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Effect of Temperature on the Transport Properties and Morphology of Polymeric Asymmetric Membranes

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ABSTRACT

Polymeric membranes have not been practical for application to high temperature processes, due to the thermal instability of most polymers. New materials are being developed with higher glass transition temperatures and a greater degree of thermal stability. Use of these polymers to perform gas separations at higher temperatures is promising; however, the performance of the membrane as the process approaches the polymer's glass transition temperature is unknown. This study was conducted to explore this issue. Gas flux and helium/nitrogen ideal selectivities through heat treated integrally-skinned asymmetric polysulfone membranes were measured. Membrane morphology was also evaluated through bubble point tests and SEM micrographs. Experiments demonstrated that as the polymer is exposed to temperatures approaching the polymer glass transition temperature, internal pores begin to collapse, causing both the gas flux and selectivity to decrease.

INTRODUCTION

Polymeric membranes are currently employed to separate gases. In certain applications, polymeric membranes offer significant advantages over other separation techniques because they operate without the addition of energy to produce two more purified streams. Polymeric gas separation membranes have found many industrial applications including the production of purified nitrogen from air; the separation of carbon dioxide from natural gas; and the separation of hydrogen from refinery gases (1,2). However, the range of environments in which polymeric membranes have found use is rather limited. Use at temperatures of greater than about 100 °C is uncommon.

New polymers with glass transition temperatures significantly higher than those conventionally used for gas separation membranes are now available (3,4,5). These materials offer the potential of application in many challenging environments. However, the question of what happens to the morphology of a membrane upon extended exposure to these environments remains. This study was conducted to address this issue.

The performance of integrally skinned asymmetric polysulfone membranes as they are heated to their glass transition temperature is evaluated. The gas transport properties of the membranes were monitored as were the macroscopic structures.

BACKGROUND

Polymeric membranes have become widely used for the separation of gases at moderate temperatures and pressures. In this system, a feed mixture is contacted with the membrane, and components from the feed sorb into and diffuse through the membrane due to an imposed chemical potential difference. Separation selectivity is determined solely by the selection of the polymer to be used.

The rate of transport is dependent upon the membrane material, its effective thickness, and the operating temperature and pressure.

Polymers have been used extensively in membrane production because they can achieve a high selectivity at an acceptable transport rate.

Yet, polymers have limitations. Current polymeric membranes cannot treat mixtures at elevated temperatures. However, polymers with glass transition temperatures above 200 °C have recently been introduced suggesting that polymeric membranes may find use at higher operating temperatures (3,4,5). However, the relationship between glass transition temperature and operating temperature has not clearly been established.

The upper use temperature for polymeric membranes is influenced by a number of factors. First, the polymer must be chemically stable in the operating environment at the expected use temperature. As the temperature increases, chemical degradation reactions which cause chain scission and structural failure become more likely. The precise temperature at which polymer degradation becomes significant is dependent upon the operating environment and upon the chemical composition of the polymer. This value can be readily estimated through use of thermal gravimetric analysis. Changing the structure of the polymer to decrease the likelihood of chemical attack is the only mechanism for increasing the use temperature.

Second, the ability of the membrane to achieve the desired separation is influenced by temperature. For most separations of interest, the permeability of the components through the polymer increase with temperature, but the separation selectivity decreases (6,7). The optimum combination of flux and selectivity for each separation will occur at different temperatures for different polymers.

Finally, if asymmetric membrane structures are to find application at temperatures far above room temperature, the mechanical strength of the microporous support layer must be sufficiently strong to prevent pore collapse even at temperatures approaching the polymer's glass transition temperature.

Asymmetric membrane structures

Permeate production rates are controlled by the membrane area available, the effective separating layer thickness and the separating layer permeability. To achieve economically acceptable membrane areas, the thickness of the separating layer has been reduced to less than a few microns through the preparation of asymmetric membranes (8).

Asymmetric structures, shown schematically in Figure 1, combine the properties of a thin, but selective separating layer, with a thick, non-selective support that introduces negligible resistance to transport (9). This asymmetric structure, first developed by Loeb and Sourirajan (10), has provided a mechanism for membrane separations to be used in the variety of applications currently employed. Modifications to these structures were made by Henis and Tripodi (11), in the development of the multi-layer composite, and by Riley (12) and Ward (13) and others (14) in the development of the thin film composite membrane.

