PII: S0032-3861(97)00384-4

Polymer Vol. 39 No. 11, pp. 2227–2233, 1998
© 1998 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/98/$19.00+0.00

Separation of water–alcohol mixture by using polymer membranes — 6. Water–alcohol pervaporation through terpolymer of PVA grafted with hydrazine reacted SMA

Wen-Yen Chiang* and Ching-Liang Chen
Department of Chemical Engineering, Tatung Institute of Technology,
40 Chungshan N. Rd., 3rd Sec., Taipei 10451, Taiwan, R.O.C.
(Received 15 July 1996; revised 18 February 1997)

The pervaporation separation of water–alcohol mixture was carried out using grafted terpolymer membrane at −10–50°C. PVA-g-ST/MA-Hz (III) terpolymer was prepared by graft copolymerization of styrene (ST)-maleic anhydride (MA) hydrazine (Hz) copolymer (ST-co-MA-Hz) (II) onto poly(vinyl alcohol) (PVA) by a condensation-coupling reaction through esterification that was performed between the hydroxy groups of PVA and the anhydride groups of ST-co-MA-Hz (II) copolymer. The ST-co-MA-Hz (II) copolymer was prepared by the chemical reaction of ST-co-MA (I) and Hz in dioxane. The ST-co-MA (I) copolymer was prepared by the copolymerization of MA and ST in dimethyl sulfoxide (DMSO) by using azobisisobutyronitrile (AIBN) as an initiator.

In order to obtain a membrane high in both selectivity and permeation rates, a series of PVA-g-ST/MA-Hz were synthesized with different compositions. Water was permeated through membrane preferentially in all ranges of water–alcohol feed compositions in this study. The permeation rate decreased and the selectivity increased as the PVA content in membrane rose. The effects of the molecular size of the permeating species on both permeation and separation were also investigated. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: graft terpolymer; poly(vinyl alcohol); pervaporation)

INTRODUCTION

The pervaporation process is a useful membrane separation technique for a wide variety of organic liquid mixtures. This method is expected to be useful particularly for the separation of close-boiling points, azeotropic liquid mixtures and others. However, this separation technique has not yet been put to practical use owing to the delay in the development of a membrane with high selectivity, ample flux and good durability during the operation. Much experimental work has been conducted in the development of very effective membranes in this field[1–11].

Recently, a method has been found for ethanol production by fermenting starch, sugar and cellulose. Since ethanol is obtained in a 5–10 wt% aqueous solution, an enormous amount of energy accounting for about 60% of production cost is consumed in the distillation process. Much work has been conducted in recent years in an atempt to save energy in water–alcohol separation in the membrane process.

A specific and selective separation of the water–alcohol mixture by membrane can be realized by incorporating a group into membranes, a process that may cause a strong interaction, such as a hydrogen-bonding interaction. Differences in the strength of the hydrogen-bonding interaction between membrane–water and membrane–alcohol may lead to a selective separation by membrane.

Polyvinyl alcohol (PVA) has many hydroxy groups and an excellent film-forming ability. However, being water soluble and having high crystallinity, pure PVA cannot be easily used for pervaporation. When heat-treated PVA membranes are used for the separation of alcohol and water, it is found that although the flux is very low, the membranes possess a high degree of selectivity toward water. Therefore, a useful procedure to improve the permeability characteristics of PVA membranes while still maintaining the selectivity lies in the graft copolymerization of hydrophobic monomers onto the PVA backbone.

From this point of view, a series of graft terpolymers based on the PVA backbone with different hydrophilic–hydrophobic ratios were synthesized in our previous papers[1–8]. Moreover, the purpose of this study is to develop and investigate new durable membranes that have high flux rates and acceptable selectivity for separating the alcohol–water system through pervaporation. The dependence of permeation behavior on the membrane composition as well as operating conditions were investigated.

EXPERIMENTAL

Materials

PVA BF-17, a product of Chang Chun Petrochemical Co., Taiwan, $D_p = 1700$, degree of saponification of 98.5–99.2 mol% and viscosity of 25–30 cp was used. Maleic anhydride (MA), styrene (ST), 1,4-dioxane and dimethyl sulfoxide (DMSO) of reagent grades were purchased from Wako Pure Chemical Industries. ST monomer was purified successively by washing with a 10 wt% aqueous solution of sodium hydroxide to remove the inhibitor, and then with

---

* To whom correspondence should be addressed

distilled water several times. Afterwards it was dried with calcium chloride and stored at −5°C overnight and then distilled below 60°C under reduced pressure. Hydrazine (Hz) was washed with aqueous sodium hydroxide, aqueous phosphoric acid and distilled water before being dried with anhydrous sodium carbonate. It was then distilled under reduced pressure. MA was purified through recrystallization from chloroform, and the crystals were dried under vacuum at room temperature. The initiator, azobisisobutyronitrile (AIBN), was recrystallized from dry methanol and dried under vacuum. Reaction solvents of dioxane and DMSO were purged by nitrogen to remove water before use.

