

Swelling Behavior of PDMS–PMHS Pervaporation Membranes in Ethyl Acetate–Water Mixtures

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Received 21 November 2003; accepted 29 February 2004

DOI 10.1002/app.20596

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

ABSTRACT: Pervaporation composite membranes were prepared with a three-layer structure: a PP support, a PEI microporous structure, and a PDMS–PMHS selective layer. Swelling tests were performed in water, ethyl acetate, and four different ethyl acetate–water mixtures, to calculate the diffusional and swelling parameters. Moreover, the dynamic–mechanical properties of the membranes were obtained before and after the swelling experiments, and their relaxation spectra were characterized with the Fuoss–Kirkwood equation and analyzed in terms of the free volume parameter. It was found that the ethyl acetate possesses high

affinity with the composite membranes and that the absorption of these small molecules substantially modifies the viscoelastic behavior and structure of the active layer. The combination of swelling experiments and the study of the mechanical relaxations proved to be an appropriate technique to investigate the behavior of pervaporation membranes immersed in different mixtures. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1384–1393, 2004

Key words: polysiloxanes; composite membranes; swelling; viscoelastic properties; pervaporation

INTRODUCTION

The separation of some specific mixtures, such as diluted organic compounds, azeotropic mixtures, aromatic and aliphatic hydrocarbons, and close boiling point compounds, presents poor performance if it is carried through conventional separation technologies. However, in these cases, pervaporation appears as a suitable membrane separation method with both economical and technological benefits and low energy consumption.^{1–3} Some of the investigation about pervaporation has been focused on the separation of some volatile organic compounds (VOCs), so as to make use of this technique in effluent treatments, recovery of valuable organic substances, and biotechnological applications.^{4–8}

Several polymeric materials have been tested as active layers for the separation of VOCs from aqueous solutions by pervaporation. Hydrophobic materials such as poly(dimethyl siloxane) (PDMS) have a tendency to discourage the passage of water molecules while it allows larger organic molecules to pass through. However, PDMS presents handicaps in forming ultrathin films and it also possesses bad mechan-

ical properties. To avoid these disadvantages, composite membranes with a thin skin that acts as a selective layer can be employed.^{9,10} In this work, the employed membranes have a three-layer structure as follows: a nonwoven polypropylene (PP) support to improve their mechanical properties, a poly(ether imide) (PEI) microporous structure, and a silicone active layer. This active layer was prepared from a mixture of poly(dimethyl siloxane) (PDMS) and poly(methyl hydrogen siloxane) (PMHS).

In previous studies,^{11,12} some different VOC aqueous mixtures were subjected to pervaporation experiences with PDMS–PMHS composite membranes to compare their behavior. It was stated that ethyl acetate aqueous solutions had excellent pervaporation performance in these types of membranes, both in terms of total flux and selectivity. Therefore, in this work the study has been focused on the behavior of the active layer of the membranes in different mixtures of ethyl acetate in water (2.5, 5, 7.5, and 10% v/v), including the pure compounds (pure water and pure ethyl acetate). Swelling experiments were performed with the composite membranes in the different solutions to obtain the diffusion coefficient. Also, the dynamic–mechanical relaxation spectrum at low temperatures for the swollen membranes was studied so as to calculate the free volume parameter of the membranes and to investigate its relationship with the diffusion coefficient.

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EXPERIMENTAL

Materials

The composite membranes have three layers made of PP, PEI, and silicone (both PDMS and PMHS). Polypropylene was commercial grade FO-2431 from Freudenberg. Poly(ether imide) was Ultem 1000 from General Electric Polymers. Dimethylacetamide (DMAc) was used as solvent without further purification. Poly(methyl hydrogen siloxane) was a silicone oil hydrofugant H-619, and PDMS was 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. Di-*n*-butyl tin dineodecanoate (Metatin Kat 730, 20% Sn) was supplied by Acima Chemical Industries Ltd. Perchloroethylene, toluene, and *n*-hexane P.A. were analytical grade from Scharlau. Water was double distilled before use. The solvent used as penetrant was ethyl acetate in reagent grade.

Preparation of samples

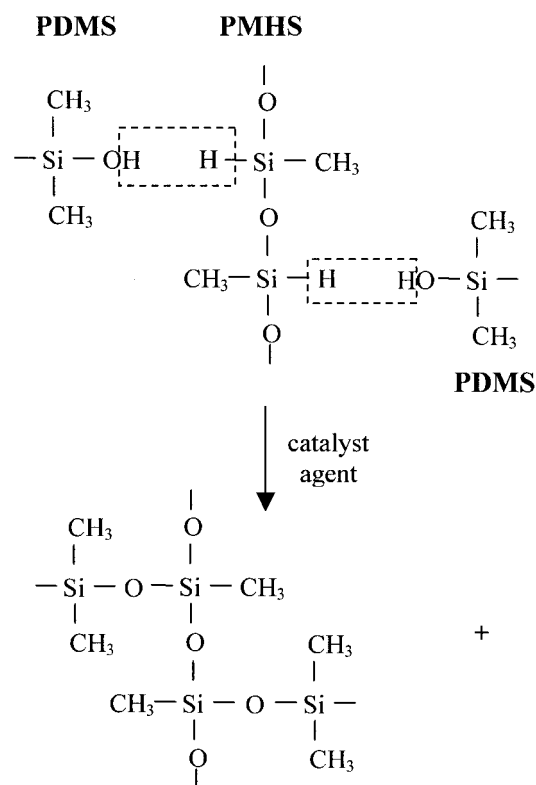
The procedure for the preparation of the silicone composite membranes was as follows: first the microporous PEI structure was formed by casting a DMAc solution 15% (w/w) PEI on a nonwoven PP support, following the phase inversion method.^{13,14} Afterward, the selective layer was prepared from a mixture 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 PDMS ratio and hydrolyzed by catalyst action by means of a heat treatment at 85°C in an oven during 2 h.

The catalyst agent 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 previous studies,^{11,15} it was stated that an optimum amount of catalyst agent 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% (w/w) ratio.

