TRANSPORT PROPERTIES OF POLYIMIDE/SILICA COMPOSITE MEMBRANES

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Polyimide/silica composite membranes were prepared by the sol-gel reaction of tetraethoxysilane, methyltriethoxysilane or phenyltriethoxysilane in the solution of polyamic acid prepared by condensation of equimolar amount of pyromellitic dianhydride, 3,3',4,4'-biphenyl-tetracarboxylic dianhydride or 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride with 4,4'-oxydianiline in N-methyl pyrrolidone. Silica-coated polyimide membranes were also prepared by the sol-gel method. Gas permeation for H₂, CO₂, CO, O₂, N₂ and CH₄ and water vapor permeation were reported. A slight reduction in gas permeability was observed for the composite membrane. The permeability of water vapor increased in polyimide/silica composite membranes, while silica coating resulted in a reduction of the permeability. Transient sorption and desorption experiments were also investigated at water vapor activity of 0.5. An increase in permeability of water vapor can be attributable to an increase in solubility of water vapor due to the presence of hydroxy species of silica.

1. Introduction

Polyimide with excellent thermal, mechanical and chemical stability, and high dielectric strength have attracted much attention for their potential use in the electronics industry. The moisture absorption and permeation of polyimide is, however, a problem for microelectronics applications. Consequently, there have been several investigations of water sorption and transport in polyimides.[1-4] We have already reported the effects of physical and chemical structure on the sorption and diffusion of water in polyimides.[5] In this report, we focus on transport properties of polyimide/silica composite membranes. Water vapor permeation, and transient sorption and desorption of water vapor are reported.

2. Experimental

The molecular structures of the polyimides and silanes used in this study are shown in Figure 1. Polyimide membranes were obtained by casting solutions prepared by condensation of equimolar amount of pyromellitic dianhydride (PMDA), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) or 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) with 4,4'-oxydianiline (ODA) in N-methyl pyrrolidone and subsequent thermal imidization at 200°C for 20 hr in vacuum. Kapton-H and Uplex-R were commercially available from Toray Du Pont and Ube Industries, respectively. Polyimide/silica composite membranes were prepared by hydrolysis of tetraethoxysilane (TEOS), methyltriethoxysilane (MTES) or phenyltriethoxysilane (PTES) in the solution of polyamic acid derived from equimolar amount of dianhydride (PMDA, BPDA or 6FDA) and diamine (ODA) and subsequent thermal imidization at 200°C for 20 hr in vacuum, as described in the literature.[6] Silica-coated polyimide membranes were prepared by the sol-gel method.[7, 8] PMDA-ODA or Kapton-H membrane was immersed into ethanol solution of TEOS or TEOS/MTES for 1 min and pulled up at 0.2 cm/sec, followed by drying at 60°C for 20 min and heating at 400°C for 20 min. The composition of the coating solution was silane/ethanol/water=0.14/1/14 (molar ratio) and the time for hydrolysis of the solution was 10 hours.

Polyimides

Silanes

Fig. 1 Structures of polyimides and silanes used in this study

Water vapor permeation was carried out at 105°C under a total pressure of 0.101 MPa. Feed vaporized by a super heater was introduced to the upstream side of a flat membrane set in a permeation cell. The cell was placed in a thermostated air-bath. The downstream side was evacuated through a vacuum line. Permeate was condensed and trapped by liquid nitrogen. The effective membrane area was 22.1 cm² and the downstream pressure was maintained below 130 Pa. After the membrane was equilibrated, the permeation data were collected under steady state conditions.

Transient sorption and desorption experiments were carried out at 50°C and water vapor activity of 0.5, using a sorption apparatus equipped with a quartz spring. Integral sorption from, and desorption to, zero pressure were investigated. Figure 2 shows typical normalized sorption and desorption curves. Plots of M_t/M_∞ versus $t^{1/2}$ were linear, where M_t and M_∞ refer to the mass sorbed or desorbed at time t and at infinite time, respectively. Diffusion coefficients (D) for sorption and desorption were determined from the initial slopes according the equation: $M_t/M_\infty = 4x(Dxt/pxl^2)^{1/2}$, where l is membrane thickness. The diffusion coefficient D used in this study was calculated as the average of that for sorption and desorption. The permeability coefficient P was evaluated as the product of D and solubility coefficient S : $P = D \times S$.

Permeability coefficients were measured at 10 atm and 35°C for H₂, CO₂, CO, N₂ and CH₄ gases and at 2 atm and 35°C for O₂ and N₂ gases by the vacuum time-lag method.

Fig. 2 Typical normalized sorption and desorption curves of water vapor in polyimide/silica composite membrane (PMDA-ODA/TEOS(20))

3. Results and Discussion

Polyimide membranes have high permeability of water vapor as shown in Table 1. In comparison with the permeability of hydrogen, water vapor permeates through the polyimide membrane two order faster than hydrogen.[9] This can be attributed to large solubility coefficient of water vapor. It is well known that polyimide membranes are thermally and chemically stable. Thus, they seem to be useful in the application to dehumidification of gases, air and organic vapors. On the other hand, for microelectronics application, water vapor adsorption and permeation of polyimide is a long-standing reliability problem.

