

Characterization of Poly(dimethylsiloxane)-Poly(methyl hydrogen siloxane) Composite Membranes for Organic Water Pervaporation Separation

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ABSTRACT: Hydrophobic composite membranes with a crosslinked poly(dimethylsiloxane)-poly(methyl hydrogen siloxane) selective layer were prepared by using a new laboratory made catalyst agent. The pervaporation separation of five organic solvent–water mixtures was carried out with these composite membranes, together with swelling experiments in the same feed mixtures. The volatile organic compounds employed were ethanol, methanol, 1-butanol, acetone, and ethyl acetate. The pervaporation and swelling experiments revealed that both the 1-butanol and the ethyl acetate solutions showed the highest affinity for the composite membrane. When these components were employed as feed solutions, the membranes showed both high selectivity and high permeation. Mechanical–dynamical experiments of swollen and nonswollen composite membranes were also performed. The relaxation spectra were analyzed in terms of the interaction of the components of the different mixtures with the composite membrane, and the free volume corresponding to the each sample was obtained. Once the membranes had reached an equilibrium swelling, a decrease in the free volume was observed. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 546–556, 2001

Key words: pervaporation; composite membrane; silicone membrane; swelling ratio; mechanical relaxation; volatile organic compounds

INTRODUCTION

During the few last years the removal of volatile organic compounds (VOCs) from liquid mixtures at a low concentration level by pervaporation has gained further interest, especially in the recovery and recycling of substances from

effluent streams, as well as in environmental and biotechnological applications. Although the pervaporation separation of many industrial solvents such as alcohols and ketones, esters, halogenated hydrocarbons, and mixtures of them has been widely studied, few applications have come to an industrial scale. The cause for this is probably the lack of high performance specific materials and membranes. The separation of each organic solute, or mixture of them, from aqueous solutions requires a specific type of membrane due to the various natures of the organic solvents employed.¹

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In this work, different crosslinked composite membranes were prepared using a new catalyst agent. The membranes had the following three layers: a nonwoven polypropylene (PP) support, a poly(ether imide) (PEI) microporous structure, and a silicone selective layer. This active layer was prepared from a mixture of poly(dimethylsiloxane) (PDMS) and poly(methyl hydrogen siloxane) (PMHS).

The composite membranes thus obtained were employed for the pervaporation separation of different VOCs from aqueous solutions. Liquid transport in pervaporation takes place by three consecutive steps described commonly as a solution—diffusion model.² The first step is the sorption of the components from a liquid mixture on the membrane surface; the second step is the diffusion of the sorbed components across the membrane due to the concentration gradients of the individual permeants; and the third step is the evaporation from the membrane into the vapor phase on the downstream side of the system.

According to this model the permeability of a membrane is a function of the solubility and diffusivity of the components of the mixture into the polymeric membrane.³

The goal of this study was to examine the permeation and sorption behavior of different VOC–water mixtures through the PDMS-PMHS composite membranes. Pervaporation and swelling experiments were performed with ethanol, methanol, 1-butanol, acetone, and ethyl acetate–water mixtures (5 vol % VOC ratio). The dynamical–mechanical relaxation spectrum at low temperatures for composite membranes swollen in the solutions described above was also studied. The swelling ratio and the pervaporation behavior of the membrane swollen in each solution were interpreted in terms of the interaction of each solvent mixture with the membrane polymers and the free volume obtained from the relaxation process.

EXPERIMENTAL

Materials

The PP was commercial grade FO-2431 from Freudenberg. The PEI was Ultem 1000 from General Electric Polymers. Dimethylacetamide (DMAc) was used as a solvent. The PMHS was a silicone oil hydrofugant H-619, and the PDMS was the dense fluid 331-V50.000 from Siliconas

Hispania S.A. 2-Ethylhexanoic acid zinc salt (Kemisol O Zn 22, 22% Zn) was supplied by Unión Derivan, S.A., and di-*n*-butyl tin dineodecanoate (Metatin Kat 730, 20% Sn) was supplied by Acima Chemical Industries, Ltd. Toluene, perchloroethylene, and *n*-hexane P.A. were analytical grade from Scharlau. Water was double distilled before use.

The reagent grade solvents used as penetrants were ethanol, methanol, 1-butanol, acetone, and ethyl acetate.

A commercial silicone composite membrane manufactured by Sulzer was also employed in the pervaporation experiments. Its performance was compared to that of the composite membranes prepared in our laboratory.

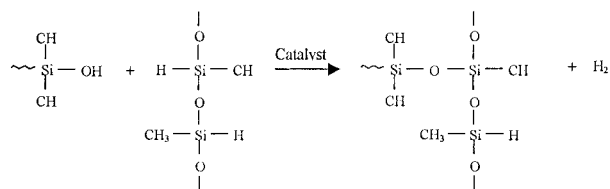
Preparation of Samples

The procedure employed for the preparation of the silicone composite membranes was as follows: first the microporous structure was formed from PEI by casting a DMAc solution (15% w/w PEI) on a nonwoven PP support, following the phase inversion method.^{4,5} Then the selective layer was prepared from a mixture of PDMS and PMHS by casting a hexane solution on the microporous structure. The silicone hydrofugant (PMHS) and dense fluid (PDMS) in a 40% (w/w) PDMS/PMHS ratio were dissolved with hexane in a 1.7 mL g⁻¹ PDMS ratio and hydrolyzed by catalyst action through a heat treatment at 85°C in an oven for 2 h.