By the effect of the catalyst agent, a crosslinking reaction occurs in which the Si—H bonds of the PMHS react with the hydroxyl groups of PDMS, liberating hydrogen, as shown in Scheme 1. To prevent the formation of a porous structure in the active layer of the composite membrane, all nascent hydrogen was removed.

Swelling test

To measure the weight increase suffered by the membranes during the swelling process, the following procedure was followed.¹⁶ First, six samples of the membrane were cut into rectangular shape with dimen-



Scheme 1 Formation of the PDMS—PMHS active layer.

sions 12 × 60 mm. The thickness of each sample was measured several times and the mean was obtained as the representative value. The membranes then were dried in an oven at 65°C for 4 h, to obtain the weight of the dry samples. Afterward, the six samples were immersed in the six different mixtures (0, 2.5, 5, 7.5, 10, and 100% v/v ethyl acetate), which were kept at a constant temperature of 40°C inside a thermostatic bath. The membranes were periodically removed from the solution and blotted with tissue paper to remove the liquid on their surface. The membranes were weighed and replaced inside each ethyl acetate aqueous solution. This procedure was repeated for each sample until an equilibrium swelling was reached. The amount of solution absorbed into the membranes and the swelling ratio were calculated from the weight increase of the samples. The swelling ratio (*S*) is defined as follows:

$$S = \frac{W_s - W_d}{W_d} \quad (1)$$

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

Dynamical-mechanical measurements

The viscoelastic measurements were carried out in a dynamic-mechanical thermal analyzer (Polymer Lab-

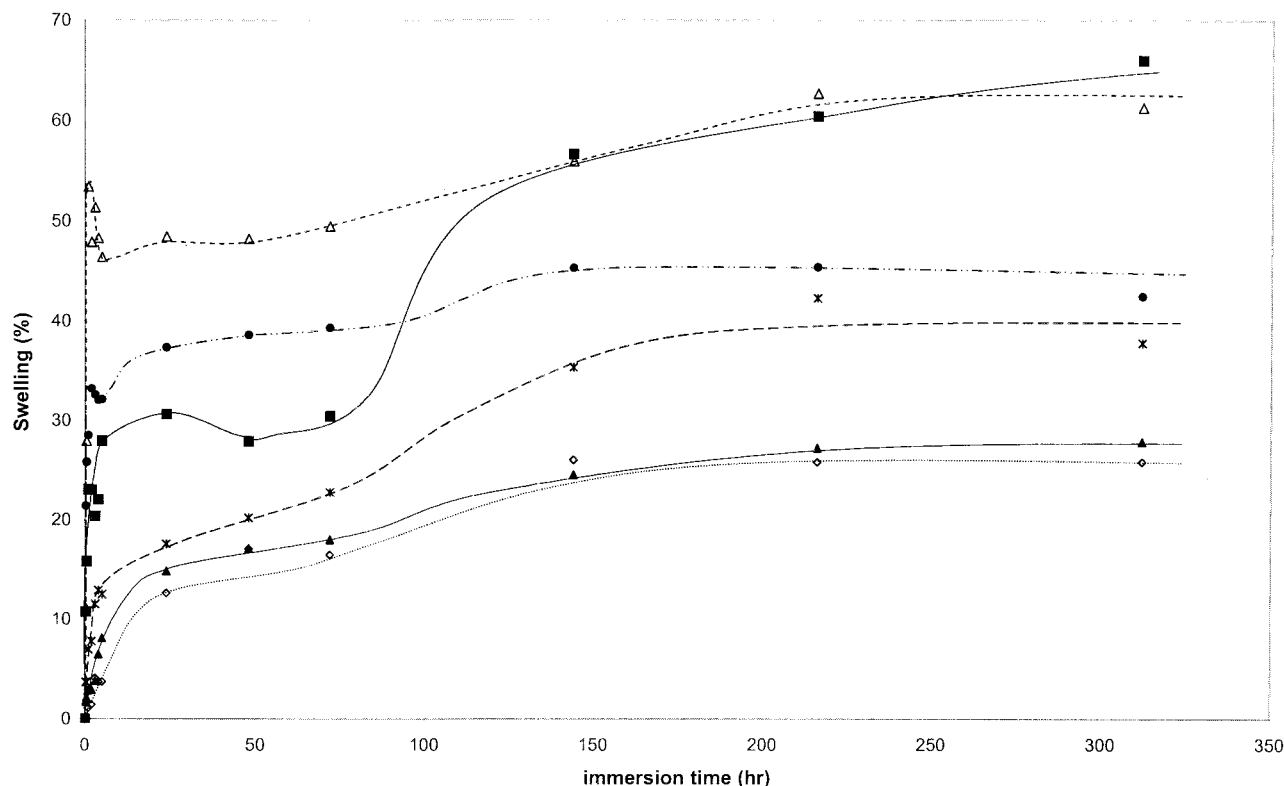


Figure 1 The swelling ratio as a function of time for the membranes immersed in different ethyl acetate aqueous solutions: (◇) 0% (v/v) ethyl acetate; (▲) 2.5% (v/v) ethyl acetate; (*) 5% (v/v) ethyl acetate; (●) 7.5% (v/v) ethyl acetate; (△) 10% (v/v) ethyl acetate; and (■) 100% (v/v) ethyl acetate.

oratories Ltd., MARK II DMTA). The sinusoidal flexural deformation was applied to the rectangular samples of the membrane in the double-clamped cantilever mode. Measuring scans were performed between -140 and -70°C at a heating rate of 1°C for the frequencies of 0.3, 1, 3, 10, and 30 Hz. The values of damping ($\tan \delta$), the storage modulus (E') and loss modulus (E'') were thus obtained. The viscoelastic measurements were first performed on the dry samples and they were repeated after the swelling experiment.

RESULTS AND DISCUSSION

Swelling behavior

The swelling behavior of PDMS-PMHS composite membranes immersed in water, ethyl acetate, and different ethyl acetate aqueous solutions was studied until the equilibrium was reached. As has been reported in previous works,¹² ethyl acetate shows high affinity with PDMS-PMHS membranes compared with other VOC-water mixtures that exhibited worse swelling performance.

