

Hybrid Membranes Based on SiO₂/Polyether-*b*-Polyamide: Morphology and Applications

MAURÍCIO L. SFORÇA,¹ INEZ V. P. YOSHIDA,¹ CRISTIANO P. BORGES,² SUZANA P. NUNES³

¹ Instituto de Química, Universidade Estadual de Campinas, 13083-970, Campinas, S.P., CP. 6154, Brasil

² Prog. Eng. Química/COPPE, Universidade Federal do Rio de Janeiro, 21845, Brasil

³ GKSS, Forschungszentrum, 21502 Geesthacht, Germany

Received 13 July 2000; accepted 15 October 2000

ABSTRACT: Hybrid materials were prepared incorporating silica networks by the sol-gel process into the poly(amide-*b*-polyether) block copolymer PEBAX®. PEBAX®/silica hybrids were characterized by transmission electron microscopy, atomic force microscopy, differential scanning calorimetry, and X-ray diffraction. The pervaporation of phenol from dilute aqueous solutions through hybrid membranes was investigated. Films prepared with lower silica contents showed better dispersed inorganic networks and were more selective in the pervaporation of phenol/water solutions. Films prepared with higher silica contents had a clear phase-separated morphology with lower performance in pervaporation. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 178–185, 2001

Key words: hybrid organic-inorganic; membrane-separation process; polyether-*b*-polyamide block copolymer; tetraethoxysilane; atomic force microscopy

INTRODUCTION

The polymerization of metal alkoxides to produce glasses is commonly carried out through the sol-gel process. More recently, the sol-gel process has also been used to develop new hybrid organic-inorganic materials by the incorporation of highly crosslinked inorganic networks into organic polymeric matrices.^{1–3} The inorganic component changes the mechanical and thermal characteristics of the organic matrix as well as the ion conductivity^{4,5} and ability of swelling and transporting gases.^{6,7}

Applications of organic-inorganic hybrids in many fields, such as nonlinear optics,⁸ optics and

electronics,⁹ solid electrolytes,¹⁰ catalysis,¹¹ biomaterials and biomedical materials,^{12–13} and membranes,¹⁴ have been described.

In the area of membranes, the introduction of an inorganic component into an organic matrix has been used to improve, for instance, the selectivity of hydrocarbons in silicone membranes.⁶ Organic-inorganic hybrids have also been used in the development of gas-separation membranes⁷ and for the facilitated transport of ions.¹⁴

In this study, hybrid membranes consisting of elastomeric block copolymer and silica were obtained. The elastomeric polymer used was poly(ether-*block*-polyamide) (PEBAX®), which exhibits exceptional selectivities for aromatic hydrocarbons in pervaporation¹⁵ and gas separation.¹⁶ These characteristics are dependent on the block nature and composition of the copolymer.

Although quite successful in the pervaporation of phenol/aqueous solutions with low phenol contents, films of PEBAX® 4033 swell considerably

Correspondence to: I. V. P. Yoshida (valeria@iqm.unicamp.br).

Contract grant sponsor: FAPESP; contract grant number: 95/03636-3; contract grant sponsor: CNPq.

Journal of Applied Polymer Science, Vol. 82, 178–185 (2001)
© 2001 John Wiley & Sons, Inc.

when the phenol content is higher than 2000 mg/kg and may even dissolve at higher concentrations, limiting the range of application. The idea here was to introduce an inorganic component to the PEBAX® film to reduce swelling and enlarge the concentration range of application of these membranes.

SiO₂/PEBAX® hybrid membranes were characterized by transmission electron microscopy (TEM), atomic force microscopy (AFM), differential scanning calorimetry (DSC), and X-ray diffraction. The performance of these membranes was evaluated in pervaporation and gas-separation experiments.

EXPERIMENTAL

Membrane Preparation

The block copolymer PEBAX® 4033 was kindly supplied by Elf Aquitaine, and tetraethoxysilane (TEOS) was provided by Aldrich.

For SiO₂/PEBAX®4033 hybrid membranes, PEBAX® pellets (7 wt %) were dissolved in 1-butanol/1-propanol (70/30 ratio) at reflux temperature for 4 h. TEOS (15 or 25 wt %) was mixed with the PEBAX® solution at room temperature (ca. 25°C) and was followed by the addition of 0.15M HCl (TEOS/H₂O = 1/4). The solution was stirred for 24 h at ambient temperature. Casting solutions were dropped into Petri dishes, and the solvent was evaporated in an oven at 70°C. The final drying step took place in a vacuum oven at 80°C for 1 day.

