440	1.5	110.0	0.53
SPI-5	455	1.6	103.0	0.61
SPI-10	456	1.8	89.0	0.71
SPI-15	455	1.8	88.0	0.62
SPI-20	455	2.0	85.0	0.52
SPI-25	496	2.7	88.0	0.65
Polyimide	543	70.0	9.0	1.6

T₁₀ = decomposition temperature at 10% mass loss.

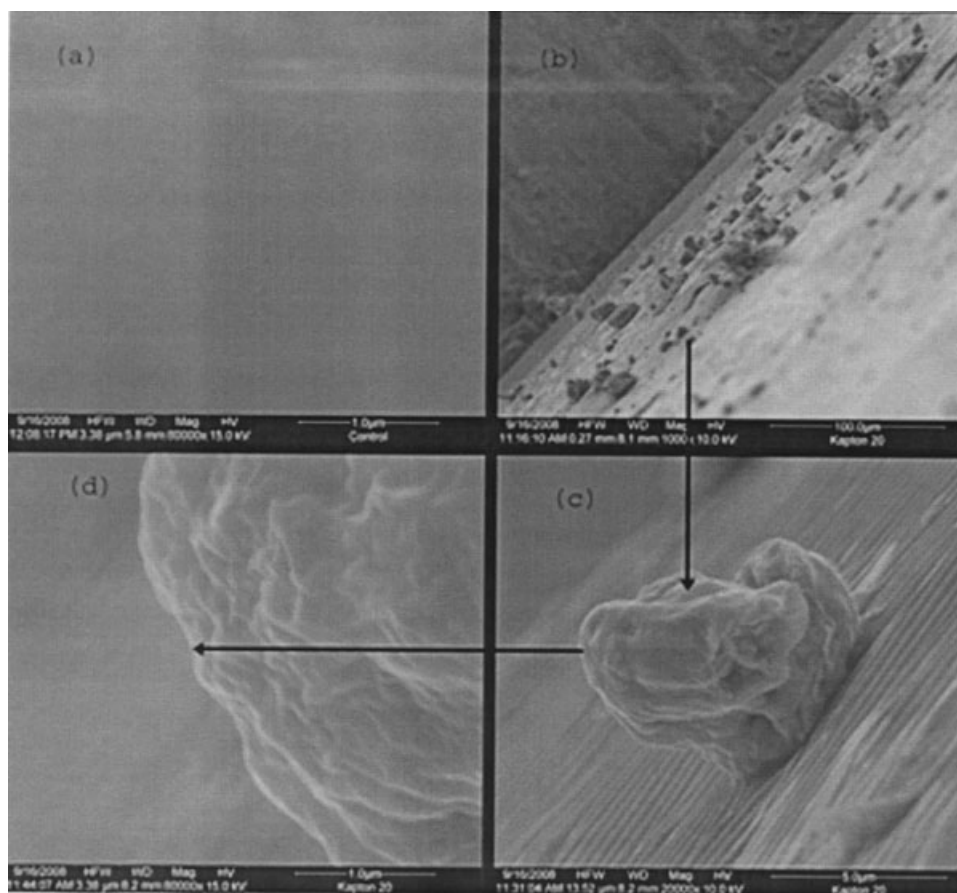


Figure 3 SEM pictures of (a) surface of PDMS membrane, (b) cross-section of SPI-25 membrane at 1000x, (c) 2000x, and (d) interface of PI particle and PDMS matrix at 80,000X.

about 400°C for pure PDMS to about 500°C for 25 wt % PI filled PDMS membrane. Interestingly, the mass loss is much larger for the PI-filled PDMS than that for pure PDMS. One possible explanation may be that the presence of PI particles helps to protect PDMS from thermal attack. On the other hand, the presence of PI particles also interferes with the cross linking of PDMS at the curing stage and makes PDMS less cross-linked. The former effect helps to raise the decomposition temperature, while the latter effect makes PDMS easier to decompose into smaller and thus more volatile products, leading to a more rapid mass loss.

