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Thermomechanical Stability of Polymer–Ceramic Composite Membranes

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ABSTRACT

The mechanical stability of thin-film polymer–ceramic composite membranes has been evaluated in a variety of processing steps with temperatures ranging from 25 to 350°C. Although not measured in this work, references for similar materials indicate that the coefficients of thermal expansion for the two layers of the membrane are considerably different. Upon heating, this difference led to the development of thermally-induced stresses. These stress could be relieved if the membrane were heated in an unrestrained manner; however, they were sufficient to cause membrane failure if not relaxed. Heating to temperatures above the glass transition of the polymer resulted in defect formation in that layer due to flow into the ceramic support. These results indicate that, if properly handled, the membranes are sufficiently stable to be used over a wide range of temperatures. However, serious consideration must be given to these issues in the design of larger-scale devices.

INTRODUCTION

The development of membranes for high temperature gas separation has produced a class of hybrid composite materials with both organic and

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inorganic components (1–6). The configuration of these materials varies greatly, ranging from a dense metal layer supported on silicone rubber (1) to thin polymeric layers supported on highly porous ceramic supports (2–4, 6). To date, these materials have remained in the developmental stages. However, the outstanding separating properties of polyimide–ceramic composite membranes for the removal of hydrogen from hydrocarbon systems at 300°C and their utility in the improvement of the operation of butane dehydrogenation reactors have provided strong motivation to evaluate the ability to move the development of these materials forward (7).

The success of polymer–ceramic composite membranes for use in reactor applications and other high temperature gas separation applications relies, in part, on the stability of these materials in the separation environment. In this environment, stress can be generated in the various layers of the membranes by the sorption of condensable components and the thermal cycling of the membranes. Comparable behavior has been observed in similar composite devices utilized in the microelectronics industry (8–12).

The ability to minimize the stress generated in the membrane, and to relieve that which does occur, is paramount to the successful application of these materials.

BACKGROUND

A growing field of literature is available relating to the mechanical stability of polymer–inorganic laminate structures. This literature focuses on the stresses of thin-film composite materials that are generated in a variety of situations. Stresses generated as the result of the removal of casting solvents (13), the thermal "curing" of thin layers of poly(amic acid) to produce polyimides (8, 11), and exposure of the composite materials to highly sorbing components (12, 14, 15) have been investigated.

Composite structures are produced from the application of a thin film of polymer on an inorganic support. The strength of the support is markedly higher than that of the polymer layer, and the thermal expansion coefficients of the individual layers are not well matched. Finally, the support layers do not absorb solvents and they do not undergo swelling and shrinkage during casting or exposure to process stream components as the polymer layers generally do.

Tong and coworkers extended the use of a relatively simple bending-beam technique commonly employed in metal stress studies to measure the stresses developed in multilayer materials (10). In this technique, a film of polymer on an inorganic support is prepared, and one end of the rectangular composite is clamped into a bracket. The deflection of the free end (δ) generated by thermal cycling or sorption-induced swelling is measured by either an optical microscope or a laser beam (16). Provided the sample exhibits uniform stress during heat treatment and the adhesion between the two layers is strong, Eq. (1) can be used to calculate the end deflection of the composite material (17):

$$\sigma = \frac{E_s t_s^2}{3(1 - \nu_s)L^2 t_f}\,\delta \tag{1}$$

where σ is the film stress (psi), E_s is Young's modulus for the support (psi), t_s is the support thickness (cm), ν_s is Poisson's ratio for the support beam, L is the unclamped length of the support beam (cm), t_f is the thickness of the polymer layer (cm), and δ is the end deflection of the composite (cm).

For thermal treatment, the film stress measured is the sum of thermal and intrinsic stresses; i.e.,

$$\sigma = \sigma_{\text{thermal}} + \sigma_{\text{intrinsic}} \tag{2}$$

The thermal stress is caused by the thermal expansion coefficient mismatch between the polymer film and the inorganic support at two different temperatures. It can be calculated by (10):

$$\sigma_{\text{thermal}} = \frac{E_f}{(1 - \nu_f)}\,\Delta\alpha\Delta T \tag{3}$$

where E_f is Young's modulus for the polymer film (psi); ν_f is Poisson's ratio for the polymer film; $\Delta\alpha = \alpha_s - \alpha_f$, where α_s and α_f are the thermal expansion coefficients for the support beam and polymer film, respectively (°C^{-1}); and $\Delta T = T - T_0$, where T is the film temperature (°C) and T_0 is the reference temperature (°C), taken here as the casting temperature of the polymer layer.

