

# Novel Poly(vinyl alcohol)-Tetraethoxysilane Hybrid Matrix Membranes as Oxygen Barriers

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**ABSTRACT:** Novel type of membranes based on poly(vinyl alcohol) crosslinked with tetraethoxysilane have been prepared by solution casting and solvent-evaporation method. The membranes thus formed were characterized by Fourier transform infrared spectroscopy (FTIR) to study the chemical interactions, X-ray diffraction (XRD), and thermogravimetry (TGA) to investigate morphological and thermal properties. Membranes were prepared in two different thicknesses (30 and 55  $\mu\text{m}$ ) and used for measuring the oxygen permeability under varying feed pressures (maintaining the desired pressure differential across the membrane) in the range from 1 to

50  $\text{kg}/\text{cm}^2$  pressure. Oxygen permeability of the membranes ranged from 0.0091 to 1.6165 Barrer for 30  $\mu\text{m}$  and 0.0305 to 0.1409 Barrer for 55- $\mu\text{m}$  thick membranes by increasing the feed pressures on the feed side. Except at 50  $\text{kg}/\text{cm}^2$  pressure, the observed oxygen permeability values are almost close to total permeability. Membranes of this study could be useful as oxygen barriers for applications in food packaging industries. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 273–278, 2007

**Key words:** poly(vinyl alcohol); hybrid matrix membranes; gas separation; packaging material; oxygen permeability

## INTRODUCTION

Membrane-based gas separation (GS) has evolved as an important unit operation in chemical industries, competing successfully with several other conventional-type separation techniques, such as cryogenic distillation, pressure-swing adsorption, and simple absorption.<sup>1,2</sup> The last decade has witnessed an exponential increase in the development of novel polymeric membranes as the effective, economic, and flexible tools in gas-separation problems. Commercial exploitation of polymeric membranes for air separation, recovery of hydrogen from nitrogen, carbon monoxide, and methane mixtures, and removal of carbon dioxide from natural gas have been widely reported.<sup>3,4</sup> In such applications, high fluxes and excellent selectivities have relied mostly on glassy polymeric membranes that base separations on differences in gas sizes. However, this technology has focused on utilizing materials near the ambient temperature. The development of novel polymers offer-

ing important combinations of high selectivity, high permeability, good mechanical stability, and processability at ambient temperatures and pressures has been quite slow.<sup>5</sup> In general, the flexible polymer films have favorable properties like low cost, good barrier properties against moisture and gases, heat sealable to prevent leakage of contents, possess both wet and dry strengths, easy to handle, and add little weight to the final product. Thus, they fit closely to the shape of the food, thereby wasting little space during storage and distribution. In food packaging applications, oxygen barrier properties of the polymers are important, since many food materials require the specific atmospheric conditions to sustain their freshness and quality during the storage. Hence, food materials are increasingly being packed in a protective atmosphere with a specific mixture of gases, thereby ensuring optimum quality and safety of the product. However, to ensure a constant gas composition inside the packaging film, the polymer should have certain specific oxygen barrier properties.

The majority of food packaging films consist of a layer of ethyl vinyl alcohol (EVOH) or polyamide (PA6) combined with low density polyethylene (LDPE) with a combination of gas barrier properties of PA6 or EVOH, having the required water vapor transport properties and appropriate mechanical strengths. Gas barrier properties of PA6 and EVOH are sensitive to moisture, while LDPE creates an effective water vapor barrier ensuring that moisture

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does not interfere with the properties of PA6 or EVOH. Similarly, poly(lactic acid) (PLA) and poly(hydroxy alcanoate) films possess moisture-sensitive gas-barrier properties. Some interesting developments have been made to improve the water vapor and gas transport properties of biobased materials using plasma coatings or production of nanocomposites of the modified clay materials.<sup>6–8</sup> The mineral oil-based polymers have shown a fixed ratio between oxygen and carbon dioxide permeabilities.<sup>9</sup> In packaging industries, flexible packaging films for oxygen sensitive products such as vegetables, fruits, meats, and electronic materials are generally made of multilayer structures. Each of these layers brings a specific property to the material such as high oxygen barrier and good adhesion to the substrate. The current trend is to reduce the number of these layers, while keeping the same mechanical strength and technical characteristics.<sup>10</sup>

