Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Performance of Composite Membranes of Poly(ether-*block*-amide) for Dehydration of Ethylene Glycol and Ethanol

S. Sridhar[a]; S. Kalyani[a]; Y. V. L. Ravikumar[a]; T. S. V. N. Muralikrishna[a]
[a] Membrane Separations Group, Chemical Engineering Division, Indian Institute of Chemical Technology, Hyderabad, India

To cite this Article Sridhar, S. , Kalyani, S. , Ravikumar, Y. V. L. and Muralikrishna, T. S. V. N.(2010) 'Performance of Composite Membranes of Poly(ether-*block*-amide) for Dehydration of Ethylene Glycol and Ethanol', Separation Science and Technology, 45: 3, 322 — 330
To link to this Article: DOI: 10.1080/01496390903409468
URL: http://dx.doi.org/10.1080/01496390903409468

Separation Science and Technology, 45: 322–330, 2010

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390903409468

Performance of Composite Membranes of Poly(ether–*block*–amide) for Dehydration of Ethylene Glycol and Ethanol

S. Sridhar, S. Kalyani, Y. V. L. Ravikumar, and T. S. V. N. Muralikrishna
Membrane Separations Group, Chemical Engineering Division, Indian Institute of Chemical Technology, Hyderabad, India

---

Poly(ether–*block*–amide) (Pebax 2533) membrane was synthesized on a poly(vinylidene fluoride) (PVDF) ultraporous substrate to study the separation of synthetic ethylene glycol/water and ethanol/water mixtures by pervaporation. The membrane was characterized by FTIR spectroscopy, DSC, SEM, and XRD to assess intermolecular interactions, thermal stability, surface morphology, and crystallinity, respectively. Equilibrium sorption studies were carried out in pure liquids and binary alcohol-water mixtures of different compositions to assess polymer-liquid interactions. Pebax 2533 membrane exhibited the requisite potential for dehydration of the alcohols by showing a selectivity of 1254 and water flux of $0.05\,\mathrm{kg\,m^{-2}\,h^{-1}}$ for the ethanol azeotrope, whereas the corresponding selectivity for 95% ethylene glycol feed was 978 with a similar flux. The effect of operating parameters such as feed composition and permeate pressure on membrane performance was evaluated. The membrane exhibited considerable feasibility for scale-up with significant potential for alcohol dehydration.

Keywords alcohol dehydration; membrane characterization; Pebax 2533 membrane; pervaporation

INTRODUCTION

The block copolymer membranes for separation of azeotropic and close boiling liquid mixtures by pervaporation (PV) have potential advantages such as low-energy requirements, effective separation of azeotropes, eco-friendly nature, and easy operation compared to azeotropic distillation (1–3). The first PV membrane, a composite of Poly(acrylonitrile) (PAN) support with Poly(vinyl alcohol) (PVA) skin layer developed by Gesellchaft Fuer Trenntechnik (GFT), Germany, showed high selectivity and flux for alcohol dehydration. Composite membranes (4,5), charged membranes (6,7), poly ion complex membranes (8), copolymer (9), and graft copolymer membranes (10,11) have also been used in specific PV separation problems. Often, the goal of membrane modification was to create a material with enhanced barrier properties in terms of flux and selectivity. Pebax 2533 is a block copolymer with 80% ether groups and 20% amide segments.

The limited literature on Poly (ether–*block*–amide) (Pebax) membranes have shown promise for PV (12) and gas separation (13) applications and therefore extensive investigations are worthwhile. Some Pebax grades possess high affinity for water. Therefore, this block copolymer was chosen to study the separation of water from ethanol and ethylene glycol (EG) individually. The availability of a wide range of co-polymers allows unique insights into structure-property relationships, which play a vital role in polymer selection. Depending on the composition of the copolymer, Pebax grades can exhibit two glass transition temperatures far below and above room temperature. Pebax 2533 grade presently used in this study is comprised of 80% ether block and 20% amide block. Pebax has been evaluated for the separation of acetone/water mixtures by PV (14). Copolymer properties were predicted by Rezac et al. (15), based on the transport properties of homopolymers made from the monomer units of Pebax. The transport properties of the water through polyamide have been reviewed by Razumovskii et al. (16). The present study intends to provide an insight into the PV–based dehydration of ethanol and ethylene glycol using predominantly rubbery Pebax membranes.

EXPERIMENTAL

Materials

Poly(vinylidine fluoride) (PVDF) used to prepare the ultraporous substrate for Pebax membrane was procured from Permionics, Vadodara. Pebax 2533 was purchased from M/s Autofina, France. Ethanol and ethylene glycol of analytical grade were purchased from Loba Chemicals, Mumbai, India. Deionized water of conductivity of $0.02\,\mathrm{mS\,cm^{-1}}$ was generated in the laboratory for the preparation of feed solutions.

Synthesis of Pebax 2533 Membrane

Composite membranes of poly(ether–*block*–amide) (Pebax) for pervaporation were prepared on polyvinylidene

---

Received 23 December 2008; accepted 30 September 2009.

Address correspondence to S. Sridhar, Membrane Separations Group, Chemical Engineering Division, Indian Institute of Chemical Technology, Uppal Road, Hyderabad 500007, India. Tel.: +91-40-27191394; Fax: +91-40-27193626. E-mail: sridhar11in@yahoo.com

(PVDF) ultrafiltration substrate by solution casting and solvent evaporation technique. Ultra-porous PVDF substrate was prepared by the phase inversion technique from a 20% (w/v) solution of the polymer in N,N′-dimethyl formamide solvent which also contained 4% LiCl salt as an additive. The film was cast onto a non-woven polyester fabric and gelled in an ice-cold water bath for 5 min. The molecular weight cut off (MWCO) of PVDF support was determined to be approximately 100000 Daltons using aqueous solutions of polyethylene glycol. For Pebax 2533, a bubble-free solution of 20% (w/v) of the polymer in isobutanol was prepared at 100°C and cast on PVDF substrate to the desired thickness using a doctor's blade. Solvent was evaporated in an oven at 150°C for 3–5 min to obtain Pebax 2533 composite membrane.