Mechanical properties of various PI-filled PDMS membranes were evaluated at room temperature on a Miniature Material Tester, Rheometric Science according to ASTM D 882-02. Tests were carried out with strain rate of 5%/min. At least three measurements were performed for each membrane sample and the average values are reported in this study. As observed from Table I, the use of PI as filler increases its tensile strength from 1.5 MPa to 2.7 MPa at the expense of elongation at break. SPI-25 membrane with sufficient value of tensile strength and thermal stability prompted us to choose the membrane for PV application.

The uniformity of PI particles distribution in PDMS solution is clear from SEM images taken at various magnifications [Fig 3(a,b)]. Figure 3(c,d) indicated that PI filler particles were completely wetted by PDMS as no air gap is visible at the interface of PDMS and PI filler.

Sorption studies

According to the solution-diffusion theory, mass transport in PV consists of sorption of the permeant at the liquid side of the membrane and desorption at the low pressure side of the membrane. Sorption in PV produces membrane swelling and causes loosening of the polymer matrix facilitating diffusion of the permeants. The degree of sorption calculated using eq. (1) indicated that the membrane SPI-20 and SPI-25 have highest sorption of Tol and Bz and lowest sorption for water when compared with other membranes having low PI filler (Fig. 4). The increase in sorption of Tol and Bz in PI-filled PDMS membrane compared to those of unfilled PDMS membrane might be due to the hydrophobic nature of PI filler. Also increased swelling of SPI-25 membrane with respect to Tol may be attributed to the higher polar-polar interactions of Tol compared with Bz.

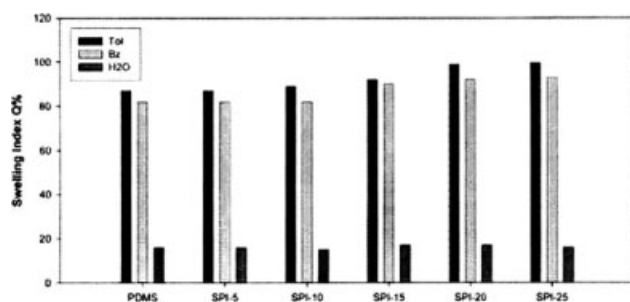


Figure 4 Swelling index of various polymer membranes in toluene, benzene, and H₂O.

The earlier observations on the sorption characteristics of PDMS-PI membrane are also supported by vapor sorption isotherms for Toluene, Benzene, and water using automated sorption analyzer IGA. The isotherms plotted in Figure 5 provide the dynamics and magnitude of sorption over entire P/P_0 (corresponding to concentration or activity) ranging from 0.06 to 0.98. The isotherm for pure Tol and pure Bz lie toward the ordinate and for water toward the abscissa, implying that interaction of PDMS-PI with Tol and Bz is higher than those of water for any concentration. This result in almost 4–5 times higher vapor sorption of Tol and Bz than water.

Pervaporation characteristics

The PV potential of a membrane is assessed in terms of two important parameters namely, flux (J), i.e. the mass crossing the membrane per unit area in a unit time and selectivity (α_p) towards the preferentially permeated component. The flux values are generally normalized with respect to thickness of the mem-