The development of more ecofriendly polymeric systems is a current trend. Among all the possibilities of combining different properties (polymer blends, polymer grafting, copolymerization, etc.), our attention has been focused on the use of biocompatible and biodegradable hybrid-mixed matrix membranes comprising a combination of organic base and inorganic fillers prepared by special methods.<sup>11–13</sup> Hybrid membranes having high crosslink density with the highest possible degree of interpenetration are the better candidates. In this direction, we thought of using poly(vinyl alcohol) (PVA), a widely used polymer, to prepare membranes by adding tetraethoxysilane (TEOS) as the crosslinking agent. PVA is an environmentally benign polymer and hence an attempt has been made to develop novel hybrid PVA membranes crosslinked with TEOS that could exhibit good oxygen barrier properties.

## EXPERIMENTAL

### Materials

PVA (MW = 125,000 with a degree of hydrolysis  $\approx$  86–89%) and HCl were purchased from s.d. Fine Chemicals, Mumbai, India. Tetraethoxysilane (TEOS) was purchased from E. Merck (India), Mumbai, India. All other chemicals were of reagent grade samples and were used without further purification. Double-distilled water was used throughout the research.

### Membrane preparation

PVA (5 g) was dissolved in 100 mL of deaerated distilled water at 60°C. To this solution, a known amount of TEOS was added along with 1 mL of HCl as a catalyst. The whole mixture was stirred overnight at 60°C to complete the reaction. The reaction is of sol-gel type and the resulting homogeneous

solution was cast on a glass plate with the help of a doctor's knife. The membrane formed was dried at ambient temperature, and peeled off from the glass plate. During reaction, 2.5 wt % of TEOS was added (i.e., 0.125 g of TEOS) for crosslinking to take place. Two membranes of different thicknesses (30 and 55  $\mu\text{m}$ ) were prepared. The membrane thickness was measured at different points using a micrometer screw gauge to an accuracy of  $\pm 2$  mm, but the average thickness was considered in all calculations. The membranes of two different thicknesses (30 and 55  $\mu\text{m}$ ) formed were designated as PVA-TEOS-30 and PVA-TEOS-55, respectively.

