Separability of SO_2 from SO_2/N_2 Mixture through Sulfoxide-Modified Poly(Vinyl Alcohol) and Cellulose Membranes

KIYOKAZU IMAI, TOMOO SHIOMI,* YASUYUKI TEZUKA, HIROKO ITAMOCHI, and MASAMITSU MIYA

Department of Materials Science and Technology, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Niigata 940-21, Japan

SYNOPSIS

Separability of SO_2 from mixtures of SO_2 and N_2 gases was studied for membranes of poly(vinyl alcohol) (PVA) and cellulose modified with methyl, ethyl, t-butyl, and phenyl vinyl sulfoxides. Of these sulfoxide-modified polymers, the phenyl vinyl sulfoxide-modified PVA membranes were found to give the best separation of SO_2. In the phenyl vinyl sulfoxide-modified PVA membranes, the permeability coefficient of SO_2 increased with sulfoxide content while separability of SO_2 was maximum at a sulfoxide content of 23.5 mol %; the separation factor of SO_2 was about 170 at this sulfoxide content. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The membrane techniques for separation of sulfur dioxide (SO_2), which is a major air pollutant, have been studied because of their facile and economic ways.[1-3] We recently reported that sulfoxide-modified poly(vinyl alcohol) (PVA)[4,5] and cellulose[6] were useful polymeric materials for a permselective membrane of SO_2. The idea for the molecular design of these materials provided by us is based on the introduction of sulfoxide compounds, in which solubility of SO_2 is very high,[7] to a gas barrier polymer with a covalent bond. We synthesized a series of sulfoxide-modified PVA[5,8,9] and cellulose[6] with various degrees of substitution and found that they had high permeability of SO_2.[4-6]

As is well known, permeability of gas is governed by solubility and diffusivity of the gas molecule in the membrane. In the present membranes, solubility is a major factor to high permeability. On the other hand, the high solubility may bring plasticizing or swelling of the membrane materials, which leads to poor separability of gas mixtures. Therefore, it is important in practical use to determine optimum with respect to varieties of sulfoxide groups and their content.

In this report, we will present separability of SO_2 from the SO_2/N_2 gas mixture for a series of vinyl sulfoxide-modified PVA and cellulose derivatives with various degrees of substitution.

EXPERIMENTAL

Materials

A series of sulfoxide-modified poly(vinyl alcohol) and cellulose was synthesized through the Michael-type addition reaction of the starting polymer with vinyl sulfoxides by the method described previously.[5,6,9] Poly(vinyl alcohol) (PVA) and cellulose were kindly supplied by Kuraray Co. (PVA-117H, $DP = 1700$) and Asahi Chemical Co. (Avicel-PH101, $DP = 250$), respectively. Methyl vinyl sulfoxide (MVSO), ethyl vinyl sulfoxide (EVSO), and t-butyl vinyl sulfoxide (BVSO) were prepared by $NaIO_4$ oxidation of their respective alkyl vinyl sulfides according to the method described.[8] Phenyl vinyl sulfoxide (PVSO) commercially available was purified by fractional distillation.

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* To whom correspondence should be addressed.

Characterization

The degree of substitution or sulfoxide content was determined by ^{1}H-NMR measurements (apparatus, JEOL PMX-60 or JEOL JNM GX270) for PVA derivatives and by elemental analyses for cellulose derivatives.

DSC thermograms were recorded at a heating rate of 10°C/min using a SEIKO DSC20 with SSC/580 thermal controller and data system.

Preparation of Membrane

Membranes of vinyl sulfoxide modified PVA and cellulose were prepared by casting from the following solutions on a Teflon-coated plate: 8 wt % and 3.5 wt % aqueous solutions were used for the alkyl vinyl sulfoxide-modified PVA and cellulose, respectively, and 8 wt % and 3.5 wt % dimethyl sulfoxide (DMSO) solutions for the PVSO modified-PVA and cellulose, respectively. The casting solvent was evacuated by keeping the solution in a desiccator containing anhydrous calcium chloride for 1 week for the water solutions and in an oven thermostatted for 2 weeks at 40°C for the DMSO solutions. The resulting membrane was dried in vacuo for two days at 40°C.
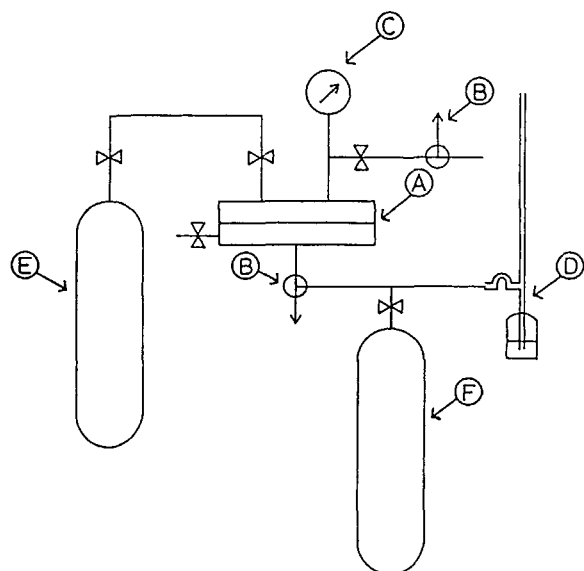