Given an understanding of the intrinsic stress of the composite material, one can estimate the degree of deflection expected in polymer–inorganic composites from the measured thermal expansion coefficients and mechanical properties of the individual layers.

EXPERIMENTAL

The goal of the work reported is to determine the mechanical stability of polymer–ceramic composite membranes. Stability was measured by heating the membranes in a variety of environments from room temperature to approximately 350°C. Thermal stress was monitored indirectly by evaluating the failure rate of the membranes in these environments. Further, the interfacial adhesion strength was monitored.

Materials

Polymer–Ceramic Composite Membrane

Membranes were prepared using the thermally stable 6FDA-IPDA polyimide as the polymer layer and a highly porous ceramic as the support (6). Each membrane was evaluated at room temperature for the separation of helium from nitrogen. This evaluation provided a means of determining both the perfection and thickness of the polymer layer. Only membranes with helium/nitrogen selectivities of greater than 47 (the selectivity of a film of polyimide with a thickness of about 2.8 mil), an indication of a "defect-free" polymeric layer, were used for further evaluation, unless otherwise indicated.

Gases

Instrument-grade normal butane (minimum purity of 99.5 mol%), ultrahigh purity grade hydrogen (minimum purity of 99.99 mol%), ultrahigh purity grade helium (minimum purity of 99.99 mol%), and ultrahigh purity grade nitrogen (minimum purity of 99.99 mol%) were purchased from Matheson Gas products and used as received without further purification.

Equipment

Mixed gas permeation measurements were completed in the constant volume–variable pressure permeation system employed in our labs (18) with a permeate pressure of less than 20 torr and a total feed pressure of 15.8 ± 0.1 psia. The system was modified slightly to accommodate the measurement of mixed gas permeation of composite membranes to temperatures of 300°C. A commercially supplied test cell (Millipore Corporation, Bedford, Massachusetts) was sealed with either standard Kal-rez or Teflon gaskets which were temperature stable to approximately 320°C. The feed flow was maintained at or above 21 cm^3(STP)/min.

Procedure

Interfacial Adhesion Strength Testing

Evaluation of the physical integrity of the polymer–ceramic interface was completed using gas permeation experiments. The composite was tested in the normal fashion at 35°C and 75 psia upstream to determine gas flux characteristics. Then the composite was placed in the test cell

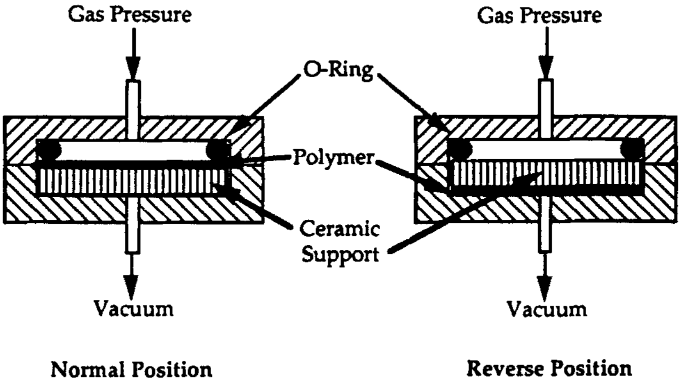

FIG. 1 Membrane orientation used to evaluate the potential for delamination in the composites. "Normal" position used for regular gas permeation testing. "Reverse" position used only to measure the strength of the polymer–ceramic interface.

with the ceramic support facing the upstream gas pressure and the polymer layer on the permeate side of the cell where the pressure was maintained at less than 10 mmHg absolute. A schematic of the normal and reverse positioning is presented in Fig. 1. If the adhesion strength of this interface is low, the polymer may delaminate and the gas transport rates through the composite may increase significantly. The reverse position mounting is especially likely to cause such delamination failures if an intrinsically poor adhesion exists.

RESULTS

Thermal Cycling of Membranes in a Restrained Environment

The ultimate application of the polyimide–ceramic composite membranes prepared here is in a reactor environment at several hundred degrees Celsius. For the membranes to prove successful in this application, it is necessary to heat the membranes from room temperature to the temperature of operation. For this discussion, the desired temperature of operation will be 300°C, just below the T_g of the polymer.