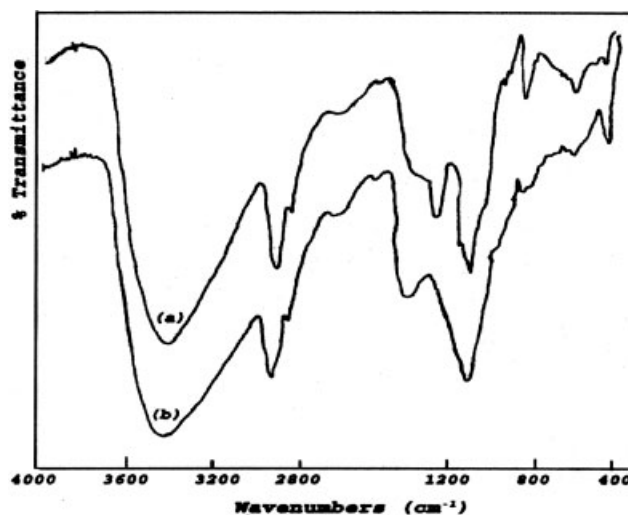
### Membrane characterization

#### Fourier transform infrared spectroscopy

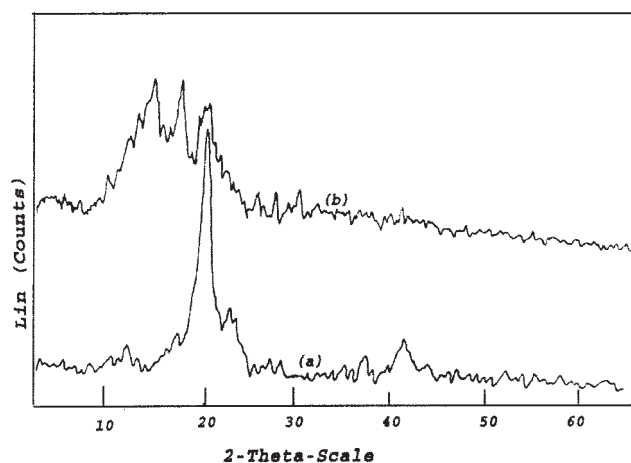
FTIR (Fourier transform infrared spectroscopy) spectra of the plain PVA and PVA-TEOS hybrid membranes were taken in the range between 4000 and 400  $\text{cm}^{-1}$  to confirm the crosslinking of PVA with TEOS using Nicolet-740, PerkinElmer-283B FTIR spectrometer (Milwaukee, WI). Membrane samples were grounded well with KBr and pellets were formed by pressing under the hydraulic pressure of 400–450  $\text{kg}/\text{cm}^2$ . FTIR spectral curves are displayed in Figure 1.

#### X-ray diffraction

A Siemens D 5000 powder X-ray diffractometer (USA) was used to study the solid-state morphology of the plain PVA and PVA-TEOS hybrid membranes. X-rays of 1.5406 Å wavelength were generated by a Cu  $K\alpha$  source. The angle of diffraction,  $2\theta$  was varied from 0 to 65° to identify any changes in crystal structure and intermolecular distances between intersegmental chains before and after the reaction. XRD



**Figure 1** FTIR spectra of (a) plain PVA and (b) PVA-TEOS-30 hybrid membrane.



**Figure 2** XRD spectra of (a) plain PVA and (b) PVA-TEOS-30 hybrid membranes.

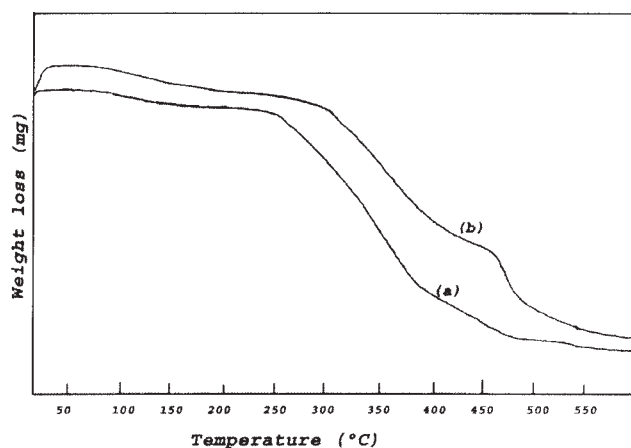
(X-ray diffraction) curves of PVA and PVA-TEOS hybrid membranes are, respectively, displayed in Figure 2.

#### Thermogravimetric analysis

Thermal stability of the plain PVA and PVA-TEOS hybrid membranes was assessed using Mettler Toledo TGA (thermogravimetric analysis)/SDTA 851<sup>e</sup> analyzer from 25 to 600°C at the heating rate of 10°C/min under nitrogen atmosphere. TGA curves are given in Figure 3.

#### Gas separation experiments

Gas separation (GS) experiments were performed using an indigenously built manifold shown schematically in Figure 4. Permeability cell was made of a SS 316, designed and fabricated at Indian Institute of Chemical Technology, India. The effective membrane area of the cell is 10 cm<sup>2</sup>. The lower part of the cell assembly is the permeate line, which is low



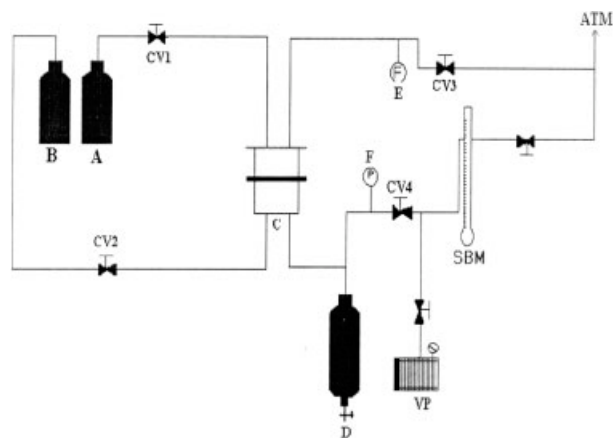
**Figure 3** TGA thermograms of (a) plain PVA and (b) PVA-TEOS-30 hybrid membranes.

