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Pervaporation of water/acetic acid through polyimide membranes from 3,3′,4,4′-benzophenone tetracarboxylic dianhydride and 4,4′-oxydianiline

Yoon Duk Moon, Boo Keun Oh, and Young Moo Lee*

Department of Industrial Chemistry, College of Engineering, Hanyang University,
Seoul 133-791, Korea

SUMMARY

Pervaporation performance of polyimide (PI) membrane from 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 4,4'-oxydianiline (ODA) was investigated at 80wt% feed acetic acid concentration and at 65℃. Imide contents in PI film were estimated by thermogravimetric analysis (TGA) method. The separation factor of PI membrane increases with the degree of imidization, while the flux was almost constant. The separation factor toward water through PI-94 membrane was about 417 with the flux of 47 $g/m^2.hr$ measured at 65°C and with 80wt% acetic acid as a feed. PI-94 showed the best pervaporation performance toward the separation of water from acetic acid solution among the PI membranes investigated. The swelling behaviors at various feed concenration were also examined.

INTRODUCTION

Pervaporation is a membrane separation process involving liquid-gas systems applicable to a variety of liquid mixtures and is especially useful for such separation near the azeotropic composition. Particularly for ethanol-water mixtures, a lot of research has been carried out to develop more efficient membranes (1-3). Yoshikawa et al. has studied the separation of water-acetic acid mixture by pervaporation through polymer membranes containing pendant carboxylic acid (4). In the case of acetic acid as organic phase, insolubility of polymer films under the exposure to acetic acid is a very considerable factor for operation. As a result, vinyl polymers (5) that are often insoluble in acetic acid were employed for pervaporation separation of water-acetic acid mixtures (4-6). However, these membranes containing vinyl or aliphatic main chains cannot be operated at high temperature due to low glass transition temperature.

Aromatic polyimide (PI) membranes are particularly stable to organic carboxylic acids and possess very high thermal stability. Several studies on high-performance polymer membranes for pervaporation have been reported recently. Maeda et al. (7) investigated the separation of water-acetic acid mixture by pervaporation through aromatic polyamide and polyamideimide membranes containing anionic groups. They also studied the effect of metal ionic crosslinking on the pervaporation performances. Ogata et al. (8) reported the permselectivity of partially imidized poly(amic acid) membranes composed of pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) for water-ethanol mixture. Effect of the degree of imidization on selectivity and flux was reported. Later Okamoto et al. (9) investigated the separation of water-ethanol mixture by pervaporation through asymmetric membrane made of commercial polyimide (ULTEM polyetherimide from GE and PMDA/ODA PI from Toray). Effect of additives and nonsolvent systems in casting

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*Corresponding author

solution was investigated. They also studied the gas permeability of the same membranes as well.

The objective of the present research is to examine the effect of various poly(amic acid) and polyimide membranes from 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and ODA on the pervaporation performance of water-acetic acid mixture. The goal of this study is to investigate the effect of imide contents in polyimide membranes on pervaporation separation efficiencies, i.e., flux and separation factor, and to compare these membranes with modified polyimide membranes. Effect of feed concentrations and swelling behaviors was studied as well.

EXPERIMENTAL

Reagents

3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA) and 4,4'-oxydianiline (ODA) were purchased from Aldrich Chemical Co. BTDA was recrystallized from acetic anhydride and dried at 170°C for 28 hours under vacuum prior to use. ODA was employed after recrystallization in ethanol. Amine-terminated poly (dimethyl siloxane) (PDMS, M_n = 4000g/mol) was obtained from Shinetsu Co. and used without any further purification. Tetrahydrofuran (THF) and 1-methyl-2-pyrrolidinone (NMP) were dehydrated with calcium hydride and distilled at atmospheric pressure and under reduced pressure, respectively. Bromine (Br_2) from Junsei Chemical Co. was employed for preparing the brominated PI membrane.

Manufacture of homopoly(amic acid) (HPAA)

To prepare the homopolyamic acid (HPAA), 0.06 mol (12.01g) of ODA was dissolved in 85ml of NMP at room temperature and added with 0.06mol (19.33g) of BTDA and 37.3ml of NMP to remove any BTDA slurry remaining in a flask under the N_2 inlet. Polymerization reaction was carried out for 4 hours to obtain clean solution and then the solution was stirred for 20 hours. Resulting solution of HPAA was precipitated three times in acetone and dried at 60°C under vacuum for one day.