The catalyst agent used was prepared in our laboratory from a solution consisting of 27.2% (w/w) Kemisol, 9.5% (w/w) Metatin, 4.8% (w/w) toluene, and 58.5% (w/w) perchloroethylene. In our previous studies^{6,7} we prepared similar silicone composite membranes employing different amounts of a commercial catalyst agent.

The pervaporation behavior of the resulting membranes was studied,^{6,7} and it was stated that an optimum amount of catalyst exists between a 7.5 and 10% catalyst ratio. In this work the catalyst agent was added to the PDMS-PMHS solution in a 7.5 wt % ratio.

During the crosslinking reaction induced by catalyst action, the Si–H bonds of the PMHS reacted with the PDMS liberating hydrogen (Scheme 1). In order to prevent the formation of a porous structure in the active layer of the composite membrane, all nascent hydrogen was removed.



Scheme 1

The PDMS-PMHS solution was cast on the microporous structure. Different amounts of casting solution (all in the range of 0.005 g cm^{-2}) were employed in the preparation of each membrane and, consequently, membranes with active layers of different thicknesses were obtained. Table I shows the amount of silicone solution coated in each sample. The thicknesses of the active layers thus obtained were in the range of $40 \mu\text{m}$ (which represents an average of measurements in three equivalent membranes). The final structure of the active layer and its mechanical behavior is dependent on the composition of the PDMS-PMHS, the heat treatment, and the catalyst ratio employed.⁶

In order for an in-depth study of the complexity of the structure of the active layer of the PDMS-PMHS composite membranes, homogeneous films made with the rubber alone were also prepared and their dynamical-mechanical response was studied separately. Crosslinked silicone films were prepared following the procedure explained above, but the PDMS-PMHS hexane solution was directly cast on a clean Teflon plate. The film thickness measured by a thickness gauge was $600 \pm 1 \mu\text{m}$.

Pervaporation Experiments

Pervaporation experiments were carried out by employing a laboratory plant described in our previous works.⁵ The pervaporation cell was capable of holding several flat membranes at a time. The experiments were performed with three flat membranes, each with independent permeate collection. The effective area in contact with the feed solution of each membrane was 78.54 cm^2 . A vac-

uum pump maintained the downstream pressure at 7 mmHg , and the permeate was collected in a trap cooled at a temperature of -22°C . The feed temperature was maintained at 40°C , and a feed flow of 4.8 L h^{-1} was used.

The feed solutions employed were the mixtures of different VOCs (ethanol, methanol, 1-butanol, acetone, and ethyl acetate) and water at a 5 vol % VOC ratio. The membranes were previously swollen in the same feed mixtures. The concentration of VOCs in the feed and permeate were determined by refraction index (± 0.0005 precision, ABBE refractometer, Shibuya Optical) and density measurements.

The pervaporation performance was characterized in terms of the steady-state flux and selectivity. The flux (J) at a steady state was obtained by

$$J = \frac{Q}{At} \quad (1)$$

where Q is the total amount permeated during the experimental time interval t , which is determined by measuring the volume of the collected sample; A is the effective membrane surface area; and J is the total flux ($\text{L m}^{-2} \text{ h}^{-1}$).

The selectivity (α) is defined in the usual manner as

$$\alpha = \frac{X_o^p/X_w^p}{X_o^f/X_w^f} \quad (2)$$

where X is the volume fraction; and the superscripts p and f and the subscripts o and w stand for the permeate, feed, VOC, and water, respectively.

In order to compare the pervaporation performance of the PDMS-PMHS composite membranes prepared in our laboratory, pervaporation experiments were also carried with the same feed mixtures using a commercial silicone pervaporation membrane. Table I summarizes the main characteristics of the membranes employed.

Table I Characteristics of Membranes

Membrane	Type of Membrane	Catalyst (% w/w)	Silicone Coated (g cm^{-2})
PV-1	Laboratory made	7.5	0.0048
PV-2	Laboratory made	7.5	0.0060
Sulzer membrane	Commercial membrane	—	—

Table II Pervaporation Data of Organic Solvent–Water Mixtures (5 vol % Organic) for Membranes at 40°C

VOC	PV-1		PV-2		Sulzer Membrane	
	Total Flux (L m ⁻² h ⁻¹)	Selectivity α	Total Flux (L m ⁻² h ⁻¹)	Selectivity α	Total Flux (L m ⁻² h ⁻¹)	Selectivity α
Ethanol	0.27	3.7	0.08	4.1	0.16	5.5
Methanol	0.29	2.7	0.08	2.8	0.165	3.05
1-Butanol	0.50	6.7	0.15	15.7	0.26	20.9
Acetone	0.49	5.6	0.15	13.3	0.335	34.1
Ethyl acetate	0.55	8.4	0.27	23.7	0.46	76.2