Reaction 1: synthesis of ST-co-MA (I)

The copolymerization reaction was carried out in a four-necked flask equipped with stirrer, thermometer, condenser and nitrogen inlet. The general experimental procedure and an example were as follows. ST 41.66 g (0.4 mol) and MA 39.224 g (0.4 mol) were dissolved in 40 ml DMSO after being stirred in an atmosphere of nitrogen. The reaction temperature was adjusted at 60°C, and 0.8 g AIBN was added as an initiator. The reaction was allowed to proceed for 5 h.

Reaction 2: synthesis of ST-co-MA-HZ (II)

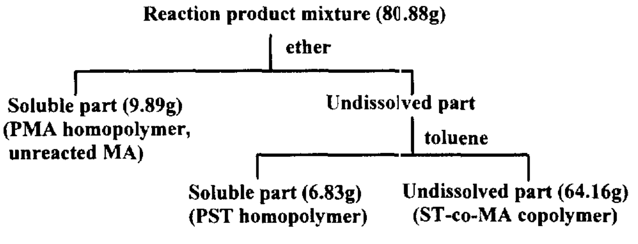
The reaction was carried out in a four-necked flask equipped with stirrer, thermometer, condenser and nitrogen inlet. Ten grams of ST-co-MA (I) was dissolved in 500 ml 1,4-dioxane and then 5 g of Hz was added. The reaction was allowed to react at 60°C for 3 h, with continuous stirring.

Reaction 3: synthesis of PVA-g-ST/MA-HZ (III)

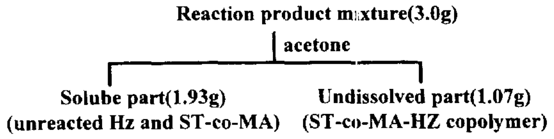
1.4 g of ST-co-MA.Hz (II) was dissolved in 50 ml of DMSO, and then 1.4 g of PVA was added. The reaction was allowed to react at 100°C with mechanical stirring under nitrogen for 12 h.

Purification of copolymer (I) and grafted terpolymers (II) and (III)

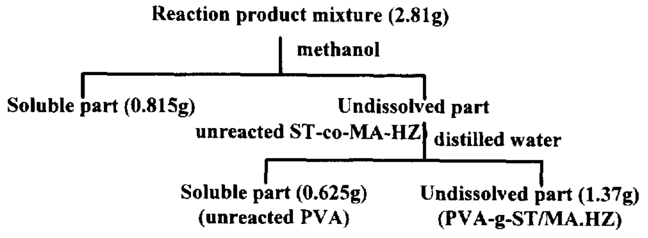
80.88 g of reaction 1 products was slowly precipitated into a large amount of ether. The filtrate solution part was condensed to obtain 9.89 g of PMA homopolymer, unreacted MA and unreacted ST. To the undissolved part was then added 300 ml of toluene for extraction. The soluble part was condensed to obtain 6.83 g of PST homopolymer. The undissolved part was dried to obtain 64.16 g of intended St-co-MA copolymer (I). The separation and purification of reaction 1 is summarized in *Scheme 1*.



Scheme 1



Scheme 2



Scheme 3

Separation and purification of reactions 2 and 3 were carried out by the same method as the one described in *Scheme 1*. The procedures are summarized in *Scheme 2* and *Scheme 3*. After the separation, all products were dried in a vacuum at room temperature.

Preparation of the membrane of graft terpolymer

1.1 g of PVA-g-ST/MA-Hz (III) was dissolved in 40 ml of DMSO. The solution was cast over a clean glass plate, which was allowed to dry at 60°C in a vacuum to constant weight to form the membrane.

Heat treatment of the membrane

All the prepared membranes were treated to enhance the mechanical strength in an oven at 100°C for 20 min before the pervaporation test.

Measurements

The measurement of various properties, such as viscosity, infrared (i.r.) spectra, gel content, water content, mechanical properties, thermal analyses was made by the same method as the one described in an earlier paper[3].

Pervaporation experiment

The apparatus and procedure for the pervaporation were essentially the same as those described in a previous report[2].

RESULTS AND DISCUSSION

Synthesis of ST-co-MA (I) copolymer

A number of publications[16–19] have indicated that ST and MA are in alternating copolymerization. In this study, the low molecular weight ST-co-MA[8] (I) was synthesized with the aprotic solvent (DMSO). The i.r. spectrum of ST-co-MA (I) was shown in *Figure 1*. The characteristic bands of anhydride groups and carbonyl groups were observed to be located at 1856 and 1779 and at 1719 cm^{-1} of MA, respectively. The intrinsic viscosity and yield of copolymer are 0.088 dl g^{-1} and 79.32%, respectively. The molecular weight of copolymer is about 4000.

