

# Swelling Behavior of Pervaporation Membranes in Ethanol–Water Mixtures

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**ABSTRACT:** Novel hydrophobic composite membranes made of crosslinked poly(dimethylsiloxane) and poly(methyl hydrogen siloxane) (PDMS–PMHS) with various amounts of catalyst were prepared. Pervaporation experiments with water–ethanol mixtures revealed that an optimum ratio of catalyst to polymer base existed. Both swelling behavior and dynamic–mechanical properties of these silicone films were studied. The swelling experiments in different mixtures of ethanol and water determined that ethanol is preferentially sorbed and that the membranes are only capable to absorb a limited quantity of solvent. Equilibrium swelling data were also used in combination with the analysis of the viscoelastic relaxation of the swollen samples to obtain the dependence of the dynamic–mechanical properties of the silicone films on the quantity of permeants sorbed into the membrane. It was observed that the permselective parameters were related with the mobility of the chains and the free volume. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1424–1433, 2000

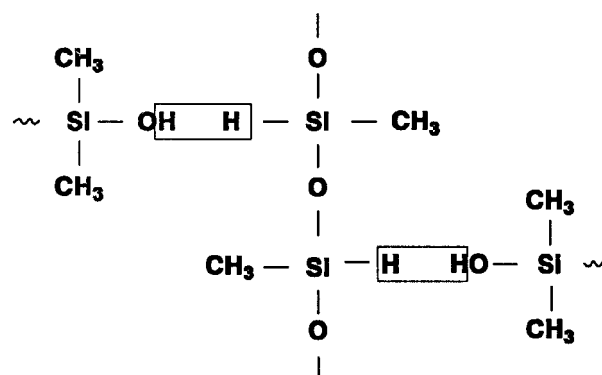
**Key words:** pervaporation; composite membrane; silicone membrane; swelling ratio; mechanical relaxations

## INTRODUCTION

Pervaporation is a method of separating azeotropic mixtures, aromatic and aliphatic hydrocarbons, and close-boiling-point compounds with low energy consumption. In recent years, there has been an increase in the use of pervaporation processes for separation of alcohol–water mixtures.<sup>1</sup> Membranes for this application can be of two types: the water and the alcohol–permselective membranes.<sup>2–5</sup> Alcohol–permselective membranes are based mostly on hydrophobic groups.

In this work, the selected membrane was a composite membrane with the following three layers: an active layer, a microporous layer, and

support. The active layer was prepared from poly(dimethylsiloxane) (PDMS) and poly(methyl hydrogen siloxane) (PMHS). The Si–H bonds of the PMHS react with the PDMS liberating hydrogen by catalyst action and crosslink the polymer. The reaction between PDMS and PMHS is schematically illustrated in Scheme 1, as follows:



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The final structure of the active layer and its mechanical behavior depend on the composition of the PDMS–PMHS and the catalyst agent. The polymeric materials employed for the support and the microporous structure were polypropylene (PP) and poly(ether sulphone) (PESU), respectively. The latter shows high levels of permeability, tensile strength, and thermal stability. This polymer composite membrane is expected to be highly permeable to ethanol because of the hydrophobicity of silicone-based polymers.

Liquid transport in pervaporation takes place by three consecutive steps described commonly as a solution–diffusion model<sup>6</sup> as follows: (1) first, sorption of the components from a liquid mixture on the membrane surface, (2) then diffusion of the sorbed components across the polymeric membrane due to the concentration gradient of individual permeants, and, finally, (3) evaporation from the membrane into the vapor phase on the downstream side of the system. According to this model permeability of a membrane is a function of solubility and diffusivity of the components of the mixture into the polymeric membrane.<sup>7,8</sup>

In the present article, pervaporation of ethanol–water solutions was conducted with hydrophobic composite membranes. A comparative study of the swelling characteristics of the silicone layer and its dynamic–mechanical relaxation spectrum was also carried out. The relationship between the swelling behavior and the free volume<sup>9,10</sup> of the polymer obtained from the relaxation process was used to elucidate the interaction of the components of the mixture with the membrane in the separation mechanism.

## EXPERIMENTAL

### Materials

Polypropylene (PP) of commercial-grade FO-2431 from Freudenberg. Poly(ether sulphone) (PESU) from BASF Española, S.A. Dimethylacetamide (DMA) was used as solvent without further purification. Poly(methyl hydrogen siloxane) (PMHS) silicone oil hydrofugant H-619, poly(dimethylsiloxane) (PDMS) dense fluid 331-V50.000, and catalyst CH-12 from Siliconas Hispania S.A., and *n*-Hexane P.A. of analytical grade from Scharlau. Water was distilled before use.

### Preparation of the Samples

Two types of membrane configuration have been made with PDMS and PMHS, three-layer com-

posite membranes with the rubber coated into a microporous support membrane, and homogeneous films made with the rubber alone. The former were used for pervaporation experiments, and the latter were employed in swelling experiments and in dynamic–mechanical measurements.

### Composite Membrane Fabrication

The microporous layer was prepared from poly(ether sulphone) by casting a dimethylacetamide solution (15% *w/w* polyethersulphone) on a non-woven polypropylene support following the phase inversion method.<sup>11</sup> Selective layer was prepared from PDMS and PMHS by casting an hexane solution on the microporous support in a ratio of 0.0175 g cm<sup>-2</sup>. Silicone hydrofugant (PMHS) and dense fluid (PDMS) to 33% *w/w* PDMS-to-PMHS ratio were dissolved with hexane in a 1.75 mL g<sup>-1</sup> PDMS ratio and hydrolyzed by catalyst action through a heat treatment at 75°C in an oven under vacuum during 4 h. All nascent hydrogen was removed in order to prevent the formation of a porous structure in the silicone film. The thickness of the active layer, was in the range of 28 to 65 μm (which represents an average of measurements in three equivalent membranes).