Membrane Characterization

Fourier Transform Infrared (FTIR) Studies

The FTIR spectrum of Pebax membrane was scanned in the range between 4000 cm^{-1} and 400 cm^{-1} using Nicolet-740, Perkin-Elmer-283B FTIR Spectrometer by KBr pellet method.

X-Ray Diffraction (XRD) Analysis

A Siemens D 5000 powder X-ray diffractometer was used to study the solid-state morphology of Pebax membrane in powdered form. X-rays of 1.5406 Å wavelengths were generated by a CuK source.

Differential Scanning Calorimetry (DSC)

DSC experiments were performed in an organ atmosphere by taking of 7.1 mg of sample films on a Perkin-Elmer DSC Model 7 instrument. Measurements were performed over the temperature range of 30°C to 300°C at a heating rate of 5°C/min in thermatically-sealed aluminum pans. Membrane samples were allowed to attain steady state with the solvents and the sample pan-conditioned in the instrument before running the experiment.

Scanning Electron Microscopy Studies

Scanning electron micrographs (SEM) are taken for the Pebax 2533 membrane, using a software controlled digital scanning electron microscope–JEOL JSM 5410, Japan.

Determination of Ion Exchange Capacity (IEC)

The ion exchange capacity (*IEC*) indicates the number of milliequivalents of ions in 1 g of the dry polymer. To determine the degree of substitution by acid groups, Pebax membrane was soaked in 50 ml of 0.01 N sodium hydroxide solution for 12 h at ambient temperature. Then, 10 ml of the solution was titrated with 0.01 N sulfuric acid. The sample was regenerated with 1 M hydrochloric acid, washed free of acid with water and dried to a constant weight. The *IEC* was calculated according to:

$$IEC = \frac{B - P * 0.01 * 5}{m}$$

where *IEC* was the ion exchange capacity ($\mathrm{meq\,g}^{-1}$), *B* the amount of sulfuric acid used to neutralize blind sample soaked in NaOH (ml), *P* the amount of sulfuric acid used to neutralize the sulfonated membrane soaked in NaOH (ml), 0.01 the normality of the sulfuric acid, '5' the factor corresponding to the ratio of the amount of NaOH taken to dissolve the polymer to the amount used for titration, and m the sample mass (g).

Sorption Characteristics

A pre-weighed sample was immersed in pure water and ethanol and ethylene glycol as well as binary mixtures of different compositions and allowed to reach sorption equilibrium at room temperature (for at least 10 h). The swollen sample was removed from the solvent mixture, wiped with tissue paper to remove the surface liquid, and immediately weighed. The process was repeated until the films attained steady state as indicated by constant mass after a certain period of soaking time. The degree of swelling (DS), which characterizes the ability of the membrane to absorb the liquid mixture, was obtained as the ratio of mass of swollen polymer (*Ms*) and mass of dry polymer (*Md*). The sorption represents the fraction of extracted liquid mixture by the membrane.

Pervaporation Procedure

Experiments were carried out with an indigenously constructed pervaporation manifold (Fig. 1) operated at a low vacuum in the permeate side. The membrane area in the pervaporation cell assembly was approximately 20 cm^2. The experimental procedure was described in detail elsewhere (17). Permeate was collected for a duration of 8–10 hours. Tests were carried out at room temperature (30 ± 2°C) and repeated twice using fresh feed solution. The collected permeate was weighed after allowing it to attain room temperature in a Sartorius electronic balance (accuracy: 10^{-4} g) to determine the flux and then analyzed by gas chromatography to evaluate membrane selectivity.

Flux and Selectivity Equations

In pervaporation the flux *J* of a given species, say faster permeating component *I* of a binary liquid mixture comprising of *i* (water) and *j* (ethanol) was given by

$$J_i = \frac{W_i}{At}$$

where *Wi* represents the mass of water in permeate (Kg), *A* was the membrane area (m^2) and *t* represents the

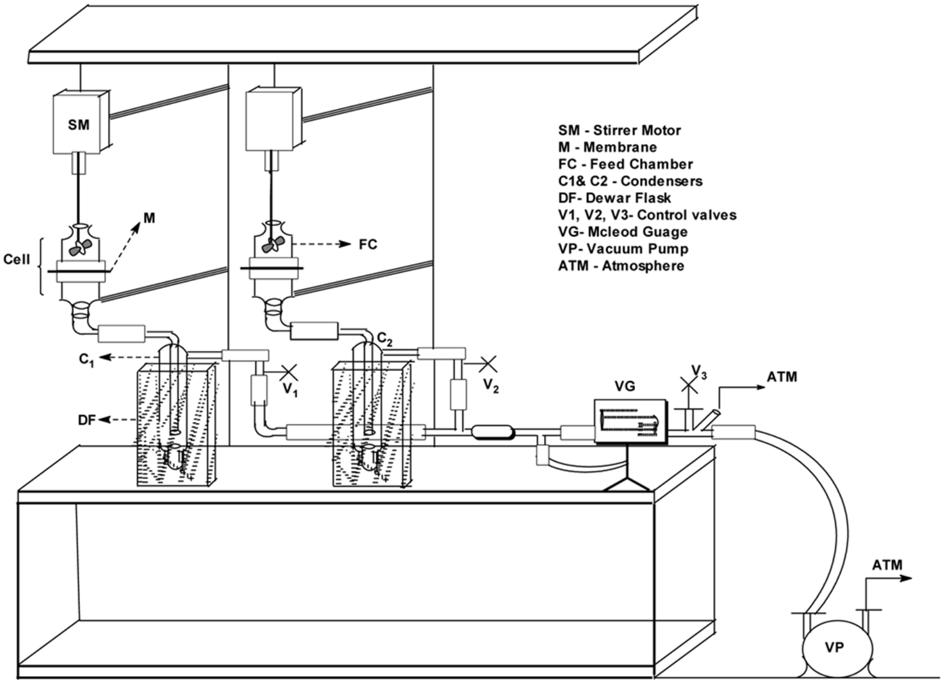


FIG. 1. Schematic of laboratory vacuum pervaporation set-up.