These highly sophisticated designs rely upon a gradual increase in the size of pores present in the support layer from the skin side to the permeate side. This gradual increase is necessary to support the fragile skin layer, which is nonporous and may be only a few hundred ångstroms thick. Lacking this support structure, the fragile skin layer could be easily damaged when exposed to high pressure operation.

Polymer moduli decrease with increases in temperature. The behavior of a typical, non crystalline polymer is shown schematically in Figure 2 (15). At low temperatures, the polymer is in the "glassy" state with a high modulus. As the temperature is increased, a transition region is transversed with a dramatic decrease in modulus and then the "rubbery" state is entered. The temperature at the transition point between the "glassy" and "rubbery" state is called the glass transition temperature. At considerably higher temperatures, the polymer may experience another decrease in modulus and enter a "flow" state where its properties are closely related to liquids.

This change in polymer modulus may be an important consideration in determining the useful operating temperature for a polymer. If it is desirable for the polymer to maintain its geometric structure, then operation in the glassy state may be necessary. Operating in the "rubbery" state, the "flow" state, or close to the glass transition temperature may lead to changes in structure due to a loss in modulus.

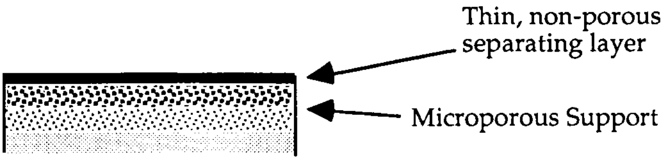

FIGURE 1. Typical asymmetric membrane structure.

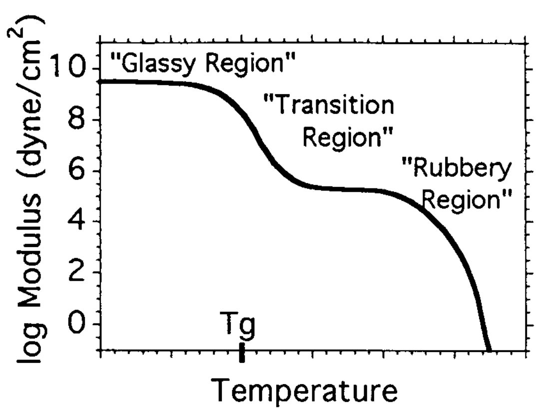

FIGURE 2. The effect of temperature on polymer modulus (15).

If the polymer modulus is insufficient, structural changes to the membrane may occur. Mazur and Chan report on decreases in the CO_2 permeance through a cellulose acetate asymmetric membrane as a function of time (16). The membrane was used to recover CO_2 from natural gas. Decreases in the gas flux were reported, but no information about the operating selectivity was provided (16). Substructure compaction due to exposure to high feed pressures was believed to be responsible for this behavior.

Compaction of the substrates of ultrafiltration membranes has been reported by several researchers (17, 18, 19, 20). In each case, compaction is attributed to high operating feed pressures. In some cases, decreasing the feed pressure results in an increase in the operating flux. In others, the compaction appears to be irreversible and is unaffected by decreasing pressure. The effects of temperature have not been widely reported.

EXPERIMENTAL

Materials

Polymers. Polysulfone, Udel® 1800, was kindly supplied by the Amoco Chemical Corporation. The measured Tg of 185 °C ± 3 °C agreed well with that reported by VanKrevlin of 190 °C (15). Reagent grade solvents were purchased from Aldrich and Fisher and used as supplied.

The helium and nitrogen permeability coefficients of a solution-cast polysulfone film at 30 °C are calculated to be 12.8 and 0.204 Barrer, respectively, from reported values at 24 °C and activation energies for permeation (9).

Gases. Helium and nitrogen, used for transport evaluation were purchased from South East Air Gas and had a minimum purity of 99.9 %.

Procedure.