Figure 1 shows the evolution of the swelling ratio with the immersion time for the composite membranes in six different mixtures (pure water, pure

ethyl acetate, and 2.5, 5, 7.5, and 10% v/v ethyl acetate). As a whole, it can be observed that the different swelling curves present several stages: an initial stage with a fast increase of the swelling ratio, a second stage in which the absorption degree presents a moderate increase, and a final stage in which the equilibrium has been reached.

The swelling of the membrane immersed in pure water is relatively low, due to the hydrophobic nature of the silicone active layer. Nevertheless, as the concentration of ethyl acetate in the mixtures increases, the swelling ratio of the membranes grows gradually. This fact could be expected because of the affinity of ethyl acetate with the composite membranes. On the other hand, a peculiar behavior could be detected in the membranes immersed in the mixtures with higher ethyl acetate concentration (from 7.5% v/v ethyl acetate). In these samples, a momentary decrease of the swelling ratio can be observed after its initial fast growth. This fact might suggest a slight decomposition of the active layer of the composite membranes, motivated by the interactions between the molecules of ethyl acetate and the PDMS-PMHS layer. This strange swelling behavior becomes more noticeable as the ethyl acetate concentration in the mixtures increases, and it is particularly evident for the sample immersed in pure ethyl acetate.

TABLE I
Equilibrium Swelling and Diffusion Coefficients for the Membrane Samples
Immersed in Different Ethyl Acetate Aqueous Mixtures

Sample	Equilibrium swelling (%)	Diffusion coefficient $D \times 10^{-13}$ (m ² /s)
Swollen in 0% ethyl acetate (v/v)	25.8	0.2443
Swollen in 2.5% ethyl acetate (v/v)	27.9	0.3959
Swollen in 5% ethyl acetate (v/v)	40.0	0.6349
Swollen in 7.5% ethyl acetate (v/v)	45.3	9.4541
Swollen in 10% ethyl acetate (v/v)	61.9	20.9219
Swollen in 100% ethyl acetate (v/v)	65.8	3.2528

Table I and Figure 2 show the dependence of the equilibrium swelling on the composition of the ethyl acetate aqueous mixtures. As can be observed, the equilibrium swelling ratio increases markedly with the concentration of ethyl acetate in the mixtures until a saturation point is reached. In this level, the concentration of ethyl acetate is such that the decomposition of the silicone layer may start and this could be the reason that the equilibrium swelling ratio does not increase noticeably. Some authors¹⁷ have reported that the equilibrium swelling of the membranes is related to the permeation rate in the pervaporation process. Therefore, the optimum performance of PDMS—PMHS membranes in pervaporation processes with ethyl acetate aqueous mixtures would take place with feed solutions between 7.5 and 10% v/v of ethyl acetate,

although certain decomposition of the active layer could appear in this range of concentrations.

To further investigate the transport phenomena through the membranes, basic diffusion studies were performed for these systems. According to Fick's diffusion law, the ratio of the amount of solvent sorbed at a certain time t (M_t) to the amount sorbed at equilibrium (M_∞) depends on the square root of time, following the equation:

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

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.

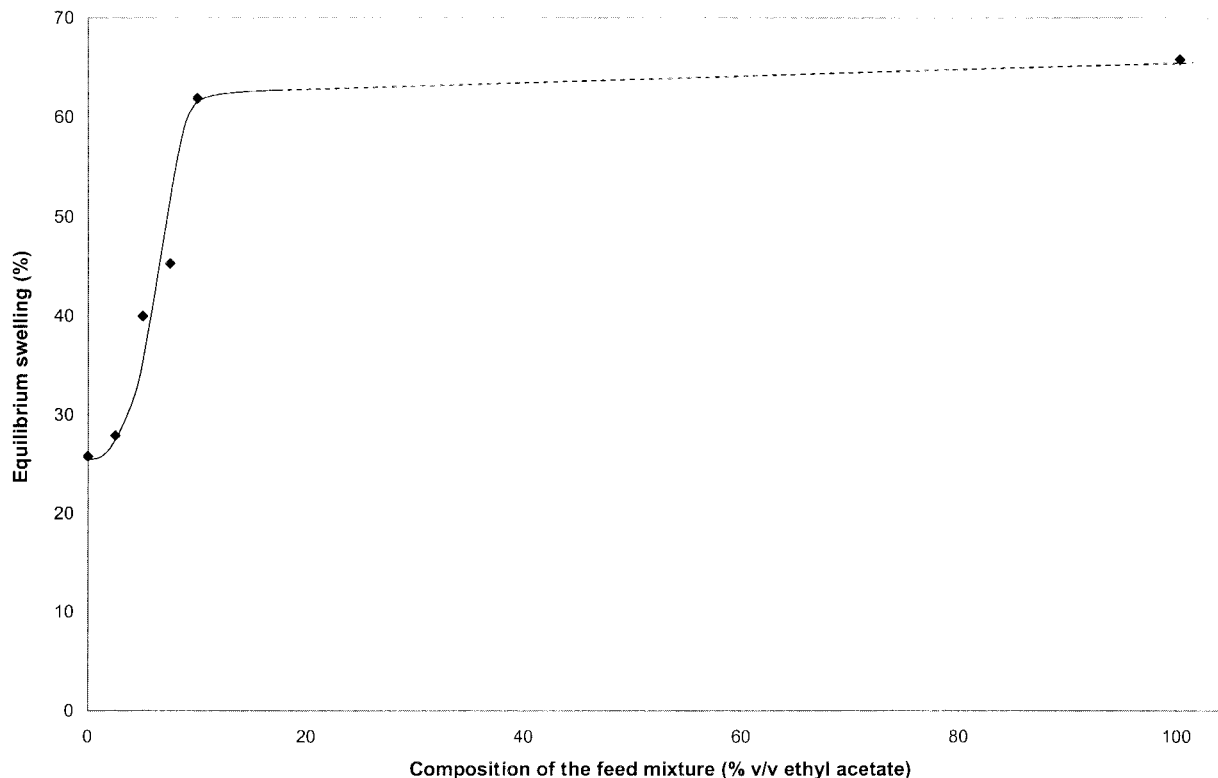


Figure 2 The relationship of the equilibrium swelling with the concentration of ethyl acetate of the feed mixtures.