evaluation time (h). The membrane selectivity (α) was the ratio of the permeability coefficients of water and ethanol and can be calculated from their respective percentages in feed and permeate as given below.

$$\alpha = \frac{y(1-x)}{x(1-y)}$$

Here, y was permeating mass content of water (%) and x was its feed mass content. Pervaporation separation index (PSI) was a measure of the separation capability of a membrane and was expressed as a product of selectivity and flux (18).

$$\mathrm{PSI} = J \times \alpha$$

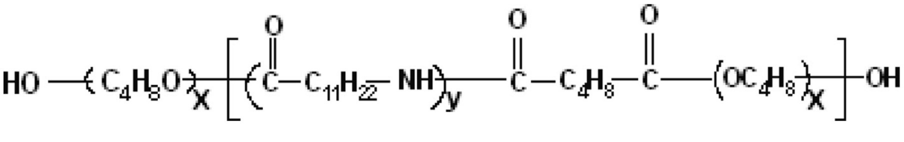
Analytical Procedure

The feed and permeate samples were analyzed using a Nucon Gas Chromatograph (GC Model 5765) installed with Thermal Conductivity Detector (TCD) and packed column of 10% DEGS on 80/100 Supelcoport of 1/8 ID and 2 meters length. The oven temperature was maintained at 70°C (isothermal) while the injector and detector temperatures were maintained at 150°C each. The sample injection size was 1 μl and pure hydrogen was used as the carrier gas at a pressure of $1\,\mathrm{kg\,cm^{-2}}$. The GC response was calibrated for this particular column and conditions with known compositions of ethanol-water mixtures and the calibration factors were fed into the software to obtain a correct analysis for unknown samples.

RESULTS AND DISCUSSION

Ion Exchange Capacity (IEC)

The amount of residual amide, ether and acetate groups in Pebax membrane was estimated from ion exchange capacity (IEC) studies. The IEC of Pebax was found to be $0.55\,\mathrm{meq\,g^{-1}}$, which was equivalent to the total number of the above functional groups present in the membrane. This was also confirmed by the general chemical structure of Pebax as given in Fig. 2 which was a thermoplastic elastomer consisting of rigid polyamide linear blocks and flexible polyether linear blocks (19,20). The Pebax membrane layer was peeled off the support before characterization by different methods.



$$\mathrm{HO}-\!\left(\mathrm{C_4H_8O}\right)_X\!\left[\left(\overset{\overset{\displaystyle O}{\|}}{C}-\mathrm{C_{11}H_{22}}-\mathrm{NH}\right)_y-\overset{\overset{\displaystyle O}{\|}}{C}-\mathrm{C_4H_8}-\overset{\overset{\displaystyle O}{\|}}{C}-\left(\mathrm{OC_4H_8}\right)_X\right]\!-\mathrm{OH}$$

FIG. 2. Chemical structure of poly(ether–*block*–amide) (Pebax) [Amide Y = 0.2, Ether X = 0.8].

Fourier Transform Infrared (FTIR) Studies

An FTIR spectrum of Pebax is shown in Fig. 3. The characteristic peaks at 1740 and 1100 cm^{-1} are attributed to $-\mathrm{C{=}O}$ and $-\mathrm{C{-}O}-$ stretching vibrations, respectively. Two peaks observed at 1640 and 3300 cm^{-1} indicate the presence of $\mathrm{H{-}N{-}C{=}O}$ and $\mathrm{N{-}H}$ groups, respectively. It is expected that the $\mathrm{N{-}H}$ groups would have preferential interaction with water present in the feed solutions through hydrogen bonding. Absorption band of the ester carbonyl stretching appear from 1700 to 1800 cm^{-1}. Two absorption bands have overlapped in this range: one at 1739 cm^{-1}, which is the absorption band of hydrogen-bonded carbonyl, while the other is at 1780 cm^{-1} representing the free ester carbonyl, which appears as a shoulder band attached to the first band. Mixing of hard and soft segments of the polymer is also possible and may increase with increasing feed temperature.

DSC Studies on Pebax 2533 Membrane

Figure 4 shows the DSC curve of Pebax where two endothermic peaks are evident whose maxima occur approximately at 50°C and 240°C. These endotherms can be attributed to fusion of the crystalline fraction of the blocks of the soft poly(ethylene oxide) (PEO) and the rigid polyamide (PA), respectively. The peak observed at 50°C is the melting temperature (T_m) of PEO, whereas the peak at 240°C corresponds to T_m of PA. The difficulty in identifying T_g may be attributed to the interference of melting signals of polyamide crystallites. The existence of two widely apart endothermic peaks for the polymer reconfirms literature reports that Pebax has a microphase-separated structure in the solid state (21).

Figure 4 corroborates the structure of Pebax displayed in Fig. 2. The selectivity of the polymer could be attributed to the hard segment comprised of amide groups. Pebax 2533 consists of 80% ether groups (soft block) and 20% amide groups (hard block). The soft block is flexible and allows permeation of both water and alcohol molecules. The difference in permeation rates through the ether block depends only on the diffusion coefficients. The smaller water molecule can diffuse faster compared to ethanol or ethylene glycol. The hard amide block is rigid and restricts the movement of the bigger sized alcohol molecules which are the less polar compared to water. The amide group is involved in hydrogen bonding with the water molecules which get preferentially sorbed in the hard block and get transported into the permeate side.