Membrane Preparation. Integrally-skinned asymmetric membranes were prepared following the methods of Pinnau (9). Membrane casting solutions were 12.1 wt.% polysulfone, 52.3 wt.% methylene chloride, 21.1 wt.% 1,1,2-trichloroethane and 14.5 wt.% 2-methyl-2-butanol. The casting solution was close to the thermodynamic instability limit, i.e., binodal composition. Methanol was used as the quench medium.

The polysulfone solution was cast on a glass plate with a knife gap of 180 μm. A gas stream (air at 100% relative humidity) was blown across the membrane surface for a period of 15 seconds. Interfacial phase separation in the cast membrane occurred immediately at the onset of blowing. After an additional free-standing evaporation period of 15 seconds, the membranes were immersed in the methanol quench medium. The membranes remained in the quench medium for 6 hours. Following removal from the quench bath, the membranes were air dried for 24 hours and then dried in a vacuum oven at 100 °C for 6 hours.

Heat Treatment. The ultimate goal of this study was to determine the influence of high temperature exposure on the gas transport properties of asymmetric membranes. To remove compaction caused by combined temperature and pressure effects, a simplification was made. Membranes were exposed to high temperatures for a predetermined period under no differential pressure, cooled, and their gas transport properties measured at room temperature. At room temperature and 50.0 psi, there was negligible compaction due to a pressure effect, as is confirmed by repeated measurements of membranes used for error analysis. Thus any differences measured before and after heat treatment are due to thermal and not mechanical forces.

Membranes were placed on a glass plate in a preheated oven and heated under a vacuum of less than 1 cmHg for a period of 21 hours. Following the heating period, the samples were removed to laboratory air and allowed to cool. Measurement of gas transport properties was completed immediately following this period.

Heat treatment temperatures of 100 °C, 130 °C, 160 °C, 175 °C, and 190 °C (the polymer Tg) were employed.

Gas Transport Evaluation. Pure gas pressure-normalized fluxes reported in this study were measured at 30 °C for membrane samples with a surface area of 13.8 cm^2. A constant pressure-variable volume test apparatus was employed, and a feed pressure of 50 psi was used. The permeate side of the sample was maintained at atmospheric pressure and purged with the test gas prior to measurement.

Only membrane samples which were judged to be essentially defect free were used in this evaluation. Based on the reported permeabilities, a defect-free membrane sample should have an ideal selectivity of 62.8 for the separation of helium from nitrogen. Membranes with a minimum selectivity of 80% of the dense film value were used. At this level, it is recognized that some surface pores are present in the samples. However, the number (and size) of these pores is limited. Resistance-model calculations which assume that any surface defects exhibit Knudsen selectivity of 2.63 and that the substrate has negligible resistance show that for a membrane with a selectivity of 50, the skin layer is less than $5x10^{-4}$ % porous.

Experimental Accuracy. Three control membrane samples were used to estimate experimental accuracy. The gas flux through these membranes was measured each time one of the heat treatment series was completed, for a total of twelve replications. Since the membranes were never heat treated, variability in the results can be attributed entirely to experimental inaccuracies.

Field Emission Scanning Electron Microscopy. Photomicrographs of membrane cross-sections were taken with a Hitachi S-800 field emission electron microscope. The membrane samples were fractured cryogenically in liquid nitrogen and subsequently coated with a thin layer (less than 0.01 μm) of gold/palladium alloy using a vacuum evaporator.

Bubble Point Evaluation. Evaluation of the bubble point of a few selected membranes was made. The standard ASTM-F316 procedure was followed in this evaluation. The membranes were soaked in isopropanol for 24 hours. Gas was applied to the top of the soaked sample. The pressure at which the gas passes through the sample point is defined as the bubble point pressure, P_{bp}. Calculation of the largest pore diameter was completed using the Young-Laplace equation (1):

$$r = \frac{2\gamma}{P_{bp}} \cos\theta \qquad (1)$$

where r is the diameter of the largest pore (cm); γ is the isopropanol-air surface tension (dynes/cm); and P_{bp} is the pressure applied at the bubble point (dynes/cm^2); and θ is the contact angle. At the bubble point, $\cos\theta$ equals 1. Isopropanol surface tension at 24 °C was taken to be 20.82 dynes/cm (21).

