

# Properties of Rubbery Polymers for the Recovery of Hydrogen Sulfide from Gasification Gases

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Received 15 June 2001; accepted 19 December 2001

**ABSTRACT:** Polydimethyl siloxane (PDMS) and two polyether–polyamide copolymers (trade name Pebax) were evaluated for their ability to transport and separate gasification gases. Specifically, the permeabilities of hydrogen, carbon monoxide, carbon dioxide, and hydrogen sulfide were evaluated at temperatures up to 200°C. The permeabilities of all gases were approximately ten times faster through the PDMS than the Pebax materials. The permeabilities through all materials at all temperatures evaluated were  $H_2S > CO_2 > H_2 > CO$ . As the temperature increased, the permeabilities of all gases increased through the Pebax. Conversely, for PDMS, hydrogen and carbon monoxide permeabilities increased with temperature while those of  $H_2S$  and  $CO_2$  decreased. The  $H_2S/H_2$  selectivities range from 1.2 (PDMS at 200°C) to 10.3 (Pebax 2533 at 35°C). The activation energies for permeation of these polymer/penetrant pairs are reported. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2436–2444, 2002

**Key words:** hydrogen sulfide; carbon monoxide; permeation

## INTRODUCTION

Gasification is the process of converting organic compounds into combustible gases by reacting with steam or oxygen. These gases are then cleaned and burned in a gas turbine to produce electric power. Heat from the turbine exhaust can be recovered to produce steam that, in turn, produces more electricity. Gasification has thermodynamic and environmental advantages over the conventional combustion of fuel to produce electricity. Gasification processes have lower emissions of  $CO_2$ ,  $NO_x$ , and  $SO_2$  than conventional combustion processes. They also have higher potential thermodynamic efficiencies than conven-

tional processes (43 vs 35% for coal-fired power plants).<sup>1</sup>

Gasification processes have been considered for fuels ranging from coal to black liquor from the manufacture of paper to biomass.<sup>1–4</sup> For those systems with significant sulfur content, hydrogen sulfide will be produced as a product of gasification. This hydrogen sulfide gas must be removed before the gas may be sent to the turbine. Failure to do so could result in the production of  $H_2SO_4$  in the gas turbine, which in the presence of the water produced therein, could lead to corrosion of the turbine blades.

The typical method for sulfur removal from gasification systems has been through the use of wet scrubbing of the gas at temperatures of less than 100°C.<sup>1</sup> Since the gasification reactions occur at much higher temperatures, cold gas cleaning requires equipment to cool the gas and forfeits some of the thermal energy of the stream. Therefore, alternatives to this technique are under investigation. The use of high temperature adsorp-

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Contract grant sponsor: Georgia Tech—Institute of Paper Science & Technology.

*Journal of Applied Polymer Science*, Vol. 85, 2436–2444 (2002)  
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tion to selectively remove  $H_2S$  from the stream has been reported.<sup>1</sup> While the results hold some promise, questions relating to bed regeneration and short lifetime remain unanswered. Polymeric membranes for the recovery of hydrogen sulfide from these high-pressure feed streams are a potential alternative to the strategies that have been considered to date. In the optimum configuration of this design, the hydrogen sulfide would permeate through the membrane into a low-pressure reservoir. The residual gases would be available at high pressure and moderate temperature to be feed to a gas turbine.

Literature reports<sup>5</sup> of the transport of the hydrogen sulfide through poly(dimethyl siloxane) indicate that the permeability of this component should be approximately twice that of carbon dioxide and the  $H_2S/H_2$  selectivity should be on the order of 8. The transport properties of carbon monoxide, a major stream component for the present application, have not been thoroughly investigated. This study evaluates the relative rates of transport of hydrogen, carbon dioxide, carbon monoxide, and hydrogen sulfide through polymers at temperatures ranging from 35 to 200°C. One of the questions addressed in this evaluation is the influence of temperature on the performance of the polymeric membrane. Maintaining high temperatures will result in high thermal efficiency. High temperature may also increase the permeability of gases through the membrane, resulting in a reduced membrane size. Unfortunately, high temperature will also reduce the sorption capacity of the membrane and alter the separations that can be achieved.