Swelling Test

The increase in weight of the membranes during the swelling process was determined following the procedure reported by Ruckenstein and Chen.⁸ The composite membranes were cut into the shape of a slab with dimensions of 12 × 50 mm. The slabs were first dried at 65°C in a vacuum oven for 2 h, and the weight of the dried membranes was determined. The dry slabs were then immersed in various organic solvent and water mixtures (5 vol % VOC ratio) at 40°C. The membranes were periodically removed from the mixtures and the solution on the surface of the membranes was carefully wiped with tissue paper, then the membranes were weighed. The amount of solution absorbed into the membranes and the swelling ratio were calculated from the weight increase of the samples. This process was carried out for each organic solvent and water solution until an equilibrium swelling was reached. The swelling ratio of the membrane (S) is defined as

$$S = \frac{(W_s - W_d)}{W_d} \quad (3)$$

where W_d and W_s represent the weight of the dry and swollen membranes, respectively.

Dynamical–Mechanical Measurements

The mechanical spectroscopy was performed in a dynamic–mechanical thermal analyzer (Mark IV DMTA, Polymer Laboratories Ltd.) with deformation applied in the cantilever flexure double-clamping mode. Measuring scans were performed between –140 and –80°C in a frequency–temperature sweep test mode with 5°C steps and frequencies ranging between 0.1 and 100 Hz with

five points per decade. The values of the damping ($\tan \delta$), storage modulus (E'), and loss modulus (E'') were obtained.

RESULTS AND DISCUSSION

Pervaporation Experiments with Different VOC–Water Mixtures

Pervaporation experiments were carried out with the different composite membranes described in Table I. The selectivity and total flux for the different membranes and the VOC–water mixtures studied are summarized in Table II. The PDMS-PMHS composite membranes showed very good pervaporation performance. Usually most polymer membranes with high permselectivity have disappointingly low fluxes, which would indicate that, although the polymer is efficient at separating molecules, diffusion through the membrane is low, resulting in no economic benefit. On contrary, the PDMS-PMHS composite membranes possessed both high selectivity and high permeation. As shown in Table II, the total flux obtained with membrane PV-1 was even higher than that obtained with the commercial membrane for all the VOCs studied. With respect to the selectivity, the commercial membrane showed the highest selectivity for all the solutions employed, but membrane PV-2 presented very similar values.

A comparison of the performance of the two different PDMS-PMHS membranes studied showed that PV-2 had a very high selectivity but its flux was lower than that of PV-1. This was due to the fact that the silicone active layer of membrane PV-2 was thicker than that of membrane PV-1. This was confirmed by the larger quantity of silicone deposited on the microporous layer of

membrane PV-2 during membrane preparation (see Table I).

A comparison of the different VOCs used showed that the order of increasing permeability and increasing selectivity was methanol \leq ethanol $<$ acetone $<$ 1-butanol $<$ ethyl acetate–water solution.

The order of increasing permeability established with the three alcohols studied was methanol \leq ethanol $<$ 1-butanol, independent of the membrane employed. As shown in Table II, ethanol and methanol solutions had very similar total fluxes, but the total flux obtained with the 1-butanol–water solution was substantially higher than the former. These results were in accordance with other studies where it was stated that, in general, the permeability of alcohols increases with increasing chain length (i.e., decreasing polarity).²

Pervaporation is a process that combines evaporation of volatile components of a mixture with their permeation through a membrane. Its selectivity depends on the following three factors concerning the nature of the molecule: affinity to the membrane material, the bulkiness of the molecule, and the vapor pressure of the feed solution. Generally, for glassy polymers the permeability is mainly determined by the diffusivity (depending on the size of the permeating molecules) while for elastomeric polymers the solubility contribution is decisive.¹⁰ Moreover, membrane swelling plays an important role in determining the permselectivity and the pervaporation performance of the membranes. Separation can be obtained from different transport rates of permeants through a membrane, but the physical–chemical interaction of the membrane material with permeating molecules should also be taken into account.

Many works sought to study the solution–diffusion mechanism occurring in the pervaporation separation of different mixtures.^{11–13} Most frequently, the solubilities and diffusivities are determined from sorption and pervaporation rate measurements. Time-lag experiments allow the diffusion coefficient and the solubility to be determined from the approach to steady state in a permeation experiment. Sorption equilibria and diffusion coefficients of molecules sorbed into a polymer are also usually studied by performing sorption–desorption experiments by means of a microbalance.¹⁴

Our work was also aimed at studying the transport phenomenon occurring in the pervaporation separation of a mixture in terms of solution and diffusion processes, but other techniques were employed. The diffusion mechanisms were studied in terms of the swelling behavior of the

membranes. The interaction of low molecular weight components in the polymeric membrane were analyzed in terms of a modification of the relaxation spectra of swollen and nonswollen samples, which was related to the solution mechanisms occurring in the membrane.