For the sake of simplicity, the nomenclature of the films is represented by the percentage of their components, so 15/85 SiO₂/PEBAX® 4033 is the representation of the film formed by the addition of 15 wt % TEOS to a PEBAX® 4033 solution to produce a hybrid containing silica (SiO₂).

Gas Separation

The gas permeability measurements of hybrid membranes were carried out with a commercially available test cell (Gelman Science Inc., Ann Arbor, MI) with pure H₂, N₂, O₂, CH₄, and CO₂ gases. The effective membrane area was 9.62 cm². The permeation rates were measured at a 4-bar pressure difference (1 bar at the permeate side) with bubble flow meters. Before each measurement, the membrane was kept dry under vacuum. The measurements were performed in triplicate.

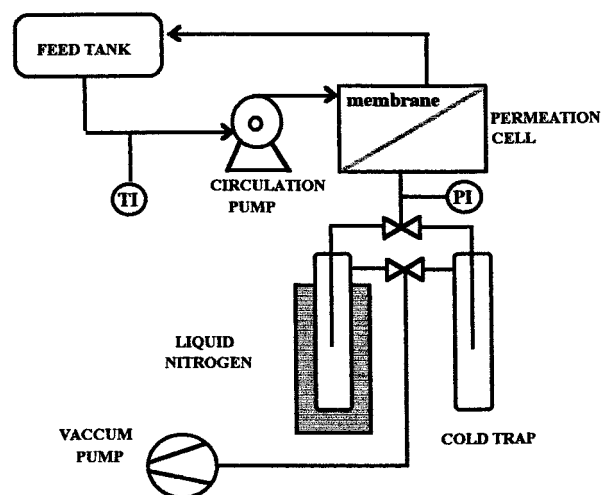


Figure 1 Test apparatus for pervaporation experiments.

Sorption

SiO₂/PEBAX® 4033 hybrid films of known weights were immersed in appropriate chemicals (methanol, ethanol, propanol, butanol, and phenol) at 50°C ($\pm 0.1^\circ\text{C}$) with a controlled-temperature bath. The films were removed at different times, slightly pressed between soft paper, and weighed. We calculated the solubilities of permeants in the polymers by taking into account the solvent uptake at equilibrium, when no further weight changes were observed. The measurements were performed in triplicate.

Pervaporation

Pervaporation experiments were conducted in an apparatus with continuous feed circulation, as represented in Figure 1. The test cell provided a central feed inlet and a peripheral feed outlet; the membrane area was 69.4 cm², and the permeate pressure was kept below 2 mbar. The feed solution at 50°C was circulated from a reservoir at a flow rate of 350 mL/min. The permeate was collected in weighted traps cooled with liquid nitrogen and, after appropriated dilution, was analyzed by gas chromatography.

DSC

DSC measurements were performed on a TA Instruments MDSC 2910 from -150 to 250°C at a heating rate of $10^\circ\text{C}/\text{min}$ for pure PEBAX® 4033 and SiO₂/PEBAX® 4033 films.

Wide-Angle X-Ray Diffraction (WAXD)

The WAXD measurements were performed on a Zeiss URD6 X-ray diffractometer with Cu K α radiation (wavelength = 1.54 Å).

Microscopy Characterization

Samples were cut in an Leitz–Reichert–Jung FC4E Ultracut microtome. The TEM images were taken with a Zeiss CEM 902 transmission electron microscope. The AFM measurements were performed under ambient conditions, in the contact mode, on a commercially available Topometrix Discoverer TMX 2010 AFM scanner. Cantilevers were monocrystalline silicon with a pyramidal tip of about 20 nm at the radius of the apex.

RESULTS AND DISCUSSION

AFM

Figure 2 shows the AFM topography images of PEBAX[®] 4033 and SiO₂/PEBAX[®] 4033 hybrid films. The surface of the PEBAX[®] 4033 film was homogeneous and rugous.