RESULTS

The influence of heat treatment on transport through integrally-skinned asymmetric polysulfone membranes is provided in Table 1. In this Table, the helium and nitrogen fluxes of membranes before and after heat treatment are provided, as are the calculated ideal selectivities for these samples.

TABLE 1: Influence of Heat Treatment Temperature on Gas Transport Properties

Treatment Temperature (°C)	*Properties of Membranes Prior To Heat Treatment* Helium Flux (GPU)	Nitrogen Flux (GPU)	He/N2 Selectivity	*Properties of Membranes Following Heat Treatment* Helium Flux (GPU)	Nitrogen Flux (GPU)	He/N2 Selectivity
100	23.63 ± 2.48	0.51 ± 0.13	46.2	19.23 ± 2.02	0.41 ± 0.10	47.3
100	125 ± 13.13	2.70 ± 0.69	46.2	97.50 ± 10.24	2.11 ± 0.54	45.3
130	173.90 ± 18.26	3.45 ± 0.88	55.4	149.70 ± 15.72	5.23 ± 1.34	31.5
130	183.30 ± 19.25	4.12 ± 1.05	48.9	102.10 ± 10.72	2.44 ± 0.62	45.9
130	153.10 ± 16.08	3.14 ± 0.80	53.5	105.30 ± 11.06	2.67 ± 0.68	43.3
160	95.14 ± 10.00	1.82 ± 0.47	57.5	29.24 ± 3.07	0.96 ± 0.25	33.6
160	137.50 ± 14.44	2.30 ± 0.59	65.7	48.98 ± 5.14	1.02 ± 0.26	52.7
160	157.10 ± 16.50	2.85 ± 0.73	60.6	54.39 ± 5.71	1.98 ± 0.50	30.1
175	163.70 ± 17.19	2.56 ± 0.66	70.4	22.63 ± 2.38	0.68 ± 0.17	36.4
175	120.50 ± 12.65	1.99 ± 0.51	66.6	25.34 ± 2.66	0.75 ± 0.19	37.1

Experimental Repeatability and Precision. The experimental errors present in the data are also provided in Table 1. The percentage error for each measurement (for example, for the measurement of helium flux) was obtained by dividing the standard deviation of a control series by the average value measured. The average experimental uncertainty for the helium flux measurement and nitrogen flux measurement was 10.5 % and 25.6%, respectively.

Influence of Heat Treatment on Surface Pores. The heat treatments employed did not seem to influence the size of the largest surface pores. The largest skin layer pore size of a membrane sample with a helium/nitrogen selectivity of 46 was measured before and after heat treatment at 100 °C. Following heat treatment, the selectivity was unchanged, as was the largest skin layer pore size. The largest pore size was determined to be 900 ± 50 Å before and 950 ± 50 Å following heat treatment.

A second sample which originally had no surface pores larger than 150 Å was also evaluated. Prior to heat treatment, no surface pores were measured and the helium/nitrogen selectivity was 53. Following heat treatment at 100 °C, no pores were detected and the helium/nitrogen selectivity was unchanged.

Influence of Heat Treatment on Gas Transport Properties. The influence of exposing integrally-skinned asymmetric polysulfone membranes to temperatures above room temperature was evaluated by monitoring the ability of the membranes to transport gases at room temperature. Since the initial properties of the membranes used in this evaluation varied somewhat, the results have been analyzed in terms of the ratio of the property following heat treatment divided by the property prior to heat treatment. In this way, an increase in gas flux following exposure to heat is seen as a value of the ratio greater than one; no change results in the ratio equaling one, and a decrease in properties results in a value of the ratio less than one.