Swelling Behavior

Swelling experiments were performed with different slabs of membrane PV-1, which was the membrane that showed the highest flux and relatively high selectivity in the pervaporation experiments described previously. Swelling in various VOC–water mixtures (5 vol % VOC ratio) was carried out until equilibrium swelling was reached.

Figure 1 compares the swelling ratio of the PDMS-PMHS composite membrane as a function of time in five different VOC–water mixtures. The membranes showed a relatively high swelling ratio in all the solutions. This confirmed the high affinity for organic solvents of the PDMS-PMHS membranes. Equilibrium swelling was reached by about 50 h in all cases. The highest swelling ratio was obtained in the ethyl acetate–water solution, followed by the 1-butanol–water solution. This was in agreement with the pervaporation results that confirmed that the solution preferentially permeated was also the ethyl acetate–water solution, followed as well by the 1-butanol–water solution. On the other hand the ethanol solution presented the lowest swelling performance. Swelling in the ethanol solution was even lower than that of methanol, which was supposed to be the solution with less affinity for the PDMS-PMHS membranes, according to the pervaporation results.

In order to compare the amount of solvent sorbed in each VOC–water mixture, the ratio of the amount of solvent sorbed at time t (M_t) to the amount sorbed at equilibrium (M_∞) versus the square root of the time is plotted in Figure 2. The diffusion coefficient of solutions in the PDMS-PMHS composite membranes can be obtained from the slope of the curves thus obtained, according to Fick's law¹⁵

$$\frac{M_t}{M_\infty} = \frac{4}{\pi} \left[\frac{D \times t}{L^2} \right]^{1/2} \quad (4)$$

where M_t and M_∞ are the amount of solvent sorbed at time t and at equilibrium, respectively; D is the diffusion coefficient; and L is the specimen thickness.

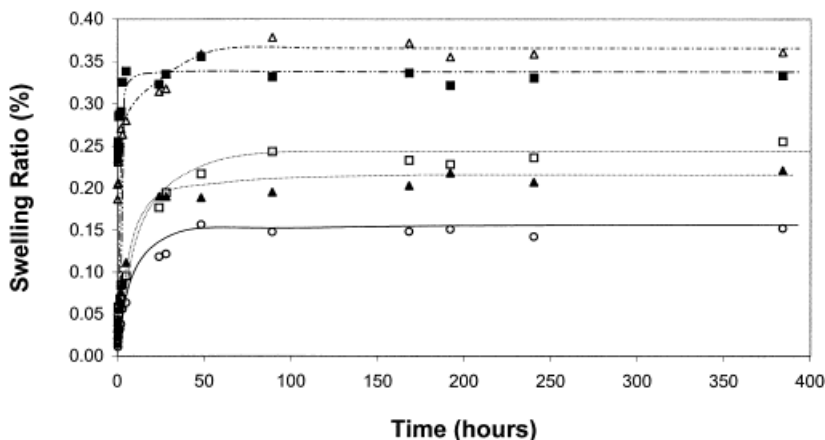


Figure 1 The swelling ratio of PV-1 membrane strips with different VOC–water solutions as a function of time: (○) 5% ethanol, (■) 5% 1-butanol, (□) 5% methanol, (▲) 5% acetone, and (△) 5% ethyl acetate.

Figure 2 shows that, for small times of permanence, a linear dependence of swelling with time could indeed be established, but for larger times of permanence swelling became parabolic with the square root of time. This probably meant that the diffusion coefficients changed when the membranes were highly swollen. The swelling finally reached equilibrium after 50 h of permanence in the solution. This result suggested that the PDMS-PHMS composite membrane had a maximum quantity of solvent that was capable of absorbing, independent of the mixture used.

A comparison of the slopes of the curves obtained revealed that the slope corresponding to the 1-butanol–water mixture was the steepest, followed by the ethyl acetate–water solution. Thus, the order of an increasing diffusion coefficient of the different organic solvent–water mix-

tures was ethanol < methanol < acetone < ethyl acetate < 1-butanol–water mixture. This meant that the 1-butanol–water solution entered the PDMS-PMHS network faster, even if the equilibrium swelling reached with this solution was lower than that reached with the ethyl acetate–water mixture.

Both representations (Figs. 1, 2) allowed us to establish a general order of affinity of the membrane from the pervaporation and swelling experiments: the membrane showed high affinity for both ethyl acetate and 1-butanol while it showed less affinity for the other three components studied.