## BACKGROUND

A widely accepted physical model of transport of gases through nonporous polymeric films holds that the gases first dissolve into the polymer matrix, then diffuse through the matrix, and finally desorb from the matrix when the penetrant reaches the solid–gas interface. The extent to which the gas dissolves into the matrix is controlled by the thermodynamic interactions of the polymer and the penetrant, and has been characterized by the *solubility coefficient* of the polymer–penetrant pair,  $S_{A-B}$ . The rate of the diffusive process is described by Fick's law:

$$\text{Flux}_A = -D_{A-B} \frac{dC_A}{dx} \quad (1)$$

**Table I** Properties of Gases Evaluated in This Study<sup>16</sup>

Penetrant Gas	Critical Temperature, $T_c$ (K)	Lennard–Jones Diameter (X)
Hydrogen sulfide	373.2	3.62
Carbon dioxide	304.1	3.94
Carbon monoxide	132.9	3.69
Hydrogen	33.2	2.83

where  $dC_A/dx$  represents the concentration gradient across the polymer film and  $D_{A-B}$  is the *diffusion coefficient* of penetrant A in polymer B. The overall rate of transport through the polymer film can be related to the partial pressure driving force of the penetrant gas as

$$\text{Flux}_A = -\bar{P}_{A-B} \frac{dp_A}{dx} \quad (2)$$

where  $\bar{P}_{A-B} = S_{A-B} \times D_{A-B}$ .  $S_{A-B}$  is the solubility coefficient of penetrant A in polymer B;  $D_{A-B}$  is the diffusivity coefficient of penetrant A in polymer B; and  $\bar{P}_{A-B}$  is the permeability coefficient of penetrant A through polymer B. Equation (2) can be integrated if the partial pressure of A is known on both sides of a membrane of thickness  $l$ .

The factors that influence the numeric values of  $S_{A-B}$  and  $D_{A-B}$  are complex and not completely understood. Nevertheless, trends in the data have been observed. In general, for a given polymer, as the size of the penetrant molecule increases, the diffusion coefficient decreases.<sup>6</sup> Conversely, as the size of the penetrant increases, its condensibility also increases and the solubility coefficient increases.<sup>6</sup> These observations suggest that if the role of the membrane is to selectively remove the smallest molecule in a gas mixture, a membrane where the permselectivity is dominated by the diffusion component should be employed. Conversely, if the role is to remove a large molecule from a gas mixture, membranes with very high sorption capacity should be employed. This typically results in glassy polymers (with rather low solubility coefficients) being employed for the former case and rubbery polymers (with high solubility coefficients) for the later.

The physical properties of the gases of interest are presented in Table I. Clearly, separation based on size would not be effective. On the other hand, since the hydrogen sulfide has the highest

**Table II** Physical Properties of the Pebax Polymers Evaluated<sup>a</sup>

	Pebax <sup>7</sup>		Pebax <sup>15</sup>	
	2533	3533	2533	3533
Weight % PA	22	27	25	33
$T_{g,PTMO}$ (°C)	-76	-72	-79	-79
$T_m$ Crystalline PTMO (°C)	12	7	12	10
$T_g$ PA (°C)	65-75	65-75	nd	nd
$T_m$ Crystalline PA (°C)	137	142	134	144

<sup>a</sup> nd = not detected; PA = polyamide = nylon 12; PTMO = polytetramethylene oxide.

critical temperature, it should also have the highest solubility coefficient in a given polymer. To exploit this property, rubbery polymers were evaluated.

This program evaluated the transport ability of both polydimethyl siloxane (PDMS) and two ether-amide block copolymers with varying ratios of ether and amide. The polyether-amide copolymers investigated were Pebax grades 2533 and 3533 and are represented in Table II. These grades have high ether contents and should therefore produce high permeation rates. Prior analysis of these materials for the separation of other gases and vapors is reported.<sup>7</sup> The presence of the rigid amide block in the Pebax polymers is anticipated to moderate the influence of temperature on the transport properties. It is expected that the Pebax materials will be less permeable at low temperature. Nevertheless, it is desired that the rigid sections of the polymer will mitigate the loss in separation selectivity that is expected as the temperature is increased.

## EXPERIMENTAL

### Materials

#### Polymers

The polymers used in this study were PDMS and polyether amide block copolymers (Pebax).