The influence of heat treatment on the helium flux through the membranes evaluated is presented in Figure 3. There is a clear trend of a decrease in the helium transport rates as the temperature of the heat

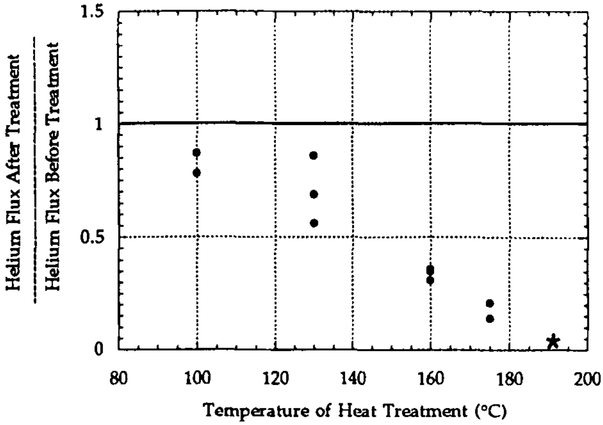

FIGURE 3. Influence of heat treatment on helium flux through integrally skinned asymmetric polysulfone membranes. [* represents a flux that is too slow to measure after heating.]

treatment increases. A similar trend is observed for the nitrogen flux through these membranes.

The membrane samples heated to 190 °C (Tg) had fluxes which were too slow to measure using the constant pressure-variable volume equipment available.

The calculated ideal helium/nitrogen selectivity for these membranes is presented in Figure 4. The selectivity initially remains approximately constant, and then decreases as the heat treatment temperature increases.

In an attempt to isolate the influence of heat treatment on the surface, transition, or substrate layer, the surface and transition layers of membranes were removed. Two sets of membranes (one as prepared and the other heat treated to 160 °C) were lightly sanded to remove the surface and transition layer. As it is difficult to know precisely how much polymer is removed and where these layers start and stop, it is extremely likely that some material from the substrate layer was also removed. Nevertheless, the nitrogen fluxes through the substrates of the two sets of membranes were equal within experimental inaccuracy.

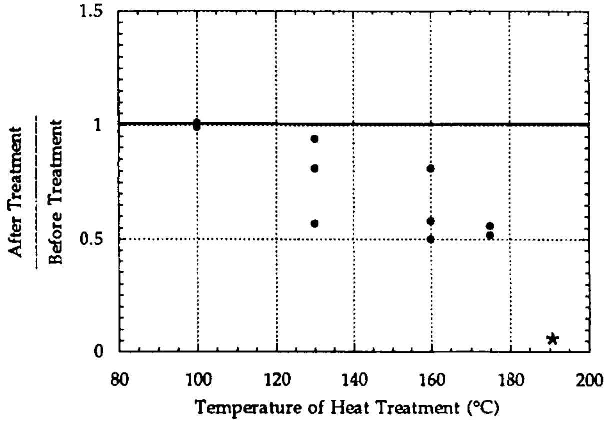

FIGURE 4. Influence of heat treatment on helium/nitrogen selectivity through integrally skinned asymmetric polysulfone membranes. [* represents a flux that is too slow to measure after heating.]

DISCUSSION

Decreases in transport rates coupled with decreases in the helium/nitrogen selectivity are believed to result from collapse of some of the pores present in the transition or support layers. If only partial pore collapse occurs, a denser, nonselective substrate layer results, with higher gas transport resistance. Thus, the overall gas flux through the membrane decreases. Due to its porous nature, the substrate retains Knudsen selectivity. As the resistance through the substructure becomes significant in comparison to the resistance through the skin layer, the selectivity of the overall membrane is influenced more by the selectivity of the substructure. Mathematical analysis of this phenomenon has been completed by numerous authors (22, 23, 24). The following relationship for two components in a series can be applied to transport through multi-layer composites:

$$R_{total} = R_{skin} + R_{substructure} \tag{2}$$

$$\frac{1}{R_{total}} = \left(\frac{P}{\ell}\right)_{i,total} \tag{3}$$

where R is the resistance of the layer in question; P is the permeability coefficient of gas i through the membrane; and ℓ is the effective membrane thickness.