Synthesis of ST-co-MA-HZ (II) copolymer

The reaction between hydrazine and ST-co-MA copolymer is described below. From the i.r. spectrum of the resultant (*Figure 1*), it can be seen that ST-co-MA-Hz (II) contains the characteristic bands of hydrazine groups (3333 cm^{-1}). The composition of the product was obtained by the elemental analysis of nitrogen. The composition and

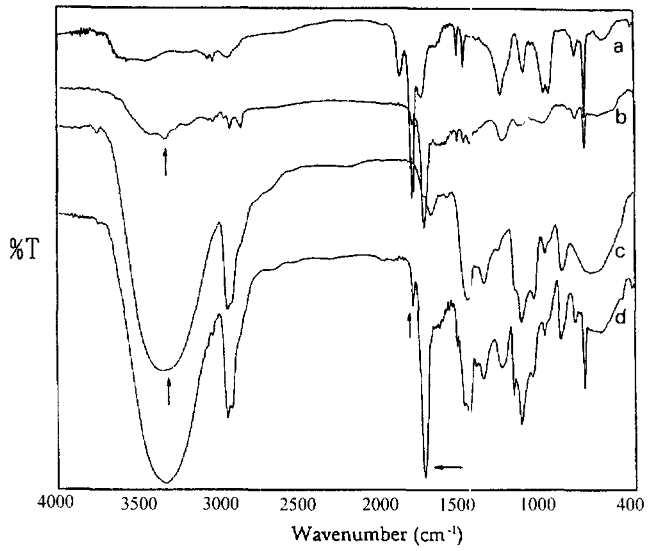


Figure 1 Infrared spectra of ST-co-MA (a), ST-co-MA-Hz (b), PVA (c) and PVA-g-ST/MA-Hz (d)

viscosity of resultants at different feed ratios are shown in *Table 1*.

Synthesis of PVA-g-ST/MA (III) terpolymer

The coupling reaction between the hydroxy groups in PVA and the anhydride groups in ST-co-MA proceeds as described below. The major difficulty encountered in the synthesis of this terpolymer was gel formation due to the presence of many hydroxy groups in the PVA backbone and many anhydride groups in ST-co-MA-Hz (II). Therefore, the reaction temperature and concentration must be carefully controlled to prevent the gel reaction from occurring.

Table 2 demonstrates that an increase of the PVA feed (wt%) results in an increase of the PVA content but a decrease of the ST-co-MA-Hz (II) content in PVAg-ST/MA-Hz (III). *Figure 2* shows the effect of the PVA content in PVA-g-ST/MAHz (III) on the integral of X-ray peak. *Figure 3* shows the DSC thermogram of PVA, ST-co-MA, ST-co-MA-Hz and PVA-g-ST/MA-Hz. From the above two figures, the crystallinity of PVA deteriorated when ST-co-MA-Hz was introduced as branches.

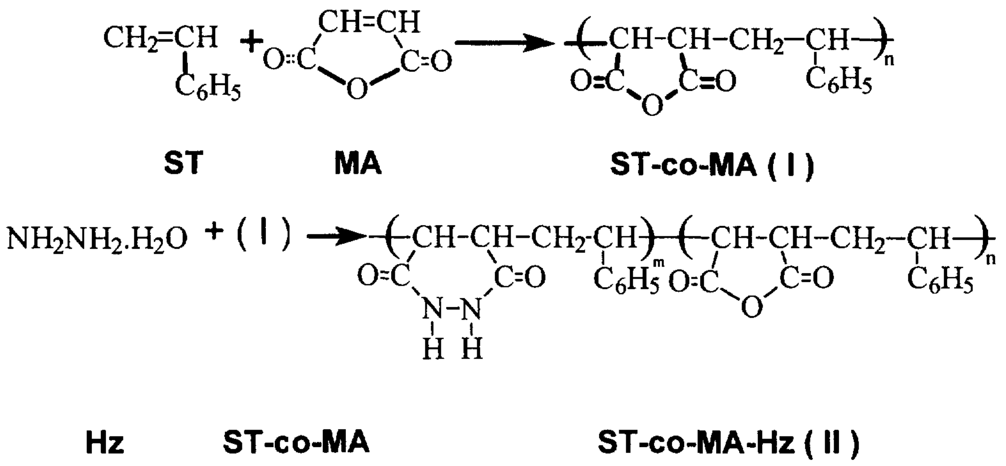


Table 1 Synthesis of ST/MA-Hz terpolymer

Number	Hz (g)	ST-co-MA[a] (g)	St-co-MA-Hz (g)	Yield (%)	[η][b] (dl g^{-1})	N (%)[c]	Percentage reaction of Ma[d]
1	0.80	2.00	0.92	32.71	0.11	8.85	66.80
2[e]	1.00	2.00	1.01	33.29	0.12	9.55	72.40
3	1.20	2.00	1.07	33.43	0.12	10.41	79.20
4	1.50	2.00	1.18	33.71	0.13	10.73	81.90