SEM Studies on Pebax 2533 Membrane

The surface and cross-sectional morphologies of PVDF substrate and Pebax composite are combined together for comparison purpose. From Fig. 5(a), it can be noticed that the surface of the PVDF shows the presence of fine pores which become much tighter and appear to be distributed uniformly across the membrane. The pores in the PVDF ultrafiltration substrate completely disappear upon coating it with Pebax as evidenced from Fig. 5(b), which shows a defect-free morphology. The cross-sectional views of PVDF and Pebax composite are shown in Figs. 5(c) and (d) respectively. Fig. 5(c) reveals the penetration of the ultraporous PVDF substrate into the macropores of the non-woven polyester fabric whereas from Fig. 5(d), it appears that the Pebax layer penetrates into the PVDF substrate (22).

X-Ray Diffraction (XRD) Studies

The XRD spectrum of Pebax membrane shown in Fig. 6 indicates that the polymer was crystalline. The XRD pattern shows sharp diffraction peaks at around 14° and 17° of 2θ and broad peak around at 25° of 2θ, which correspond to the amide, ether, and acetate groups of the co-polymer.

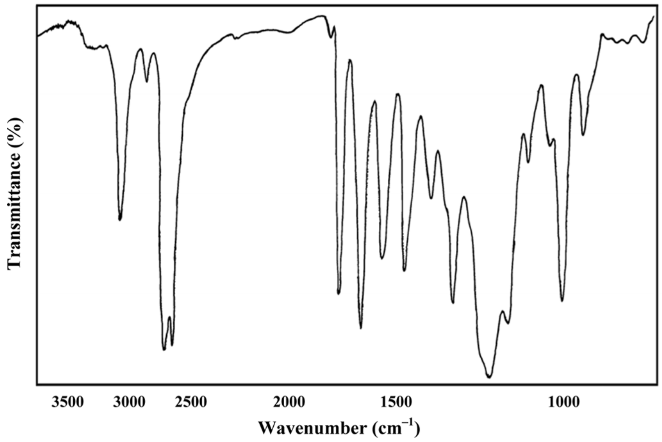


FIG. 3. FTIR spectra of Pebax 2533 membrane.

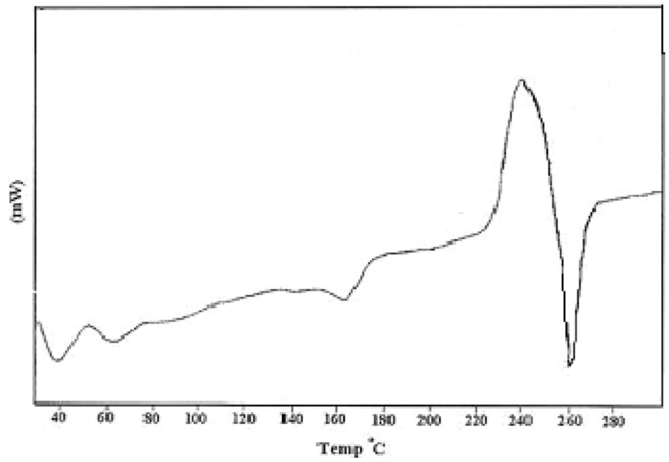
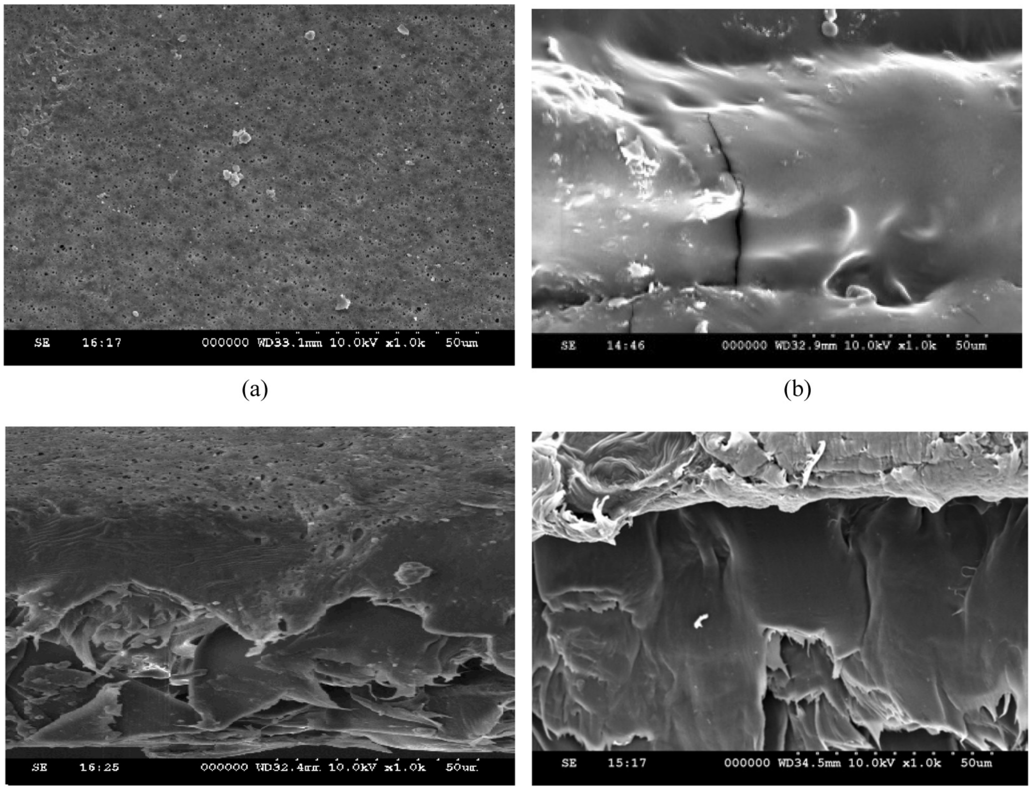


FIG. 4. DSC thermogram of Pebax 2533 membrane.