The simplest heating procedure is to seal the membranes into a housing at room temperature and then heat to the desired temperature. Several membranes were tested in this manner. In each case the membrane failed prior to reaching the test temperature. A list of representative membranes, their room temperature properties, and the approximate temperature at

TABLE 1
Effect of Membrane Properties on the Failure Temperature When Heated in a Constrained Environment

He flux (GPU)[a,c]	α-He/N$_2$[a]	Polymer thickness[b] (μm)	Failure temperature (°C)
9.0	60.1	7.0	80
9.6	62.4	6.5	87
10.9	64.8	5.8	100
186	34.7	0.34	130
140	32.7	0.45	192

[a] At 25°C.

[b] Based on helium flux, assuming a defect-free polymer layer.

[c] 1 GPU = 10^{-6} cm^3(STP)/(cm^2·s·cmHg).

which failure occurred is presented in Table 1. Failure was indicated by a rapid increase in permeate pressure.

Examination of the membranes following failure indicated that all were destructively fractured. Most appeared to fracture at the center, with radial fractures running from that point as shown in the schematic shown in Fig. 2.

It is believed that the strength of the composite membranes was not sufficient to withstand the stress generated upon heating. Estimates of the maximum strength of the membranes and the induced stresses generated were made to gain an understanding for the magnitude of these values.

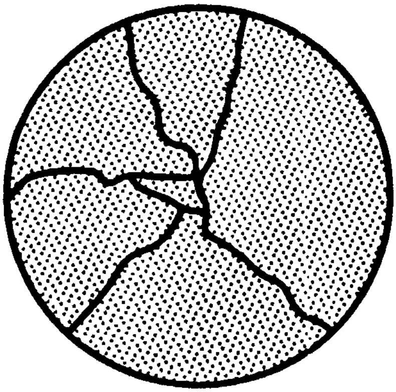

FIG. 2 Schematic of a membrane fractured as a result of constrained heating.

Modulus of Rupture of Ceramic Supports

In terms of strength, the important consideration for this application is the modulus of rupture. The modulus of rupture is defined as the fracture strength of a specimen for which the stress is applied via a bending mode (19). For disc-shaped samples, the modulus of rupture is typically measured under four-point loading as illustrated in Fig. 3. This situation is remarkably similar to the configuration used in gas permeation testing, where there is continuous contact around the perimeter of the disc. The sample bends in response to a stress generated by thermal cycling. Therefore, the induced thermal stresses can be estimated if the modulus of rupture for these materials is known.

The moduli of rupture for many ceramics have been reported in the literature. The modulus of rupture for aluminum oxide, the material of the ceramic supports studied here, has been reported to be between 30 and 50 × 10^3 psi (19) for a completely dense sample. The ceramic support materials used here are highly porous. Porosity is normally deleterious to the mechanical integrity of a ceramic piece with the magnitude of Young's

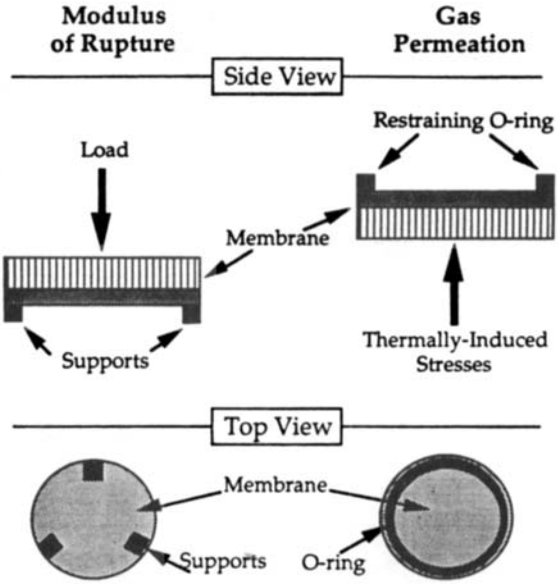

FIG. 3 Schematic of sample in modulus of rupture test apparatus and gas permeation test cell.

modulus, Y, decreasing with the volume fraction porosity, ϵ, according to (19):

$$Y = Y_0(1 - 1.9\epsilon + 0.9\epsilon^2) \tag{4}$$

where Y_0 is Young's modulus of the nonporous material (psi). In order to obtain an estimate of the modulus of rupture as a function of porosity, we will apply this equation directly, substituting modulus of rupture for Young's modulus.

The bulk porosity in the ceramic material used here is approximately 50%. Therefore, the modulus of rupture of the porous material is between 8,250 and 13,750 psi.