AFM images from polymer surfaces have to be examined with great care to avoid misinterpretations associated with image artifact due to probe damage. In this case, probe-induced image artifact damage was easily identified, either as streaks parallel to the probe motion or as small apparent indentations caused by mechanical vibration. Surface shading simulation can be done with the instrument software at various angles. However, the morphological features described in the previous paragraph were consistently observed in various surface regions of each sample, as well as in repeated scans of the same area.

The hybrid surfaces showed significant differences in the images. Particles can be observed over the hybrid surface film, which can be associated with the formation of silica clusters. Because PEBAX[®] 4033 has a hydrophobic character, the interaction between the SiO₂ and polymer phases was minimized, inducing the phase segregation. Some silica domains can be observed on the surface of the hybrid sample in Figure 2(b). The number of domains considerably increased with a higher SiO₂ content in Figure 2(c).

TEM

Figure 3 shows TEM images of 15/85 and 25/75 SiO₂/PEBAX[®] 4033 hybrid films.

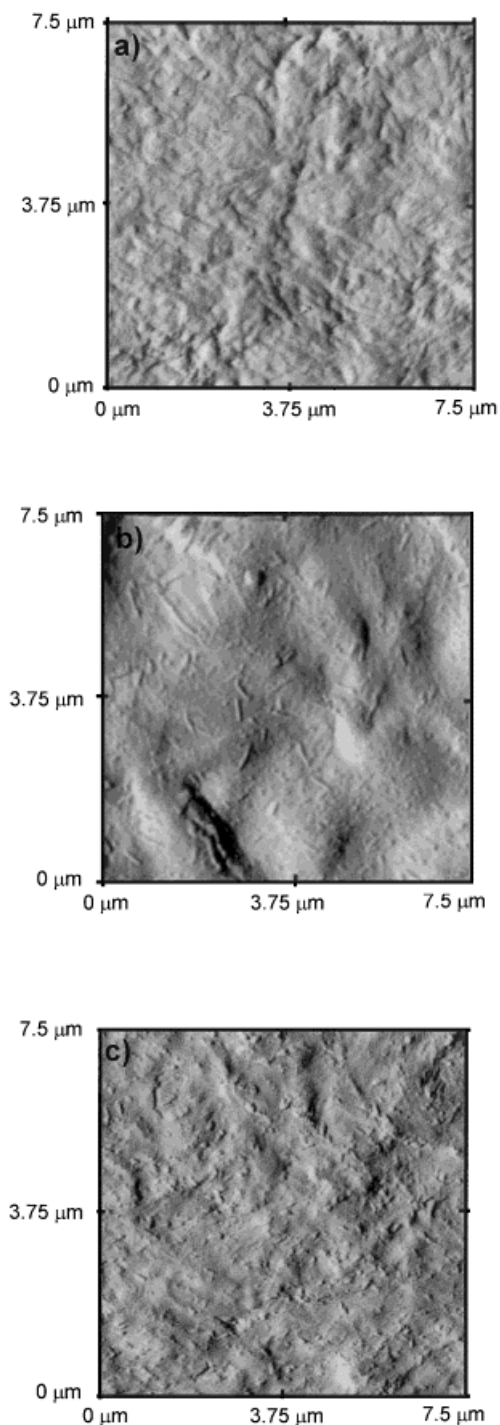


Figure 2 AFM images of (a) PEBAX[®] 4033, (b) 15/85 SiO₂/PEBAX[®] 4033, and (c) 25/75 SiO₂/PEBAX[®] 4033.

A quite smooth morphology was observed for the 15/85 hybrid in comparison with the 25/75 hybrid, in which phase separation was much more evident.