(a) (b)

(c) (d)

FIG. 5. SEM pictures of (a) surface of PVDF substrate, (b) surface of Pebax composite, (c) cross-sectional view PVDF substrate, (d) cross-sectional view of Pebax composite membrane.

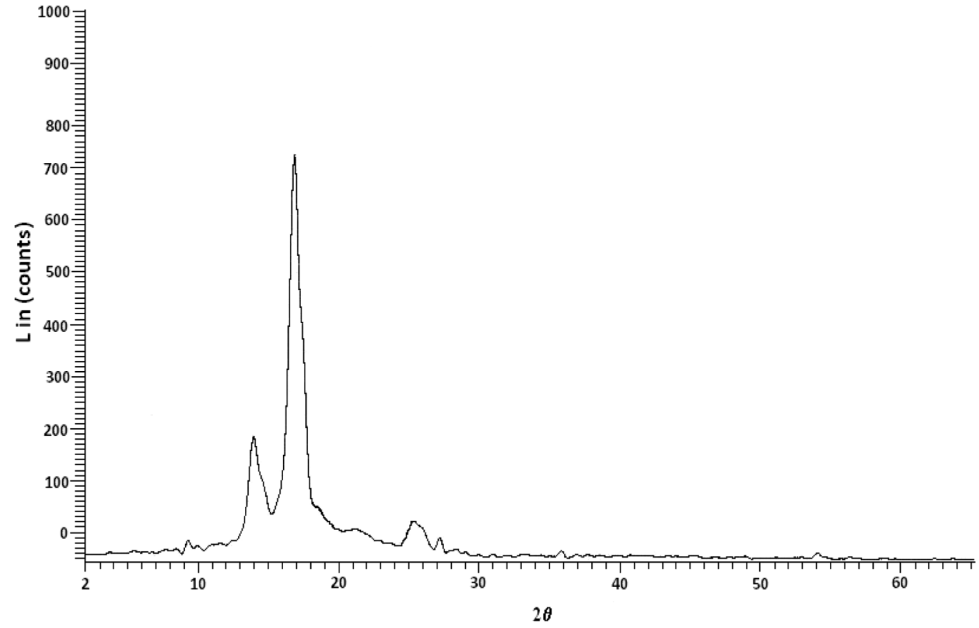


FIG. 6. XRD spectra of Pebax 2533 membrane.

TABLE 1
Flux, degree of swelling and PSI of Pebax membrane for varying feed composition of ethanol/water mixture

Mass % of water in feed	Mass % of water in permeate	Flux (J) ($kg\,m^{-2}\,h^{-1}$)	PSI	Degree of swelling
4.79	98.44	0.0515	64.6	1.15
10.47	96.06	0.0715	14.6	1.26
19.88	92.62	0.098	5.0	1.32
31.24	88.30	0.127	2.1	1.41
49.63	85.36	0.1735	1.02	1.52

This spectrum supports the structure of Pebax membrane displayed in Fig. 2.

Effect of Feed Composition

The relation between liquid feed composition and PV performance over a wide range of feed mixture at room temperature was investigated using Pebax membrane keeping other operating parameters such as permeate pressure (0.5 mm Hg) and membrane thickness (20 μm) constant. The effect of feed composition on flux, PSI and degree of swelling of the membrane in aqueous ethanol and ethylene glycol were shown in Tables 1 and 2. A rise in the mass percentage of water in feed produces an increase in the flux from 0.05 to 0.17 $kg\,m^{-2}\,h^{-1}$ and a drop in selectivity from 1254 to 6 for ethanol/water mixture and correspondingly a flux enhancement from 0.05 to 0.11 $kg\,m^{-2}\,h^{-1}$ and selectivity reduction from 978 to 8 for ethylene glycol/water mixture (Figs. 7 and 8). Mass transport through the membrane occurs by a solution diffusion mechanism, in which the molecular transport of liquids is governed by interactions between the liquid molecules and the polymer chains. The Pebax membrane shows a high degree of sorption, which increases with increase in mass percentage of water in both the binary mixtures. From Fig. 9, it can be seen that the percentage of water uptake from the binary feed mixture increases the % of sorption from 15.1 to 52.6% with increase in feed water from 4.8 to 49.6 mass% for ethanol/water system and from 20.5 to 46.3% with increase in feed water from 5.3 to 40.7 mass% for ethylene glycol/water system. As the membrane has more affinity for water molecules than ethyl alcohol and ethylene glycol, it exhibits selectivity to water in case of both the feed systems considered in this study. Moreover, water being a smaller molecule, diffuses faster than both the alcohols. An increase in the feed water concentration enhances flux. However, increased swelling has a negative impact on membrane selectivity since the swollen and plasticized upstream membrane layer allows some ethanol and ethylene glycol molecules also to escape into the permeate side along with water. It can been seen from Tables 1 and 2 that the PSI is more influenced by selectivity than flux and attains higher values at lower feed water concentrations.

Effect of Permeate Pressure

The permeate pressure was varied from 0.5 to 10 mm Hg to study the permeation characteristics at a constant membrane thickness of 20 μm and feed water compositions of ethanol and ethylene glycol. Ethanol forms the azeotrope with water at 95.6 mass% of ethanol but ethylene glycol does not form azeotrope with water. 94.7 mass% of ethylene glycol in the feed was taken to study the effect of permeate pressure. At lower pressures the influence of the driving force on the diffusing molecules in the membrane was high and will result in the components being swept out immediately from the permeate side enhancing mass transfer rates. The membrane exhibits considerable lowering of flux from 0.052 to 0.03 $kg\,m^{-2}\,h^{-1}$ as well as a reduction in selectivity from 1254 to 102 for ethanol/water azeotropic feed composition with increase in pressure from 0.5 to 10 mm Hg as seen in Fig. 10. In case of ethylene glycol/water system the flux reduces from 0.06 to 0.03 $kg\,m^{-2}\,h^{-1}$ and selectivity drops from 884 to 70 with an increase in permeate pressure from