Table 1 Solubility(S), diffusion(D) and permeability(P) coefficients for water vapor in polyimide membranes at 50°C and activity 0.5

Membrane (silica wt%)	S	D	P
PMDA-ODA	9.1	1.66	15.1
Kapton-H	5.5	0.64	3.6
PMDA-ODA/TEOS(20)	10.4	1.81	18.8
PMDA-ODA/PTES(14)	7.6	2.91	22.1
BPDA-ODA	6.2	1.28	7.8
Upilex-R	3.2	0.44	1.4
6FDA-ODA	4.7	4.60	21.6

S is in $\text{cm}^3(\text{STP})\text{cm}^{-3}\text{cmHg}$, D is in $10^{-8}\text{cm}^2\text{s}^{-1}$ and P is in $10^{-8}\text{cm}^3(\text{STP})\text{cmcm}^{-2}\text{s}^{-1}\text{cmHg}^{-1}$.

Water vapor permeation among the polyimide/silica composite membranes are compared in Table 2, together with the results of silica-coated polyimide membranes. Although the permeability depends on the acid dianhydride moiety in the order 6FDA>PMDA>BPDA, the permeability through polyimide/silica composite membranes increased for a given dianhydride moiety and it increased with an increase in silica content. Changing the silane from TEOS to PTES also resulted in an increase in the permeability of water vapor. In order to determine the individual contributions of solubility and diffusivity to the permeability, transient sorption and desorption experiments were carried out for PMDA-ODA/TEOS composite membrane (Figure 1). The results are shown in Table 1. A slight increase in solubility of water vapor seems to be attributable to the presence of hydroxy species of silica due to incompleteness of polycondensation to form silica structure as suggested by A. Morikawa et al.[10] FTIR spectra of the composite membrane showed a broad and weak band at $3700\text{--}3100\text{ cm}^{-1}$ ascribed to OH stretching. Polar hydroxy groups probably increase solubility of water.

Table 2 Water vapor permeability at 105°C

Membrane (silica wt%)	ρ	P
Polyimide membranes		
PMDA-ODA	1.398	14.8
Kapton-H	1.473	4.05
BPDA-ODA	1.366	5.53
6FDA-ODA	1.433	15.7
Polyimide/silica composite membranes		
PMDA-ODA/PTES(14)	1.382	16.1
PMDA-ODA/PTES(29)	1.362	23.6
PMDA-ODA/PTES(52)	1.345	24.1
BPDA-ODA/TEOS(20)	1.444	7.81
BPDA-ODA/PTES(20)	1.350	7.15
6FDA-ODA/TEOS(20)	1.510	20.1
6FDA-ODA/PTES(13)	1.418	16.0
Silica-coated polyimide membranes		
PMDA-ODA/TEOS-MTES		11.7
Kapton-H/TEOS-MTES		2.27

ρ (density) is in gcm^{-3} and P is in $10^{-8}\text{cm}^3(\text{STP})\text{cmcm}^{-2}\text{s}^{-1}\text{cmHg}^{-1}$

On the other hand, silica coating by the sol-gel method resulted in a reduction of the permeability as suggested by N. Tohge et al.[8] The thickness of the coated-silica membrane was about $0.1\ \mu\text{m}$ judging from the cross-sectional view of SEM observation. According to a series resistance model for gas permeation of the composite membrane [11], the permeability of water vapor through silica membrane coated on Kapton-H can be estimated to be $\approx 10^{-10}\ \text{cm}^3(\text{STP})\text{cmcm}^{-2}\text{s}^{-1}\text{cmHg}^{-1}$.

Table 3 shows the gas permeability coefficients through polyimide/silica composite membranes at 35°C . A slight reduction in permeability was observed for the composite membranes. On the contrary to water vapor permeation, solubility were little affected and diffusivity decreased judging from the individual estimation of solubility and diffusivity. Thus, for the reduction of water solubility and diffusivity through the polyimide/silica composite membranes, further studies is needed to complete the sol-gel reaction by heating at higher temperature like in the case of the preparation of silica-coated polyimide membranes and to make silica particles dispersed homogeneously at the molecular level.

Table 3 Permeability coefficients (P) for polyimide/silica composite membranes at 35°C

Membrane (silica wt%)	P [$10^{-10} \text{cm}^3(\text{STP})\text{cmcm}^{-2}\text{s}^{-1}\text{cmHg}^{-1}$]					
	H ₂	CO ₂	O ₂	N ₂	CO	CH ₄
PMDA-ODA	7.18	2.36	0.604	0.0916	0.172	0.0625
PMDA-ODA/TEOS(20)	7.43	2.22	0.560	0.0823	0.148	0.0510
PMDA-ODA/PTES(14)	12.4	5.16	1.24	0.218	0.402	0.179
PMDA-ODA/PTES(29)	17.8	11.2	2.47	0.504	0.884	0.504
BPDA-ODA	3.54	0.582	0.171	0.0213	0.0413	0.0119
BPDA-ODA/TEOS(20)	3.02	0.521	0.145	0.0186	0.0365	0.0109
6FDA-ODA	40.7	16.7	3.88	0.733	1.16	0.341
6FDA-ODA/TEOS(20)	23.4	6.01	1.72	0.369	0.565	0.240

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