### Silicone Film Fabrication

Silicone films were prepared following the procedure used for the fabrication of the active layer explained above, but the hexane solution was directly cast on a clean Teflon plate instead of on a microporous support. Film thickness measured by a thickness gauge was 0.8–1.0 mm.

### Pervaporation Experiments

Pervaporation experiments were carried out in a laboratory plant with different composite membranes. The plant used was a normal vacuum pervaporation apparatus consisting of a cell made of stainless steel with circulation of the liquid over the membrane.<sup>11</sup> The plant was capable to hold eight membranes at a time. The effective area in contact with the feed solution of each membrane was equal to 78.54 cm<sup>2</sup>. A vacuum pump maintained the downstream pressure at 1 mm Hg, and the permeate was collected in a trap cooled at a temperature of –25°C. Feed temperature was maintained at 25°C and a feed flux of 4.8 L h<sup>-1</sup> was used.

Membranes used were all composite membranes with the following three layers: a PP sup-

**Table I Catalyst Ratio Dependence of Pervaporation Performance**

Membrane	Catalyst (% w/w)	Selectivity $\alpha$	Flux J ( $\text{l m}^{-2} \text{h}^{-1}$ )
A	5	6.74	0.117
B	7.5	6.80	0.108
C	10	7.14	0.099

port, a PESU microporous layer, and PDMS–PMHS active layers using different catalyst concentrations ranging from 5 to 10%. Feed mixture was a 11 vol % ethanol solution. Pervaporation was carried out with membranes previously swollen during 12 hours in the same feed mixture. Selectivity and flux were measured.

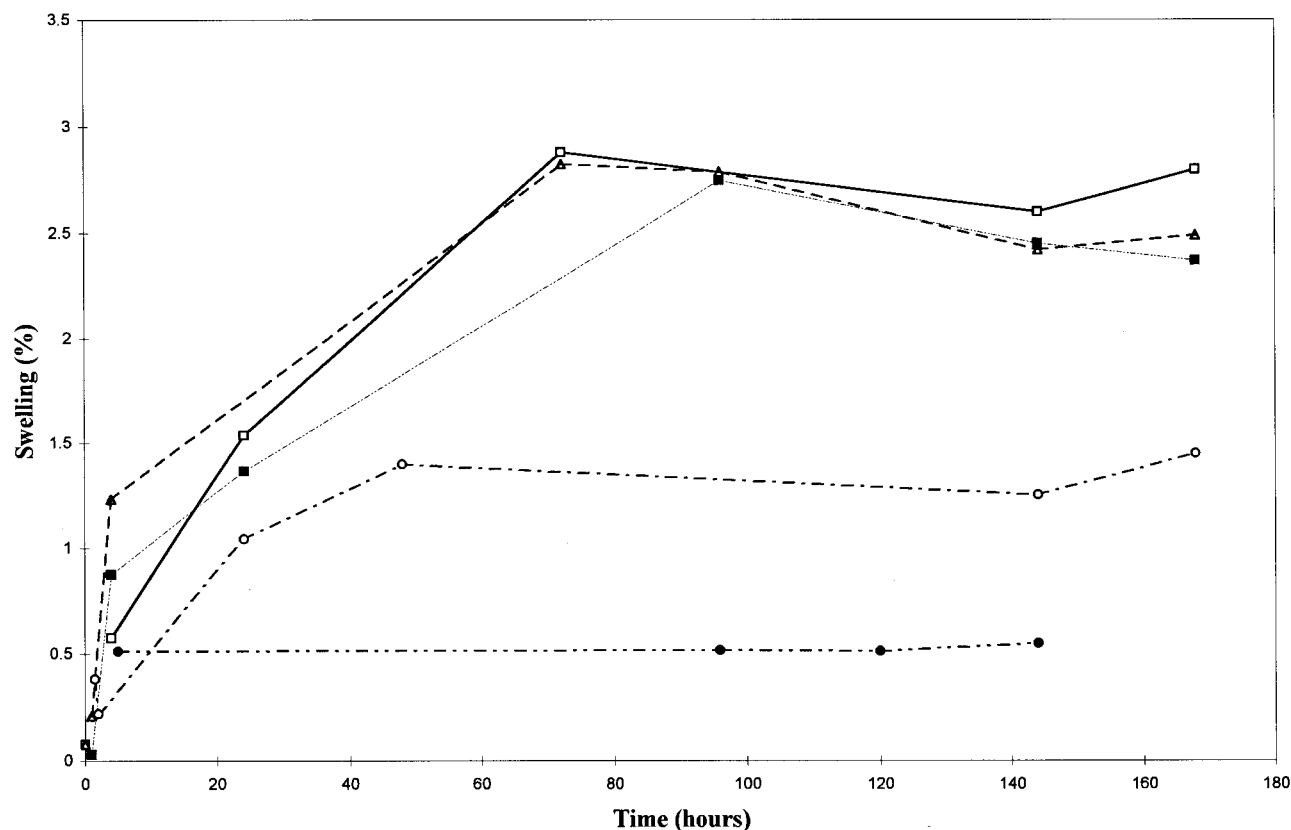
### Swelling Test

The increase in weight of the membranes during the swelling process was determined following