[a] The intrinsic viscosity of ST-co-MA used was 0.083
[b] Measured in DMSO at 30°C
[c] Found by elemental analysis
[d] Calculated from N (%) in the composition of equation
[e] The sample was selected to react with PVA for terpolymer preparation

Table 2 Synthesis of PVA-g-ST/MA-Hz graft terpolymer

Number	PVA feed (wt%)	St-co-MA-Hz (wt%)	Content of PVA in PVA-g-ST/MA-HZ[a] (wt%)	Yield (%)	[η][b] (dl g^{-1})	N (%)[c]	Integral of X-ray peak
1	66.7	33.3	75.2	39.2	4.9	3.4	730.2
2	58.3	41.7	62.9	44.9	4.2	3.8	607.4
3	50.0	50.0	57.3	48.8	3.4	4.5	478.2
4	41.7	58.3	52.1	52.5	2.3	5.1	396.9
5	33.3	66.7	43.3	41.0	1.5	5.3	337.5

[a] The intrinsic viscosity of ST-co-MA-HZ used was 0.117
[b] Measured in DMSO at 30°C
[c] Found by elemental analysis

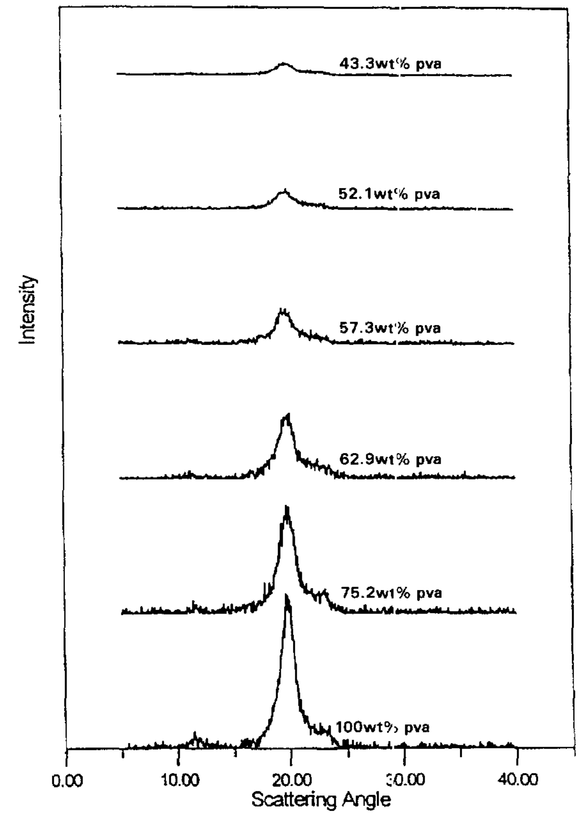


Figure 2 Effect of the content of PVA in PVA-g-ST/MA-Hz on integral of X-ray peak

Figure 1 shows the i.r. spectra of ST-co-MA-Hz (II), PVA and PVA-g-ST/MAHz. (III). The i.r. spectrum of PVA-g-ST/MA-Hz (III) contains the characteristic band of anhydride groups (1856 and 1779 cm^{-1}) and carbonyl groups (1719 cm^{-1}) of the grafted ST-co-MA-Hz (II) side chain.

Heat treatment of graft terpolymer

The mechanical strength of the PVA-g-ST/MA-Hz (IIIa) membrane is too weak to use in this study. In order to enhance the mechanical strength, all the membranes with different compositions were treated by heating at 100°C for 20 min to form a cross-linking network structure such PVA-g-ST/MA-Hz (IIIb), which is a result of the interchain ester linkage during the heat treatment. Similar ester linkages involving polyacid and PVA have been reported in the literature[3,8,12,13]. The differences of tensile strength and elongation at break before and after heat treatment are shown in *Figures 4 and 5*.