TABLE 2
Effect of feed composition of ethylene glycol/water mixtures on flux, degree of swelling and PSI of Pebax membrane

Mass % of water in feed	Mass % of water in permeate	Flux (J) ($kg\,m^{-2}\,h^{-1}$)	PSI	Degree of swelling
5.31	98.21	0.0485	47.4	1.20
9.71	98.96	0.058	51.3	1.25
19.16	88.77	0.078	2.6	1.39
31.36	86.32	0.0905	1.2	1.43
40.71	84.90	0.114	0.9	1.46

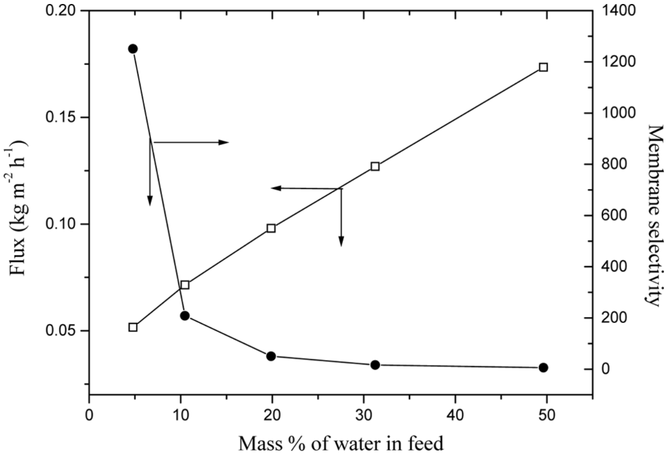


FIG. 7. Effect of ethanol/water feed composition on Pebax membrane selectivity and flux.

0.5 mm Hg to 10 mm Hg (Fig. 11). Under high vacuum conditions diffusion through the membrane was the rate determining step of the PV process and the diffusing water molecules experience greater driving force, which enhances the desorption rate at the downstream side. Lower vacuums reduce the driving force, thus slowing down desorption of molecules. In such cases the relative volatilities of the two components of the mixture govern the separation character of the membrane.

Comparison of Present Work with Literature

Data from literature (22–31) on pervaporation-based separation of ethanol/water and ethyleneglycol/water systems are summarized in Table 3 for comparison with Pebax 2533 membrane used in the present work. The data in the table indicates that the performance of Pebax 2533 membrane is on par with most other membranes, especially for dehydration of ethylene glycol, where a selectivity of 978 was observed. Some of the membranes reported in literature

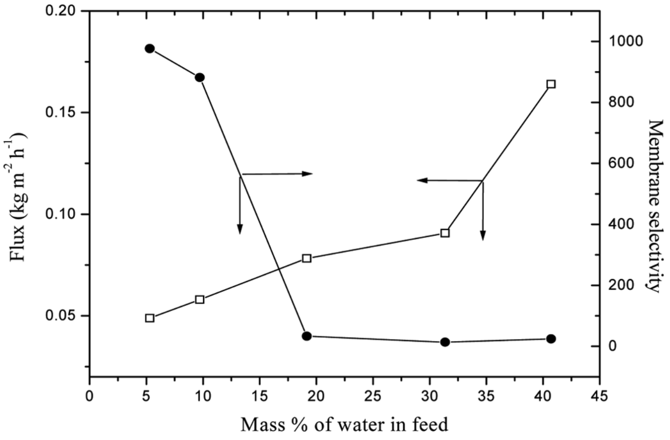


FIG. 8. Influence of ethylene glycol/water feed composition on Pebax membrane performance.

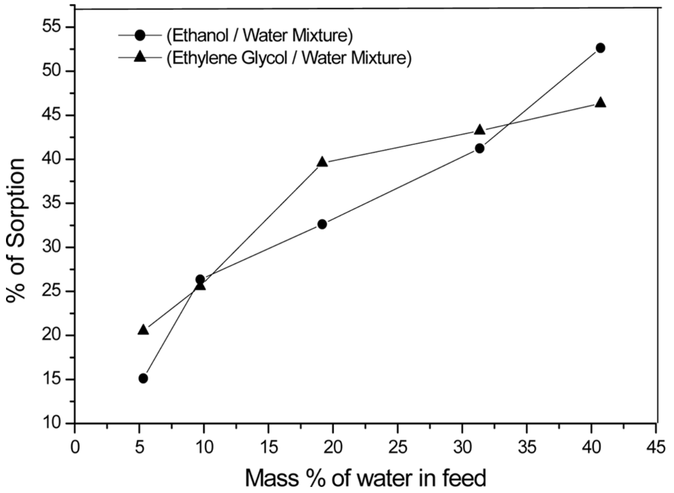


FIG. 9. Effect of ethanol/water and ethylene glycol/water compositions on sorption of Pebax membrane.

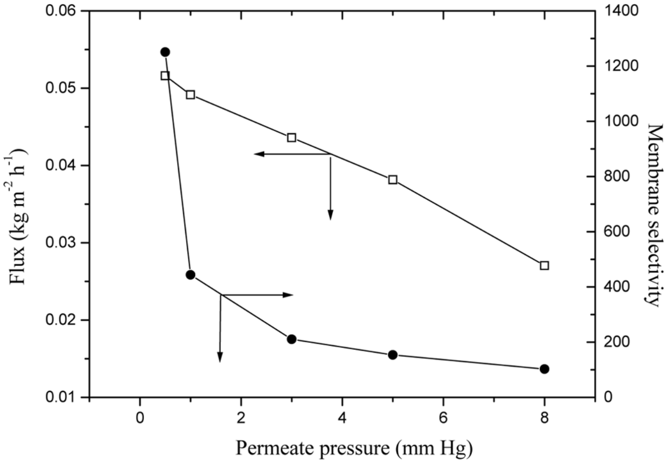


FIG. 10. Effect of permeate pressure on flux and selectivity of Pebax membrane for ethanol/water azeotropic feed composition.