Equation (2) has been previously employed by Pinnau to model the separation of oxygen and nitrogen through integrally-skinned asymmetric membranes to evaluate the influence of substructure resistance on overall membrane performance (24). The same method can be applied to determine the effect of the polysulfone skin and substructure resistance on the helium/nitrogen ideal selectivity. The model assumes that there is no overlap in the skin and substructure layers (i.e., no components are in parallel). Equation (2) can be expanded (23, 24):

$$\frac{1}{\left(\frac{P}{\ell}\right)_{i,total}} = \frac{1}{\left(\frac{P}{\ell}\right)_{i,skin}} + \frac{1}{\left(\frac{P}{\ell}\right)_{i,substructure}} \tag{4}$$

Assuming all the flow through the substrate is Knudsen flow, and all flow through the skin is flow through a dense film at a temperature of 30 °C, Equation (4) can be simplified for nitrogen as:

$$\frac{1}{\left(\frac{P}{\ell}\right)_{N_2,total}} = \frac{\ell_{skin}(\mu m)}{0.204\ (\text{Barrer})} + \frac{1}{\left(\frac{P}{\ell}\right)_{N_2,Knudsen}} \tag{5}$$

A similar equation can be written for helium. The solution to Equation (5) was varied by altering the effective thickness which contributed to the resistance of each layer, until the model compared with experimental data. Selectivities were calculated from the helium and nitrogen total resistances. The model predictions and experimental data are presented in Figure 5. The initial straight line of Figure 5 represents the area where resistance of the substructure is negligible, resulting in a selectivity equal to the dense film selectivity of 62.8. As the substructure provides more resistance, the overall selectivity decreases. As the resistance of the substructure becomes appreciably greater than that of the skin layer, the membrane selectivity approaches the He/N_2 Knudsen selectivity of 2.63. Data points on Figure 5 represent the selectivity of the

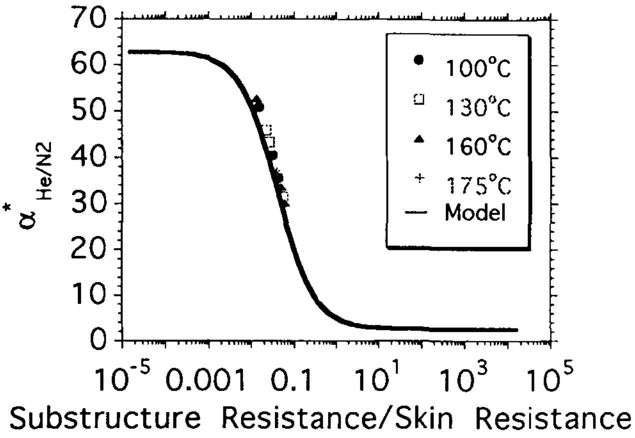

FIGURE 5. The effect of substructure resistance on the helium/nitrogen selectivity of an integrally-skinned asymmetric polysulfone membrane.

heat treated membranes. From this plot, one can see that increased substructure resistance decreases the overall selectivity of the heat treated membranes.

Evaluation of these equations provided a clear appreciation of the influence of the support layer resistance on the overall transport properties. Exposure to temperatures well below the glass transition temperature caused an increase in the gas transport resistance of the substrate layer and a decrease in the ideal selectivity of the membranes.

The cross sections of selected membranes were analyzed with scanning electron microscopy and are shown in Figure 6. However, no dramatic changes in the morphology were observed except for the membrane heated to its Tg. Although major differences were not demonstrated in the cross sections in Figure 6, clear pore collapse is evident in the magnification of the transition layer shown in Figure 7. In this membrane, the thickness of the skin layer has clearly increased and the relative porosity of the transition layer decreased.

Figure 8 presents a schematic of the proposed membrane structure before and after heating. In this schematic, the relative thicknesses of the skin and transition layer are significantly increased in comparison to the substrate. The "as prepared" sample is shown on the left, and the heat treated sample on the right. The skin layer is essentially nonporous and consists only of condensed polymer chains. The substrate layer is comprised of a highly porous polymer matrix. The average pore size here is on the order of 10 μm. As is depicted in Figure 8, neither the skin layer nor the substrate is markedly influenced by the heat treating processes. The transition layer, which consists of a gradient of pores of increasing size and number, shows the most significant changes upon heating. The smallest pores are completely eliminated by heating. Larger pores are decreased in size.