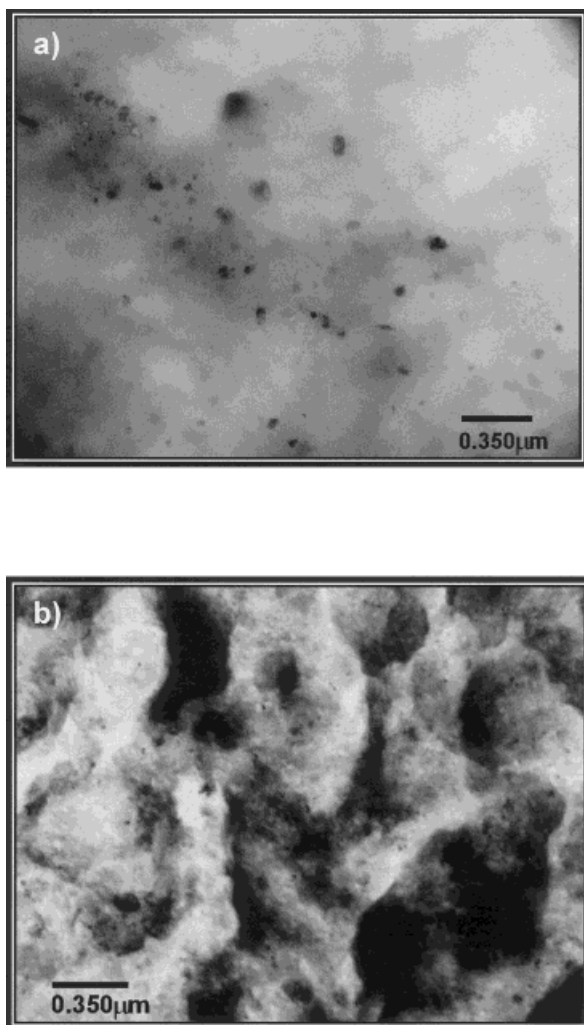


Figure 3 TEM images of (a) 15/85 SiO₂/PEBAX® 4033 and (b) 25/75 SiO₂/PEBAX® 4033.

DSC

The DSC measurements provide indirect information on the compatibility and size of the phase-separated domains of the hybrid film structure. Figure 4 shows DSC scans of pure PEBAX® 4033 and hybrid films.

PEBAX® 4033 has a glass-transition temperature (T_g) around -35°C (related to T_g of polyether groups) and a crystallization peak (T_c) around 210°C associated with the polyamide block. The 15/85 SiO₂/PEBAX® 4033 hybrid film showed a less defined T_g , and T_c could not be observed. These results suggest that the elastomeric phase and silica network are better dispersed at a molecular level.

Higher silica contents in the hybrid films led to the presence of the two PEBAX® 4033 transitions,