Figure 1   Apparatus for gas permeability measurement using mixed gases. (A) permeation cell; (B) sampling line for gas chromatograph measurement; (C) pressure gauge; (D) soap film flow meter; (E) sample gas cylinder; (F) helium gas cylinder.
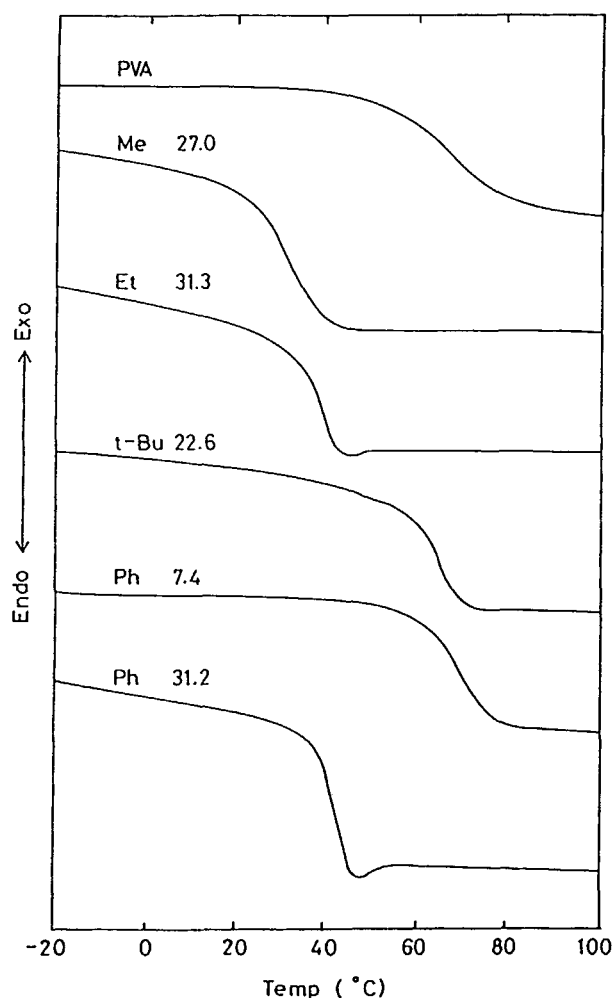

Figure 2   DSC thermograms for PVA and sulfoxide-modified PVAs. The numerical values indicate the degree of substitution.

Gas Permeation Measurements

The apparatus used for permeability measurements of the mixed gas of SO_2 and N_2 is shown in Figure 1. The total volume of the gas mixture permeated through the membrane was detected with a soap film flow meter, and its composition was analyzed with a gas chromatograph using Porapak P (Waters Associates, Inc.).

The membrane was supported in the permeation cell. Both feed and permeate sides of the apparatus were degassed and purged with helium gas. The SO_2/ N_2 gas mixture was supplied to the feed side from the gas cylinder containing the mixed gas, and then the pressure and composition of the supplied mixture gas were measured; those were 2.5 atm and SO_2/N_2 = $\frac{2}{3}$ (by volume), respectively, through the present experiments. The volume and composition of the

Table I   Permeability of SO₂/N₂ Mixture through Sulfoxide-Modified PVA Membrane

Run	R^a	Sulfoxide Content (mol %)	Thickness (μm)	Temperature (°C)	$P(SO_2)^b$	$\alpha(SO_2/N_2)^c$
1	CH₃	22.4	66	23	18.2	54
2	C₂H₅	11.7	82	23	19.2	—^{d}
3		18.8	87	23	8.5	60
4	t-C₄H₉	17.9	76	21	26.5	2
5	C₆H₅	11.5	143	18	16.5	78
6		16.4	154	22	33.4	113
7		23.5	102	23	47.0	170
8		27.8	98	16	48.1	96

^{a} Substituent in vinyl sulfoxide.
^{b} Permeability coefficient of SO₂, P: (cm³(STP)·cm)/(cm²·s·cmHg) × 10¹⁰.
^{c} Separation factor: $\alpha(SO_2/N_2)$ = [permeated (SO₂/N₂)]/[supplied (SO₂/N₂)].
^{d} Not determined.

permeated gas were measured at a certain time interval until the constant flow rate was attained.