The PDMS films were cast from commercially available components (General Electric: RTV615) with no fillers or additives. As solvent, toluene was used. The sample was dried at room temperature for two weeks and at 100°C for 48 h under vacuum (vacuum pump equipped with an aluminum oxide back-diffusion trap). The density of PDMS is reported<sup>8</sup> to be 1.02 g/cm<sup>3</sup>. The thickness was evaluated with a thickness gauge. Films with

thicknesses of 500 μm were evaluated. The glass transition temperature,  $T_g$ , was measured using differential mechanical thermal analysis to be -123°C. This is in good agreement with the published value.<sup>8</sup>

Pebax, in pellet form, was kindly supplied by Elf Atochem (Philadelphia, Pennsylvania). Pebax 2533 and 3533 were evaluated. The Pebax series studied here consisted of varying nylon 12, the hard rigid segments, and polytetramethylene oxide (PTMO), the soft flexible segments. The relative presence of each segment and the physical properties of the polymers have been previously determined and the results reported in Table II.

Pebax films were melt extruded using a Haake Buckler extruder fitted with a flat film die. The extrusion temperature ranged from 140 to 180°C depending on the material. The motor speed was varied between 5 and 30 rpm. Sample thickness was controlled by the motor speed and the speed of the take-up roller. The film thicknesses employed ranged from 340 to 390 μm.

All films were optically clear and remained so throughout the preparation and testing process. Samples were dried under vacuum for 14 days at 40°C. The vacuum pump was equipped with an aluminum oxide back-diffusion trap. Following drying, all samples were stored in a desiccator until further use. The density of the Pebax grades tested was reported<sup>9</sup> to be 1.01 g/cm<sup>3</sup>.

### Gases

Hydrogen (99.995%) and carbon dioxide (99.8%) were obtained from Air Products and used as received. Carbon monoxide (99.99%) was obtained from Matheson Gases and Equipment and used as received. Two different hydrogen sulfide/hydrogen gas mixtures were used over the course of experimentation. One contained 2.85 volume per-

cent hydrogen sulfide in hydrogen. The other contained 3.31 volume percent hydrogen sulfide in hydrogen. Both were also obtained from Matheson Gases and Equipment and used as received.

### Gas Transport Analysis

A constant volume/variable pressure apparatus was used to measure pure gas permeability coefficients for  $H_2$ ,  $CO_2$ , and  $CO$ . All polymer/penetrant pairs were evaluated at  $35.0 \pm 0.1^\circ C$ . PDMS was evaluated at temperatures up to  $200.0 \pm 0.1^\circ C$ . Pebax 2533 was evaluated at temperatures up to  $100^\circ C$ . For these evaluations, the permeation cell and a gas preheater were heated to desired test temperature. The system was maintained at operating temperature for a minimum of 2 h and then permeation measurements were made. In all cases, the feed pressure was  $10 \pm 0.05$  atm. On the permeate side of the film, the gas pressure was less than 10 torr and considered negligible. These techniques have been described in greater detail elsewhere.<sup>10</sup>

The permeability of hydrogen sulfide was evaluated using a  $H_2S$ /hydrogen gas mixture. In these mixed gas runs, the stage cut was kept low to ensure that the  $H_2S$  concentration in the retentate was >98% of the  $H_2S$  concentration in the feed. This was verified through analysis of the feed and retentate compositions. The pressure in the permeate system was allowed to increase to greater than 10 torr during which time the rate of gas transmission through the film was measured. Subsequently, the permeate receiver volume was isolated from the film and the vacuum pump. The entrapped gas (pressure of approximately 10 torr) was diluted with hydrogen to increase the total pressure to about 1 atmosphere. The hydrogen sulfide content of the diluted permeate gas was analyzed using a Perkin Elmer GC equipped with a Flame Photometric Detector. The concentration of  $H_2S$  in the original, undiluted permeate gas was calculated through knowledge of the dilution ratio and the concentration of  $H_2S$  in the diluted gas.

## RESULTS AND DISCUSSION

The permeability properties of the selected polymers were evaluated at  $35^\circ C$  and 10 atm feed pressure. These conditions were selected because they (1) provide a reasonable estimate of the conditions currently employed in cold gas cleanup

(i.e., wet scrubbers) and (2) they are the standard conditions used for the evaluation of polymeric materials. Thus, comparison between the permeabilities measured here and those reported in the literature should be possible. The measured permeability coefficients for each gas through PDMS and Pebax 2533 and 3533 are presented in Table III. As expected, the relative rate of penetrant transport through all three materials is  $H_2S > CO_2 > H_2 > CO$ . This order of permeation provides for the possible use of these membranes for gasification cleanup.