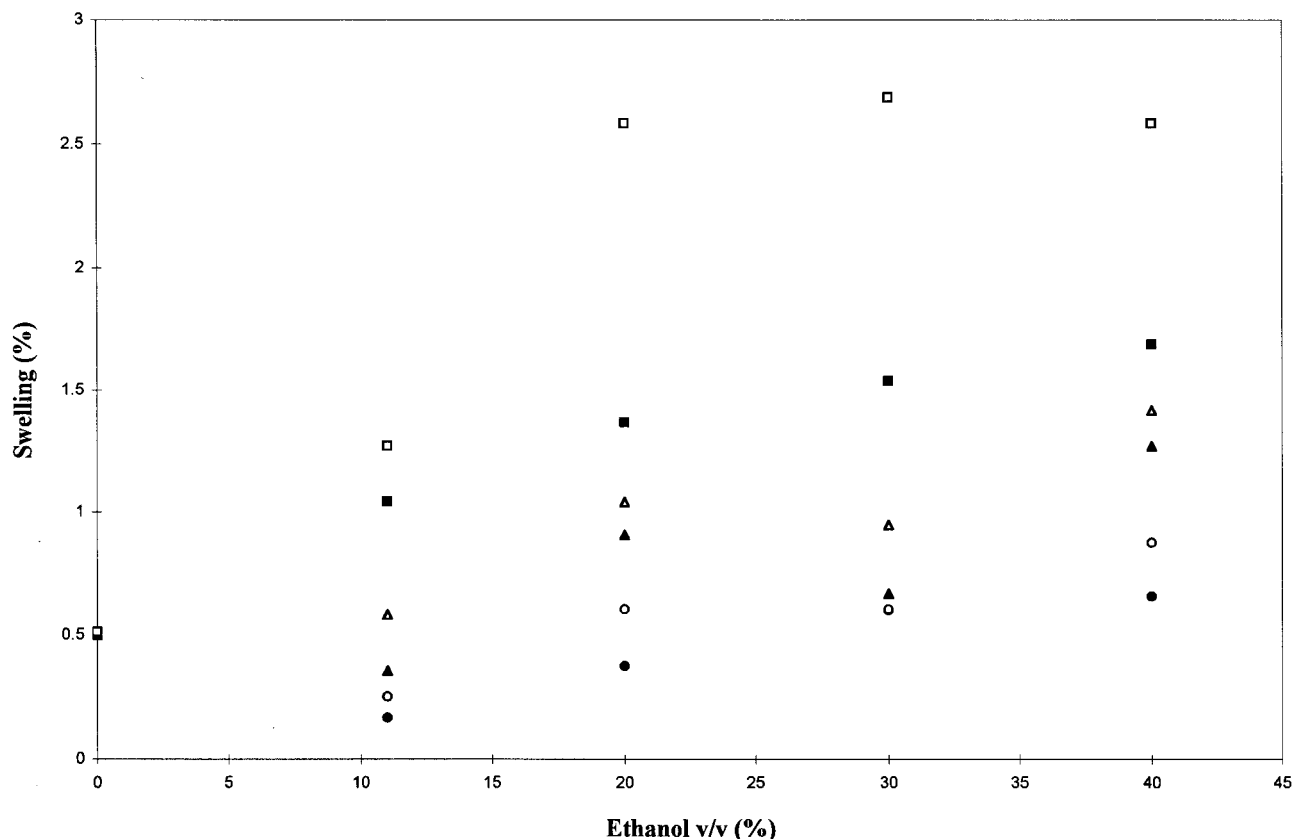
the procedure reported by Ruckenstein and Chen.<sup>12</sup> Membrane strips of 0.5 g were immersed in a flask filled with one of the different mixtures of ethanol and water at 25°C temperature. The membranes were periodically removed from the mixture, blotted quickly with filter paper to remove the solvent attached on their surfaces, and weighted. The swollen membranes were then dried at 60°C in a vacuum (0.4 bar) oven to determine the weight of the dried membranes. 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 ethanol–water solution until an equilibrium swelling was reached. The swelling ratio of the membrane ( $S$ ) is defined as

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

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



**Figure 1** Swelling of PDMS–PMHS films with varying ethanol concentrations in the solution as a function of time: (●) 0% ethanol; (○) 11% ethanol; (■) 20% ethanol; (□) 30% ethanol; (△) 40% ethanol.



**Figure 2** Swelling of PDMS–PMHS films against ethanol concentration in the feed, obtained at various instants of time: (●) 1 h; (○) 3 h; (▲) 6 h; (△) 12 h; (■) 24 h; (□) 120 h.

### Dynamical–Mechanical Measurements

The mechanical spectroscopy was performed in a dynamic–mechanical thermal analyzer (Polymer Laboratories Ltd., MARK II DMTA), with deformation applied in the cantilever flexure double-clamping mode. Measuring scans were performed between  $-140$  and  $150^{\circ}\text{C}$  at a heating rate of  $2^{\circ}\text{C min}^{-1}$  for the frequencies of 1, 3, 10, and 30 Hz. The values of damping ( $\tan \delta$ ), the storage modulus ( $E'$ ), and loss modulus ( $E''$ ) were obtained.

## RESULTS AND DISCUSSION

### Catalyst Ratio and Performance Plant

Pervaporation experiments were carried out with three different composite membranes prepared by the method explained above and by only altering the amount of catalyst added. Pervaporation performance was characterized in terms of the steady state flux and the permselectivity. The flux  $J$  at a steady state was obtained by