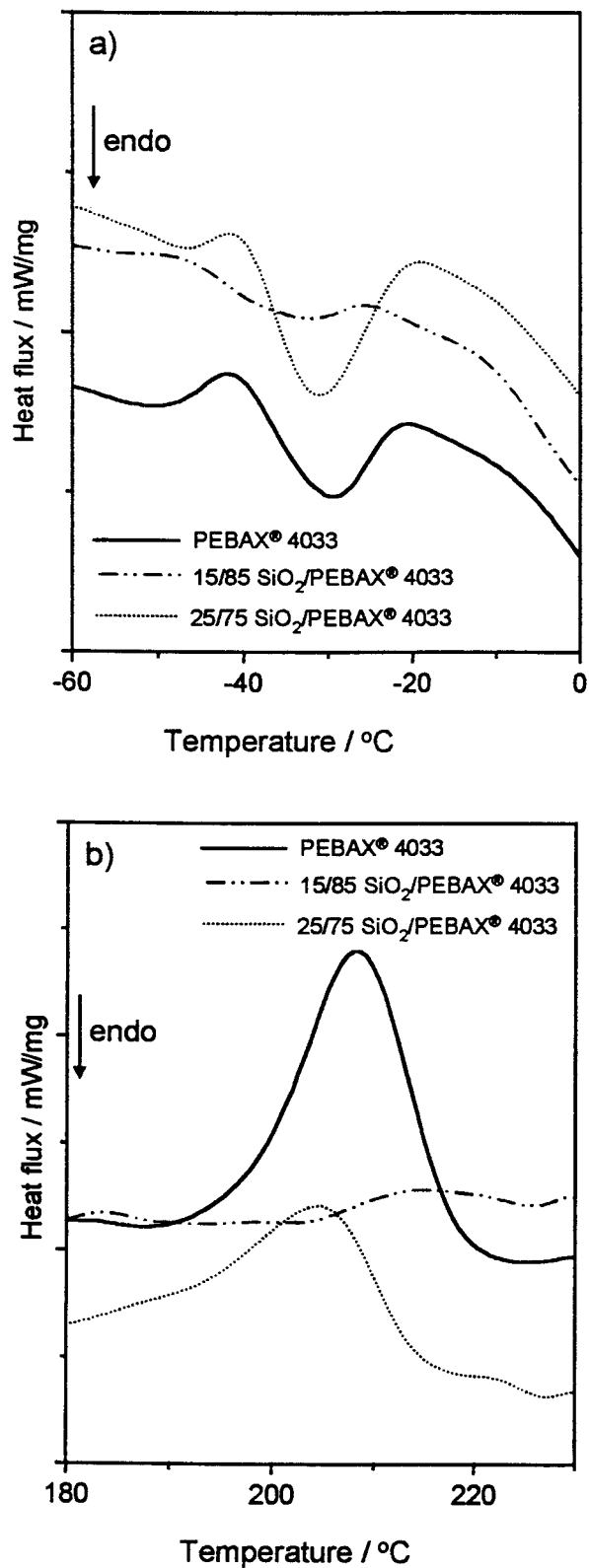


Figure 4 DSC curves of the PEBAX® 4033 film and SiO₂/PEBAX® 4033 hybrid film: (a) T_g related to the polyether group and (b) T_c related to the polyamide group.

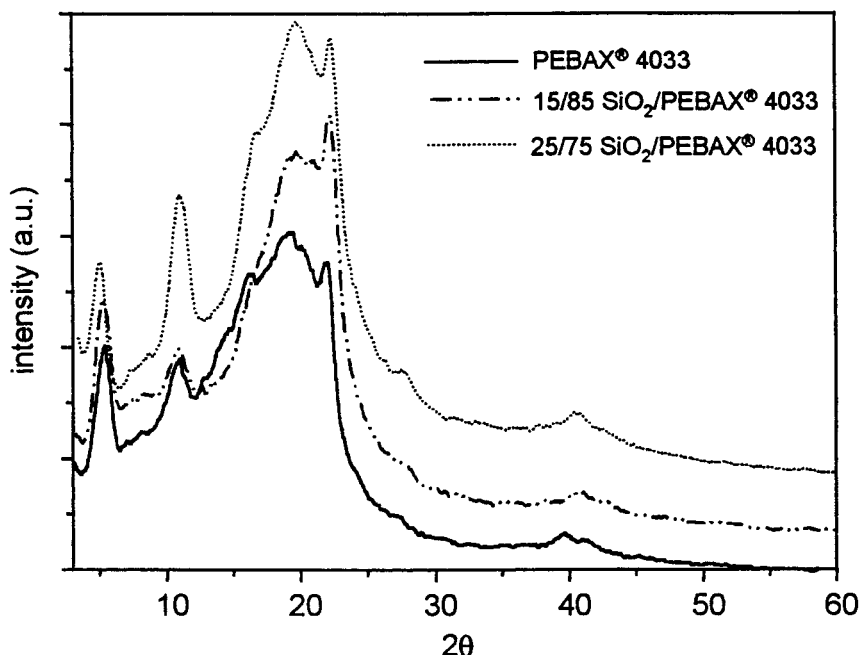


Figure 5 X-ray diffractograms of PEBAX® 4033, 15/85 SiO₂/PEBAX® 4033, and 25/75 SiO₂/PEBAX® 4033.

suggesting the separation of organic and inorganic phases in higher domain sizes, enough to be distinguished by the DSC technique, which is in agreement with the morphology observed by TEM.

X-Ray Diffraction

Figure 5 shows the X-ray diffraction patterns of PEBAX® 4033 and SiO₂/PEBAX® 4033 solution-cast films. PEBAX® 4033 is a partially crystalline polymer, with a narrow diffraction peak at 5° (2θ) and an amorphous halo that almost obscures the presence of diffractions at 10.7, 16.4, 19.5, and 22.1° (2θ).

Although the patterns obtained for all the films were similar, the 15/85 SiO₂/PEBAX® 4033 hybrid had a less intense diffraction peak at 10.7°, indicating that the SiO₂ network disturbed the

arrangement of specific sites of the organic polymer chains. With a higher SiO₂ content, phase separation was favored. The phase quite poor in SiO₂ could better crystallize, giving a higher diffraction peak at 10.7°.

