Preparation of Plasma-grafted Membranes and Their Pervaporation Properties to Aromatic/Non-aromatic Mixtures

Katsuhiro Yoshimatsu, Hongyuan Wang, Hidetoshi Kita and Ken-ichi Okamoto

*Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi
University, Ube, Yamaguchi, 755-8611, Japan*

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1. Introduction

Pervaporation has gained widespread acceptance in the chemical industry as an effective process for separation of azeotropic mixtures and close-boiling mixtures.[1,2] The process operates with a liquid feed, which contacts the upstream membrane face, and a vapor permeate under vacuum or a stream of inert gas. It has been applied to the dehydration of organic liquids (ethanol, isopropyl alcohol, ethylene glycol, etc) but its application to separate organic liquid mixtures such as aromatic/aliphatic hydrocarbon or alcohols/ethers is very limited because of low selectivity due to swelling of polymer membranes. However, the separation of organic liquid mixtures offers potentially the largest opportunity for energy and cost savings and pervaporation is one of most promising membrane separation processes for such separations. Not a few articles, therefore, have reported the pervaporation membrane prepared by various methods such as copolymerization, graft polymerization, polymer alloys, crosslinking, concentrated emulsion polymerization, and microphase separation.[3]

In our previous papers [4-6], we have reported on the preparation of composite membranes by plasma-induced graft polymerization of glycidyl methacrylate (GMA) onto a porous substrate of high density polyethylene which provides the restraint of membrane swelling. The membranes

showed good stability and higher pervaporation performance; that is, the permeation flux of 0.30–0.37 kg/m²h and separation factor of 19–22 at 70°C for benzene (60 wt%) / cyclohexane (40 wt%) than plasma-grafted methyl acrylate (MA) membrane reported by Yamaguchi et al.[7,8] In this communication, we report plasma-graft polymerization of polyethyleneglycol monomethacrylate (PME), where ethylene oxide segment has higher affinity for benzene, to elucidate how benzene affinity of graft polymer could affect the pervaporation performance for benzene / cyclohexane through plasma-grafted membrane.

2. Experimental

2.1 Membrane Preparation

A porous polyethylene film with a thickness of 25 μm and a pore size of 0.003 μm was supplied by Tonen Chemical Co. Ltd. and was used as the substrate for plasma-graft polymerization. Polyethyleneglycol monomethacrylate (PME; $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$, $n=2$) was supplied by NOF Corp. and was used without further purification. The apparatus and the procedure of plasma-graft polymerization was the same as that described previously.[4-6] Plasma was generated by an inductive coupled rf(13.56 MHz) power source. After the substrate of 8x8 cm² in size was placed in a reactor made of pyrex

glass tubing, with a round bottom. the reactor was evacuated and Ar gas was injected into the reactor. The Ar plasma treatment was carried out at a pressure of 10 Pa and a discharge power of 10 W for 2-3 min.

After the plasma treatment, a previously degassed aqueous PME solution (3 vol%) containing AIBN (200 ppm) was introduced into the reactor under vacuum without exposure to air. The graft polymerization was carried out in a shaking constant-temperature bath at 30-40°C for 90-240 min. Then, the grafted membrane was immersed in acetone to remove the homopolymer and the unreacted monomer, and dried. The membrane was weighed before and after the graft polymerization in the dry state, and the grafting yield was determined as the weight of grafted polymer₂ per unit area of the porous substrate (mg/cm²).

2.2 Pervaporation

Pervaporation experiments were carried out for benzene / cyclohexane or benzene / n-hexane liquid mixtures at 25-70°C according to a literature method.[9] The effective membrane area was 19.6 cm². The downstream pressure was maintained below 130 Pa. The volume of feed solution was about 100 mL. The permeate was collected in a trap at liquid nitrogen temperature. The permeation flux Q in kg/(m²h) was calculated from the weight of permeate. Feed and permeate compositions were determined by gas chromatography. The separation factor α is defined as

$$\alpha = y(1-x) / x(1-y)$$

where x and y are weight fractions (%) of benzene in feed and permeate, respectively.

3. Results and discussion

The relationship between the grafting yield and the grafting time is shown in Figure 1. The yield increased with increases in the grafting time and temperature. Especially, the yield increased with increasing time at above 40°C. Compared with the previous results of GMA and MA, the grafting yield was in the order of MA > PME $\approx$ GMA. The membrane thickness increased with an increase in the grafting yield. The membrane of which grafting yield exceeded 2 mg/cm² displayed a significant enlargement both in thickness and size, indicating the graft polymer was formed on the surface of the substrate as observed in the MA and GMA-grafted membranes.[4-6]