Viscoelastic Relaxations

In order to further investigate the effects of the absorbed molecules on the behavior of the com-

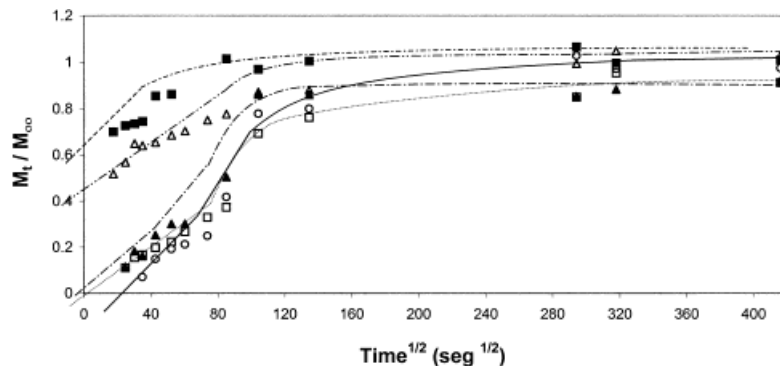


Figure 2 The normalized swelling of PV-1 membrane strips with different VOC–water solutions: (○) 5% ethanol, (■) 5% 1-butanol, (□) 5% methanol, (▲) 5% acetone, and (△) 5% ethyl acetate.

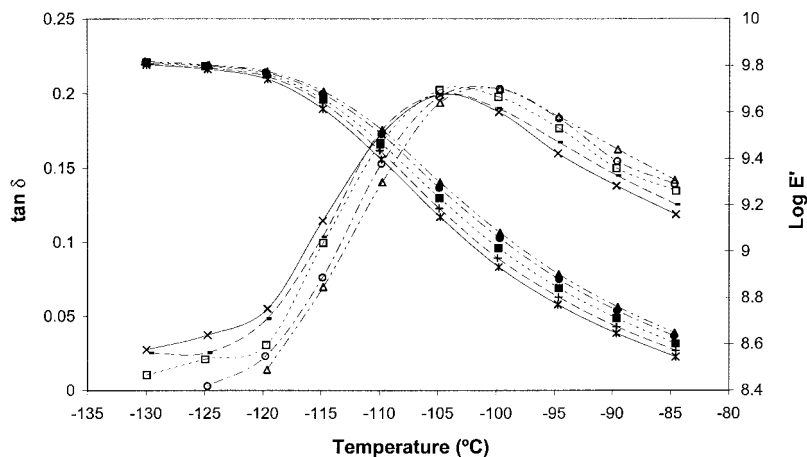


Figure 3 The temperature dispersion of the loss tangent ($\tan \delta$) and storage modulus (E') of crosslinked PDMS-PMHS films made with 7.5% catalyst ratio at different frequencies: (\times) $\tan \delta$ at 2.51 Hz, (—) $\tan \delta$ at 6.31 Hz, (\square) $\tan \delta$ at 15.85 Hz, (\circ) $\tan \delta$ at 39.81 Hz, (\triangle) $\tan \delta$ at 63.09 Hz, ($*$) $\log E'$ at 2.51 Hz, ($+$) $\log E'$ at 6.31 Hz, (\blacksquare) $\log E'$ at 15.85 Hz, (\bullet) $\log E'$ at 39.81 Hz, and (\blacktriangle) $\log E'$ at 63.09 Hz.

posite membranes, dynamical–mechanical experiments were performed. First the silicone active layer was characterized. Crosslinked PDMS-PMHS films with a final structure similar to that of the active layer of the composite membrane were prepared. Figure 3 represents their corresponding relaxation spectrum in terms of $\tan \delta$ and $\log E'$ as a function of temperature at different frequencies. The PDMS-PMHS film showed a well-developed process centered at -103°C (15.85 Hz), which was conventionally designated as the α -mechanical relaxation and can be attributed to the glass transition of the PDMS-PMHS.¹⁶ Moreover, a slight shoulder appeared at around -95°C , which might be explained in terms of the crosslinking of an initially linear polymer.⁶ In our previous studies^{6,7} we stated that the mechanical relaxation of the PDMS-PMHS films became more complex as the percentage of catalyst used or the curing time increased. In fact, as the crosslinking of the sample increased, the main relaxation shifted to higher temperatures and broadened and an overlapped shoulder appeared, all together with a reduction of the intensity of the relaxation peak. Although in this work a new self-made catalyst agent was used, the resulting structure was comparable to that obtained in our previous studies.

Dynamical–mechanical experiments of swollen and nonswollen strips of membrane PV-1 were performed. Once the strips were immersed in each VOC–water mixture and had reached equilibrium swelling, their mechanical–dynamical re-

sponse was obtained by means of a Mark IV DMTA. The values of $\tan \delta$ and $\log E'$ at a 15.85-Hz frequency of all the samples tested are plotted as a function of temperature in Figures 4 and 5, respectively. Similar spectra were obtained at other frequencies, but they are not included for the sake of clarity.

Figures 4 and 5 show that the dynamical–mechanical response of the membranes was modified when the membranes were swollen in different organic–water solutions. Figure 4 shows that the temperatures of the maximum of the α peak of the swollen membranes compared to that of the nonswollen membrane shifted to higher values, independent of the mixture employed. The solution that led to a higher shifting of the temperature was the ethanol–water solution, while the rest of the solutions had very similar shifting.