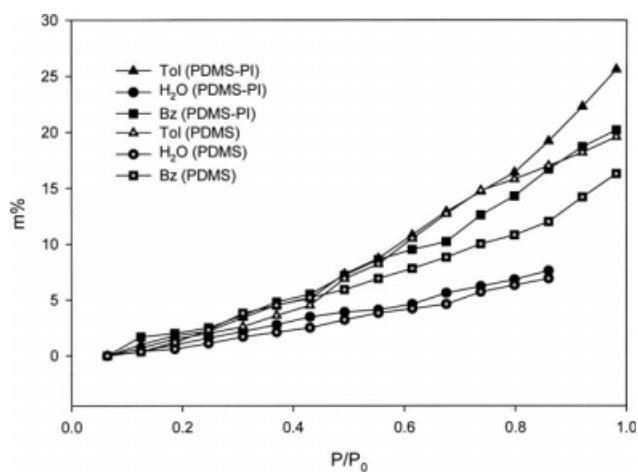


Figure 5 Sorption Isotherm of Tol, Bz, and H₂O vapors on SPI-25 at 30°C. P , Pressure (mbar); P_0 , saturation vapor pressure (mbar); P/P_0 , relative pressure \approx activity or concentration; w , weight of sample; m , mass uptake of vapors (%).

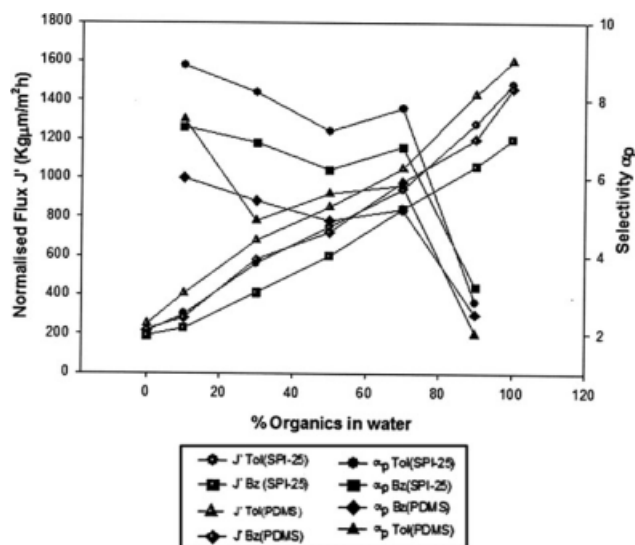


Figure 6 Normalized flux and selectivity at $30 \pm 1^\circ\text{C}$ as a function of feed composition.

brane. The PV performance of the PDMS membrane and modified SPI-25 membrane are shown in Figure 6. Both the membranes were investigated for Tol and Bz flux and selectivity for the entire range of Tol/water and Bz/water feed compositions (Fig. 7). For SPI-25 membrane, the normalized flux values increased with increasing amount of Tol/Bz in the feed, varying from 210 $\text{g } \mu\text{m}^2/\text{h}$ for pure water, 1480 $\text{g } \mu\text{m}^2/\text{h}$ for pure Tol, and 1200 $\text{g } \mu\text{m}^2/\text{h}$ for pure Bz. For Tol the separation factor varied between 8.9 and 7.8 with the feed Tol concentration upto 70% and then decreased to 2.8 at 90% Tol. For Bz, the separation factor varied between 7.3 and 6.8 with the feed Bz concentration upto 70% and then decreased to 3.2 at 90% Bz. This may be explained by the effect of plasticity of polymer chains on the separation process. When the feed concentration increases, Tol/Bz tends to plasticize the

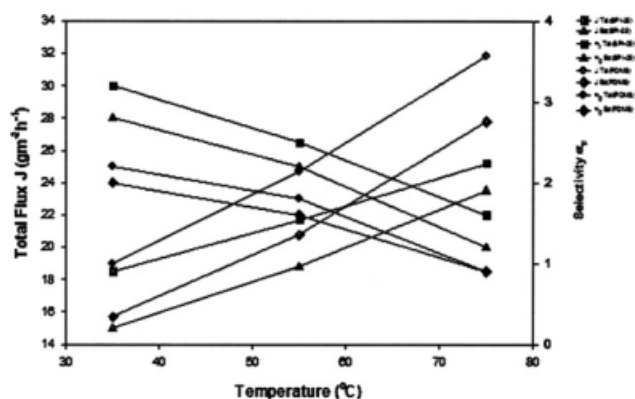


Figure 7 Temperature dependence of total flux (J) and selectivity (α_p) in the pervaporation of Tol/H₂O and Bz/H₂O through SPI-25 membrane.