At  $35^\circ C$ , PDMS has gas permeabilities that are approximately ten times those of the Pebax materials. However, the ability of the PDMS to discriminate between the gases is somewhat lower than that of the Pebax materials. The highly flexible Si–O linkages in the PDMS backbone are the basis of its high flexibility and minimal discrimination ability. On the other hand, the rigid semicrystalline polyamide segments in the Pebax material is the basis of its discriminatory ability. For the PDMS, the relative rate of hydrogen sulfide to hydrogen transport is approximately 6.5 while Pebax 2533 has an  $H_2S/H_2$  selectivity of over 10. The carbon dioxide/hydrogen selectivity of Pebax 2533 (5.8) is also significantly higher than that measured for PDMS (4.2). Finally, the carbon dioxide/carbon monoxide selectivity for Pebax is nearly twice that of PDMS (15.7 vs 8.4).

As the content of glassy and crystalline amide segments in the Pebax polymer increases (3533 vs 2533), the permeability coefficients decrease slightly. Nevertheless, there is little difference between the measured selectivities for the two Pebax grades evaluated.

It is informative to compare the hydrogen permeabilities measured for the three polymers using (1) pure hydrogen and (2) a hydrogen–hydrogen sulfide mixture. For the latter, the permeabilities of hydrogen and hydrogen sulfide were calculated based on their relative compositions in each stream. For all polymers, hydrogen permeability in the mixed gas experiment is higher than that from the single gas experiment. This suggests that the hydrogen sulfide has plasticized the polymer matrix and facilitated the transport of hydrogen.

Also presented in Table III are the permeabilities of some of the polymer–penetrant pairs obtained from the literature. In the case of PDMS, the values measured here are in fair agreement with those reported in the literature. The values are consistently lower than those measured by

Table III Permeabilities and Selectivities of Pebax and PDMS at 35°C<sup>a</sup>

Polymer	$P_{\text{CO}_2}$		$P_{\text{CO}}$		$P_{\text{H}_2}$		$P_{\text{H}_2\text{S}}$ Mixed 3%	$\alpha_{\text{CO}_2\text{H}_2}$ Ideal		$\alpha_{\text{CO}_2\text{CO}}$ Ideal		$\alpha_{\text{H}_2\text{CO}}$ Ideal		$\alpha_{\text{H}_2\text{S}/\text{H}_2}$ Real		$\alpha_{\text{H}_2\text{S}/\text{CO}_2}$ Ideal	
	Pure Gas	Pure Gas	Pure Gas	Pure Gas	Pure Gas	Mixed 97%		Mixed 3%	Ideal	Ideal	Ideal	Ideal	Ideal	Real	Ideal		
PDMS	3700	440	890	940	6100	—	—	4.2	8.4	2.0	6.5	1.7	—	—	—	—	—
PDMS <sup>b</sup>	4500	—	940	—	7500	—	—	4.8	—	—	8.0	1.7	—	—	—	—	—
PDMS <sup>c</sup>	2700	300	550	—	8400	—	—	—	—	—	—	3.1	—	—	—	—	—
Pebax 2533	350	22	60	70	720	—	—	5.8	15.7	2.7	10.3	2.1	—	—	—	—	—
Pebax 3533	230	14	46	54	510	—	—	4.9	16.3	3.3	9.4	2.3	—	—	—	—	—
Pebax 3533 <sup>d</sup>	243	—	—	—	888	—	—	—	—	—	—	3.7	—	—	—	—	—

<sup>a</sup> (Permeabilities reported in Barrer, 1 Barrer =  $10^{-10}$  cm<sup>3</sup> (STP) cm/cm<sup>2</sup> s cm Hg). Pure gases measured at 10 atm feed pressure. H<sub>2</sub>/H<sub>2</sub>S mixture evaluated at 10 atm total feed pressure (9.7 atm H<sub>2</sub>; 0.3 atm H<sub>2</sub>S).

<sup>b</sup> Reference 5; pure gases CO<sub>2</sub>; Pressure = 8 atm; H<sub>2</sub>S; Pressure = 0.3 atm; H<sub>2</sub>; Pressure = 10 atm.

<sup>c</sup> Reference 11; no information regarding test conditions.