Additional support for the compaction argument can be found from Brown's work with latex dispersions (25). Brown used a force balance to approximate the conditions necessary for pore collapse in a drying latex film(25):

$$G_t > 5.43\frac{\sigma}{R} \qquad (6)$$

where G_t is the polymer modulus; σ is the surface tension; and R is the radius of the pore (between three spherical particles). The aforementioned model assumes that the polymer is elastic and its volume does not vary. It also assumes that the force due to polymer curvature, Van der Waals forces, gravitational forces, and repulsion due to coulombic forces are negligible when compared to the force caused by capillary pressure and the force maintaining particle shape (25). Application to present work at 130 °C yields:

$$R < 9.1 \text{ Å} \qquad (7)$$

where the surface tension of the polysulfone is calculated to be 67 dynes/cm (15); and the modulus at 130 °C is approximately 0.4 GPa (26). Therefore, pore sizes smaller than about 20Å in diameter could collapse at 130 °C. This calculation explains the lack of morphological changes observed in the SEM data for samples heated below Tg. It is difficult to view pore sizes smaller than approximately 50Å with the SEM (27). As

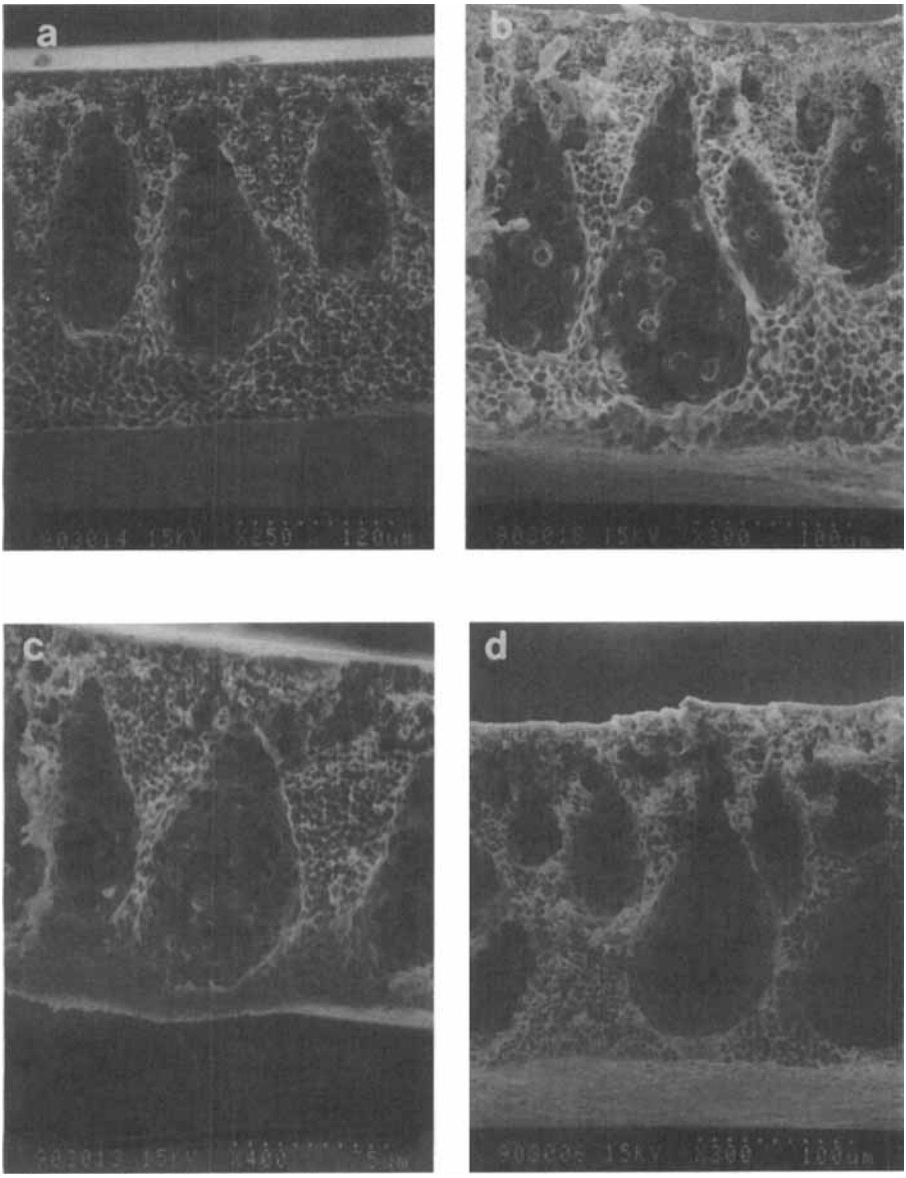

FIGURE 6. Scanning electron micrographs of the cross-section of heat treated membranes: (a) 100 °C, (b) 130 °C, (c) 165 °C, (d) 175 °C, and (e) 190 °C. (Note: The magnifications for each micrograph are slightly different.)