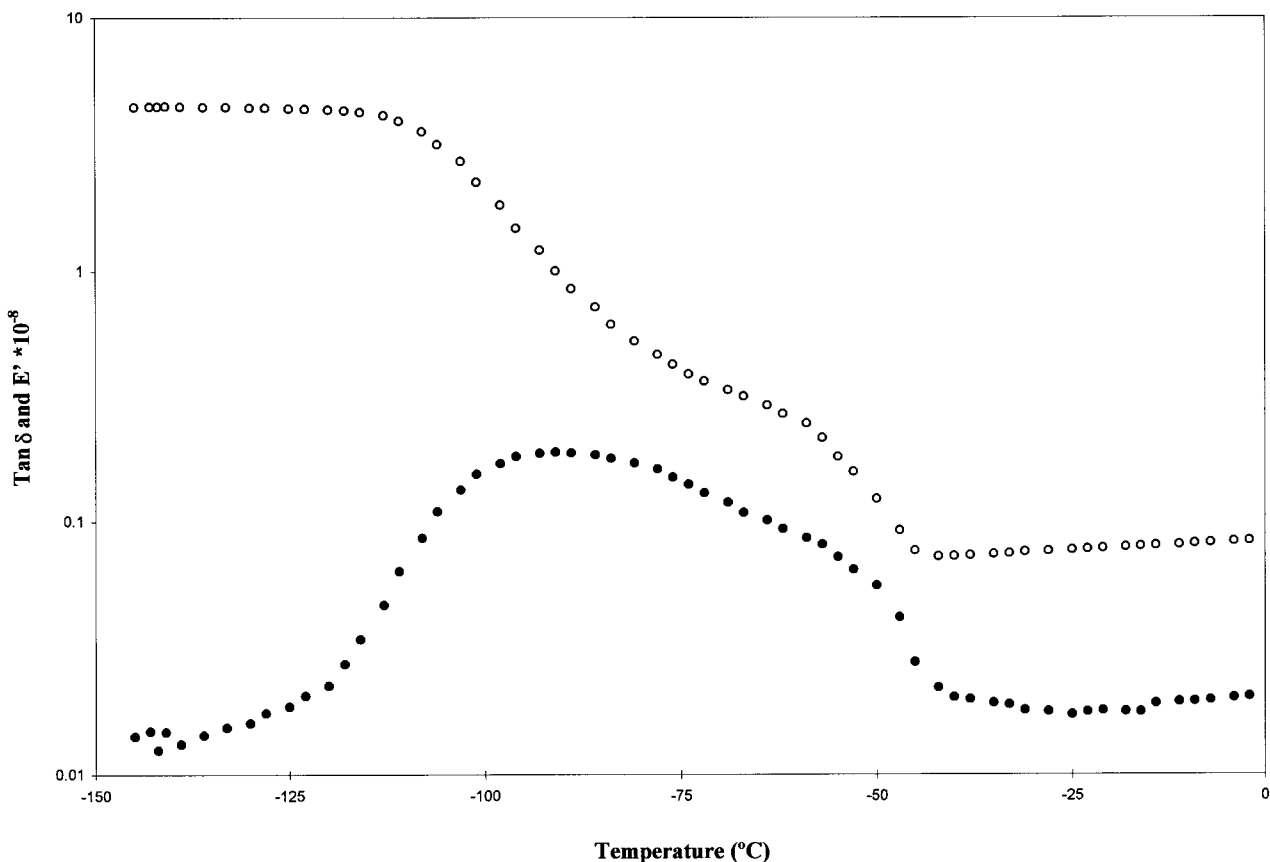
$$J = \frac{Q}{At} \quad (2)$$

where  $Q$  is the total amount permeated during the experimental time interval  $t$  at the steady state, and  $A$  is the effective membrane surface area. The total flux  $J$  is measured in  $\text{L m}^{-2} \text{h}^{-1}$ . The selectivity  $\alpha$  is defined in the usual manner as

$$\alpha = \frac{X_e^p/X_w^p}{X_e^f/X_w^f} \quad (3)$$

where  $X$  is the volume fraction, the superscripts  $p$  and  $f$  stand for permeate and feed, and the subscripts  $e$  and  $w$  stand for ethanol and water.

Table I summarizes selectivity and flux for the three different membranes. As the content of catalyst increases, permselectivity of ethanol increases substantially at the expense of flux. This appears to be due to reduced chain mobility of the PDMS–PMHS molecules. The complexity of the structure of the silicone samples increases as the



**Figure 3** Temperature dispersion of loss tangent ( $\tan \delta$ ) and storage modulus ( $E'$ ) of PDMS-PMHS films made with 10% catalyst ratio, at 10-Hz frequency: (●)  $\tan \delta$  and (○)  $E'$ .

catalyst content is increased, as explained in a previous article,<sup>13</sup> at the same time that the movement of the chains is strongly obstructed.<sup>14</sup> Crosslinking, therefore, has an effect on the diffusivity of the permeant molecules and on the partial permeation rate of ethanol and water.

Moreover, Table I shows that the increase in selectivity is not linear. In order to analyze the dependence of the pervaporation parameters on the catalyst ratio, the relative increase in selectivity and flux have been calculated as follows:

$$\text{Relative increase in selectivity} = \frac{\Delta\alpha}{\Delta\% \text{ catalyst}} \quad (4)$$

$$\text{Relative increase in flux} = \frac{\Delta J}{\Delta\% \text{ catalyst}} \quad (5)$$