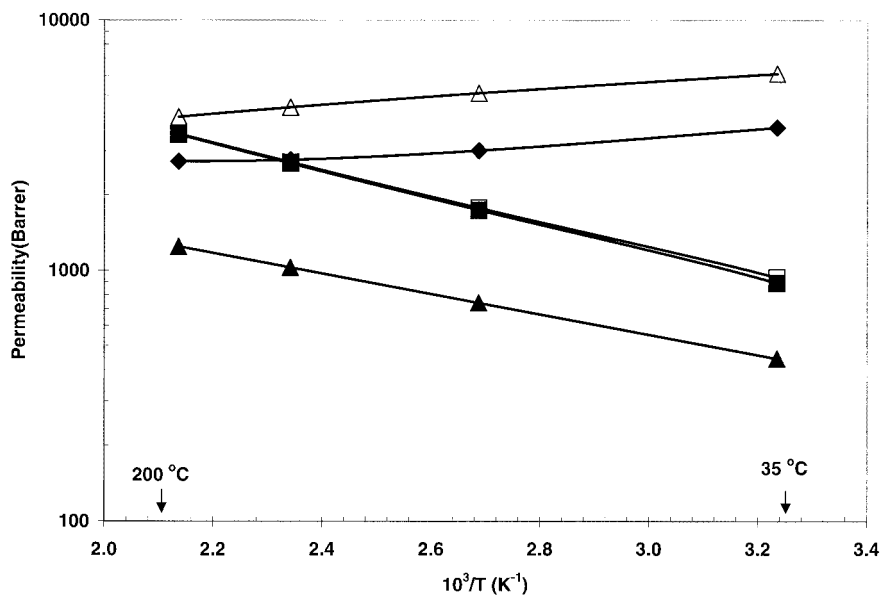
<sup>d</sup> Reference 12; mixed gas of (CH<sub>4</sub>/CO<sub>2</sub>/H<sub>2</sub>S:70.8/27.9/1.3 mol %) pressure = 10 atm, T = 35°C.

Stern and Bhide,<sup>5</sup> but higher than those of Fenstermaker.<sup>11</sup> The hydrogen sulfide permeability reported by Stern was measured using pure H<sub>2</sub>S.<sup>5</sup> The value presented in Table III is an estimate of the H<sub>2</sub>S permeability at 0.3 atm feed pressure. The H<sub>2</sub>S/H<sub>2</sub> selectivity reported by Stern has also been calculated from the pure gas data. It is well documented that mixed gas selectivities are consistently lower than those calculated from pure gas data for systems with a highly sorbing component (such as H<sub>2</sub>S). Thus, the higher selectivity reported by Stern is consistent with the differences in the evaluation technique. Comparison with the Fenstermaker data is a bit more difficult because of a lack of experimental details provided in the reference. While the permeabilities of the gases measured here are of the same order as those reported by Fenstermaker, those permeabilities are consistently lower and permselectivities consistently higher. This difference could result from a difference in the measurement temperature or feed composition or pressure or material differences such as molecular weight or extent of crosslinking.

While there is less data available for the Pebax polymers, the comparisons possible would indicate reasonable agreement with the literature reports. Chatterjee and co-workers have reported on the ability of Pebax 3533 to separate acid gases.<sup>12</sup> They reported CO<sub>2</sub> permeabilities essentially equivalent to those evaluated here. The reported hydrogen sulfide permeability coefficient is nearly twice that reported here, but the hydrogen sulfide partial pressure was 4.5 times higher. Chatterjee provided no measure of the carbon monoxide or hydrogen permeabilities.

Increasing the system temperature over a small range has been shown to result in a reduction in the permeability of hydrogen sulfide through Pebax<sup>13</sup> and PDMS<sup>5</sup> polymers. The data reported are available over only a small temperature range and do not describe the influence of temperature on hydrogen or carbon monoxide through these polymers. Therefore, the influence of temperature on these properties was evaluated. Because the 35°C data for Pebax 2533 and 3533 were similar, only the 2533 was evaluated as a function of temperature. Results from these evaluations are presented as Arrhenius plots in Figures 1 and 2.