pressure maintained area by applying vacuum (0.04 mmHg) using a high vacuum pump (Toshniwal, Mumbai, India). The upper part of the cell assembly represents the feed line, wherein the gaseous mixture was pressurized as per the required pressure through a cylinder using the control valve. Feed and permeate lines in the manifold were made of 1/4 in. diameter SS piping networked by means of the compression fittings. The vacuum line (permeate line) built-up a network of high vacuum rubber glass valve connection to provide a negative pressure as high as possible (usually, 0.05 mmHg).

#### Permeability measurements-continuous flow method

In the present study, a continuous flow method was used to perform the permeability experiments. In the feed compartment, permeate gases transport through the membrane into a flowing stream of inert gas swept in the permeate compartment. The stream flowing towards permeate side was analyzed to determine the component concentration. The product of concentration and stream flow rate gives the permeation rate. The continuous flow method was most preferred because the measurement of low and high permeation rates are easily done by varying the carrier gas flow rate at a controlled rate to bring the concentration of the penetrant in the permeate stream within the detectable range of gas chromatography (GC).

Oxygen permeability was determined by maintaining a desired pressure differential across the membrane. All experiments were performed at 30°C and permeate line was evacuated by a vacuum pump to remove any impure gases or traces present in the



**Figure 4** Gas separation manifold. Letters: (A) feed gas, (B) carrier gas, (C) membrane cell, (D) sample collection bottle, (E) feed pressure gauge, (F) permeate pressure gauge; CV1, CV2 are feed and permeate line control valves; CV3, CV4 are feed and permeate line outlet valves; VP, vacuum pump; SBM, soap bubble meter; and ATM, atmosphere.

permeate line. The feed gas mixture was introduced slowly into the upper part of the chamber by means of a mass flow controller, but the outlet control valve was closed until the dial gauge indicated the applied pressure. Hydrogen was used as a carrier gas to sweep the permeated gas to SS 316 gas sample container (100 mL capacity) for subsequent GC analysis. Samples were collected after attaining the steady state permeation. Experiments were repeated thrice to check for reproducibility, which typically reproduced within 3% standard errors.

Flow rate of the carrier gas was controlled and kept constant by means of a needle valve, which was measured by using a soap-bubble meter connected to the end of the permeate line. Permeate stream was collected after 3 h of equilibration of the membrane with the feed gas. The sample collection duration was 6–8 h; the composition of feed and permeate streams were determined by GC. Permeabilities were expressed in Barrers (1 Barrer =  $10^{-10}$  cm<sup>3</sup> (STP) cm cm<sup>-2</sup> s<sup>-1</sup> cmHg<sup>-1</sup>). The flux ( $J$ ), partial pressure difference across the membrane ( $\Delta P$ ), and permeability ( $K$ ) were calculated, respectively, using eqs. (1)–(3):

$$\text{Flux} = \left( \frac{\text{Permeate peak area}}{\text{Feed peak area}} \right) \times \left( \frac{\text{Carrier gas flow rate}}{\text{Membrane area in the cell}} \right) (\text{cc/s cm}^2) \quad (1)$$

$$\Delta P = (\text{Total permeate pressure} \times \text{mole fraction in permeate})(\text{cm Hg}) \quad (2)$$

$$\text{Permeability } (K) = \left( \frac{\text{Flux} \times h}{\Delta P} \right) (\text{Barrer}) \quad (3)$$

where  $h$  is thickness of the membrane.