RESULTS AND DISCUSSION

Sulfoxide Modified PVA

The DSC thermograms for a series of sulfoxide-modified PVA are shown in Figure 2. The results indicate that the polymers (see Table I) used for gas-permeation measurements are glassy at measurement temperatures. Also, another thermal analysis[10] gave no peak of melting point for MVSO-modified PVA with a substitution degree more than ∼ 15 mol %.

The permeation coefficient of SO₂ gas was obtained using the equation

$$Q = P\Delta p/l \qquad (1)$$

where Q(cm³ (STP)/cm² s) is the flow rate of the component gas, P(cm³ (STP)cm/cm²s cmHg) is the permeation coefficient, Δp is the partial pressure differential between the SO₂ gases in the feed and permeate sides, and l (cm) is the thickness of the membrane. The flow rate of SO₂ gas in the permeated mixture was determined from the total flux and the composition of the mixture at a constant flow rate. Figure 3 shows an example of gas chromatograms of the supplied and permeated SO₂/N₂ mixtures.

As shown in Table I, the permeation coefficients of SO₂ for the BVSO and PVSO membranes are larger than that for the MVSO membrane. Namely, the bulkier the substituent, the higher the SO₂ permeability. This tendency was found for the perme-
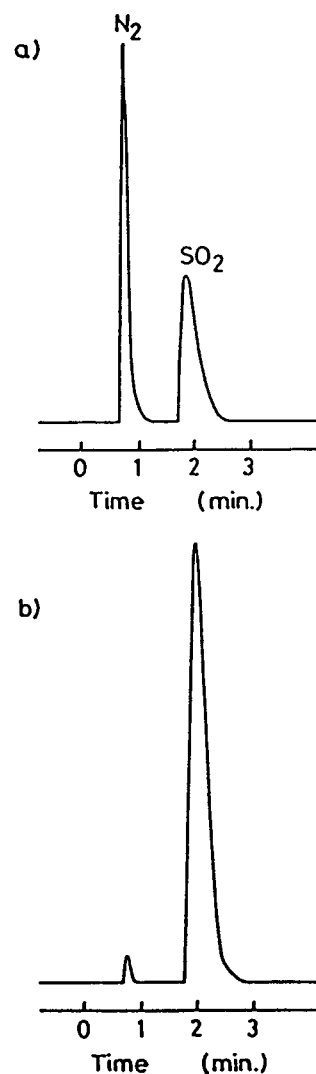

Figure 3   Gas chromatograms of SO₂/N₂ mixture in (a) feed and (b) permeate sides through the 16.4 mol % phenyl vinyl sulfoxide-modified PVA membrane.
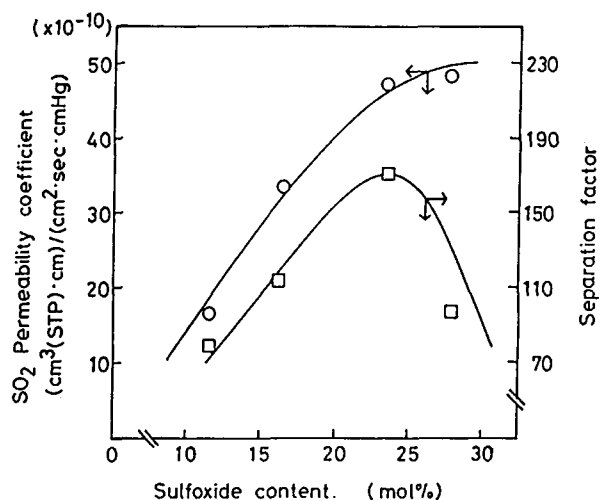
Figure 4 Plots of the SO_2 permeability coefficient (O) and separation factor (□) against the sulfoxide content for the phenyl vinyl sulfoxide-modified PVA membrane.

ability of the pure gas of SO_2 as reported in the previous papers.[4-6]

Separability of the SO_2 gas from the mixed gas was evaluated using the separation factor α defined by[3]

$$\alpha = [y/(1 - y)]/[x/(1 - x)] \qquad (2)$$

where y and x are the fractions of SO_2 in the permeate and feed sides, respectively. The values of α are summarized in the seventh column of Table I.