Gas Permeability

In nonporous membranes, the transport of gases is well described by the solution–diffusion mechanism,¹⁷ which involves three steps: the solubility of permeants into the polymer, the diffusion through the polymer matrix, and the desorption at the permeate side. Hence, the permeability (P) of a certain polymer can be written as the product of a solubility coefficient (S) and a diffusivity coefficient (D). Therefore, the permeate flux (J) can be correlated to the permeability times the drive

Table I Gas Permeability of PEBAX® 4033 and SiO₂/PEBAX® 4033 Membranes

Membrane	Permeability/10 ⁻¹⁰ (cm ³ cm s ⁻¹ cm ⁻² cmHg ⁻¹)				
	H ₂	N ₂	O ₂	CH ₄	CO ₂
PEBAX® 4033	15 ± 1	2.6 ± 0.3	7.1 ± 0.1	9.0 ± 2	76 ± 7
15/85 SiO ₂ /PEBAX® 4033	12 ± 2	2.8 ± 0.2	5.7 ± 0.9	9.4 ± 2	71 ± 8
25/75 SiO ₂ /PEBAX® 4033	21 ± 1	5.8 ± 0.2	12.6 ± 0.9	19 ± 2	139 ± 15

Table II Gas Selectivity of PEBAX® 4033 and SiO₂/PEBAX® 4033 Membranes

Membrane	Selectivity					
	H ₂ /CH ₄	CO ₂ /CH ₄	CO ₂ /N ₂	H ₂ /N ₂	O ₂ /N ₂	CO ₂ /H ₂
PEBAX® 4033	1.6 ± 0.4	8 ± 2	29 ± 4	5.8 ± 0.8	2.7 ± 0.3	5.0 ± 0.6
15/85 SiO ₂ /PEBAX® 4033	1.3 ± 0.3	7.6 ± 1.8	25 ± 3	4.3 ± 0.8	2.0 ± 0.3	6.0 ± 1.2
25/75 SiO ₂ /PEBAX® 4033	1.1 ± 0.1	7.2 ± 1.1	25 ± 3	3.6 ± 0.2	2.1 ± 0.2	6.6 ± 0.8

force, that is, the pressure difference (Δp) divided by the membrane thickness (l):

$$J = P \frac{\Delta p}{l} \quad (1)$$

The ideal separation factor α , which is an index of the overall selectivity of a polymer, can be expressed in the following terms:

$$\alpha_{A/B} = \frac{P_A}{P_B} \quad (2)$$

where P_A and P_B are the permeabilities for gases A and B .

The hybrid films used in gas permeation experiments had a thickness of 60–130 μm .

The 15/85 SiO₂/PEBAX® 4033 film induced no significant changes in the membrane performance. However, the 25/75 SiO₂/PEBAX® 4033 membrane had a higher permeability for all gases, as shown in Tables I and II. The higher segregation of SiO₂ domains in the last membrane probably generated small cavities between the phases, reducing the film resistance to gas transport.

Sorption

The solubility of the PEBAX® 4033 film and the hybrids containing silica was evaluated by the

equilibrium absorption of the samples when introduced into some solvents.

Table III shows the percentage of organic solvent absorption in the elastomeric and hybrid films.

Pure PEBAX® 4033 and 25/75 SiO₂/PEBAX® 4033 films absorbed more solvent than the 15/85 SiO₂/PEBAX® 4033 hybrid film. All the films were soluble in pure phenol at 50°C.

According to microscopy, 15/85 SiO₂/PEBAX® 4033 had a more homogeneous structure with better dispersion of the SiO₂ phase. It seems that, at this composition, the inorganic phase forms a network that reduces the swelling of the organic polymer reach matrix.

However, in the 25/75 SiO₂/PEBAX® 4033 hybrid film, the inorganic component is not well dispersed in the polymer matrix. It is distributed in large domains with less influence on the swelling of the matrix as a whole.

Pervaporation

Pervaporation is a separation process in which a multicomponent liquid is passed across a membrane that preferentially permeates one or more of the components. A partial vacuum is maintained on the permeate side of the membrane, so that the permeating components are removed as a vapor mixture.

The transport model for the pervaporation is also based on a solution–diffusion mechanism.