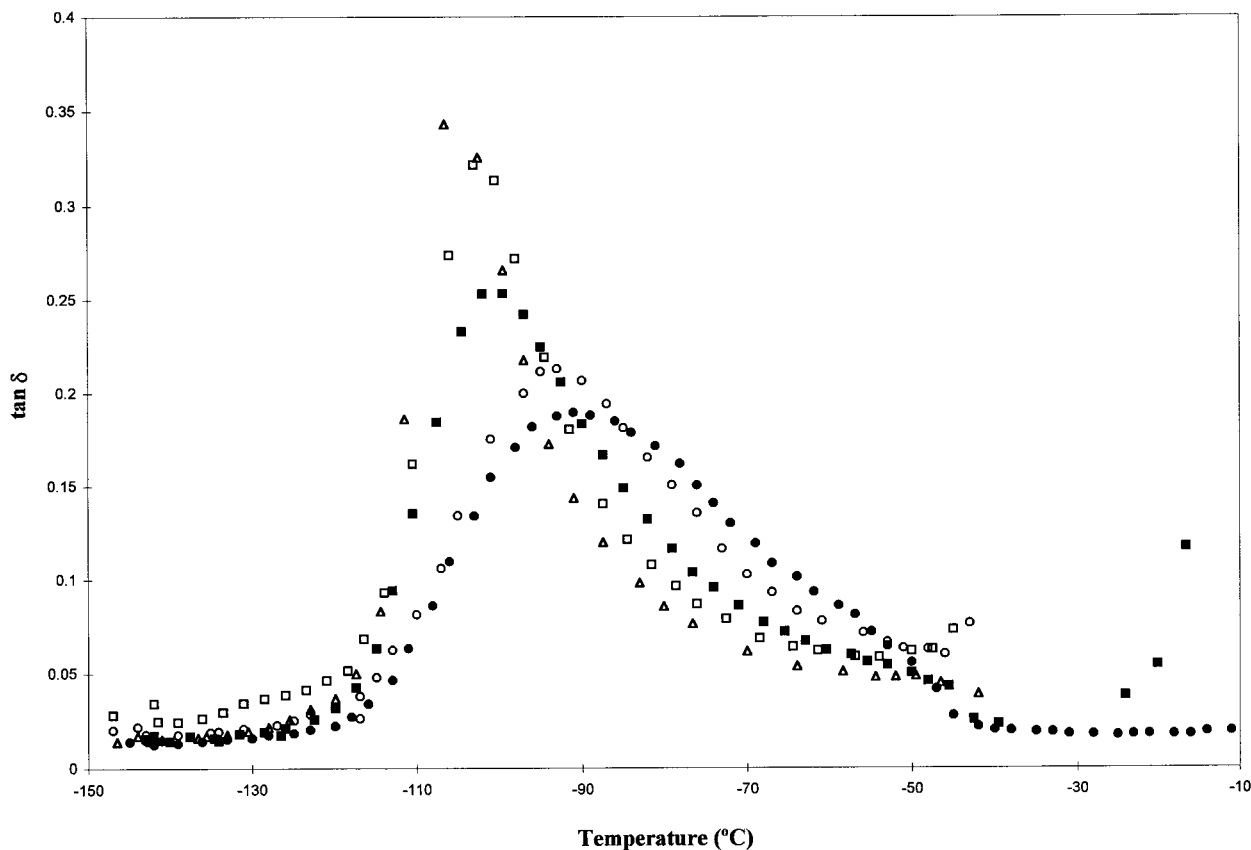
Comparing membranes A and B, the relative increase in  $\alpha$  is equal to 0.024. While for membranes B and C, the relative increase in  $\alpha$  is equal to 0.136, which is much higher than the preced-

ing. However, in both cases, the rate of variation of flux remains constant and equal to  $-0.0036$ . These results show that the increase in selectivity is larger between 7.5 and 10% than between 5 and 7.5% catalyst ratio, while the flux decreases linearly. Therefore, one can conclude the optimum content of catalyst is between 7.5 and 10%.

### Swelling Experiments

According to the solution-diffusion model, the preferential sorption plays an important role in determining the permselectivity. Thus, swelling experiments for silicon films made with 10% catalyst ratio were conducted with various mixtures of ethanol and water.

Figure 1 compares the swelling ratio of the PDMS-PMHS layer as a function of time in five different compositions of ethanol-water mixtures (0, 11, 20, 30, and 40 vol % ethanol). The swelling increases rapidly with the amount of ethanol in the ethanol-water solution. The swelling of pure water is relatively low, and the equilibrium swell-



**Figure 4** Plot of  $\tan \delta$  versus temperature at 10-Hz frequency for silicone films obtained with 10% catalyst ratio and swollen in various ethanol–water mixtures: (●) not swollen; (○) 11% ethanol; (■) 20% ethanol; (□) 30% ethanol; (△) 40% ethanol.

ing in this solution is reached in few hours. This confirms the low affinity for water of the PDMS–PMHS membranes. With respect to ethanol–water mixtures, the equilibrium time increases with the amount of ethanol in the solution.

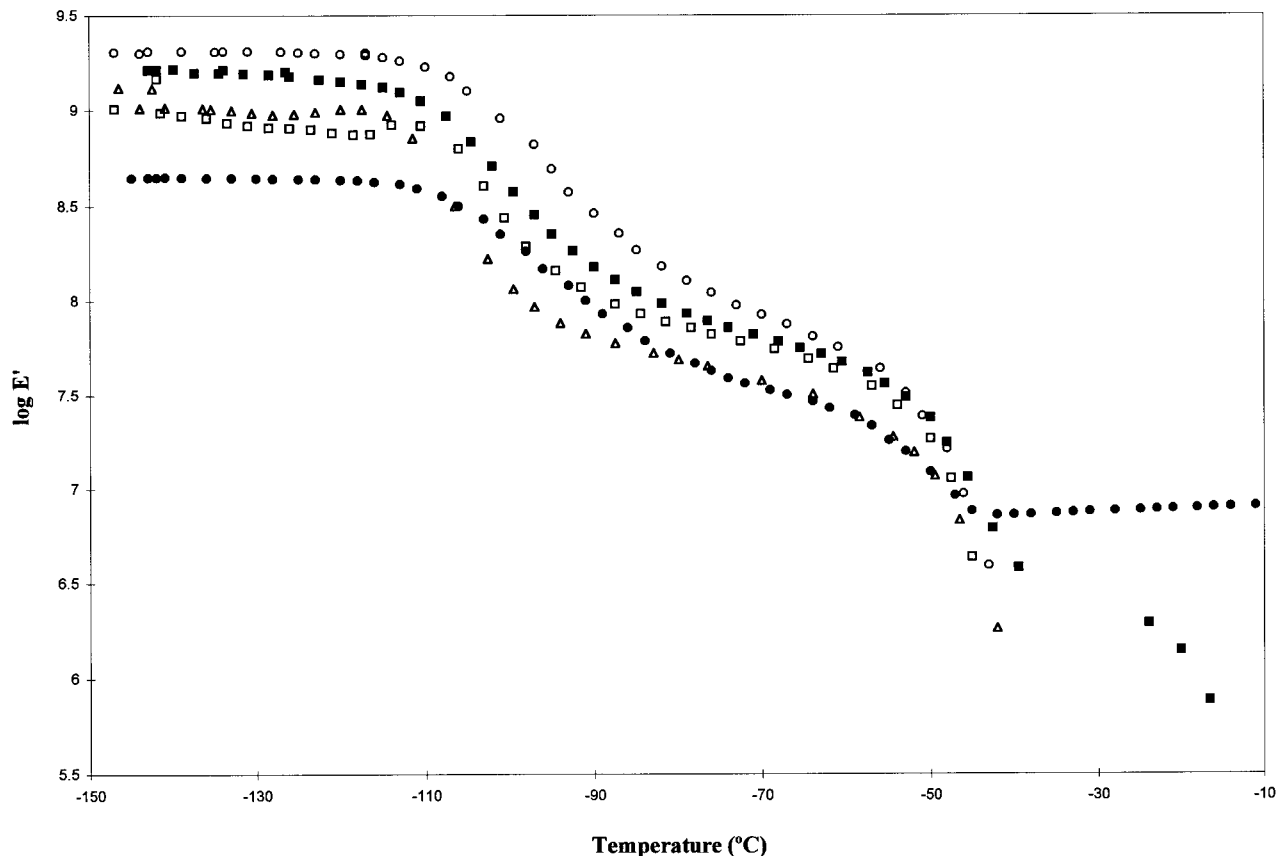
Further, in Figure 2, the dependence of swelling on the feed composition at different swelling times is plotted. For low ethanol concentrations, the membranes exhibit an increase in swelling with the amount of ethanol in the feed, and an equilibrium is reached near a composition of 30 vol % ethanol. Some authors<sup>15</sup> consider that swelling of membranes is related to the permeation rate in the pervaporation process. From their observations, it can be seen that the permeation rate of PDMS–PMHS membranes will be maximum when the pervaporation is performed with feed mixtures of 30 to 40 vol % ethanol content.