Preparation of polyimide (PI) membranes

Dried and yellow HPAA powder was dissolved in NMP to 20wt% and the solution was cast on a glass plate and preheated for 20 minutes at 70°C. It was thermally baked in a static air oven at various curing conditions as can be seen in Table I, to prepare partially imidized PI films and fully cured PI (PI-100) membranes.

Preparation of poly (imide-siloxane) (PIS) film

To prepare the siloxane containing polyamic acid (SPAA), 13.7ml of PDMS previously dissolved in 84.1ml of THF was reacted with HPAA prepared from ODA (1.1815g=0.0059mol), BTDA (1.901g=0.006mol), and NMP (175.75ml). Resulting solution of SPAA was precipitated in methanol, filtered and dried at 60°C under vacuum for one day. PIS film was manufactured following the preparation method for PI-94 membrane.

Preparation of brominated polyimde film (Br -PI-94) film

Bromonation was carried out by dipping the PI-94 film in mixed solution composed of Br_2 and water (50:50, v/v ratio) and the mixed solution was magnetically stirred at room temperature under the exposure of UV-light (10).

Preparation of partially cured asymmetric PI film (As-PI)

HPAA solution (20wt% in NMP) was cast on a glass plate and preheated for 20 minutes at 70°C and immersed in water at room temperature for one day. The light yellow asymmetric HPAA film was obtained and then thermally treated at 120°C for two hours.

Table I. Thermal curing conditions for preparing BTDA and ODA PI films.

Sample degradation	Thermal treatment	Imide content*(%)
PI - 14	120°C, 2.5hr	14
PI - 64	120°C, 2.5hr / 170°C, 1hr	64
PI - 91	120°C, 1hr / 200°C, 1hr / 300°C, 1hr	91
PI - 94	120 °C, 2.5hr / 200°C, 1hr / 250°C, 1hr	94
PI - 100	120°C, 1hr / 200°C, 1hr / 300°C, 4hr	100

* see. Ref. 18 and 19.

Characterization

Chemical structure of HPAA and PI was confirmed by using FT-IR (Nicolet model, 5DX). Inherent viscosity (η_{inh}, dl/g) was measured at 25 °C for samples dissolved in NMP (0.5wt%), using Ubbelohde viscometer.

Thermal transition behaviors and aspects of weight loss were detected by differential scanning calorimeter (DSC, Du Pont Model 910) and thermogravimetry (TGA, Du Pont Model 951) attached to thermal analyzer 2100 computer system at a heating rate of 20 °C/min under a nitrogen purge (50ml/min).

Pervaporation experiments

A detailed description of the pervaporation apparatus is given elsewhere (1,2).

RESULTS AND DISCUSSION

FT-IR spectra for partially imidized poly(amic acid) from BTDA and ODA showed the characteristic peaks at 1660 cm^{-1} (amide I) and 1545 cm^{-1} (amide II) (not shown here). The absorption bands for PI appeared at 1,780 cm^{-1}, 1720 cm^{-1}, 1380 cm^{-1}, and 725 cm^{-1}. Intensities of the above peaks strongly increased as the thermal imidization is carried out at higher temperature and longer time (11-13). Disappearance of a peak at 1545 cm^{-1} (amide II) indicated the conversion of HPAA into PI due to the formation of imide ring after thermal cycloimidization.

Inherent viscosity of HPAA measured in NMP (0.5 wt%) at 25 °C was 0.4 dl/g. The glass transition temperature (T_g) of PI-100 was about 295 °C measured by DSC (second scan). Temperature of 10 % weight loss due to decomposition was about 576 °C and maximum temperature of derivative TGA curve was 615 °C. Tensile strength at break and elongation at break of PI film were 12.55 kg/mm^2 and 14%, respectively.

There are several reports on the calculation of imide contents using FT-IR (14-17), TGA derivative (18, 19), optical density (20) and refractive index (20). In this study, we utilized the TGA method as suggested by Omoto et al. (18). Degree of imidization (%) was calculated from the equation $(W_0 - W_T) / W_0$, where W_0 and W_T are the percent weight loss for cyclization of uncured and cured films at any temperature T (°C), respectively. Typical TGA derivative curves for polyimides from BTDA-ODA are shown in Figure 1. As the film is cured the area under the derivative curve decreases. Imide contents were calculated to be 14, 64, 91, 94, and 100%, and designated as PI-14, PI-64, PI-91, PI-94, and PI-100, respectively.