Table III Pure Organic Solvent Absorption at 50°C of PEBAX® 4033 and SiO₂/PEBAX® 4033 Hybrid

Membrane	Sorption (wt %)				
	Methanol	Ethanol	<i>n</i> -Propanol	Phenol	Water
PEBAX® 4033	22	26	75	Dissolved	Nondetectable
15/85 SiO ₂ /PEBAX® 4033	7	16	37	Dissolved	Nondetectable
25/75 SiO ₂ /PEBAX® 4033	19	28	44	Dissolved	Nondetectable

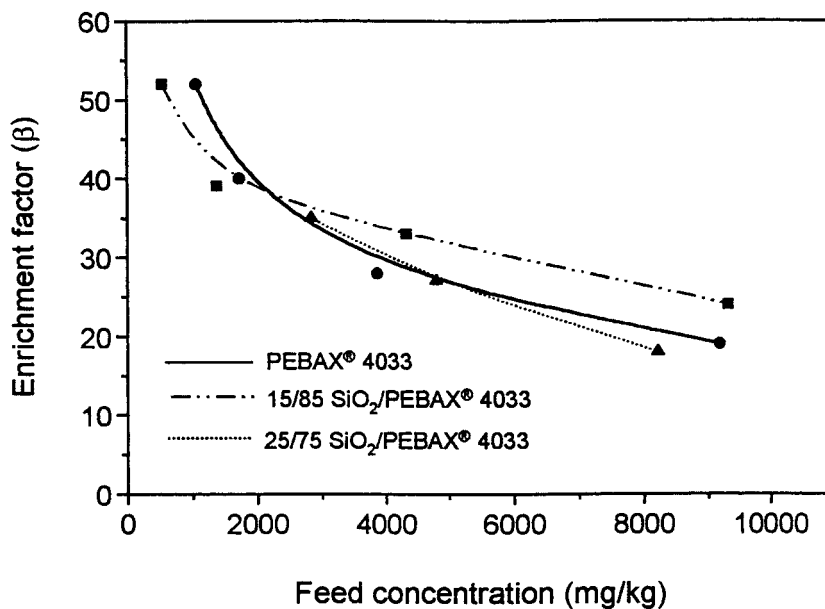


Figure 6 Enrichment factor as a function of the feed concentration of phenol of the PEBAX® 4033 film and the hybrid SiO₂/PEBAX® 4033 film.

However, because of higher swelling of the polymer matrix and coupling of fluxes, it is more complex than gas permeation. In the pervaporation of an aqueous solution with diluted organics, the solubility limit of the organic in water leads to high activity to the organic at the feed side. Because the activity at the permeate side is kept at very low values (vacuum), a large driven force is established to the organic solute and to the water. Consequently, the affinity of the component and polymer or, in other words, the sorption step, is very important in the selectivity of the process.

The selectivity of a membrane can be specified with the ratio of concentrations in the feed and permeate. In this article, we discuss the results in terms of the enrichment factor, which is defined as

$$\beta = \frac{c_i''}{c_i'} \quad (3)$$

where c_i' and c_i'' are the concentrations of the organic component in the feed and permeate, respectively.

Figure 6 shows the behavior of the enrichment factor as a function of the feed concentration, in the pervaporation process, for PEBAX® 4033 and hybrid films. The 15/85 SiO₂/PEBAX® 4033 film promotes an increase in the enrichment factor of the phenol, although the 25/75 SiO₂/PEBAX®

4033 hybrid film basically did not show variation in this value.

As discussed in the Sorption section, the 15/85 SiO₂/PEBAX® 4033 hybrid has the SiO₂ network dispersed in the polymer matrix, which precludes the swelling effect caused by the phenol solution, extending the application range for phenol removal to 10,000 mg/kg. The most important factor observed in this membrane is the water flux resistance caused by the silica network. The silica segregation in the 25/75 SiO₂/PEBAX® 4033 film decreased the enrichment factor (in comparison with the hybrid film containing 15 wt % TEOS) of the phenol solution caused by the higher transport of water through the membrane. This can be easily seen in a comparison of the water-normalized fluxes as a function of the phenol feed concentration (see Fig. 7). In Figure 7, the results of Bøddeker et al.¹⁵ are also represented for comparison.