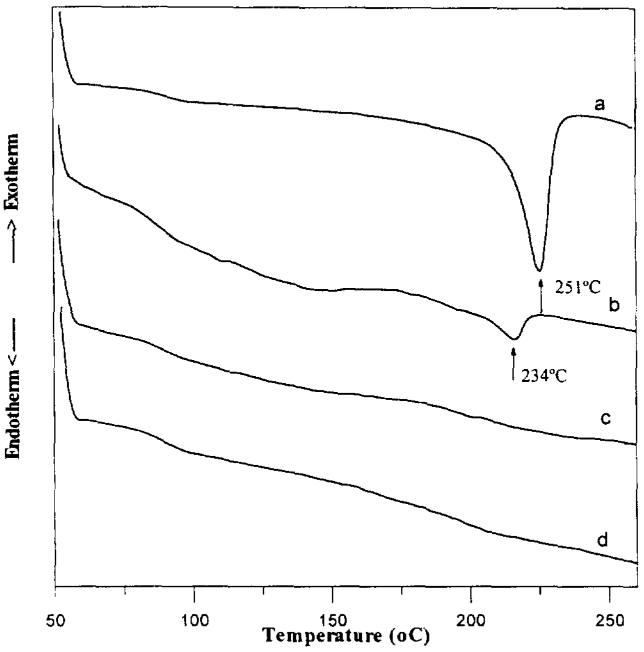
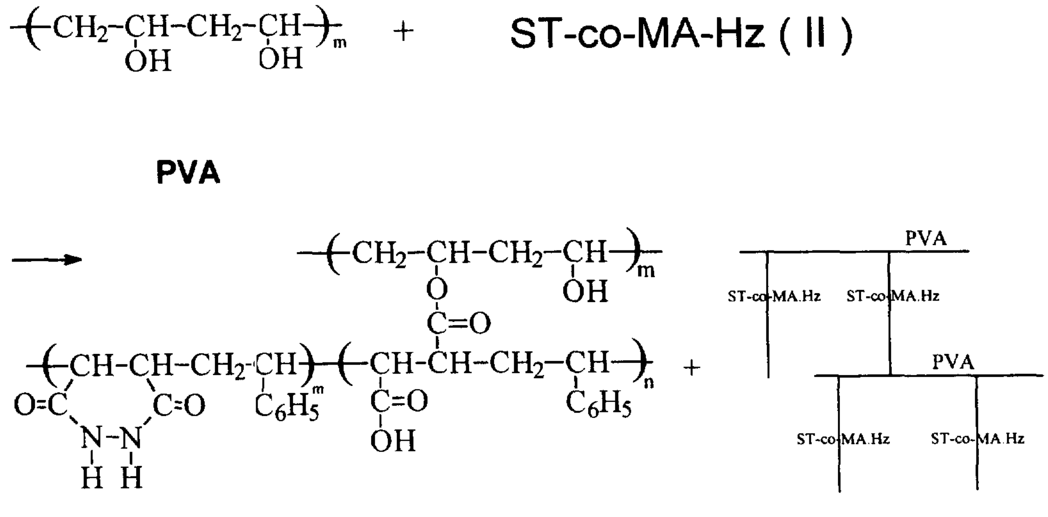


Figure 3 DSC thermogram of PVA (a), PVA-g-ST/MA-Hz (b), ST-co-MA-Hz (c) and St-co-MA (d)

Water–alcohol pervaporation

The relationships between the swelling ratio in water–alcohol mixtures at 30°C and the composition of graft terpolymer membranes are shown in *Figure 6*. Water causes swelling of the membranes to a far greater degree than alcohol. Moreover, the swelling ratio increases monotonically with the increase in the PVA level in the membrane because of the increase of hydrophilicity. As the water concentration increases, so does the swelling ratio. It should be noted that the membranes in the water–ethanol system have a larger swelling ratio than in the water–methanol system. It is well known that the degree of swelling of the polymer membrane by water–alcohol mixture increases



PVA-g-ST/MA-Hz (IIIa)

PVA-g-ST/MA-Hz (III$_b$)

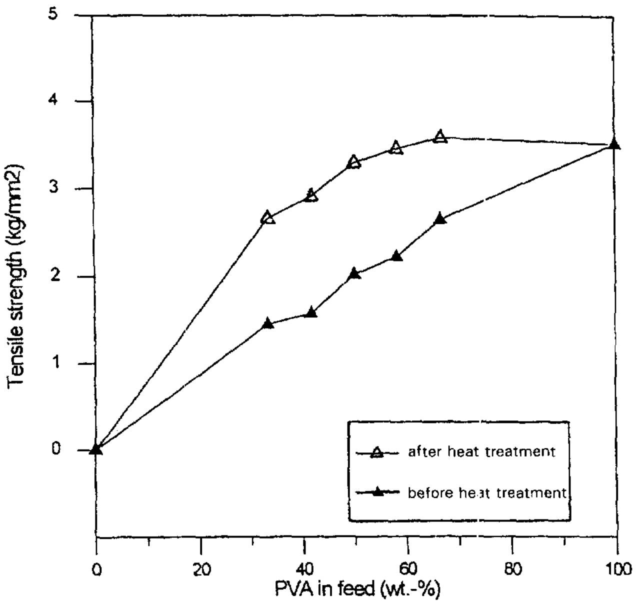


Figure 4 Effect of the content of PVA in feed on the tensile strength of PVA-g-ST/MA-Hz