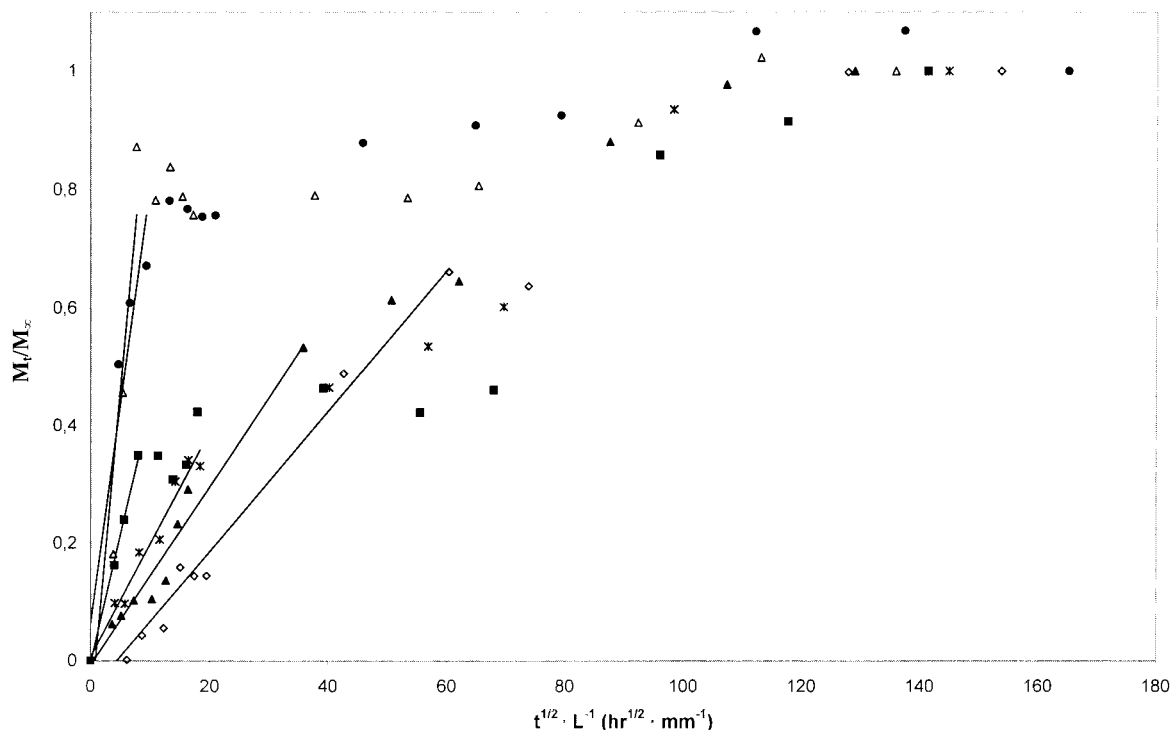


Figure 3 Dependence of the amount of solvent sorbed with Fick's law: (\diamond) 0% (v/v) ethyl acetate; (\blacktriangle) 2.5% (v/v) ethyl acetate; (\times) 5% (v/v) ethyl acetate; (\bullet) 7.5% (v/v) ethyl acetate; (\triangle) 10% (v/v) ethyl acetate; and (\blacksquare) 100% (v/v) ethyl acetate.

Figure 3 represents the amount of solvent absorbed in the composite membrane for each mixture, according to Fick's law. This figure shows that, for small times of permanence, the studied systems follow Fickian behavior, since a linear dependence of the ratio of solvent sorbed with the square root of time can be established. However, for higher times of immersion, a different diffusional behavior is observed. This behavior may be explained because of the fact that when the membranes become swollen, they change their permeation and absorption properties. The diffusion coefficients at the initial stage of diffusion for the different systems have been obtained from the slopes of the linear plot of M_t/M_∞ with $t^{1/2}/L$. From the comparison of the values of these diffusion coefficients, which are shown in Table I, it can be stated that the increase of the concentration of ethyl acetate in the feed solutions motivates a faster entrance of the solvent particles inside the PDMS-PMHS membranes. Only the membrane swollen in pure ethyl acetate exhibits a different behavior, which could be explained from the decomposition of its active layer.

From the results of the swelling experiments, it can be stated that ethyl acetate shows high affinity with the silicone active layer since the diffusion coefficient and the swelling equilibrium increase for higher ethyl acetate concentrations in the feed mixtures. In addition to this, for mixtures with concentrations from 7.5% v/v ethyl acetate, a slight decomposition of the

active layer may have taken place, which could become evident for the membrane swollen in pure ethyl acetate. This phenomenon is quite important, since it suggests that PDMS-PMHS composite membranes could only be employed for separating low-concentration ethyl acetate aqueous mixtures, as long as the active layer may decompose with high ethyl acetate concentrations. However, to verify these statements, the viscoelastic behavior of the swollen membranes will be analyzed in terms of their dynamic-mechanical properties.

Viscoelastic relaxations

Dynamic-mechanical experiments at low temperatures were performed on the PDMS-PMHS composite membranes before and after the swelling test, so as to study the effect of the absorbed molecules on the viscoelastic behavior of the membranes. In previous works,^{11,12,15} the effect of the swelling on the viscoelastic properties of the composite membranes was studied for several VOC aqueous mixtures, and it was observed that the absorption of the small molecules of the mixtures substantially changes the dynamic-mechanical response of the membranes. However, this effect on their viscoelastic behavior is different, depending on the type of VOC employed in the swelling experiment.