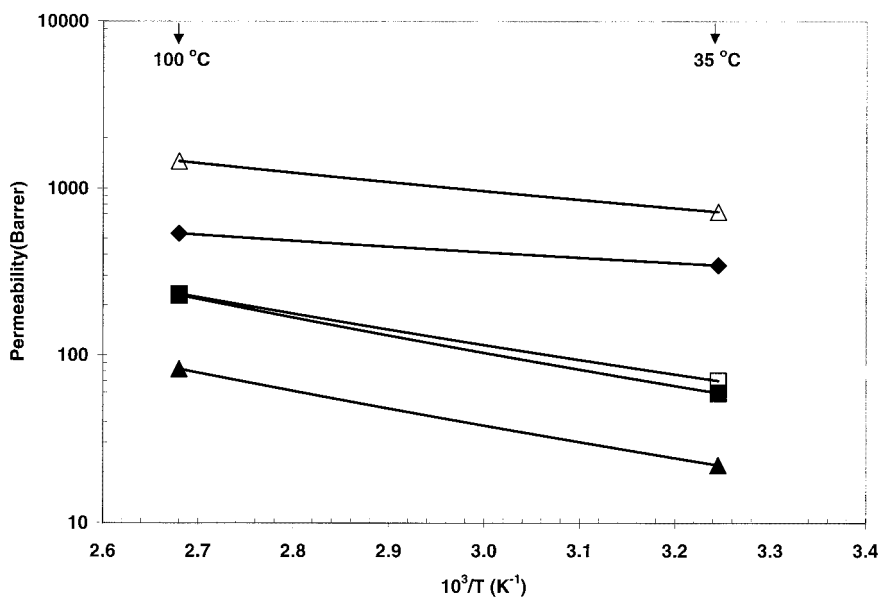
Figure 1 presents the influence of temperature on the transport of gasification gases through PDMS. All four gases follow the expected Arrhenius relationship. The highly sorbing hydrogen



**Figure 1** Influence of temperature on the permeability of gases through PDMS, plotted as an Arrhenius relationship.  $\Delta$  H<sub>2</sub>S (mixed),  $\blacklozenge$  CO<sub>2</sub>,  $\square$  H<sub>2</sub> (mixed),  $\blacksquare$  H<sub>2</sub> (pure), and  $\blacktriangle$  CO. Pure gas experiments completed with 10 atm feed pressure. Mixture experiments completed with 0.3 atm H<sub>2</sub>S pressure and 9.7 atm hydrogen pressure.

sulfide and carbon dioxide actually have lower permeabilities as the temperature of the system is increased. Hydrogen and carbon monoxide show increasing permeabilities with system tempera-

ture. As a result, the hydrogen sulfide/hydrogen selectivity of PDMS decreases with temperature, from 6.5 at 35°C to 1.2 at 200°C (see Fig. 3). From the slopes of the lines in Figure 1, the activation



**Figure 2** Influence of temperature on the permeability of gases through Pebax 2533, plotted as an Arrhenius relationship.  $\Delta$  H<sub>2</sub>S,  $\blacklozenge$  CO<sub>2</sub>,  $\square$  H<sub>2</sub> (mixed),  $\blacksquare$  H<sub>2</sub> (pure), and  $\blacktriangle$  CO. Pure gas experiments completed with 10 atm feed pressure. Mixture experiments completed with 0.3 atm H<sub>2</sub>S pressure and 9.7 atm hydrogen pressure.

**Table IV** Measured Activation Energies for CO<sub>2</sub>, CO, H<sub>2</sub>, and H<sub>2</sub>S Through PDMS and Pebax 2533<sup>a</sup>

Polymer	Activation Energy (kJ/mol)				
	CO <sub>2</sub> Pure Gas	CO Pure Gas	H <sub>2</sub> Pure Gas	H <sub>2</sub> Mixed 97%	H <sub>2</sub> S Mixed 3%
Pebax 2533	6.5	19.4	19.8	17.7	10.3
PDMS	-2.4	7.8	10.3	10.0	-3.0
PDMS <sup>5</sup> filled					-6.8

<sup>a</sup> Note that the data available from refs 5 is at only 10, 35, and 55°C. The activation energy was calculated at 0.3 atm feed pressure. Polymer contained 4.0 vol % silica filler.

energies for permeation have been calculated and are reported in Table IV.

Figure 2 presents the influence of temperature on the transport of gasification gases through Pebax 2533. Again, Arrhenius relationships are observed, although, with the limited data available, it is not possible to conclusively rule out other types of behavior. Nevertheless, activation energies have been calculated and reported in Table IV.