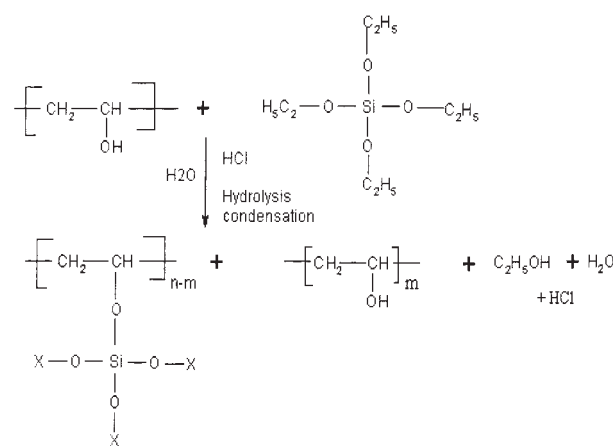
### Analytical procedure

Feed and permeate samples were analyzed by Nucon GC (Model 5765, Mumbai, India) installed with a thermal conductivity detector, using Haysep "Q" column. The oven temperature was maintained at 50°C (isothermal), while the injector and detector temperatures were maintained at 150°C each. The sample injection size was 0.5 mL and pure hydrogen was used as a carrier gas at a pressure of 0.9 kg/cm<sup>2</sup>. The GC response was calibrated for this particular column and conditions with the known binary feed mixture compositions. Calibration factors were fed into the software to obtain the correct analysis for unknown samples.

## RESULTS AND DISCUSSION

### Reaction of PVA and TEOS

Polycondensation reaction was carried out as per the procedure reported earlier.<sup>11,14,15</sup> While preparing



[where X = C<sub>2</sub>H<sub>5</sub>, Si(OX)<sub>3</sub>, or PVA chain]

**Scheme 1** Reaction scheme of poly(vinyl alcohol) and tetraethoxysilane; [where X = C<sub>2</sub>H<sub>5</sub>, Si(OX)<sub>3</sub>, or PVA chain].

PVA/TEOS hybrid matrix membranes, TEOS was hydrolyzed in the presence of an acid catalyst (HCl) producing the silanol groups. The resulting silanol groups yielded siloxane bonds because of the dehydration or dealcoholysis reaction with other silanol or ethoxy groups during the membrane drying process. These reactions have led to cohesive-type interactions between siloxane and hydroxy groups of PVA as shown in Scheme 1.

### Membrane characterization

#### FTIR

Crosslinking of PVA with TEOS is confirmed by FTIR spectra displayed in Figure 1. A broad peak at 3200 cm<sup>-1</sup> for plain PVA represents O—H stretching vibrations of the hydroxyl group. Broadness of this peak was decreased for the hybrid matrix membrane because of the incorporation of TEOS group, since the —OH groups of PVA could participate in the condensation reactions with the silanol groups of TEOS, resulting in the formation of a covalent crosslinking bond with —OH of PVA. In the region of 1000–1100 cm<sup>-1</sup>, multiple bands have appeared for plain PVA due to C—O stretching vibrations. In case of hybrid matrix membrane, the intensity of this peak was increased, indicating the formation of Si—O—C bonds<sup>16,17</sup> between linear alkyl chain (—CH<sub>2</sub>—CH—) of PVA. However, —Si—O— stretching is also observed in the same region as that of C—O stretching.

#### XRD

X-ray diffractograms presented in Figure 2 show two distinct bands giving maxima at  $2\theta = 7^\circ$ – $9^\circ$  and  $20^\circ$ . These two peaks are related to two types of crystals,<sup>18</sup> Crystal 1 and Crystal 2. Crystal 1, which cor-



**TABLE I**  
Effect of Feed Pressure on Oxygen Permeability at 30°C

Pressure applied (kg/cm <sup>2</sup> )	Permeability, <i>K</i> (Barrer)	
	PVA-TEOS-30	PVA-TEOS-55
1	0.0091	N/A
5	0.0139	N/A
10	0.0235	N/A
20	0.0676	0.0305
30	0.1948	0.0514
40	0.5612	0.1051
50	1.6165	0.1409

N/A = data not obtained.

Membrane PVA-TEOS-30 and PVA-TEOS-55 means thickness of 30 and 55 μm, respectively.