Figure 2 also shows an increase in swelling when time of permanence in the solution increases. For small times of permanence, a linear dependence of swelling with ethanol composition

can be established, while the trend of the curves changes for larger times of permanence. Swelling increases asymptotically with time until an equilibrium swelling is reached after 120 hours of permanence in the solution. This result suggests that the PDMS–PHMS film has a maximum quantity of solvent, which is capable of absorbing.

### Viscoelastic Relaxations

The effect of the absorbed molecules on the viscoelastic behavior of the silicon films was investigated. Figure 3 represents the relaxation spectrum of the PDMS–PMHS films in terms of  $\tan \delta$  and  $E'$  as a function of temperature at 10 Hz frequency. Similar spectra were obtained at 1, 3, and 30 Hz frequency, but they have not been included for the sake of clarity. The PDMS–PMHS mechanical spectrum presents a prominent absorption around  $-100^\circ\text{C}$ , which has conventionally been designated as  $\alpha$ -mechanical relaxation. Its molecular origin has been retraced to the micro-Brownian movement of segments of the



**Figure 5** Plot of  $\log E'$  versus temperature at 10-Hz frequency for silicone films obtained with 10% catalyst ratio and swollen in various ethanol–water mixtures: (●) not swollen; (○) 11% ethanol; (■) 20% ethanol; (□) 30% ethanol; (△) 40% ethanol.

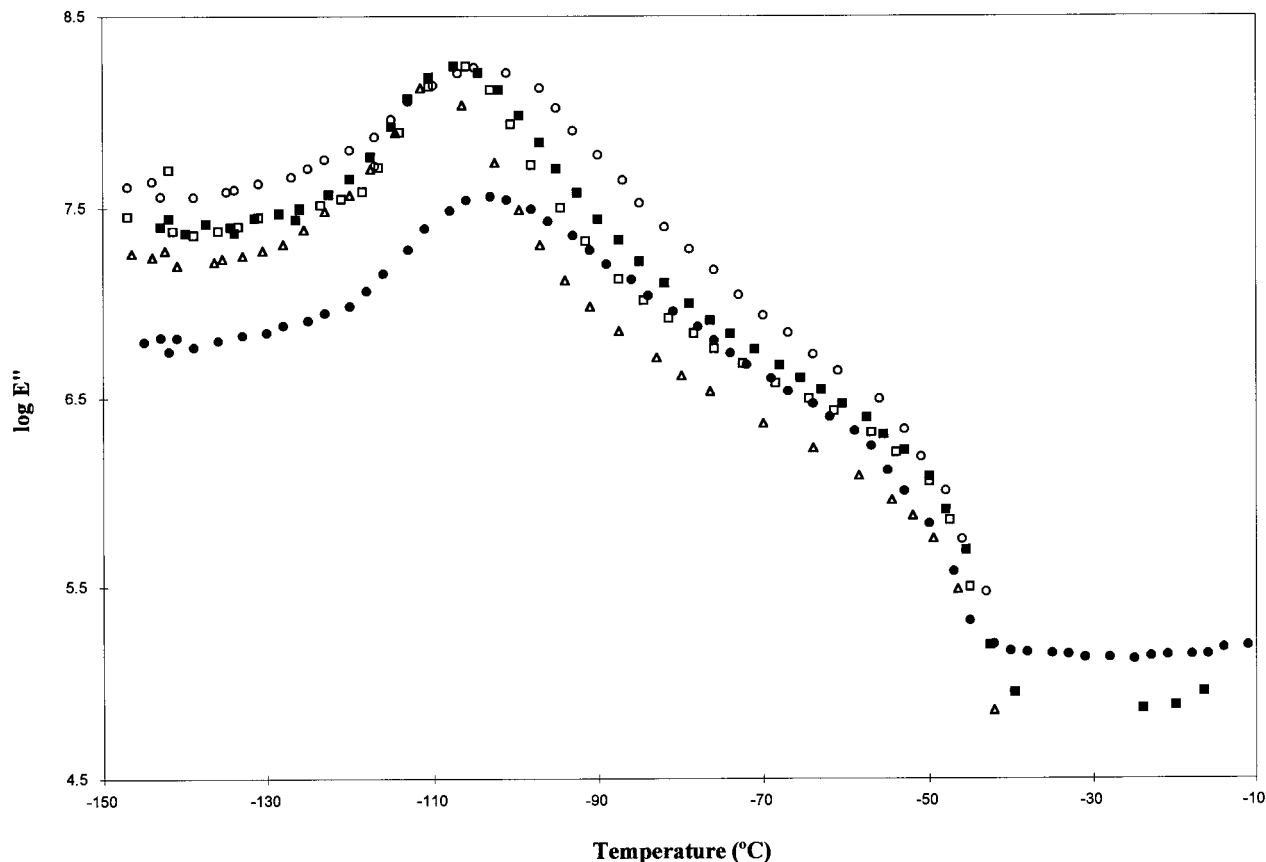
chain backbone, and it has been associated to the glass transition of the polymer.<sup>16</sup> Moreover, a slight shoulder appears around  $-80^{\circ}\text{C}$ , which might be explained in terms of the crosslinking of an initially linear polymer.<sup>13</sup>