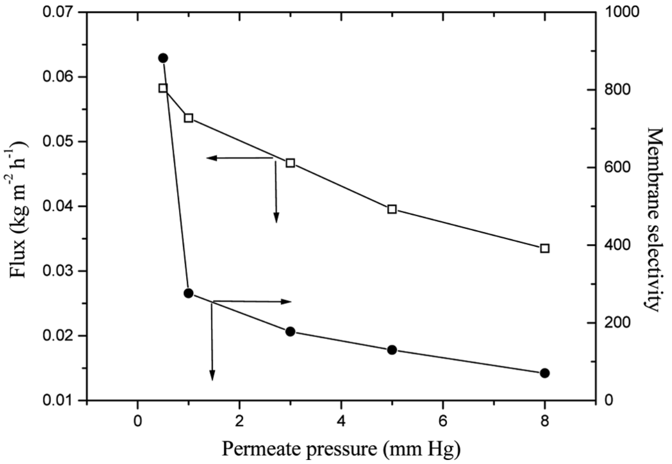


FIG. 11. Effect of permeate pressure on flux and selectivity of Pebax membrane for 94.7% ethylene glycol feed.

TABLE 3
Comparison of flux and selectivity of Pebax membrane with values reported in literature

	Feed composition (%)				Total flux (kg m^{-2} h^{-1})		Selectivity to water		
Membrane	Water	EG	Water	Ethanol	EG-Water	Ethanol-Water	EG-Water	Ethanol-Water	Ref.
CS/SA	–	–	10	90	–	0.11	–	10491	23
PVA/PSS	–	–	6.2	93.8	–	0.5	–	700	24
P-SA	–	–	5.2	94.8	–	0.24	–	2182	25
TOA	–	–	10	90	–	1.62	–	113	26
NaY	–	–	10	90	–	9.9	–	231	27
PVA4 (TMC)	10	90	–	–	0.36	–	987	–	28
PVA-GPTMS/TEOS	20	80	–	–	6.0	–	714	–	29
PVA – heat treatment	20	80	–	–	14.5	–	54	–	29
PAAM/PVA	20	80	–	–	14.0	–	96	–	30
Chitosan/Polysulfone	20	80	–	–	35.0		96	–	31
PEBAX-2533	5.3	94.69	4.8	95.2	0.048	0.05	978	1254	Present work

CS/SA—chitosan/sodium alginate; PVA/PSS—poly(vinyl alcohol)/poly(styrene sulfuric acid); P-SA—phosphorylated sodium alginate; TOA—Trioctylamine; NaY—zeolite membrane; PVA4 (TMC)—a composite membrane crosslinked by trimesoyl chloride; PVA-GPTMS/TEOS—poly(vinylalcohol)-γ-glycidyloxypropyltrimethoxysilane + tetraethyl orthosilicate; PVA—poly(vinyl alcohol); PAAM—polyacrylamide; EG—ethylene glycol.

have shown high flux but low values of selectivity. To optimize the flux and bring it within comparable range, the Pebax membrane could be cast with finer thickness of 2 μm or lower on the PVDF substrate. The ease in fabrication of these membranes associated with their low cost render them more attractive for pervaporation of aqueous alcohols.

CONCLUSIONS

In this study, Pebax 2533 membrane was used for pervaporation-based dehydration of ethanol/water and ethylene glycol/water mixture. Characterization of these membranes by FTIR and XRD confirmed its chemical structure. The membrane showed adequate thermal stability to withstand the PV experimental conditions. With increasing feed water composition, the membrane exhibited a reduction in selectivity and an improvement in flux due to increase in swelling. Higher permeate pressure caused a reduction in both flux and selectivity. Pervaporation could be combined with distillation in an integrated process wherein the former overcomes the azeotropic barrier of ethanol after which the latter can be applied to achieve final purity. In case of ethylene glycol, the membrane could be successfully applied in the form of a thin film composite for removal of small amounts of water (<10%).

ACKNOWLEDGMENTS

The authors are thankful to the Council of Scientific and Industrial Research (CSIR), New Delhi, for the Network Project (NWP-0047) Grant.

REFERENCES

1. Toti, U.S.; Aminabhavi, T.M. (2004) Different viscosity grade sodium alginate and modified sodium alginate membranes in pervaporation separation of water + acetic acid and water + isopropanol mixtures. *J. Membr. Sci.*, 228: 199–208.
2. Rautenbach, R.; Albrecht, R. (1985) The separation potential of pervaporation Part 2. Process design and economics. *J. Membr. Sci.*, 25: 25–54.
3. Dutta, B.K.; Sikdar, S.K. (1991) Separation of azeotropic organic liquid mixtures by pervaporation. *AIChE J.*, 37: 581–588.
4. Haack, J.M.; Lenk, W.; Lehmann, D.; Lunkwitz, K. (2001) Pervaporation separation of water/alcohol mixtures using composite membranes based on polyelectrolyte multilayer assemblies. *J. Membr. Sci.*, 184: 233–243.
5. Qureshi, N.; Meagher, M.M.; Huang, J.; Hutkins, R.W. (2001) Acetone butanol ethanol (ABE) recovery by pervaporation using silicalite–silicone composite membrane from fed-batch reactor of *Clostridium acetobutylicum*. *J. Membr. Sci.*, 187: 93–102.
6. Huang, S.C.; Ball, I.J.; Kaner, R.B. (1998) Polyaniline membranes for pervaporation of carboxylic acids and water. *Macromolecules*, 31: 5456–5464.
7. Kusumocahyo, S.P.; Sudoh, M. (1991) Dehydration of acetic acid by pervaporation with charged membranes. *J. Membr. Sci.*, 161: 77–83.
8. Jegal, J.; Lee, K.H. (1996) Development of polyion complex membranes for the separation of water-alcohol mixtures. III. Preparation of polyion complex membranes based on the k-carrageenan for the pervaporation separation of waterethanol. *J. Appl. Polym. Sci.*, 60: 1177–1183.
9. Park, C.H.; Nam, S.Y.; Lee, Y.M.; Kujawski, W. (2000) Pervaporation of pyridine–water mixture through poly (acrylonitrile-co-monoacryloxyethyl phosphate) membrane. *J. Membr. Sci.*, 164: 121–128.
10. Ping, Z.H.; Nguyen, Q.T.; Chen, S.M.; Ding, Y.D. (2002) Pervaporation of water–ethanol mixtures with polyacrylate-grafted polyethylene acid (PE-g-AA) membranes: Physico-chemical analysis of the transport mechanism. *J. Membr. Sci.*, 195: 23–34.