FIGURE 6. Continued.

the temperature increases, the largest pore size which can collapse also increases, due to decreasing modulus. Therefore, one could expect to see changes in the SEM data. Byelousov and Mikitayev (26) found that a sharp drop in the modulus of glassy polysulfone occurs at the glass transition temperature at approximately 190 °C. However, the modulus is not constant on approach to Tg. The modulus begins its downward slope at approximately 130 °C (26). The membranes which were treated at temperatures above 130 °C demonstrated a substantial decrease in flux.

CONCLUSIONS

The ability to use integrally skinned asymmetric, glassy polymeric membranes for the separation of gases depends upon the temperature of the application. As the temperature increases and nears the glass transition temperature, the polymeric modulus decreases allowing for

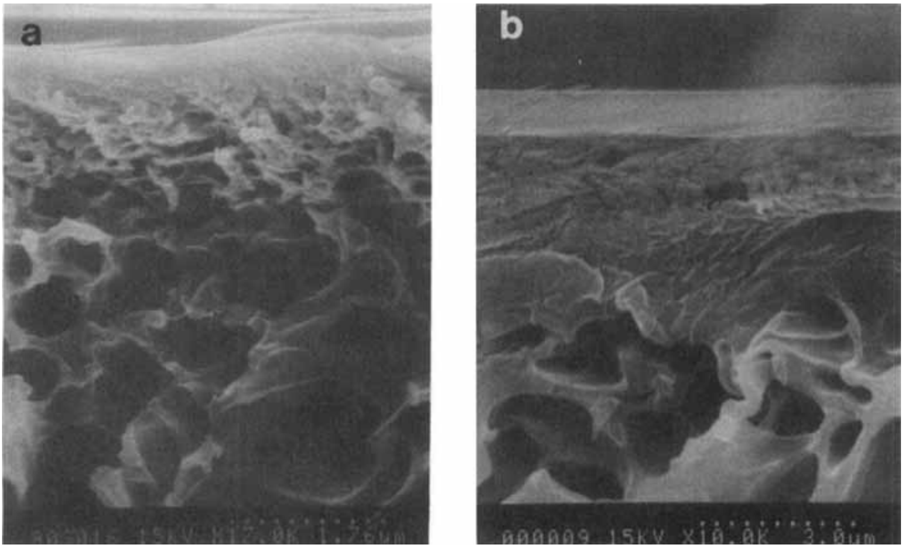

FIGURE 7. Scanning electron micrographs of the cross-section of heat treated membranes: (a) 100 °C, (b) 190 °C. (Note: The magnifications for each micrograph are slightly different.)

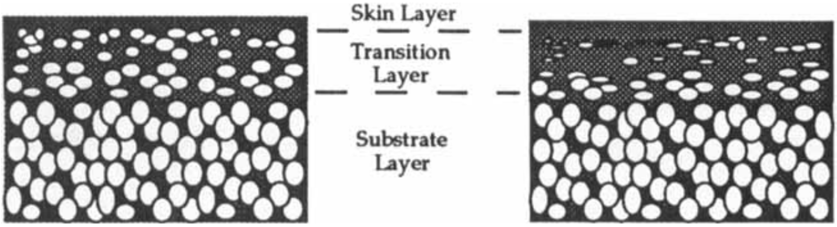

FIGURE 8: Schematic representation of the cross-section of membranes. Left: as prepared. Right: Following heat treatment and transition layer pore collapse.

morphological changes in the complex polymer microstructure. Incomplete pore collapse in the membrane substrate leads to decreased transport rates and decreased separation selectivity. In order for high temperature membranes to become industrially attractive, the compaction mechanism must be retarded or polymers which do not show as much compaction with temperature increase must be explored.

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