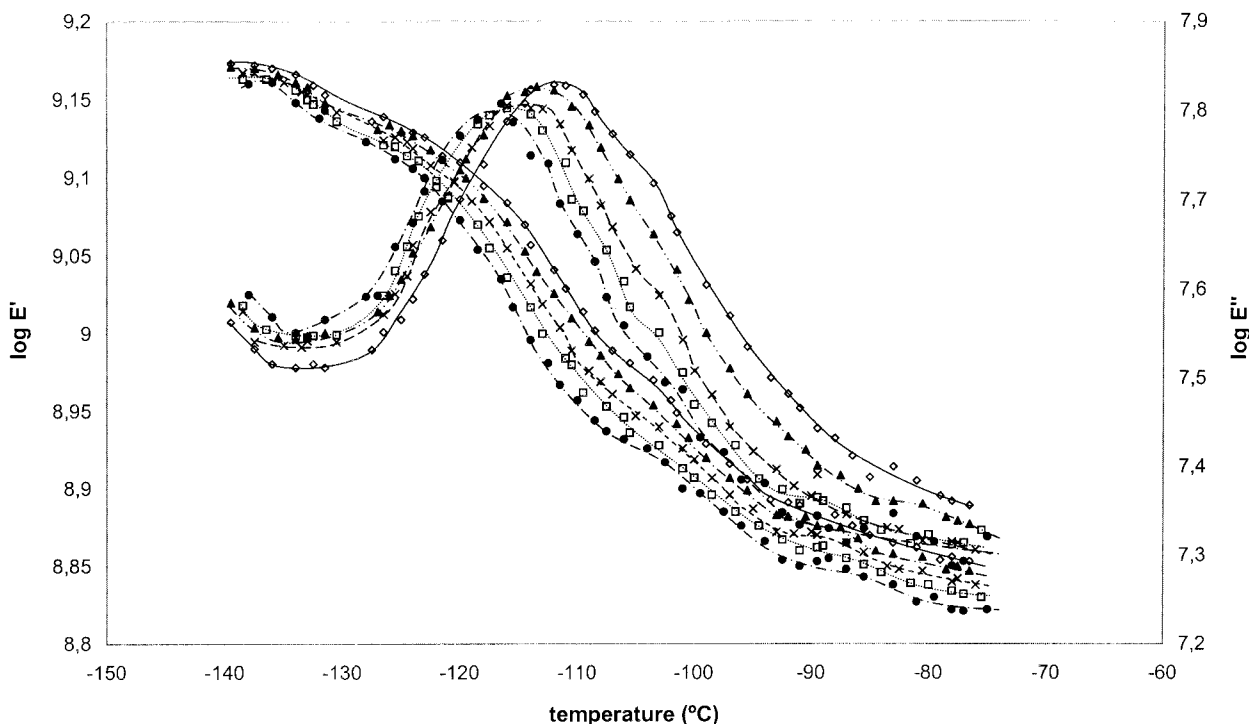


Figure 4 Plot of $\log E'$ and $\log E''$ as a function of temperature for the nonswollen membrane sample at different frequencies: (\diamond) 30 Hz; (\blacktriangle) 10 Hz; (\ast) 3 Hz; (\square) 1 Hz; and (\bullet) 0.3 Hz.

In our work, the viscoelastic properties of the PDMS–PMHS membranes (storage modulus, E' ; loss modulus, E'' ; and damping, $\tan \delta$) at five different frequencies (0.3, 1, 3, 10, and 30 Hz) were obtained by means of a Mark II DMTA, before and after they were immersed in the six different ethyl acetate aqueous solutions. As an example, the mechanical relaxation spectrum of the sample of PDMS–PMHS composite membrane before being subjected to swelling experiments is represented in Figure 4. In the figure, an α -relaxation process centered at a temperature of -113°C can be clearly observed, which can be assigned to the glass transition of the PDMS–PMHS layer.¹⁸

To analyze the effect of swelling on the viscoelastic properties of the membrane, Figure 5 shows the values of $\tan \delta$ as a function of the temperature for all the samples tested at a frequency of 10 Hz. Similar spectra were obtained at the other frequencies, but they are not included for the sake of clarity. As a whole, it can be observed that the swelling substantially modifies the shape of the relaxation curve by reducing the intensity of the α -peak and widening its profile at the temperature axis.

Some authors^{11,15,19,20} have reported that the inclusion of small molecules inside the polymeric matrix causes a plasticizing effect, seen by the shifting of the glass transition temperature to lower values. This effect can be observed in the membrane immersed in water. However, the membranes swollen in the differ-

ent ethyl acetate aqueous mixtures show a different pattern, since the temperature of the α -peak shifts to higher temperatures. This displacement of the peak is more significant for the samples immersed in lower ethyl acetate concentrations (2.5 and 5% v/v ethyl acetate) rather than for the ones swollen in higher concentrations, which could be partially decomposed by the ethyl acetate molecules. In addition to this, the shape of the relaxation curves is evidently modified for the membranes swollen in the ethyl acetate aqueous solutions, showing a more complex behavior. From these results, it can be concluded that the ethyl acetate molecules interact with the PDMS–PMHS layer in a way different from other solvent molecules, such as water, ethanol or 1-butanol, studied in previous works.^{11,12} Instead of acting as a plasticizer agent, the ethyl acetate molecules may have originated rearrangements of the polymeric chains and might have induced crosslinking reactions among some segments of the PDMS–PMHS network. This would explain why the α -peak showed a more complex and less intense structure, with a broader shape at the temperature axis. In previous studies,^{11,15} it was stated that, when the percentage of catalyst employed in the formation of the PDMS–PMHS layer or its curing time increased, the crosslinking level of the network also increased. This fact was evidenced by the shift of the peak to higher temperatures, the reduction of the intensity of the peak, and the broadening of its shape. This behavior pattern is reproduced in the samples