The PME-grafted membrane showed a benzene

Fig. 1. Relationship between grafting yield and grafting time for PME-grafted membranes

selectivity in pervaporation of benzene / cyclohexane and benzene / n-hexane. Table 1 shows characterization and pervaporation results for PME-grafted membranes together with those of GMA and MA-grafted membranes. It is to be noted that the PME-grafted membrane with a high grafting yield showed a pretty high permeation flux and a rather small separation factor. This is probably due to the presence of defects as suggested in the GMA-grafted membrane previously.[5,6]

Figure 2 shows the feed composition dependence of the permeation flux and the separation factor in pervaporation of benzene / cyclohexane through PME-grafted membranes with the grafting yield of 3.6 and 1.8 mg/cm². The permeation flux of benzene increased and the separation factor decreased with an increase in benzene fraction in feed due to the swelling of the membrane with an increase in benzene fraction in feed, which is usually observed for polymeric membranes.[6]

In conclusion, the PME-grafted membrane showed higher permeation flux with considerably smaller separation factor compared with the pervaporation performance of benzene / cyclohexane through the GMA-grafted membrane. This may be attributable to the rubbery nature of

Table 1 Characterization and pervaporation performance of plasma-grafted membranes

Monomer	Duration time of plasma treat- ment (sec)	Polymerization conditions			Grafting yield (mg/cm ²)	Thickness (μ m)	Pervaporation results			
		Monomer Conc (vol%)	Temp (°C)	Time (min)			Feed(A/B) (wt% of A)	Temp (°C)	Permeation Flux (kg/m ² h)	Separation factor α
PME	180	3.0	30	90	1.8	47	Bz/Cx(60)	50	1.4	5.5
							Bz/Cx(20)	25	0.17	5.2
								35	0.34	9.2
								50	0.76	6.9
								70	1.64	4.7
							Bz/n-Hx(20)	25	0.12	7.6
								35	0.21	8.3
								50	0.47	7.0
PME	180	3.0	30	90	2.9	62	Bz/Cx(60)	50	1.3	5.1
							Bz/n-Hx(57)	50	1.5	4.7
PME	120	3.0	30	120	3.6	40	Bz/Cx(57)	50	1.4	5.2
							Bz/n-Hx(57)	50	2.8	4.3
PME	180	3.0	40	150	11	136	Bz/Cx(56)	50	2.4	3.9
PME	180	3.0	40	240	21	192	Bz/Cx(56)	70	5.4	2.4
GMA	120	3.0	30	35	0.7	17	Bz/Cx(60)	70	0.46	14
GMA	120	3.0	30	35	1.7	26	Bz/Cx(60)	70	0.37	19
GMA	120	3.0	30	35	1.9	29	Bz/Cx(60)	70	0.30	22
							Bz/n-Hx(60)	70	0.22	12
GMA	120	3.0	30	35	2.4	26	Bz/Cx(60)	70	0.35	22
MA	120	2.0	30	45	0.9	-	Bz/Cx(50)	50	2.4	3.3
MA	70	3.0	30	30	3.2	71	Bz/Cx(50)	50	1.2	6.3
MA	120	15.0	40	20	8.0	-	Bz/Cx(50)	50	0.6	6.2

PME: polyethyleneglycol monomethacrylate, GMA: glycidyl methacrylate, MA: methyl acrylate, Bz: benzene, Cx: cyclohexane, N-Hx: n-hexane

Fig. 2. Feed composition dependence of permeation flux and separation factor for pervaporation of benzene / cyclohexane at 50°C through PME-grafted membranes;

(○△) grafting yield=3.6mg/cm²,

(□▽) grafting yield=1.8mg/cm²

PME-graft polymer as suggested previously in poly(ethylene oxide imide) segmented copolymer membrane.[9]

References

- 1) H.L.Fleming, *Chem. Eng. Progr.*, 1992, July, 46
- 2) R.Y.M.Huang, Ed., "Pervaporation Membrane Separation Processes", Elsevier, Amsterdam, 1991
- 3) X.Feng and R.Y.M.Huang, *Ind. Eng. Chem. Res.*, **36**, 1048(1997)
- 4) H.Wang, X.Lin, K.Tanaka, H.Kita and K.Okamoto, *J. Photopolym. Sci. Technol.*, **10**, 119(1997)
- 5) H.Wang, X.Lin, K.Tanaka, H.Kita and K.Okamoto, *J. Polym. Sci. Polym. Chem. Ed.*, **36**, 2247(1998)
- 6) H.Wang, K.Tanaka, H.Kita and K.Okamoto, *J. Membr. Sci.*, **154**, 221(1999)
- 7) T.Yamaguchi, S.Nakao, S.Kimura, *Macromolecules*, **24**, 5522(1991)
- 8) T.Yamaguchi, S.Nakao, S.Kimura, *Ind. Eng. Chem. Res.*, **31**, 1914(1992)
- 9) N.Tanihara, N.Umeo, T.Kawabata, K.Tanaka, H.Kita and K.Okamoto, *J. Membr. Sci.*, **104**, 181(1995)