1 Barrer = 10<sup>-10</sup> cm<sup>3</sup> (STP) cm cm<sup>-2</sup> s<sup>-1</sup> cmHg<sup>-1</sup>.

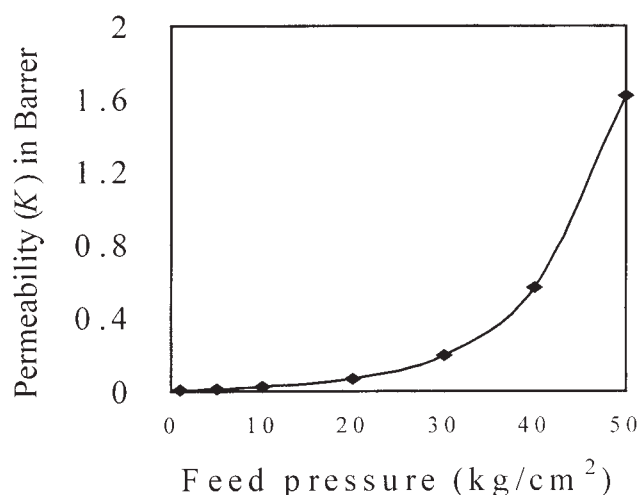
responds to peak at 12°, is responsible for the separation, as it comprises —OH groups, which has undergone a significant change after crosslinking.<sup>19</sup> A reduction in the effective *d*-spacing value from 8.49 Å for plain PVA to 8.38 Å in the hybrid matrix membrane suggests the shrinkage in cell size or intersegmental spacing. Diffraction patterns of the membrane showed that peak intensity decreased at 2θ = 20°, which confirms the formation of Si—O—C bonds between the —CH<sub>2</sub>—CH— polymer chain. Thus, the uncrosslinked PVA has more crystalline domains than the crosslinked hybrid matrix polymer. There is a shift in the position of peaks from 2θ = 9° to 24° in case of hybrid membranes. Thus, silanol groups of TEOS have crosslinked with the —OH groups in the crystalline domain, resulting in a compression of the amorphous region, thereby creating a more compact structure<sup>20</sup> and exhibiting a poor oxygen transport.

#### TGA

Thermal degradation of the membranes was examined by TGA as shown in Figure 3. The plain PVA exhibits two weight-loss stages around 260–280°C and 410–450°C followed by a final decomposition of the polymer that begins around 480°C. Weight loss in the first and second stages is attributed to the decomposition of functional groups and splitting of the main chain before the final decomposition of the polymer. The hybrid membrane also exhibits two weight loss stages ranging in the region 300–320°C and 470–480°C followed by a final decomposition at 490°C. However, the membrane is stable up to 480°C, beyond which, splitting of the main chain is likely to occur. The hybrid matrix membranes exhibit a higher thermal stability than plain PVA membrane.

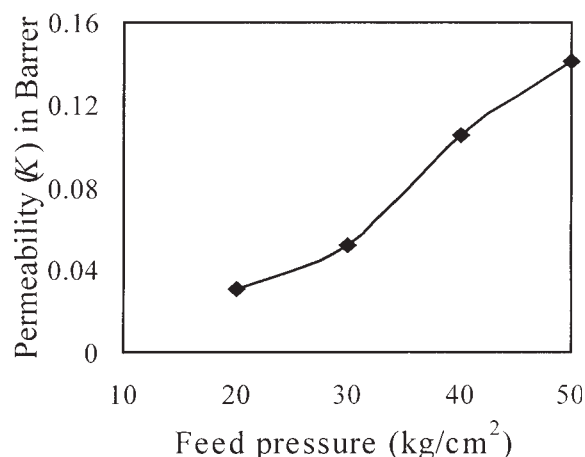
#### Membrane performance

Membranes were tested for oxygen permeability by varying feed pressures (maintaining the desired



**Figure 5** Effect of feed pressure on permeability for PVA-TEOS-30 membrane.

pressure differential across the membrane) and membrane thicknesses. The permeability (*K*) values are given in Table I. In case of PVA-TEOS-30 membrane, the pressure was increased from 1 to 50 kg/cm<sup>2</sup>. At 1 kg/cm<sup>2</sup> pressure, the permeability was 0.0091 Barrer, which has increased to 0.0139, 0.0235, 0.0676, 0.1948, 0.5612, and 1.6165, respectively, at 5, 10, 20, 30, 40, and 50 kg/cm<sup>2</sup> pressures. This dependence is shown in Figure 5. For PVA-TEOS-55 membrane at 1, 5, and 10 kg/cm<sup>2</sup> pressures, no oxygen permeability was observed. However, at 20 kg/cm<sup>2</sup> pressure, permeability was 0.0305 Barrer; at still higher pressures, viz., 30, 40, and 50 kg/cm<sup>2</sup>, permeability values were 0.0514, 0.105, and 0.1409, respectively, as depicted in Figure 6. Of the two hybrid membranes developed, the one with higher thickness (55 μm) has exhibited an improved barrier performance to oxygen, suggesting its suitability as a film for food packaging applications.