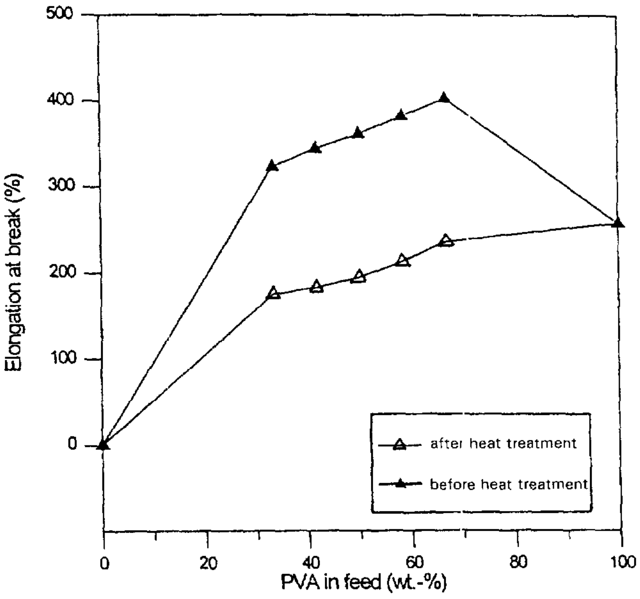


Figure 5 Effect of the content of PVA in feed on the elongation at break of PVA-g-ST/MA-Hz

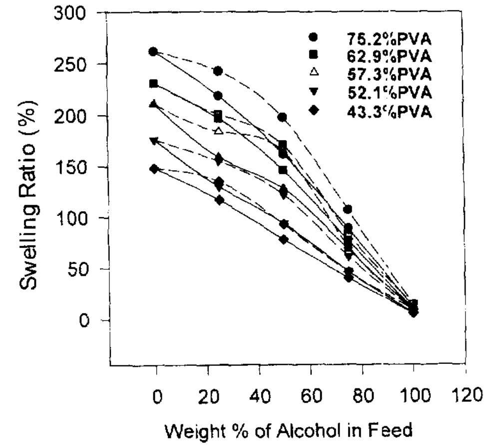


Figure 6 Dependence of swelling degree on the PVA feed wt% in water–alcohol mixture at 30°C. Water–methanol system (—); water–ethanol system (· · ·)

with the increase of the number of carbons in alcohol mixtures[14].

Figures 7 and 8 show that the separation factor and permeation flux of water are related to the PVA feed wt% and composition of feed mixtures at 30°C. The number of a higher hydroxy content shows a higher selectivity of water. Moreover, it has been postulated by several authors[15,16] that if the interaction between water and the polar group of the polymer membrane is too strong, water clusters will be formed to suppress the permeation. Therefore, there is an increase in the separation factor, but a decrease in the permeation flux as the PVA feed wt% increase. In the figures, it is also observed that the separation characteristics of the membrane for a water–methanol blend were worse than that for a water–ethanol mixture.

In our research (*Figures 6, and 8*), there is no certain relationship between the swelling ratio and the permeation flux when the membrane has different degrees of hydrophilicity. However, a high swelling degree always results in a high permeation rate of the membrane with the same composition. The separation factor increases gradually with the increase of the alcohol concentration in the feed.

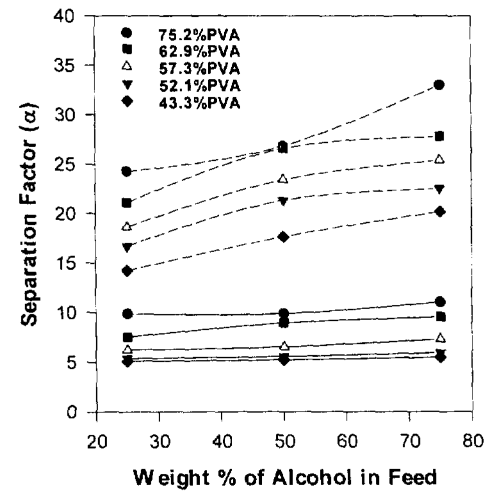


Figure 7 Dependence of separation factor on the PVA wt% and composition of feed mixture at 30°C. Water–methanol system (—); water–ethanol system (· · ·)

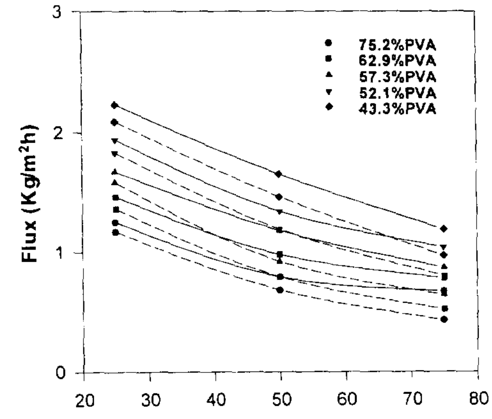


Figure 8 Dependence of permeation flux on the PVA wt% and composition of feed mixture at 30°C. Water–methanol system (—); water–ethanol system (· · ·)

Effect of molecular size and shape of alcohol

Figure 9 shows that the relation between the permselectivity and the size of alcohol molecules with 1–3 carbon atoms was investigated by using 50 wt% alcohol feed mixtures. Huang and coworkers[17,18] has shown that as the molecular weight of compounds in a given homologous series increases, the permeation flux decreases and the separation increases. The results are borne out in *Figure 9*, which shows that the separation factor increases gradually up to 38 with the increase in the number of carbon atoms in alcohol molecules while the permeation rate decreases from 1.18 to 0.61 kg m^{-2} h^{-1}. Isopropanol, with the larger cross-section, can better separate from water–alcohol mixtures than can n-propanol.