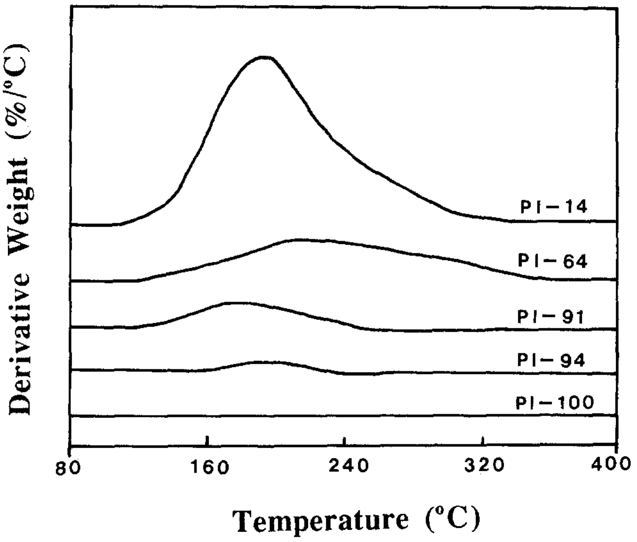

Figure 1. Dynamic TGA derivative curves for polyimide from BTDA and ODA. Numbers indicate their imide contents.

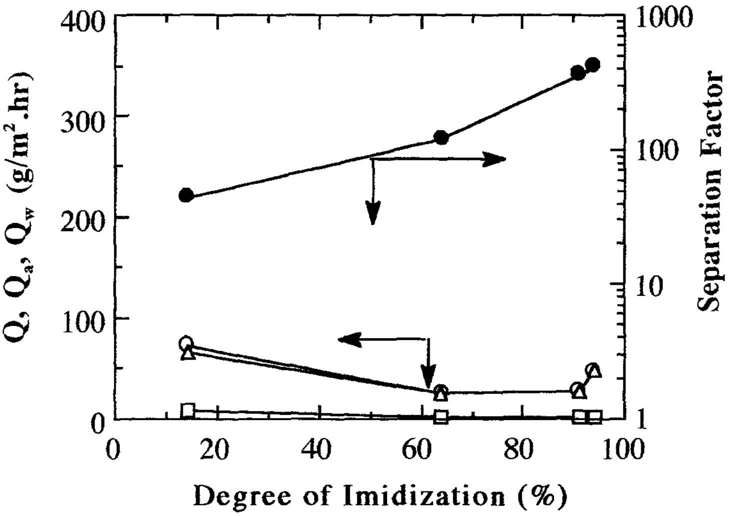

Figure 2. Effect of the degree of imidization on the separation factor (●), total flux (○), water flux (△), and acetic acid flux (□) through polyimide membrane. Feed concentration of acetic acid and termperature was 80wt% and 65°C, respectively.

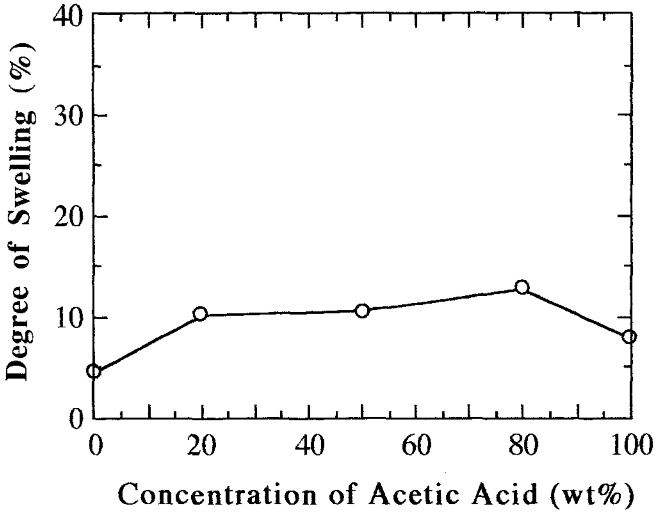

Figure 3. Swelling behaviors of PI-94 membrane as a function of acetic acid concentration measured at 65°C after equilibration.