Figure 4 shows the double plots of the permeability coefficient and separation factor against the sulfoxide contents for the PVSO membranes. The permeability coefficient of SO_2 increases with increasing sulfoxide content, while the separation factor curve has a maximum. The permeation process is controlled in general by solubility and diffusivity of the gas molecule in the membrane. In the present membrane the permeation may be solubility controlled, because the pressure dependence of the permeability coefficient was found to be very large[4] and because the sulfoxide containing compounds have a high SO_2 solubility.[7] Therefore, the permeability of SO_2 is larger with sulfoxide contents. On the other hand, the sorbed gas may bring plasticizing or swelling effect to the membrane. In fact, as shown in Figure 5, the glass-transition temperature of the membrane was lowered after the gas-permeation experiment. This plasticizing or swelling effect may enhance the permeability of N_2 as well. Namely the permeabilities of SO_2 and N_2 become competitive with each other as the sulfoxide content increases. This may be the reason for the appearance of the maximum in the separation factor curve. Even though such a plasticizing effect may be present, the
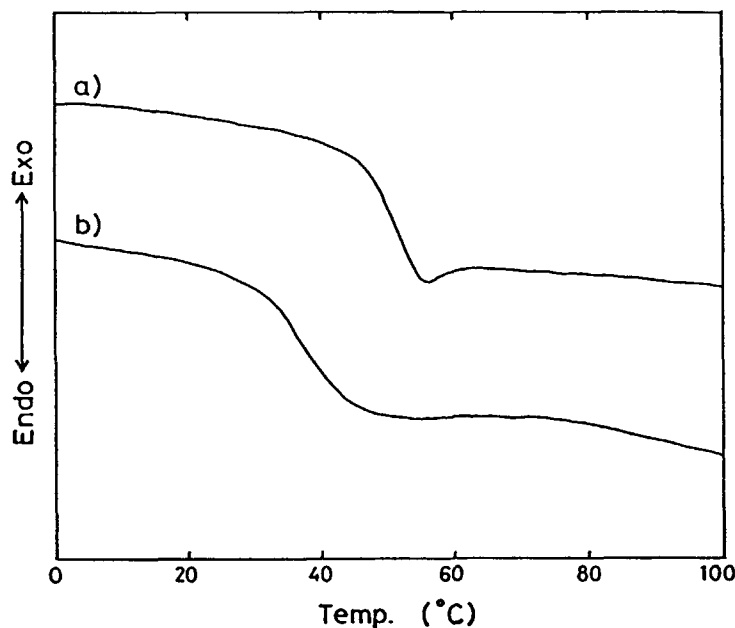

Figure 5 DSC thermograms of the 16.4 mol % phenyl vinyl sulfoxide-modified PVA membrane (a) before and (b) after gas permeation measurement, respectively.

Table II   Permeability of SO₂/N₂ Mixture through Sulfoxide-Modified Cellulose Membrane

Run	R^a	D.S.[b]	Thickness (μm)	Temperature (°C)	$P(SO_2)^c$	$\alpha(SO_2/N_2)^d$
1	CH_3	0.92	68	23	11.2	1.9
2		1.06	42	23	7.3	6.1
3	C_2H_5	0.66	109	24	7.2	2.3
4	C_6H_5	0.54	130	21	12.7	0.5
5	—[e]	2.50	140	21	75.5	21.1

[a] Substituent in vinyl sulfoxide.
[b] Degree of substituent.
[c] Permeability coefficient of SO_2, P: $(cm^3(STP) \cdot cm)/(cm^2 \cdot s \cdot cmHg) \times 10^{10}$.
[d] Separation factor: $\alpha(SO_2/N_2)$ = [permeated (SO_2/N_2)]/[supplied (SO_2/N_2)].
[e] Ethyl cellulose.

maximal value of α is as high as one of the highest values reported so far.[3]

Sulfoxide Modified Cellulose

Table II shows the results of separability in some sulfoxide-modified cellulose membranes together with that in ethyl cellulose membrane. Although the ethyl cellulose membrane indicated rather high separability for an SO_2/N_2 mixture, separability of a series of sulfoxide-modified cellulose was not so high as those of the sulfoxide-modified PVAs.

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