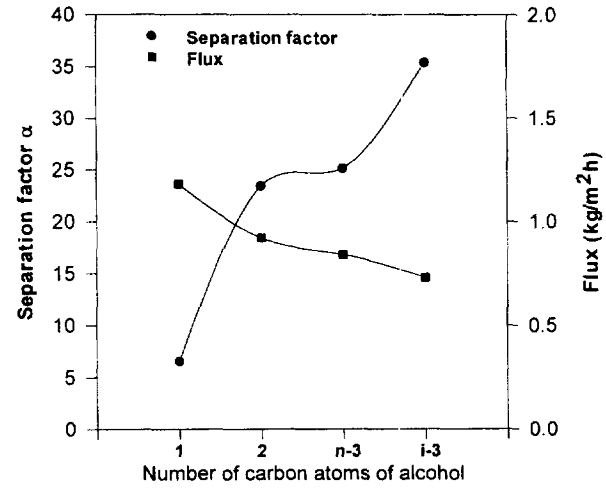


Figure 9 Effect of size and shape of permeation species on the flux and separation factor through membrane number 3 at 30°C (weight fraction of ethanol in feed is 0.5)

CONCLUSION

A condensation-coupling reaction through esterification is performed between the hydroxy groups of PVA and the anhydride groups of ST-co-MA-Hz (II) copolymer to produce the PVA-g-ST/MA-Hz (III) with the anhydride side chain. The above synthesized polymers are water-insoluble, but still have high affinity toward water. In the condensation-coupling through esterification of PVA with ST-co-MA-Hz (II), it was found that an increase in the PVA feed wt% results in an increase in the PVA content. The grafted terpolymers shows a higher water resistance and better mechanical properties than does the PVA after treatment, due to the occurrence of interchain ester linkages.

This graft terpolymer for the separation of water–alcohol mixtures by pervaporation was considered on the basis of the difference in hydrogen-bonding interaction between two components of the membranes. The experimental results show that the modified polymer was water-permselective membrane with selective permeability of water in water–alcohol mixtures.

The permeation properties of this study are compared with another published paper, which is shown in *Table 3*.

Table 3 Pervaporation separation with different membrane in 50 wt% of ethanol–water system (30°C)

Membrane	α	Flux (kg m^{-2} h^{-1})	$\alpha \times$ flux	Reference
PVA-g-ST/MA-HZ(75.2%PVA)	26.83	0.68	18.24	
PVA-g-ST/MA-HZ(62.9%PVA)	26.58	0.79	21.00	
PVA-g-ST/MA-HZ(57.3%PVA)	23.41	0.92	21.54	
PVA-g-ST/MA-HZ(52.1 %PVA)	21.32	1.19	25.37	
PVA-g-ST/MA-HZ(43.3%PVA)	17.62	1.46	25.73	
Chitosan	13.5	2.92	39.42	19
Cellulose	4.33	9.02	39.05	20
PVA/nafion blend	40	0.8	32	21
PVA-G-AA	80	0.4	32	22
PVA-g-MMA/MA	38	0.8	30.4	23
PVA-g-ST/MA	24	0.95	22.5	8
PVA-g-NSMAc/MMA	27	0.65	17.55	4
Neutralized chitosan	450	0.0039	17.55	24
PVA-CD-oligomer	30	0.5	15	25
PVA-g-NSMI/MMA	20	0.32	6.4	4
3-(N,N-dimethyl)amino-propyl acrylamide-cc-AN	528	0.01	5.28	26
Porous PVA	4.5	1.1	4.95	9
PAA/nylon 6	30	0.12	3.6	27
PVA-g-AN	4	0.7	2.8	28
PAN-EA	75	0.03	2.25	29
Poly (AA-co-maleimide)	50	0.04	2	30
1-Bu-4-VPiodide-co-AN	50	0.04	2	31
Poly (AA-co-AN)	50	0.03	1.5	32
ST-co-divinyl benzene	9	0.16	1.44	33
Nylon-g-AA	30	0.04	1.2	34
Poly (4-vinyl pyridine-co-AN)	10	0.02	0.2	35
Poly (AA-co-ST)	15	0.002	0.03	36

ACKNOWLEDGEMENTS

The authors wish to express their appreciation to Dr T. S. Lin, president of Tatung Institute of Technology, for his encouragement and support. Thanks are also due to the National Science Council for financial support under contract number NSC85-2216-E-036-007.