CONCLUSIONS

The introduction of an inorganic phase to a poly-(amide-*b*-ether) (PEBAX® 4033) matrix promoted a considerable change in its performance in sorption and pervaporation experiments and in film morphology. Films prepared with 15 wt % TEOS showed a well-dispersed inorganic SiO₂ network

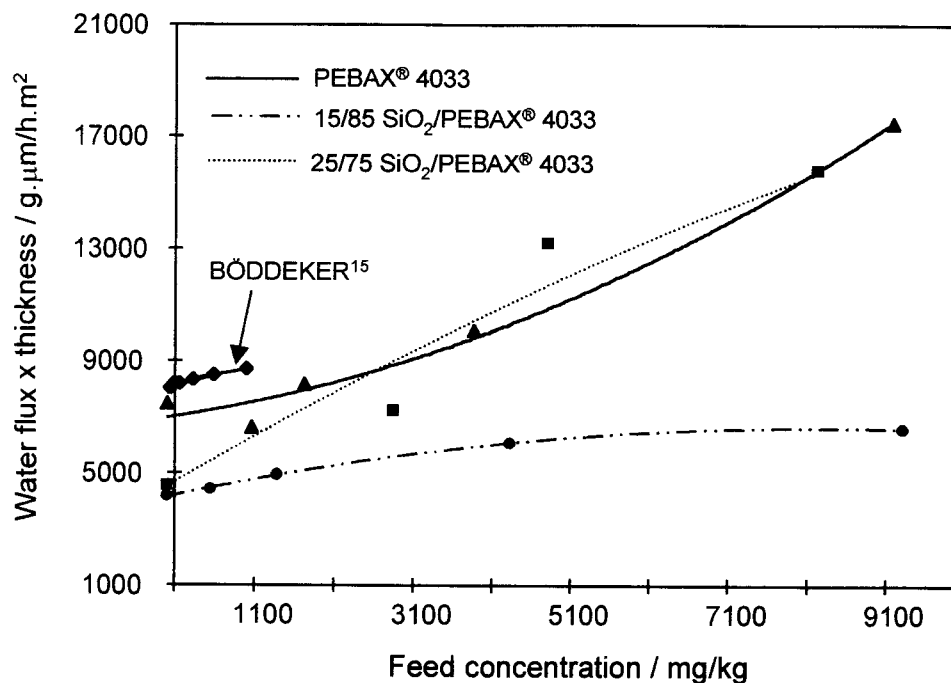


Figure 7 Normalized water flux curves of PEBAX® 4033 and SiO₂/PEBAX® 4033.

that considerably lessened the film swelling in different solvents and made the pervaporation of phenol/water solutions more selective. Films prepared with 25 wt % TEOS had a clear phase-separated morphology with lower performance in pervaporation.

REFERENCES

- Nunes, S. P.; Silveira, K. F.; Yoshida, I. V. P. *Polymer* 1995, 36, 1425.
- Nunes, S. P.; Zoppi, R. A.; Yoshida, I. V. P. *Polymer* 1997, 39, 1309.
- Nunes, S. P.; Zoppi, R. A.; Castro, C. R.; Yoshida, I. V. P. *Polymer* 1997, 38, 5705.
- Nunes, S. P.; Zoppi, R. A. *J Electroanal Chem* 1998, 445, 1–2, 39.
- Zoppi, R. A.; Fonseca, C. M. N. P.; De Paoli, M. A.; Nunes, S. P. *Acta Polym* 1997, 48, 131.
- Nunes, S. P.; Schultz, J.; Peinemann, K. V. *J Mater Sci Lett* 1996, 15, 1139.
- Nunes, S. P.; Sforça, M. L.; Yoshida, I. V. P. *J Membr Sci* 1999, 159, 197.
- Ulrich, D. R. *J Non-Cryst Solids* 1994, 100, 174.
- Wung C. J.; Wijekoon, W. M. K. P.; Prasad, P. N. *Polymer* 1993, 34, 1174.
- Ravaine, D.; Seminel, A.; Charbouillot, Y.; Vincens, M. *J Non-Cryst Solids* 1986, 82, 210.
- Schubert, V. *New J Chem* 1994, 18, 1049.
- Nitanda, J.; Wakasa, K.; Matsui, H.; Kasahara, Y.; Yamaki, M.; Matsui, A. *J Mater Sci: Mater Med* 1992, 3, 137.
- Schmidt, H. *J Non-Cryst Solids* 1985, 73, 68.
- Guizard, C.; Lacan, P. *New J Chem* 1994, 18, 1097.
- Böddeker, K. W.; Bengtson, G.; Bode, E. *J Membr Sci* 1990, 53, 143.
- Chatterjee, G.; Houde, A. A.; Stern, S. A. *J Membr Sci* 1997, 135, 99.
- Crank, J.; Park, G. S. *Diffusion in Polymers*; Academic: London, 1968.