The activation energy for permeation is comprised of two terms, the activation energy for diffusion and the heat of sorption:

$$\Delta E_{P,A-B} = \Delta E_{D,A-B} + \Delta H_{S,A-B} \quad (3)$$

where  $\Delta E_{P,A-B}$  is the activation energy for permeation of penetrant A through polymer B;  $\Delta E_{D,A-B}$  is the activation energy for diffusion of penetrant A through polymer B; and  $\Delta H_{S,A-B}$  is the heat of sorption of penetrant A in polymer B. The heat of sorption value is generally exothermic (negative).

For many glassy polymers, the heats of sorption of a variety of gases are approximately constant and the activation energy for permeation is proportional to the activation energy for diffusion. Meares has shown that the activation energy for diffusion and permeation, for systems where sorption effects are minimal, is proportional to the second power of collision diameter of the gas molecule.<sup>14</sup> For polymers in which the heat of sorption is approximately constant for the gases of interest, Meares' correlation would suggest that the activation energy for permeation should be of the following order:

$$\text{CO}_2 > \text{CO} > \text{H}_2\text{S} > \text{H}_2.$$

The experimentally measured activation energies for permeation were of the following order for PDMS:

$$\text{H}_2 > \text{CO} > \text{CO}_2 \approx \text{H}_2\text{S}.$$

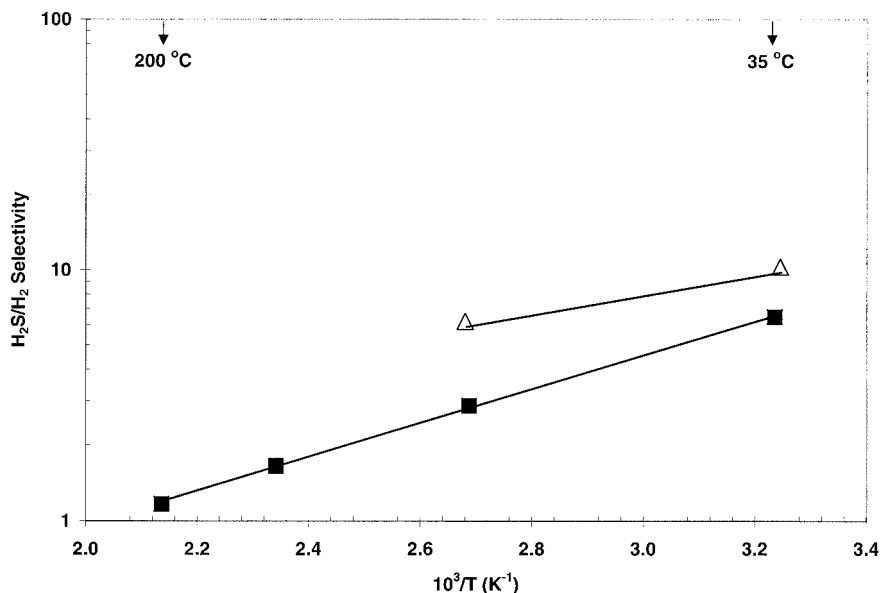
The order for Pebax 2533 was

$$\text{H}_2 \approx \text{CO} > \text{H}_2\text{S} > \text{CO}_2.$$

Clearly, based on the obvious differences in the rank order of the activation energies measured and those predicted by Meares, sorption is very important for the rubbery polymers evaluated here. The heat of sorption term is markedly different for the different gases. The negative activation energies for permeation of CO<sub>2</sub> and H<sub>2</sub>S through PDMS can only be realized if the heat of sorption for these gases is larger than the activation energy for diffusion. For all other polymer-penetrant pairs, the heat of sorption is smaller than the activation energy for diffusion. Investigation of the solubility parameters will give further insight on the effects of solubility on transport.

The measured activation energy for permeation for hydrogen is consistently lower when the data for the mixed hydrogen-hydrogen sulfide runs are compared to the values obtained from pure hydrogen. This confirms that the hydrogen sulfide is acting to plasticize the polymer matrix and reduces the resistance for hydrogen transport.