REFERENCES

1. Chiang, W. Y. and Hu, C. M., *Journal of Applied Polymer Science*, 1985, **30**, 3895.
2. Chiang, W. Y. and Hu, C. M., *Journal of Applied Polymer Science*, 1985, **30**, 4045.
3. Chiang, W. Y. and Hu, C. M., *Journal of Appied Polymer Science*, 1988, **36**, 1479.
4. Chiang, W. Y. and Hu, C. M., *Angewandt Makromole Chemistry*, 1989, **165**, 133.
5. Chiang, W. Y. and Hu, C. M., *Journal of Polymer Science, Part A: Polymer Chemistry*, 1990, **28**, 353.
6. Chiang, W. Y. and Hu, C. M., *Journal of Polymer Science, Part A: Polymer Chemistry*, 1990, **28**, 1623.
7. Chiang, W. Y. and Huang, C. C., *Journal of Polymer Science, Part A: Polymer Chemistry*, 1993, **31**, 381.
8. Chiang, W. Y. and Hsiao, C. Y., *Angewandt Makromolecule Chemistry*, 1994, **219**, 169.
9. Chiang, W. Y. and Hu, C. M., *Angewandt Makromolecule Chemistry*, 1990, **179**, 157.
10. Lee, Y. M. and Won, K., *Polymer Journal*, 1990, **22**, 583.
11. Shantora, V. and Huang, R. Y. M., *Journal of Applied Polymer Science*, 1981, **26**, 3223.
12. Reid, C. E. and Spencer, H. G., *Journal of Applied Polymer Science*, 1960, **4**, 354.
13. Gryte, C. C., Chen, J., Kevorkian, V. and Gregor, H. P., *Journal of Applied Polymer Science*, 1979, **23**, 2611.
14. Mitchell, A. G. and Wynne-Jones, W. E. K., *Transactions of the Faraday Society*, 1953, **49**, 161.
15. Aptel, P., Challard, N., Cuny, J. and Neel, J., *Journal of Membrane Science*, 1976, **1**, 271.
16. Yasuda, H. and Stannett, V., *Journal of Polymer Science*, 1962, **57**, 906.
17. Huang, R. Y. M. and Lin, V. J. C., *Journal of Applied Polymer Science*, 1968, **12**, 2615.
18. Huang, R. Y. M. and Jarvis, N. R., *Journal of Applied Polymer Science*, 1970, **14**, 2341.
19. Mochizuki, A., Sato, Y., Ogawara, H. and Yamashita, S., *Journal of Applied Polymer Science*, 1989, **37**, 3375.
20. Mochizuki, A., Sato, Y., Ogawara, H. and Yamashita, S., *Journal of Applied Polymer Science*, 1989, **37**, 3357.
21. Hirotsu, T., Ichimura, K., Mizoguchi, K. and Nakamura, E., *Journal of Applied Polymer Science*, 1988, **36**, 1717.
22. Yamasaki and Mizoguchi, K., *Journal of Applied Polymer Science*, 1994, **51**, 2057.
23. Chiang, W. Y. and Hu, C. M., *Journal of Applied Polymer Science*, 1991, **43**, 2005.
24. Mochizuki, A., Amiya, S., Sato, Y., Ogawara, H. and Yamashita, S., *Journal of Applied Polymer Science*, 1989, **37**, 3385.
25. Sun, M. and Huang, T. L., *Journal of Polymer Research*, 1995, **2**, 47.
26. Yoshikawa, M., Ochiai, S., Tangigaki, M. and Eguchi, W., *Journal of Polymer Science: Polymer Letters Edition*, 1988, **26**, 263.
27. Xu, Y. F. and Huang, R. Y. M., *Journal of Applied Polymer Science*, 1988, **36**, 1123.
28. Chiang, W. Y. and Huang, C. C., *Journal of Applied Polymer Science*, 1993, **48**, 199.
29. Chiang, W. Y. and Hu, C. M., *Journal of Applied Polymer Science*, 1991, **42**, 1829.
30. Yoshikawa, M., Yokoi, H., Sanui, K. and Ogata, N., *Journal of Polymer Science: Polymer Letters Edition*, 1984, **22**, 473.
31. Yoshikawa, M., Yukoshi, T., Sanui, K. and Ogata, N., *Polymer Journal*, 1986, **15**, 447.
32. Yoshikawa, M., Yukoshi, T., Sanui, K. and Ogata, N., *Journal of Polymer Science: Polymer Chemistry Edition*, 1986, **24**, 1585.
33. Ruckenstein, E. and Park, J. S., *Journal of Applied Polymer Science*, 1990, **40**, 213.
34. Huang, R. Y. M. and Xu, Y. F., *European Polymer Journal*, 1988, **24**, 927.
35. Yoshikawa, M., Yukoshi, T., Sanui, K. and Ogata, N., *Journal of Applied Polymer Science*, 1987, **33**, 2369.
36. Yoshikawa, M., Yukoshi, T., Sanui, K. and Ogata, N., *Polymer Journal of Science*, 1984, **11**, 653.