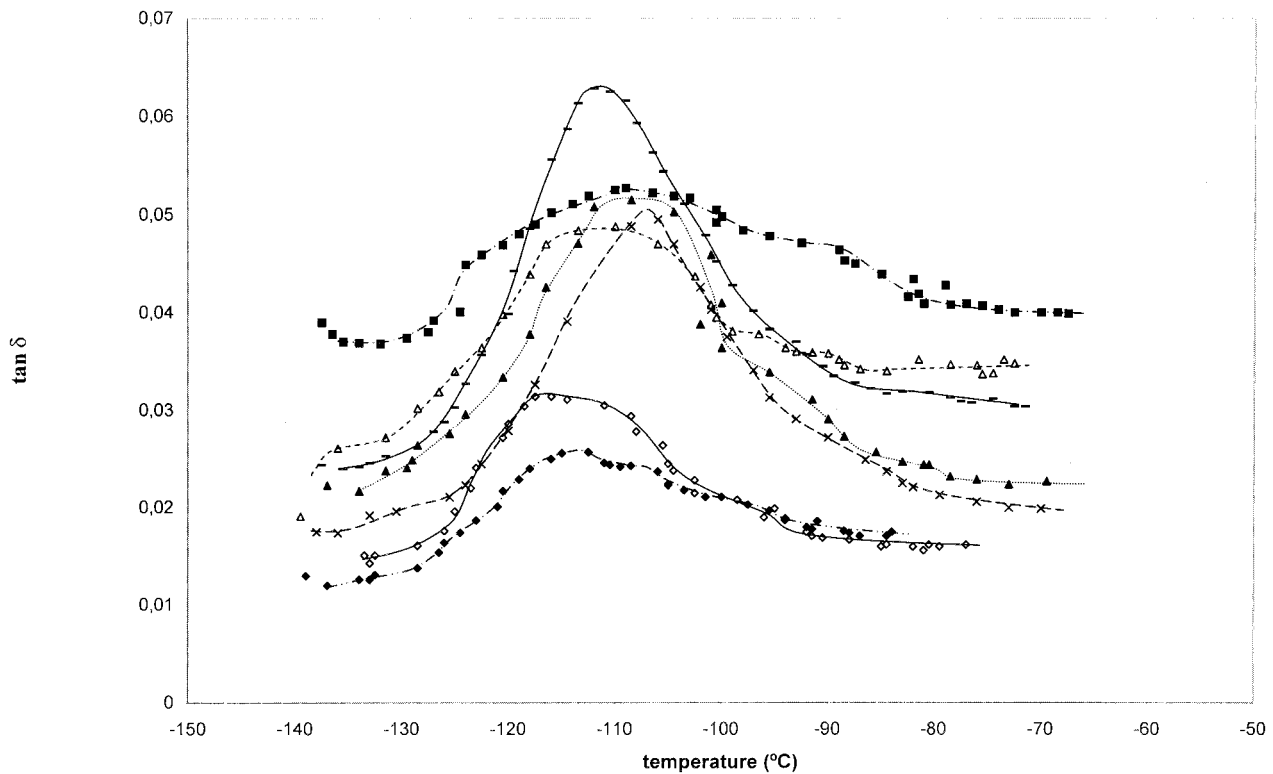


Figure 5 Plot of $\tan \delta$ versus the temperature at a frequency of 10 Hz for the composite membranes swollen in different ethyl acetate aqueous mixtures: (—) nonswollen membrane; (\diamond) 0% (v/v) ethyl acetate; (\blacktriangle) 2.5% (v/v) ethyl acetate; ($*$) 5% (v/v) ethyl acetate; (\bullet) 7.5% (v/v) ethyl acetate; (\triangle) 10% (v/v) ethyl acetate; and (\blacksquare) 100% (v/v) ethyl acetate.

swollen in ethyl acetate solutions, so similar mechanisms may act in both cases.

To further investigate the viscoelastic behavior of the composite membranes, each of the dynamic-mechanical curves was characterized following the Fuoss–Kirkwood empirical model:

$$E'' = \frac{E''_{\max}}{\cosh\left[m \times \frac{E_a}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_m}\right)\right]} \quad (3)$$

where E''_{\max} is the maximum of the loss modulus; m is the Fuoss–Kirkwood parameter, and T_m is the temperature of the maximum of the loss modulus. The fit of the experimental data of temperature and loss modulus from the dynamic-mechanical experiments allowed us to obtain the values of the parameters E''_{\max} , T_m , and the product $m \times E_a/R$ for each sample and frequency tested.

The characterization of the α -relaxation related with the glass transition of the PDMS–PMHS active layer was continued with the estimation of the free volume for all the membranes tested, to characterize the structure of the swollen membranes related to the swelling and diffusional behavior. Doolittle and Doolittle²¹ found an empirical equation to represent with high

accuracy the viscosity of ordinary liquids of low molecular weight:

$$\eta_0 = A \times \exp\left(B \times \frac{v - v_f}{v_f}\right) \quad (4)$$

where A and B are empirical constants (B is of the order of unity), v is the specific volume, and v_f is the free volume.

If we define the relative free volume at a temperature T , as $\phi = \frac{v - v_0}{v_0} = \frac{v_f}{v_0}$, the Doolittle eq. (4) can be expressed in terms of this variable in the following way:

$$\eta_0 = A \times \exp\left(\frac{B}{\phi}\right) \quad (5)$$

The Doolittle equation for viscosity can be also applied in terms of the relaxation times associated to the viscoelastic mechanism i , as follows:

$$\tau_i = A \times \exp\left(\frac{B}{\phi}\right) \quad (6)$$

$$\ln \tau_i = \ln A + \frac{B}{\phi} \quad (7)$$

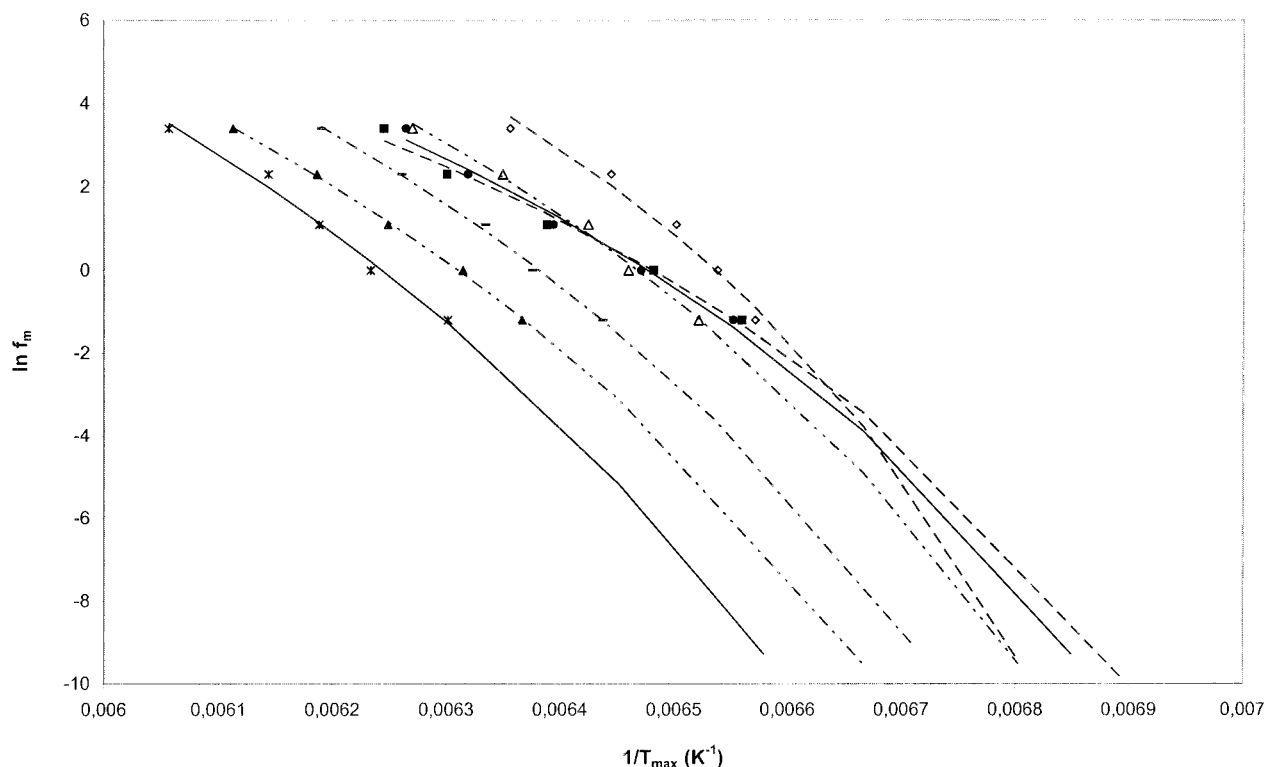


Figure 6 Plot of the relaxation times with the inverse of the temperature of the maximum for the glass transition and fit to the Vogel equation: (—) nonswollen membrane; (\diamond) 0% (v/v) ethyl acetate; (\blacktriangle) 2.5% (v/v) ethyl acetate; ($*$) 5% (v/v) ethyl acetate; (\bullet) 7.5% (v/v) ethyl acetate; (\triangle) 10% (v/v) ethyl acetate; and (\blacksquare) 100% (v/v) ethyl acetate.

It may be assumed that the specific volume is a linear function of the temperature in accordance with the relation:^{18,22}

$$v = v_0 \times [1 + \alpha_f \cdot (T - T_\infty)] \quad (8)$$

$$\phi = \alpha_f \times (T - T_\infty) \quad (9)$$

where α_f is the expansion coefficient and T_∞ is the temperature at which the free volume would be zero were it not for the formation of the glassy state.

Combining eqs. (7) and (9), we obtain the Vogel equation,²³ which correlates the relationship between the relaxation times and the temperature:

$$\ln \tau_i = A' + \frac{m_v}{T - T_\infty} \quad (10)$$

The parameter m_v , which is related with the relative free volume, was obtained by the Vogel equation. Thus, if we specify this parameter for the glass transition temperature, the relative free volume associated with the α -relaxation can be easily determined from m_v :

$$m_v = \frac{B}{\alpha_f} = \frac{B}{\phi_g} \cdot (T_g - T_\infty) \quad (11)$$

In our work, the values of the temperature of the maximum of the loss modulus (T_m) obtained from the Fuoss–Kirkwood model and their respective relaxation frequencies were fit to the Vogel equation for each of the analyzed membranes. As a first approach, the fitting of the experimental results to the Vogel equation was examined from the viewpoint of the temperature T_∞ , so it was decided to make several trials for the determination of this parameter. The estimation of T_∞ was performed using the rule of thumb that the initial value of this temperature is usually about 50°C below the glass transition temperature. Finally, it was found that the experimental values for the membranes fit reasonably well the Vogel equation when choosing values of T_∞ between -138°C and -148°C , as can be observed in Figure 6. This plot shows the relationship of the relaxation frequencies with the inverse of temperature of the maximum of the α -peak and their fitting to the Vogel equation for each of the considered membrane samples. From this fitting, the parameter m_v of Vogel equation was obtained, so the relative free volume could be easily calculated for all the membranes.

Table II presents the parameters of the Vogel equation and the temperature of the maximum of the loss modulus at 1 Hz frequency, here employed for the characterization of the α -relaxation of the different

TABLE II
Characterization of the α -Relaxation of the Membrane Samples^a

Sample	T_{\max} at 1 Hz (°K)	m_v (°K)	$\frac{\phi_g}{B \times (T_g - T_\infty)} \times 10^{-4}(\text{K}^{-1})$	T_∞ (°K)
Nonswollen	157.88	599.35	16.68	125
Swollen in 0% (v/v) ethyl acetate	152.77	536.41	18.64	125
Swollen in 2.5% (v/v) ethyl acetate	160.04	640.35	15.62	130
Swollen in 5% (v/v) ethyl acetate	161.60	755.19	13.24	130
Swollen in 7.5% (v/v) ethyl acetate	158.26	616.94	16.21	135
Swollen in 10% (v/v) ethyl acetate	156.57	523.73	19.09	130
Swollen in 100% (v/v) ethyl acetate	158.72	389.88	25.65	130

^a Temperature of the maximum of the loss modulus at 1 Hz frequency, m_v parameter of Vogel equation, relative free volume, and T_∞ .

membranes. As a whole, it can be observed that these results confirm all the statements that have been previously suggested. The sample swollen in water demonstrates that the peak has shifted to lower temperatures and that the free volume has increased, if it is compared with the nonswollen membrane. Therefore, it can be concluded that the inclusion of water molecules in the PDMS–PMHS network has a plasticizing effect on its viscoelastic behavior. On the other hand, for the samples swollen in lower ethyl acetate concentrations (2.5 and 5% v/v), the free volume has clearly decreased after the swelling experiment, which demonstrates that the active layer of these swollen membranes presents a structure with a higher crosslinking degree. Consequently, the ethyl acetate molecules in low concentrations may have acted as catalyzing agents for some rearrangements of the polymeric chains and for these crosslinking processes between the PDMS and the PMHS that conform the active network. However, for higher ethyl acetate concentrations (7.5 and 10% v/v), this decrease of the free volume after the swelling experiment is not followed. For these concentrations, the decomposition of the active layer may have started leading to higher values of the free volume than expected. Finally, for the sample swollen in pure ethyl acetate, the decomposition of the active layer motivated by the high affinity between this organic compound and the PDMS–PMHS layer is evident, since the value of the free volume is extremely high compared to the other values.