Incorporation of the rigid amide block into the Pebax polymer resulted in a reduction in the influence of sorption on the polymer and increased activation energies for permeation. The fact that all activation energies are positive indicates that all permeation rates will increase with increasing temperature. The impact of these differences on the polymer selectivity are presented in Figure 3. While both polymers exhibit a reduction in H<sub>2</sub>S/H<sub>2</sub> selectivity with increasing temperature, the rate of selectivity loss is much greater for the PDMS material than the Pebax polymer.



**Figure 3** Mixed gas H<sub>2</sub>S/H<sub>2</sub> selectivity vs temperature for △ Pebax 2533 and ■ PDMS. Experiments completed with 0.3 atm H<sub>2</sub>S pressure and 9.7 atm hydrogen pressure.

After the Pebax polymer was heated to 150°C, the material flowed into the porous metal support and lead to film failure. At this temperature, both copolymer components were above  $T_g$  and any crystals present in the polyamide phase should have melted. Under these conditions, the polymer was not sufficiently stable to withstand the pressure applied. If these or similar block copolymers are to be used for high temperature evaluations, the rigid phase must have a higher  $T_m$  or must be crosslinked to avoid these mechanical failures.

## CONCLUSIONS

The transport of H<sub>2</sub>S, CO<sub>2</sub>, H<sub>2</sub>, and CO through PDMS and Pebax polymers is strongly influenced by sorption into the polymer matrix. In PDMS, hydrogen sulfide and carbon dioxide have sufficiently exothermic heats of sorption that the overall activation energy for permeation for these gases is negative. Increasing the rigidity of the polymer (by evaluating Pebax instead of PDMS) resulted in a reduced sorption and increases in the activation energy for permeation. Investigation of the solubility parameters will give further insight on the impact of polymer penetrant interactions on transport properties. Thus, while the Pebax polymers have lower permeabilities, they are able to maintain some separation power at

elevated temperature. Nevertheless, the very low H<sub>2</sub>S/H<sub>2</sub> selectivity of these polymers at elevated temperatures will not alone be adequate for the separation of the gasification gases for the process outlined in the introduction. Nonetheless, this work provides insight into the ability to separate gasification gases using polymeric membranes. One may tailor copolymer combinations to enhance the polymer properties for the desired separation at low temperatures. It appears unlikely that passive sorption-selective polymeric membranes have the potential to be effective for H<sub>2</sub>S/H<sub>2</sub> or CO<sub>2</sub>/H<sub>2</sub> separations at elevated temperatures.

This work has been partially supported by a Georgia Tech—Institute of Paper Science & Technology Grant.

## REFERENCES

1. Cal, M. P.; Stickler, B. W.; Lizzio, A. A. *Carbon* 2000, 38, 1757–1765.
2. Lin, K. S.; Wang, H. P.; Lin, C.-J.; Juch, C.-I. *Fuel Process Tech* 1998, 55, 185–192.
3. Wang, W.; Padban, N.; Ye, A.; Olofsson, G.; Andersson, A.; Bjerle, I. *Ind Eng Chem Res* 2000, 39, 4075–4081.
4. Cayton, D. C.; Frederick, W. J., Jr. *Energy Fuels* 1996, 10, 284–292.



5. Stern, S. A.; Bhide, B. D. *J Appl Polym Sci* 1989, 38, 2131–2147
6. Baker, R. W. *Membrane Technology and Applications*; McGraw-Hill: New York, 2000.
7. Rezac, M. E.; John, T.; Pfromm, P. H. *J Appl Polym Sci* 1997, 65, 1983–1993.
8. Brandrup, J.; Immergut, E. H. *Polymer Handbook*; John Wiley & Sons: New York, 1989.
9. ELF Atochem North America, Inc., *PEBAX® Technical Brochure*.
10. Rezac, M. E.; Sorensen, E. T.; Beckham, H. W. *J Membr Sci* 1997, 136, 249–259.
11. Fenstermaker, R. W. U.S. Patent 4,370,150, 1983.
12. Chatterjee, G.; Houde, A. A.; Stern, S. A. *J Membr Sci* 1997, 135, 99–106.
13. Lokhandwala, K. A.; Baker, R. W.; Toy, L. G.; Amo, K. D. U.S. Patent 5,401,300, 1995.
14. Meares, P. *J Am Chem Soc* 1954, 76, 3425.
15. Djebbar, M. K.; Nguyen, Q. T.; Clement, R.; Germain, Y. *J Membr Sci* 1998, 146, 125–133.
16. Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill, New York, 1987.