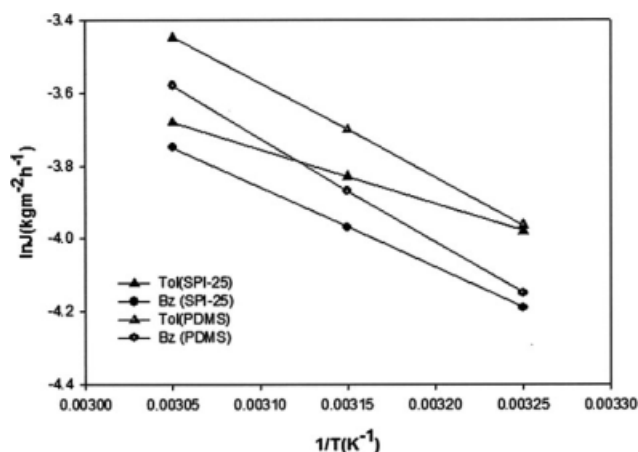


Figure 8 Arrhenius plot for PV of Tol/H₂O and Bz/H₂O (90 : 10% (w/w)) through SPI-25 membrane.

membrane, the relaxed polymer chains, thus becoming accessible to water molecules as well, thereby reducing the selectivity. The values of normalized flux for SPI-25 membrane are comparatively lower as compared with that for PDMS membrane but the selectivity is higher as compared with PDMS membrane. This may be due to the creation of torturous path for permeates diffusion by PI filler but the enrichment factor (selectivity) increases for the organics due to filling of ultra micro free volume by hydrophobic PI filler.

Temperature dependence of flux and selectivity

The PV process is known to be temperature dependent²¹⁻²³ as both flux and selectivity are influenced by the change in temperature. The dependence of PV of Bz/H₂O and Tol/H₂O binary mixture (90 : 10% (w/w)) was investigated at a temperature ranging from 35 to 75°C. From the results depicted in Figure 6, it is observed that total flux for SPI-25 membrane increases from 18.5 to 25.2 g⁻²h⁻¹ for Tol and 15.0 to 23.5 g⁻²h⁻¹ for Bz with the concomitant decrease in selectivity from 3.2 to 1.6 for Tol and from 2.8 to 1.2 for Bz. The increase in flux at higher temperature may be attributed to the increase in free volume of polymer and increased kinetic energy of the permeates, which assist their diffusivity through matrix of the membrane. The latter effect also causes the decrease in selectivity as the diffusivity of both the permeates is facilitated.²⁴

To determine the energy of activation (E_j) for the PV process, $\ln J$ was plotted against the inverse of temperature (K) in accordance with the extensively used Arrhenius type of relationship²⁴

$$J = J_0 \exp(-E_j/RT) \quad (4)$$

E_j as determined from the slope of the plot in Figure 8 was 18.3 kJ/mol for Bz and 12.5 kJ/mol for

Tol for sample SPI-25, whereas for PDMS E_j values were higher i.e. 21.9 kJ/mol for Bz and 23.27 kJ/mol for Tol. E_j thus calculated is a compounded parameter characterizing the overall temperature dependence of permeation flux.²⁴ The E_j is also dependent upon the nature of the membrane material and feed composition; the reported values range from 13 to 53 kJ/mol for various other polymers.²⁴ A comparatively lower E_j obtained in this study implies that the PV of Bz/H₂O and Tol/H₂O may be more facilitated in PDMS-PI membrane as compared to the PDMS membranes.