If we analyze the shape of the relaxation spectra in more detail, we can observe that the spectra corresponding to membranes swollen in the methanol–water and the ethyl acetate–water mixtures were significantly modified when compared to that of the nonswollen membrane. However, the changes in the spectrum observed with the methanol–water and the ethyl acetate–water solutions were different. Thus, we suggested that the modifications occurring in each solution were of different origin.

The membrane swollen in the methanol–water mixture showed a decrease in the intensity of the spectrum, but its pattern was maintained. The decrease of the maximum values of the α peak can

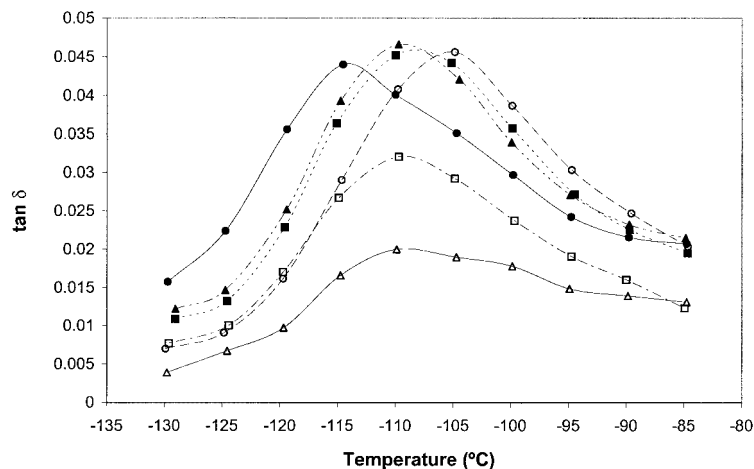


Figure 4 The plot of the $\tan \delta$ versus the temperature at 15.85-Hz frequency for PV-1 membranes swollen in various VOC–water solutions: (●) not swollen, (○) 5% ethanol, (■) 5% 1-butanol, (□) 5% methanol, (▲) 5% acetone, and (△) 5% ethyl acetate.

be partially explained by a difference in the thickness of the active layer of the membranes employed. In fact, the method employed for the deposition of the silicone active layer did not allow for very precise control over the thickness of the active layer.

On the other hand, the α relaxation corresponding to the membrane swollen in the ethyl acetate–water mixture was more complex. Not only was the intensity of the α peak reduced, but the overlapped shoulder, already described, also became more important. This effect might have been due to the high interaction of the small molecules of the penetrant with the PDMS-PMHS network. This was in agreement with the order of

affinity established for the PDMS-PMHS; the ethyl acetate–water mixture presented the highest swelling ratio.

The anomalous behavior of the PDMS-PMHS membrane swollen in the ethyl acetate–water solution may be explained in terms of intramolecular interactions of the solvent with the top layer network. The small molecules of ethyl acetate have a very high affinity for the PDMS-PMHS layer, and their inclusion in the polymer network might have induced further rearrangements of the polymeric chain similar to a crosslinking reaction. This would explain the change in the shape of the relaxation spectrum of the sample swollen in the ethyl acetate–water mixture to-

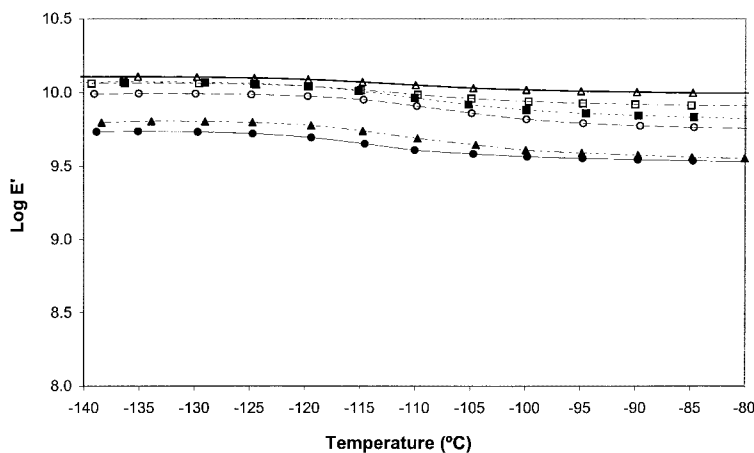


Figure 5 The plot of the $\log E'$ versus the temperature at 15.85-Hz frequency for PV-1 membranes swollen in various VOC–water solutions: (●) not swollen, (○) 5% ethanol, (■) 5% 1-butanol, (□) 5% methanol, (▲) 5% acetone, and (△) 5% ethyl acetate.

ward more complex and less intense spectra. Similar transformations of the relaxation spectrum were obtained in our previous studies^{6,7} when a higher catalyst ratio or longer curing times of the PDMS-PHMS layer were employed.

Figure 5 plots a comparison of the storage modulus of the samples swollen in different mixtures. It is shown that E' increased when the sample was swollen in any of the solutions employed. The highest storage modulus was obtained with the ethyl acetate–water mixture. This meant that the absorption of the molecules of the mixture in the composite membrane led to a more rigid PDMS-PHMS structure. This confirmed that the ethyl acetate–water solution highly interacted with the polymer matrix and that the intramolecular reactions occurring led to a higher crosslinking degree, accompanied by a higher modulus value.