Thermal Stresses of Membranes

The stresses present in the membrane are the combined sum of intrinsic stress and thermal stresses at any temperature as shown in Eq. (2). While the intrinsic stresses have not been measured directly, this term will be neglected based on the work of Tong (10), which showed that the stresses in these types of films are predominantly thermal. Therefore, for this order-of-magnitude estimation of the stress in polymer–ceramic composite membranes, it is assumed that the intrinsic stress is zero.

From Eq. (3), the thermal stress is generated by the difference in the thermal expansion coefficients of the two layers and a temperature difference. The physical parameters shown in Table 2 will be used to evaluate this thermal stress.

The thermal stress generated as a function of heating was calculated with the membrane formation temperature, 25°C, as the reference temperature, T_0, and shown in Table 3 as a function of temperature.

The stresses generated as a result of heating the composite membranes are of the same order as the modulus of rupture of the ceramic support. While the estimates of both values rely upon a number of physical param-

TABLE 2

Physical Parameters of Polyimide–Ceramic Composite Membranes

Physical parameter	Polyimide	Porous Al_2O_3 support
Thermal expansion coefficient (/°C)	50×10^{-6} (1)	9×10^{-6} (13)
Young's modulus (psi)	340,000 (7)	53×10^6 (13)
Poisson ratio	0.47 (7)	0.16 (3)
Layer thickness (μm)	0.1–10	60

TABLE 3
Thermal Stress of Polyimide-Ceramic Composite Membrane as a Function of Temperature

Temperature (°C)	Thermal stress (psi)
25	0
100	1972
150	3290
200	4600
250	5920
300	7230

eters which were measured for various other polyimides and aluminum oxides, these results are believed to be accurate in terms of an order of magnitude analysis. Based on this analysis, it does not appear possible to heat these composite membranes in a gas-tight permeation apparatus from 25 to 300°C.

Thermal Cycling of Membranes in an Unrestrained Environment

The problem experienced by these membranes was that the stresses generated upon heating could not be dissipated. When the same membrane was heated in an unrestrained environment (for example, sitting on a glass plate), fracture of the support was never observed. Membranes heated in this manner are quite stable and could be cycled from room temperature to 300°C several times with no observable differences in the room temperature gas transport properties of the membranes.

Apparently the membrane is able to relieve some of the stresses generated upon heating. The work by Tong et al. (10) supports this theory. Tong found that as the composites were heated to near the glass transition temperature of the polymer for the first time, some stresses, believed to be the result of the casting processes, were relieved. Following this initial heating, the level of stress followed the same pattern upon heating and cooling for three heating cycles.

The results thus far are for tests with heating rates of 1–5°C/min. While the ceramic layer may be viewed as an equilibrium structure, the polymer layer is clearly not in equilibrium (20). Films of glassy polymers are said to be nonequilibrium materials and, given time, the individual chains of the polymer film will become organized in such a way that the structure reaches a true equilibrium state. However, the rate of this transformation is quite slow (20). Thus, realistic time limits will govern the rate of heating or cooling.

In the testing completed, the composite membrane was quickly heated from 25 to 300°C. Stresses of 7230 psi developed in the membrane, and, if restrained, failure occurred. However, if the same membrane was heated from 25 to 300°C, over an infinitely long period, the stresses that developed as a result of the heating could be dissipated by changes in the polymer layer. The liquidlike polymer very slowly deforms to accommodate these changes. Thus, the problems of thermal stresses can be minimized by heating at an infinitely slow rate. Clearly, this is not a practical solution; therefore, other approaches were investigated.

Thermal Cycling of Membranes in Unrestrained Environment

An alternative heating procedure was attempted in which the desired membrane was placed in the test cell, the sealing O-ring was placed loosely on the surface, and the top was placed on the cell. However, the three restraining screws that hold the top and bottom plates of the cell together and create a gas-tight environment were not tightened. Rather, nitrogen was purged over the surface of the membrane and a low vacuum was pulled on the permeate side. In this configuration the membrane was heated to 300°C at a heating rate of about 1°C/min. While heating in this configuration, no membranes were observed to fail due to crack formation in the ceramic layer.

Once the membranes reached 300°C they were allowed to equilibrate at this temperature for approximately 12 hours. Following equilibration, the cell was closed and testing was initiated. The membrane remained in this configuration for tests at 300°C, and the closed cell was then slowly cooled to 250, 200, 150, and ultimately 100°C. Following brief testing at 100°C, the membrane failed.