In order to correlate the dynamics of the polymer with the swelling behavior of the samples, silicone films made with 10% catalyst ratio were immersed in different compositions of ethanol–water mixtures (11, 20, 30, and 40 vol % ethanol) during 168 hours, and dynamic–mechanical experiments were performed. The values of  $\tan \delta$ ,  $\log E'$ , and  $\log E''$  at 10 Hz frequency were plotted as a function of temperature (see Figs. 4–6, respectively). These figures show that with increasing amount of ethanol in the solution, the temperature of the maximum of the  $\alpha$ -peak shifts to lower values, and the  $\alpha$ -mechanical relaxation spectrum lengthens and narrows considerably. These observations indicate that the absorbed molecules plasticize the polymer during the sorption process.

Table II shows the relationship between the temperatures corresponding to the maximum val-

ues of  $\tan \delta$  versus temperature ( $T_{\alpha\text{-peak}}$ ) at 10 Hz and the amount of ethanol in the solution. The dependence of the percent equilibrium swelling, obtained from the swelling data at 120 h, on the ethanol concentration in the solution was also indicated. Table II shows the difference as well between the  $T_{\alpha\text{-peak}}$  corresponding to two consecutive compositions of ethanol and water ( $-\Delta T_{\alpha\text{-peak}}$ ).  $T_{\alpha\text{-peak}}$  shifts to lower temperatures with increasing amount of ethanol in the solution, as expected. The temperature difference,  $-\Delta T_{\alpha\text{-peak}}$ , decreases as the ethanol concentration in the mixture increases. This is in agreement with the swelling data, and it reflects that the ethanol sorbed has indeed plasticized the PDMS–PMHS film, but that the plasticizing effect is limited.

In order to analyze in detail the effect of the sorbed components on the viscoelastic properties of the polymer, the temperatures corresponding to the maximum values of loss modulus ( $E''$ ) versus temperature  $T_{\text{max}}$  at 10 Hz were obtained with an accuracy of  $\pm 0.01$  from the Fuoss–Kirkwood equation, as follows:



**Figure 6** Plot of  $\log E''$  versus temperature at 10-Hz frequency for silicone films obtained with 10% catalyst ratio and swollen in various ethanol–water mixtures: (●) not swollen; (○) 11% ethanol; (■) 20% ethanol; (□) 30% ethanol; (△) 40% ethanol.

$$E'' = \frac{E_{\max}}{\cosh \left[ m \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_{\max}} \right) \right]} \quad (6)$$

$$W = \frac{W_s - W_d}{W_s} \quad (8)$$

fitted to the data of the  $\alpha$ -relaxation.

$T_{\max}$  can be related to the weight fraction of the diluting constituent in the swollen sample  $W$ ,<sup>17</sup> as follows:

$$T_{\max} = T_g - KW \quad (7)$$

where  $T_g$  and  $K$  are characteristic constants that depend on the polymer.  $W$  can be, in turn, defined as

where  $W_d$  and  $W_s$  denote the weight of the dry and swollen membrane, respectively.

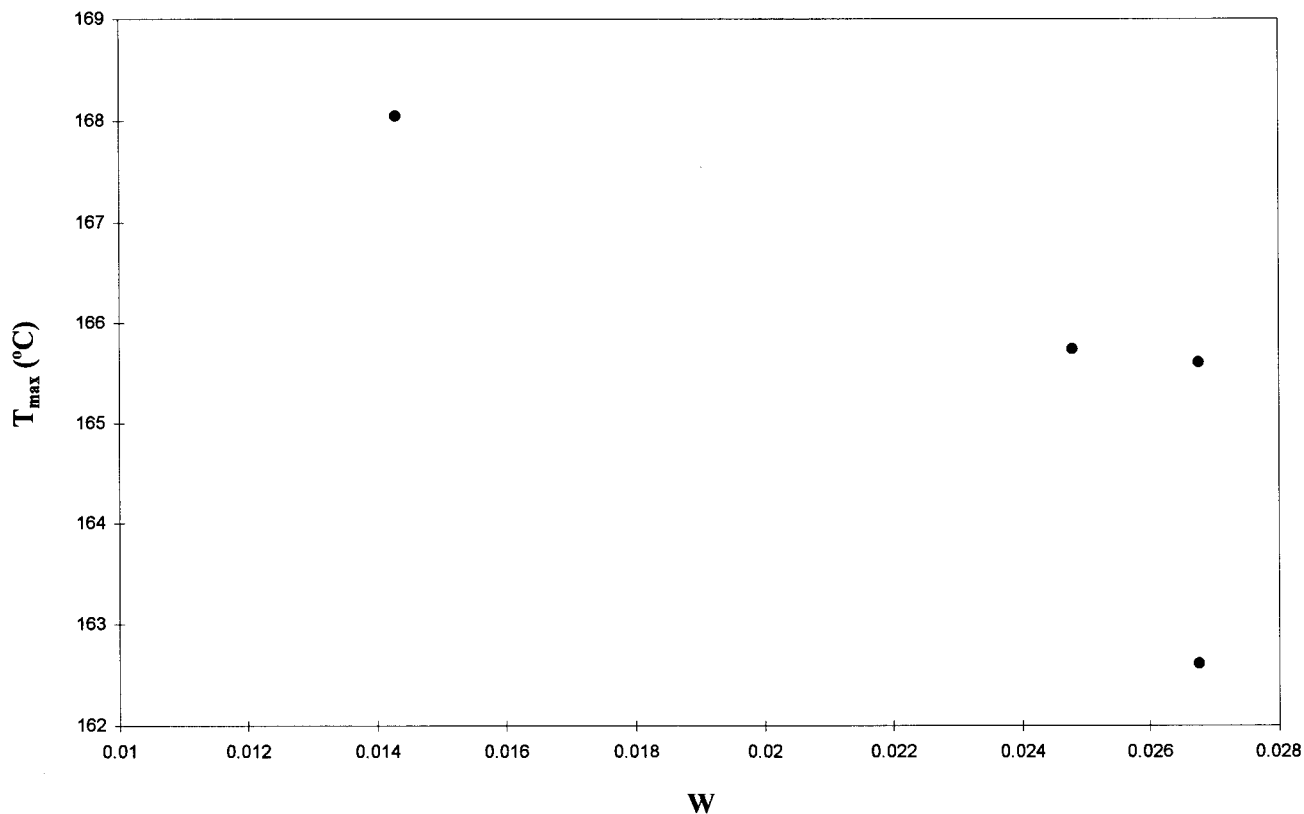
The results of eq. (7), plotted in Figure 7, are in good agreement with previous studies on plasticized polymers.<sup>18</sup> From these results, one can confirm that the ethanol molecules have plasticized the structure of the silicone.