In order to correlate the dynamics of the composite membrane with the swelling and pervaporation results and to try to clarify the effect of the sorbed components on the viscoelastic properties of the polymer, the data of the distribution of the relaxation times and the temperatures corresponding to the maximum values of the loss modulus, for all the frequencies employed, were fitted to the Vogel equation.

The viscoelastic mechanisms associated with the glass–rubber transition are in most systems dependent on the free volume, so that the relaxation time π_i , associated with the viscoelastic mechanism i , is related to the free volume by the Doolittle¹⁷ equation

$$\ln \tau_i = \ln A + B(v - v_f)/v_f = \ln A + B\phi \quad (5)$$

where v is the specific volume, v_f is the free volume, ϕ is the relative free volume at temperature T , and B is a constant whose value is believed to be close to unity. If the assumption is made that the free volume linearly increases with temperature in accordance with

$$\phi = \phi_0 + \alpha_f(T - T_0) = \alpha_f(T - T_\infty) \quad (6)$$

where α_f is the thermal dilation coefficient, T_0 is a reference temperature, and T_∞ is the temperature at which the free volume would be zero, one obtains the Vogel relationship¹⁸

$$\ln \tau_i = A + m/(T - T_\infty) \quad (7)$$

where

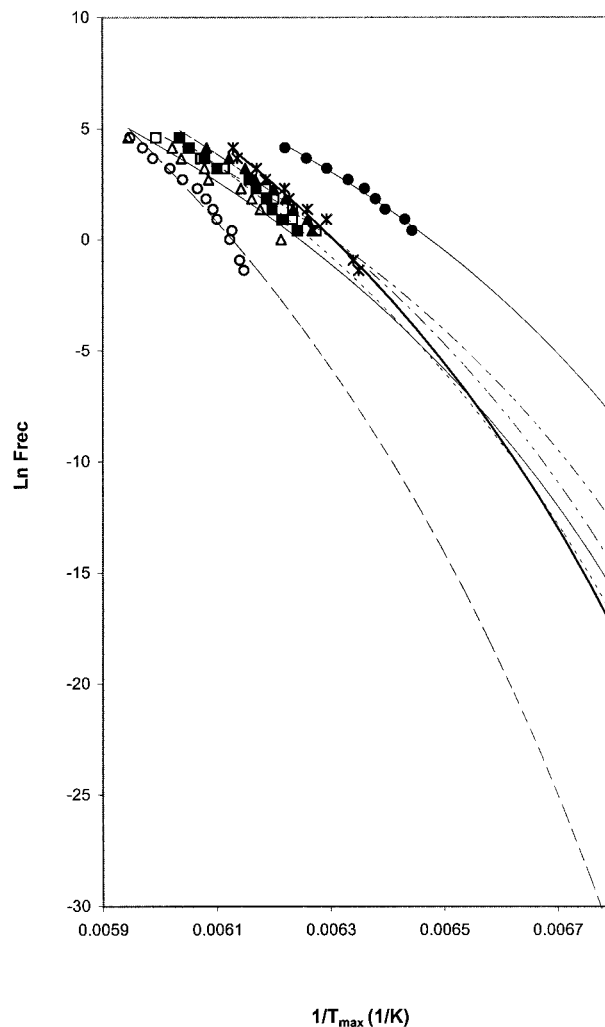


Figure 6 The plot of the logarithm of the relaxation times associated with the maximum of the α peak as a function of $1/T$ for PV-1 membranes swollen in various VOC–water solutions: (●) not swollen, (○) 5% ethanol, (■) 5% 1-butanol, (□) 5% methanol, (▲) 5% acetone, and (△) 5% ethyl acetate.

$$m = \frac{B}{\phi_g} (T_g - T_\infty) = B/\alpha_f \quad (8)$$

Figure 6 shows the plot of the relaxation times associated with the maximum of the α peak as a function of $1/T_{\max}$ for all the samples tested. Because fitting of experimental results to eq. (7) required a choice of T_∞ , trials were made until the best fitting was obtained by using the rule of thumb that this parameter was usually about 50°C below the glass transition. As shown in Figure 6, the experimental results fit the Vogel equation reasonably well for $T_\infty = -148^\circ\text{C}$. The values

Table III Parameter of Vogel Equation for α Relaxation and Values of Free Volume

Sample	m	$[\phi_g/(T_g - T_\infty)] \times 10^{-4}$
Silicone film	1132	9
PV-1 nonswollen	707	14
PV-1 swollen in 5%		
Ethanol solution	1657	6
Methanol solution	823	13
1-Butanol solution	1040	10
Acetone solution	950	11
Ethyl acetate solution	941	11

of $\phi_g/(T_g - T_\infty)$ obtained by using this procedure are presented in Table III. These values were in fair agreement with the values for ϕ_g/B reported by other authors.¹⁹

The values presented in Table III show that the nonswollen membrane had the highest free volume while the sample swollen in the ethanol-water solution had the lowest free volume. The three solutions with which better pervaporation results were obtained (ethyl acetate, 1-butanol, and acetone) led to very similar values of $\phi_g/(T_g - T)$ of around 11×10^{-4} . These solutions were supposed to show more affinity for the PDMS-PMHS composite membranes.