Figure 2 shows the effect of degree of imidization on the pervaporation flux and separation efficiency using 80wt% water-acetic acid mixture measured at 65°C. Thickness of membranes was ranging between 21-28 μm. As the membrane is imidized the flux decreases, while the separation factor toward water increases, except for PI-94 membrane. Larger flux of PI-94 compared with PI-91 might be caused by the variance in thermal treatment condition for cycloimidization (see Table I) that influences the molecular orientation of polyimides and thus the diffusion behavior. The difference in preparation method of PI-91 and PI-94 films is the first and third thermal curing steps, and more significant effect might be induced from the first curing step. PI-94 membrane was cured at 120°C for 2.5 hr, while PI-91 was prepared at 120°C for 1 hr. Longer evaporation of solvent at this temperature could accelerate the conversion of amic acid into imide ring and orientation of molecular segments (21-22). In general it is known that polyimide film manufactured on substrate (glass plate or silicon wafer) can be oriented parallel to the substrate or film surface, and that orientation of polymeric materials influences diffusion rates that may vary relative to the axis of orientation (21). The degree of orientation increases with the imide content. Thus, PI-94 is more highly ordered than PI-91, resulting in the higher separation factor. Furthermore, higher temperature in the final curing step affects the intermolecular cross-linking of polyimide (23). The flux of PI-94 is higher than that of PI-91 because of the increased free volume of PI-94 due to the lower third thermal curing temperature (250°C) and the smaller amount of intermolecular cross-links formed during PI thermal curing process (23, 24). Note that the flux and separation factor for PI-94 were 47 $g/m^2.hr$ and 417, respectively.

The swelling behaviors of PI-94 membrane were measured in aqueous acetic acid solution with varying concentration as exhibited in Figure 3. Samples were swollen at 65°C and equilibrated in three days. For water, swelling degree was only about 4%. As the concentration of acetic acid increased, however, swelling degree was in the range of 8-12% for all the concentration range tested.

Figure 4 shows the effect of concentration of acetic acid in the feed on the pervaporation performance through PI-94 membrane measured at 65°C. Flux was in the range of 40 - 70 g/m^2.hr for up to about 80 wt% acetic acid. Separation factor was about 417 when the feed was 80wt% acetic acid solution, and dropped as the feed acetic acid concentration was decreased.

Table II compares the pervaporation performance of polyimides and modified polyimides. Silicon containing polyimides (25), brominated silicone polymers (10, 26) and brominated poly(phenolphthalane terephthalate) (27) were known as gas separation membranes with better permselectivity. Weight fraction of PDMS unit in poly(imide siloxane) (PIS) membrane was about 0.3 in the reactant (28-29). Dipping method (10) was employed for preparing Br-PI-94 film. As-PI membrane was manufactured by phase inversion method (9).

As can be seen in Table II, PIS has separation factor of 117 and the flux of 11.8 g/m^2.hr. Br-PI-94 has the comparable flux with PIS, but shows the twice the separation factor of PIS. As-PI shows the remarkable flux and a very low separation factor clearly because of the porous asymmetric structure of the membrane. Among the membranes, permeation index, which is the product of pervaporation flux and the separation factor, of PI-94 was the highest.

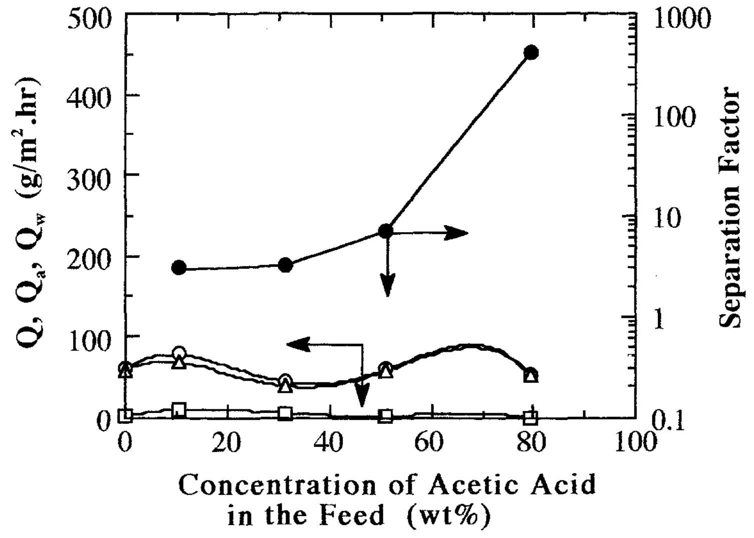

Figure 4. Effect of the acetic acid concentration in the feed on the separation factor (●), total flux (○), water flux (△), and acetic acid flux (□) through PI-94 membrane measured at 65 °C.

Table II. Comparison of pervaporation capacity of polyimide and modified polyimide membranes.*

Sample	Separation Factor	Flux ($g/m^2.hr$)	Membrane Thickness (μm)	Pervaporation Separation Index
PI-94	417	47.6	22	20.0
PIS	117	11.8	55	1.4
Br-PI-94	227	12.2	31	2.8
As-PI	2	9526.0	209	16.0

* pervaporation test was executed at 65°C and the feed was 80wt% acetic aicd.

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