11. Aminabhavi, T.M.; Naik, H.G. (2002) Pervaporation separation of water/dimethylformamide mixtures using poly(vinyl alcohol)-g-polyacrylamide copolymeric membranes. *J. Appl. Polym. Sci.*, 83: 273–282.
12. Boddeker, K.W.; Bengtson, G.; Bode, E. (1990) Pervaporation of low volatility aromatics from water. *J. Membr. Sci.*, 53: 143–158.
13. Chatterjee, G.; Houde, A.A.; Stern, S.A. (1997) Poly(ether urethane) and poly(ether urethane urea) membranes with high H_2S/CH_4 selectivity. *J. Membr. Sci.*, 135: 99–106.
14. Hollein, M.E.; Hammond, M.; Slater, C.S. (1993) Concentration of Dilute acetone ± water solutions using pervaporation. *Sep. Sci. Technol.*, 28: 1043–1061.
15. Rezac, M.E.; John, T.; Pfromm, P.H. (1997) Effect of copolymer composition on the solubility and diffusivity of water and methanol in a series of polyether amides. *J. Appl. Polym. Sci.*, 65: 1983–1993.
16. Razumovskii, L.P.; Markin, V.S.; Zaikoz, G.Y. (1985) Sorption of water by aliphatic polyamides. *Polym. Sci.*, 27: 751–768.
17. Sridhar, S.; Ravindra, R.; Khan, A.A. (2000) Recovery of monomethylhydrazine liquid propellant by pervaporation technique. *Ind. Eng. Chem. Res.*, 39: 2485–2490.
18. Kalyani, S.; Smitha, B.; Sridhar, S.; Krishnaiah, A. (2006) Blend membranes of sodium alginate and hydroxyethylcellulose for pervaporation-based enrichment of *t*-butyl alcohol. *Carbohyd. Polym.*, 64: 2006, 425–432.
19. Faruque, H.S.; Lacabanne, C. (1987) Anelastic and dielectric properties of polyether-polyamide copolymer Pebax studied by a thermally stimulated depolarization current method. *J. Phys. Appl. Phys.*, 20: 939–944.
20. Flesher, J.R. (1987) High Performance Polymers: Their Origin and Development, Seymour, R.B.; Kirshenbaur, G.E., eds.; Elsevier Science Publishing: New York.
21. Di Lorenzo, M.L.; Pyda, M.; Wunderlich, B. (2001) Calorimetry of nanophase-separated poly(oligoamide-*alt*-oligothers). *J. Polymer Sci. Part B: Polymer Phys.*, 39: 1594–1604.
22. Sridhar, S.; Aminabhavi, T.M.; Mayor, S.J.; Ramakrishna, M. (2007) Permeation of carbon dioxide and methane gases through novel silver-incorporated thin film composite Pebax membranes. *Ind. Eng. Chem. Res.*, 46: 8144–8151.
23. Kanti, P.; Srigowri, K.; Madhuri, J.; Smitha, B.; Sridhar, S. (2004) Dehydration of ethanol through blend membranes of chitosan and sodium alginate by pervaporation. *Sep. Purif. Technol.*, 40: 259–266.
24. Toutianoush, A.; Krasemann, L.; Tieke, B. (2002) Polyelectrolyte multilayer membranes for pervaporation separation of alcohol/water mixtures. *Colloids Surf. A*, 198–200: 881–889.
25. Kalyani, S.; Smitha, B.; Sridhar, S.; Krishnaiah, A. (2008) Pervaporation separation of ethanol–water mixtures through sodium alginate membranes. *Desalination*, 229: 68–81.
26. Thongsukmak, A.; Sirkar, K.K. (2009) Extractive pervaporation to separate ethanol from its dilute aqueous solutions characteristic of ethanol-producing fermentation processes. *J. Membr. Sci.*, 329: 119–129.
27. Sato, K.; Sugimoto, K.; Nakane, T. (2008) Mass-production of tubular NaY zeolite membranes for industrial purpose and their application to ethanol dehydration by vapor permeation. *J. Membr. Sci.*, 319: 244–255.
28. Hyder, M.N.; Huang, R.Y.M.; Chen, P. (2009) Composite poly(vinyl alcohol)–poly(sulfone) membranes crosslinked by trimesoyl chloride: Characterization and dehydration of ethylene glycol–water mixtures. *J. Membr. Sci.*, 326: 363–371.
29. Guo, R.; Hu, C.; Pan, F.; Wu, H.; Jiang, Z. (2006) PVA-PTMS/TEOS hybrid pervaporation membrane for dehydration of ethylene glycol aqueous solution. *J. Membr. Sci.*, 281: 454–462.
30. Burshe, M.C.; Sawant, S.B.; Joshi, J.B.; Pangakar, V.G. (1998) Dehydration of ethylene glycol by pervaporation using hydrophilic IPNs of PVA, PAA and PAAM membranes. *Sep. Purif. Technol.*, 13: 47.
31. Feng, X.; Huang, R.Y.M. (1996) Pervaporation with chitosan membranes. I. Separation of water from ethylene glycol by a chitosan/polysulfone composite membrane. *J. Membr. Sci.*, 116: 67.