We found that the entrance of small molecules in the composite membranes led to an increase in the temperature of the α peak and a decrease in the free volume. Other authors^{15,20} reported that swelling can alter the polymer structure by forcing rearrangement of the polymer chain, but the disruption of the polymer matrix due to swelling usually caused an increase in free volume. This was associated with a plasticizing effect of the absorbed molecules on the polymer, which is accompanied by a shifting of the glass-transition temperature of the swollen polymer to lower temperatures.^{6,7} Anyway, we should take into account that in this work the whole composite membrane (support, microporous structure, and active layer) was involved in the swelling and the dynamical-mechanical experiments, while other works only reported the behavior of swollen and nonswollen active layers.^{6,7} The PEI microporous layer, which is hydrophilic, might have also interacted in the absorption process of small molecules in the composite membrane.

It is known that PDMS possesses one of the greatest permeability coefficients of any polymer, because of its large free volume and low selectiv-

ity. It was already stated that the liquid mixtures employed here largely swell the composite membranes, but the permselectivity obtained was relatively high. In fact the solution that gave a higher swelling ratio was also the solution that led to a higher selectivity parameter. So it can be finally stated that a more complicated interaction between the organic solvents employed and the composite membrane was occurring.

CONCLUSIONS

The following conclusions can be drawn from this study:

1. Pervaporation experiments with different organic solvent-water mixtures (5 vol % VOC ratio) showed that the PDMS-PMHS composite membranes were organic compound selective and that they had very high total flux and high selectivity.
2. The order of increasing permeability and increasing selectivity obtained was methanol \leq ethanol $<$ acetone $<$ 1-butanol $<$ ethyl acetate-water solution.
3. From the pervaporation and swelling experiments, an order of affinity of the composite membrane could be established: the membrane showed high affinity for ethyl acetate and 1-butanol and showed lower affinity for the other three components studied.
4. The dynamical-mechanical experiments revealed that the relaxation spectra of the membranes were modified when the membranes were swollen in different VOC-water mixtures.
5. Swelling of the composite membranes in different VOC-water mixtures led to a shifting of the relaxation spectra to higher temperatures together with a decrease in the free volume. These anomalous results indicated that a more complicated interaction between the VOC and the polymeric materials of the composite membrane occurred.

REFERENCES

1. Clément, R.; Bendjama, Z.; Nguyen, Q. T.; Néel, J. *J Membr Sci* 1992, 66, 193.

2. Huang, R. Y. M. *Pervaporation Membrane Separation Processes*. Membrane Science and Technology; Elsevier: New York, 1991.
3. Vieth, W. R. *Diffusion in and through Polymers: Principles and Applications*; Hanser and Oxford University Press: New York, 1991.
4. Kim, H. J.; Jo, W. H.; Kang, Y. S. *J Appl Polym Sci* 1995, 57, 63.
5. Alcaina-Miranda, M. I. Ph.D. Thesis, Polytechnical University of Valencia, 1991.
6. Bueso-F. Moscoso, L.; Ribes-Greus, A.; Alcaina-Miranda, M. I. *J Non-Cryst Solids* 1994, 172-174, 1066.
7. Bueso, L.; Osorio-Galindo, M.; Alcaina-Miranda, M. I.; Ribes-Greus, A. *J Appl Polym Sci* 2000, 75, 1424.
8. Ruckenstein, E.; Chen, H. H. *J Appl Polym Sci* 1991, 42, 2429.
9. Yeom, C. K.; Dickson, J. M.; Brook, M. A. *Kor J Chem Eng* 1996, 13, 482.
10. Schauer, J. *J Appl Polym Sci* 1994, 53, 425.
11. Sun, Y. M.; Chen, J. *J Appl Polym Sci* 1994, 51, 1797.
12. Hoshi, M.; Kobayashi, M.; Saitoh, T.; Higuchi, A.; Nakagawa, T. *J Appl Polym Sci* 1998, 69, 1483.
13. Yeom, C. K.; Huang, R. Y. M. *J Membr Sci* 1992, 68, 11.
14. Blume, I.; Schwering, P. J. F.; Mulder, M. H. V.; Smolders, C. *J Membr Sci* 1991, 61, 85.
15. Andreopoulos, A. G.; Polyzois, G. L.; Evangelatou, M. *J Appl Polym Sci* 1993, 50, 729.
16. McCrum, N. G.; Read, B. C.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solids*; Dover Publications: New York, 1991.
17. Doolittle, A. K.; Doolittle, D. B. *J Appl Phys* 1957, 28, 901.
18. Vogel, H. *Physik* 1921, 22, 645.
19. Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980.
20. Muzzalupo, R.; Ranieri, G. A.; Golemme, G.; Drioli, E. *J Appl Polym Sci* 1999, 74, 1119.