**Figure 6** Effect of feed pressure on permeability for PVA-TEOS-55 membrane.

## CONCLUSIONS

Novel type of hybrid membranes of PVA with TEOS in two different thicknesses have been prepared and tested for oxygen gas permeability at varying feed pressures. Membranes exhibited a moderately high thermal stability as indicated by TGA enough to withstand the experimental operation at higher temperatures and pressures. Thermal stability of the membranes increased even at a very low content of TEOS of the PVA matrix, which also acted as cross-linking agent, as confirmed by FTIR. XRD results confirmed the polymer crystallinity. The hybrid matrix membrane of 30- $\mu\text{m}$  thickness gave increased oxygen permeability upon varying the feed pressures from 1 to 50  $\text{kg}/\text{cm}^2$ . The present results indicated that both the hybrid membranes could be better candidates as food packaging materials because of their good oxygen barrier properties.

## References

1. Javaid, A.; Ford, D. M. *J Membr Sci* 2003, 215, 157.
2. Kesting, R. E.; Fritze, A. K. *Polymeric Gas Separation Membranes*; Wiley: New York, 1993.
3. Stern, S. A. *J Membr Sci* 1994, 94, 1.
4. Spillman, R. W.; Sherwin, M. B. *CHEMTECH* 1990, 20, 378.
5. Pesiri, D. R.; Jorgensen, B.; Dye, R. C. *J Membr Sci* 2003, 218, 11.
6. Fischer, S.; de Vlieger, J.; Kock, T.; Gilberts, J.; Fischer, H.; Batenburg, L. *Proceedings of the Food Biopack Conference*, Copenhagen, Denmark, August 27–29, 2000; p 109.
7. Johansson, K. S. *Proceedings of the Food Biopack Conference*, Copenhagen, Denmark, August 27–29, 2000; p 110.
8. Johansson, K. S. Improved barrier properties of biodegradable polymers by means of plasma deposition of glass-like SiOx coatings. Report within the NUTEK Programme, Stockholm, Sweden; p 11486. UKI 1997, Box 5607.
9. Petersen, K.; Nielsen, P. V. *Proceedings of the Food Biopack Conference*, Copenhagen, Denmark, August 27–29, 2000; p 73.
10. Miller, J. R.; Koros, W. J. *Sep Sci Technol* 1990, 25, 1257.
11. Uragami, T.; Okazaki, K.; Matsugi, H.; Miyata, T. *Macromolecules* 2002, 35, 9156.
12. Brennan, D. J.; White, J. E.; Haag, A. P.; Kram, S. I.; Mang, M. N.; Pikulin, S.; Brown, C. N. *Macromolecules* 1996, 29, 3707.
13. Simic, V.; Boileau, S.; Bouteiller, L.; Gallez, L.; Merlin, P. *Eur Polym J* 2002, 38, 2449.
14. Sakka, S.; Ito, S.; Kamiya, K. J. *Noncryst Solids* 1985, 71, 311.
15. Feng, Q.; Xu, J.; Dong, H.; Li, S.; Wei, Y. *J Mater Chem* 2000, 10, 2490.
16. Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, 3rd ed.; Chapman & Hall: London, 1975; p 378.
17. Robertson, M. A. F.; Mauritz, K. A. *J Polym Sci Part B: Polym Phys* 1998, 36, 595.
18. Salmon, S.; Hudson, S. M. *Rev Macromol Chem Phys* 1997, 37, 199.
19. Kim, J. H.; Lee, Y. M. *Polymer* 1952, 1993, 34.
20. Burshe, M. C.; Sawant, S. B.; Joshi, J. B.; Pangarkar, V. G. *Sep Purif Technol* 1997, 12, 145.