CONCLUSIONS

PI filled PDMS membrane prepared by the incorporation of synthesized PI filler showed potential use of membrane for the pervaporative separation of Tol/H₂O and Bz/H₂O. These membranes show a substantially high normalized flux i.e. of the order of 1.48 kg $\mu\text{m}^2/\text{h}$ for Tol, 1.20 kg $\mu\text{m}^2/\text{h}$ for Bz and a lower activation energy (E_j) i.e. 12.5 kJ/mol for Tol, 18.3 kJ/mol for Bz. The composite membrane based on PDMS-PI has an excellent dimensional stability, better mechanical strength, and improved thermal stability as compared to PDMS.

The authors thank Dr P. K. Gutch and Mr. Anchal Srivastava for recording TGA and SEM images.

References

- Peng, M.; Vane, L. M.; Liu, S. X. *J Hazard Mater* 2003, 98, 69.
- Smitha, B.; Suhanya, D.; Sridhar, S.; Ramakrishna, M. *J Membr Sci* 2004, 241, 1.
- Sain, S.; Dincer, S.; Savascyi, O. T. *Chem Eng Process* 1998, 37, 203.
- Pandey, L. K.; Saxena, C.; Dubey, V. *J Membr Sci* 2003, 227, 173.
- Pandey, L. K.; Saxena, C.; Dubey, V. *Separ Purif Technol* 2005, 42, 213.
- Dubey, V.; Pandey, L. K.; Saxena, C. *J Membr Sci* 2005, 251, 131.
- Dubey, V.; Pandey, L. K.; Saxena, C. *Separ Purif Technol* 2006, 50, 45.
- Gutch, P. K.; Pandey, L. K.; Saxena, C. *J Appl Polym Sci* 2008, 110, 203.
- Li, L.; Xiao, Z. Y.; Zhang, Z. B.; Tan, S. J. *Chem Eng J* 2004, 97, 83.
- Dutta, B. K.; Sikdar, S. K. *AIChE J* 1991, 37, 581.
- Tehehnepe, H. J. C.; Bargeman, D.; Mulder, M. H. V.; Smolders, C. A. *J Membr Sci* 1987, 35, 39.
- Ray, S.; Ray, S. K. *J Membr Sci* 2006, 270, 132.
- Kumar, S.; Shah, J. N.; Sawant, S. B.; Joshi, J. B.; Pangarkar, V. G. *J Membr Sci* 1997, 134, 225.
- Ding, M. X.; He, T. B. *A New Class Materials of Polyimides*; Science Press: Beijing, 1998, pp 1-21.
- Fang, X. Z.; Yang, Z. H.; Zhang, S. B.; Gao, L. X.; Ding, M. X. *Polymer* 2004, 45, 2539.
- Sroog, C. E.; Endrey, A. L.; Abramo, S. V.; Berr, C. E.; Edwards, W. M.; Oliver, K. L. *J Polym Sci* 1965, 3, 1373.

17. Dubey, V.; Saxena, C.; Singh, L.; Ramana, K. V.; Chauhan, R. S. *Separ Purif Technol* 2002, 27, 163.
18. Hiden Analytical Limited. IGA System User Manual, Document No. HA-085-060, Issue A, Appendix E; Hiden Analytical Limited: UK, 2005.
19. Neel, J. In *Pervaporation Membrane Separation Process*; Huang, R. Y. M., Ed.; Elsevier: Amsterdam, 1991; Chapter 1.
20. Yang, C. P.; Chen, R. S.; Chen, K. H. *J Appl Polym Sci* 2005, 95, 922.
21. Yin, J.; Ye, Y. F.; Li, L.; Huang, Y.; Wang, Z. G. *Eur polym J* 1999, 35, 1367.
22. Van Krevelen, D. W. *Properties of Polymers*; Elsevier: The Netherlands, 1990.
23. Matsuura, M. *Synthetic Membrane Technology*; Kluwer: The Netherlands, 1999.
24. Wijmanns, J. G.; Baker, R. W.; Athayde, A. L. In *Membrane Process in Separation and Purification*; Crespo, J. G., Boddiker, K. W., Eds.; Kluwer: The Netherlands, 1994; p 1.