This process of unrestrained temperature changes is believed to be viable because it allows the entire membrane to deform and relax during the heating phase. Given sufficient time for both the membrane and its housing to equilibrate at the test temperature, the system appears to be very stable. While this heating technique is clearly more complicated than that first attempted, it appears to be very successful in minimizing the possibility for membrane failure as a result of heating.

Heat Treatment of Membranes to $T > T_g$

The glass transition temperature of a polymer marks a significant change in the mechanical properties of the material (21). The glass transition of the polyimide studied here is approximately 310°C. As a test of the mechanical integrity of the polymer film above this transition temperature, a number of membranes were heated to 350°C in an oven blanketed with helium. The membranes were held at this temperature for times ranging from 2 to 10 hours. Following the heating, the membranes were cooled and their properties measured at room temperature. The results for two representative samples are shown below.

The gas transport rates of both membranes increased significantly and the helium/nitrogen selectivities decreased following heat treatment. This indicates the presence of an increased concentration of surface defects following heat treatment. The formation of defects was not observed for membranes heated to less than 300°C.

At 350°C, the mechanical strength of a rubbery polyimide is significantly less than that of the same polymer in the glassy state. As a rubber, it is possible that the pressure difference across the membrane (feed pressure on the polymer side and vacuum on the permeate) could increase the rate at which the polymer layer begins to flow into the relatively large pores of the ceramic. Once the polymer layer begins to flow, defects form on the surface, causing a reduced selectivity of the membrane and a dramatic increase in the rate of gas transport consistent with the results presented in Table 4.

It appears unlikely that 6FDA-IPDA polyimide–ceramic composite membranes can be used at 350°C because the mechanical strength of the polymer layer is insufficient. However, testing at temperatures below the glass transition temperature of the polymer indicates that the polymer is sufficiently strong for extended use at temperatures up to 300°C.

Adhesion of the Polymer–Ceramic Layers

Gas flux measurements for both configurations were equivalent within the experimental error of the system. This indicated that the membrane

TABLE 4

Effect of Heating Polyimide–Ceramic Composite Membranes to 350°C[a]

	Prior to heating		After heating	
Time at 350°C (hours)	Nitrogen flux (GPU)	α-He/N_2	Nitrogen flux (GPU)	α-He/N_2
2.0	2.7	48.3	19.3	10.2
6.5	24.8	9.2	247.5	3.1

[a] 1 GPU = 10^{-6} cm^3 (STP)/(cm^2·s·cmHg).

was indeed intact when the pressure was applied to the ceramic side of the composite. If the polymer layer were to delaminate, one would expect that gas would bypass the polymer layer, travel around the edge of the polymer layer, and increase the measured flux rates. Further, the gas-separating ability of the membrane would be lessened. These phenomena were not observed. Conversely, the gas-separating factor of the composite membrane was independent of the configuration of the experiment.

Corresponding tests at high temperatures have not been completed. However, evaluation of the gas transport and mechanical strength tests completed at 300°C indicates that the adhesion strength of the polymer–ceramic interface was sufficiently strong. The adhesion strength of the polymer-ceramic bond has consistently proven to be stronger than the ceramic material itself as is exhibited by ceramic failure prior to delamination.

SUMMARY AND CONCLUSIONS

Polymer–ceramic composite membranes have been tested to measure their mechanical stability at temperatures to 300°C. The materials were shown to undergo destructive failure if heated in a constrained environment from room temperature to about 100°C. It was not possible to heat these membranes in closed housings to 300°C. However, if the membranes were not restricted in their movements, heating was completed without incident and the membranes were quite temperature stable at 300°C.

Failure is believed to be due to a bending of the membrane caused by a difference in the thermal expansion coefficients of the ceramic support and the polymer layer. This difference can generate stresses, when the material is heated to 300°C, which are on the same order as the rupture of modulus of the ceramic support. Yet, if heated in an unrestrained environment, the membrane appears capable of dissipating these stresses.

Membranes heated to 350°C in a helium environment, 40°C above the glass transition temperature of the polymer, were observed to have an increased concentration of polymer layer defects and a resulting loss in the selectivity of the membrane. Therefore, it appears unlikely that the 6FDA-IPDA polyimide membranes studied here can be used at temperature above the polymer's glass transition temperature. However, when tested at temperatures below T_g, the membranes appear quite stable.

The limitations in the handling of these materials provides insight into future materials for high-temperature gas separation. To minimize the problems noted here, future membranes should either have well-matched thermal expansions of all layers or have sufficient strength in each layer to withstand the generated stress.

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