It might be interesting at this point to examine the problem from the standpoint of the theory of free volume. The relaxation time  $\tau_i$ , associated with the viscoelastic mechanism  $i$ , is related to

**Table II** Values of  $T_{\alpha\text{-peak}}$  and Percentage of Equilibrium Swelling

Swelling Conditions	$T_{\alpha\text{-peak}}$ (°C)	$-\Delta T_{\alpha\text{-peak}}$	(%) Equilibrium Swelling
11% Ethanol	-93	—	1.45
20% Ethanol	-99.5	6.5	2.55
30% Ethanol	-103	3.5	2.75
40% Ethanol	-106	3	2.75





**Figure 7** Temperature corresponding to the maximum values of loss modulus ( $E''$ ) versus temperature  $T_{\max}$  at 10-Hz frequency as a function of the weight fraction of the diluting constituent.

the temperature by the Vogel equation,<sup>19</sup> as follows:

$$\log \tau_i = A + (m/2.303)/(T - T_\infty) \quad (9)$$

where  $T_\infty$  is the temperature at which the free volume would be zero, and  $A$  and  $m$  are constants. By assuming that all the relaxation mechanisms have the same temperature dependence, the shift factor  $a_T = \tau_i/\tau_{i,0}$ , where  $\tau_{i,0}$  is the relaxation time at the reference temperature  $T_0$ , is given by

$$\log a_T = A' + (m/2.303)/(T - T_\infty) \quad (10)$$

with

$$A' = -(m/2.303)/(T - T_\infty) \text{ and } m = B/\alpha_f \quad (11)$$

According to Doolittle's equation,<sup>20</sup>  $m$  is related to the free volume as

$$m = (B/\phi)(T - T_\infty) = (B/\phi_g)(T_g - T_\infty) \quad (12)$$

where  $\phi$  and  $\phi_g$  are the relative free volumes at  $T$  and  $T_g$ , and  $B$  is an empirical constant. Although the values of  $B$  for polymer systems are not exactly known, the values of  $\phi$  and  $\phi_g$  are customarily calculated assuming  $B = 1$ .

Table III shows the dependence of the parameters obtained from the Vogel equation fitted to the maximum values of loss modulus versus temperature at the frequencies of 1, 3, 10, and 30 Hz on the ethanol concentration. There the values of the apparent activation energies are also given, calculated from the expression,<sup>21</sup> as follows:

$$E_a = R \frac{d \ln a_t}{d(1/T)} \quad (11)$$

which, with eq. (10), gives

$$E_a = Rm \left( \frac{T}{T - T_\infty} \right)^2 \quad (12)$$

The values obtained are similar to those reported by other authors for the PDMS.<sup>22</sup> The  $(\phi/B)$  param-

**Table III Parameters of the Vogel Equation for the  $\alpha$ -Relaxation and Values of Free Volume**

Swelling Conditions	$m$	$(\phi/B) \times 10^2$	$E_a$ (at $T = 405$ K) kJ mol
Not swollen	1013	1.1	7.072
11% Ethanol	962	1.5	6.469
20% Ethanol	979	1.6	6.420
30% Ethanol	987	1.9	6.247
40% Ethanol	988	2.0	6.178

eter, which is related to the free volume, first increases with the ethanol concentration but remains almost constant for ethanol concentrations between 30 and 40 vol %. This result suggests that the entrance of solvent into the PDMS-PMHS structure produces an additional free volume in the polymer. Further, the activation energy decreases with increasing amount of ethanol in the solution, which indicates that the ethanol molecules absorbed facilitate the movement of the PDMS-PMHS chains. The fact that the increasing free volume approaches a constant value confirms that the silicone polymer has a limited relative free volume; therefore, it has a maximum quantity of solvent, which is capable of absorbing.

## CONCLUSIONS

The following conclusions can be drawn from this study.

1. Pervaporation experiments with pervaporation membranes, whose active layers were made with different catalyst concentrations, showed that an optimum amount of catalyst exists between 7.5 and 10% catalyst ratio.
2. Swelling behavior reveals that PDMS-PMHS membranes have higher affinity for ethanol than for water and that the membranes are only capable of absorbing a limited quantity of solvent.
3. The analysis of the viscoelastic relaxation of the swollen samples has determined that the molecules sorbed produce an increase in the amount free volume of the polymer. The dependence of the parameters of the Vogel equation fitted to the data of the  $\alpha$ -relaxation on the ethanol concentration confirms that the small molecules of ethanol have a plasticizing effect over the polymer and that the PDMS-PMHS layer has a limited relative free volume.

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