From these results it can be concluded that the viscoelastic experiments performed on the membranes offer interesting information about the interaction between the active layer of the membranes and the different mixtures during the swelling experiments. Ethyl acetate has high affinity with the PDMS–PMHS layer, since for lower concentrations it modifies the structure of the active layer by inducing crosslinking reactions between segments of the PDMS–PMHS. Moreover, for higher concentrations of this organic compound, the active layer becomes partially decomposed as is evidenced by the values of the free volume

for the samples immersed in 7.5, 10% v/v, and pure ethyl acetate solutions. Also, these structural conclusions have their relationship with the swelling and pervaporation behavior of the membranes in ethyl acetate aqueous mixtures. We could state that PDMS–PMHS composite membranes possess excellent swelling and pervaporation properties for the separation of low-concentrated ethyl acetate–water mixtures (until concentrations of approximately 7.5% v/v), but for higher concentrations of the feed mixtures these membranes could not be employed, because of the decomposition of the active layer.

CONCLUSION

From the results of this study, the following conclusions can be made:

Ethyl acetate shows high affinity for the PDMS–PMHS active layer, since the swelling ratio increases when the concentration of ethyl acetate in the feed aqueous mixtures is higher. However, for feed solutions with high ethyl acetate content (from 7.5% v/v ethyl acetate), a slight decomposition of the active layer can be observed. Therefore, PDMS–PMHS composite membranes can only be employed for separating low-concentrated ethyl acetate–water mixtures (until 7.5–10% v/v), since the active layer decomposes with higher concentrations of ethyl acetate in the feed mixture.

The equilibrium swelling increases with the ethyl acetate concentration in the feed mixture until a saturation point is reached, which agrees with the beginning of the decomposition of the membrane. From the diffusion studies it can be stated that the swelling behavior at initial times follows the Fickian model. The diffusion coefficients at this stage of absorption were obtained and it was found that higher concentrations of ethyl acetate in the feed mixtures favor the inclusion of the small molecules of solvent inside the membranes.

The swelling modifies substantially the viscoelastic behavior of the composite membranes. The absorption of ethyl acetate molecules inside the membranes leads

to a displacement of the α -relaxation peak to higher temperatures and a change on its shape, showing a more complex pattern. This fact could indicate that ethyl acetate interacts with the PDMS—PMHS layer originating rearrangements of the polymeric chains and crosslinking reactions among some segments of the network. This conclusion was confirmed by the study of the free volume related to the glass transition relaxation. For lower concentrations of ethyl acetate (2.5 and 5% v/v), the values of free volume decrease compared to the nonswollen membranes. However, for higher concentrations (7.5, 10% v/v, and pure ethyl acetate) this tendency is not followed, motivated by the decomposition of the active layer.

References

1. Jonquières, A.; Clément, R.; Lochon, P.; Néel, J.; Dresch, M.; Chrétien, B. *J Membr Sci* 2002, 206, 87.
2. Lipnizki, F.; Field, R. W.; Ten, P.-K. *J Membr Sci* 1999, 153, 183.
3. Doghieri, F.; Nardelle, A.; Santi, G. C.; Valentini, C. *J Membr Sci* 1994, 91, 283.
4. Shaban, H. I.; Ali, S. H.; Mathew, J. *J Appl Polym Sci* 2001, 82, 3164.
5. Chang, Y. H.; Kim, J. H.; Lee, S. B.; Rhee, H. W. *J Appl Polym Sci* 2000, 77, 2691.
6. Yeom, C. K.; Kim, H. K.; Rhim, J. W. *J Appl Polym Sci* 1999, 73, 601.
7. Poddar, T. K. *J Membr Sci* 1997, 132, 229.
8. Ji, W.; Sikdar, S. K.; Hwang, S. *J Membr Sci* 1994, 93, 1.
9. Watson, J. M.; Baron, M. G. *J Membr Sci* 1996, 110, 47.
10. Qariouh, H.; Schué, R.; Schué, F.; Bailly, C. *Polymer Int* 1999, 48, 171.
11. Bueso, L.; Osorio-Galindo, M.; Alcaína-Miranda, M. I.; Ribes-Greus, A. *J Appl Polym Sci* 2000, 75, 1424.
12. Osorio-Galindo, M.; Iborra-Clar, A.; Alcaína-Miranda, M. I.; Ribes-Greus, A. *J Appl Polym Sci* 2001, 81, 546.
13. Kim, H. J.; Jo, W. H.; Kang, Y. S. *J Appl Polym Sci* 1995, 57, 63.
14. Alcaína-Miranda, M. I. PhD Thesis, Universidad Politécnica de Valencia, 1991.
15. Bueso, L.; Ribes-Greus, A.; Alcaína-Miranda, M. I. *J Non-Cryst Solids* 1994, 172–174, 1066.
16. Ruckenstein, E.; Chen, H. H. *J Appl Polym Sci* 1991, 42, 2429.
17. Ruckenstein, E.; Chen, H. H. *J Membr Sci* 1992, 66, 205.
18. Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980.
19. Andreopoulos, A. G.; Polyzois, G. L.; Evangelatou, M. *J Appl Polym Sci* 1993, 50, 729.
20. Muzzalupo, R.; Ranieri, G. A.; Golemme, G.; Drioli, E. *J Appl Polym Sci* 1999, 74, 1119.
21. Doolittle, A. K.; Doolittle, D. B. *J Appl Phys* 1957, 28, 901.
22. Riande, E.; Díaz-Calleja, R.; Masegosa, R. M.; Prolongo, M. G.; Salom, C.; Marcel Dekker: New York, Basel, 2000.
23. Vogel, H. *Physik* 1921, 22, 645.