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Dehydration of water–alcohol mixtures by pervaporation and vapor permeation through surface resintering expanded poly(tetrafluoroethylene) membranes

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Abstract

For the purpose of separating aqueous alcohol mixtures by the use of the pervaporation and vapor permeation techniques, a surface resintering expanded poly(tetrafluoroethylene) (e-PTFE), membrane was investigated. The surface properties of the modified e-PTFE membranes were characterized by atomic force microscopy, scanning electron microscopy, and contact angle meter. The X-ray diffraction measurements show that the crystallinity of the e-PTFE membrane decreases with increasing the surface resintering temperature. The surface roughness decreases with the surface resintering temperature increases. The membrane exhibited water selectivity during all process runs. The effects of feed composition, surface resintering temperature, and molar volume of the alcohols on pervaporation and vapor permeation were investigated. Compared with the e-PTFE membrane without surface modified, the e-PTFE membrane with surface resintering treatment effectively improve the separation factor for pervaporation of aqueous alcohol mixtures. The separation performances of e-PTFE membranes in vapor permeation are higher than that in pervaporation.

Keywords: Expanded poly(tetrafluoroethylene); Surface resintering; Pervaporation; Vapor permeation

1. Introduction

Azeotropic mixtures have been industrially separated by means of extractive distillation techniques, which account for a large portion of the cost of alcohol production. Thus, separation by membranes is one of the most promising processes as an energy-efficient technology. Pervaporation with polymeric membranes is considered to be an interesting alternative process for the concentration or dehydration of azeotropic mixture solutions. The earliest work on the separation of azeotropic mixtures by pervaporation technique was developed in the mid-1950s [1,2]. Other applications include the separation of isomeric mixtures close-boiling components, heat-sensitive mixtures, removal of water from the esterification reaction and the elimination of impurity traces. Basically, the efficiency of the pervaporation process depends mainly on the intrinsic properties of the polymers used to prepare membrane. Thus, to make a careful choice in an appropriate material for pervaporation is exceedingly important. Poly(tetrafluoroethylene) (PTFE) is a potential film material because of its attractive combination of chemical, physical, and thermal resistant. Because of its high melting point and difficult to dissolve in organic solvents, therefore, sintering is a very suitable technique for preparing films

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from PTFE. Stretching under high temperature then sintering is one of the technique allowing porous membrane to be obtained from organic materials. However, only microfiltration membranes can be prepared via sintering. The membranes porosity is too high to obtain a highly selectivity for the membranes prepared via stretching methods. Many researchers have focused their attention on improving the PTFE membrane separation performance by using ^{60}Co γ-ray irradiation [3–5]. Tealdo et al. studied the permeability and selectivity of styrene-grafted and sulphonated PTFE membranes toward binary mixtures of water and ethanol [3]. Aptel et al. studied the liquid transport through membranes prepared by ^{60}Co γ-ray irradiation grafting of polar monomers onto PTFE films [4,5]. The radiation induced grafting of acrylic acid onto PTFE films by the pre-irradiation method was reported by Hegazy et al. [6]. Hoffmann et al. investigated the evaporation of alcohol/water mixtures through porous PTFE membrane [7]. Nevertheless, to our knowledge there are few reports on investigating the effect of surface resintering on the surface morphology, pervaporation and vapor permeation performance of expanded poly(tetrafluoroethylene) (e-PTFE) membranes. The purpose of this work is to study the relationship between the surface roughness and the pervaporation and vapor permeation performance of e-PTFE membranes. The effect of heat treatment conditions on the surface morphology were studied by scanning electron microscopy, atomic force microscopy (AFM), and water contact angle measurements. In addition, the effects of feed composition, the molar volume of alcohols, and the surface resintering temperature on the pervaporation and vapor permeation performances of the modified e-PTFE membranes were investigated.

2. Experimental

2.1. Materials

The starting PTFE fine powder (Teflon 65N) with a number average molecular weight ($M_n = 3 \times 10^6$–6×10^6) provided by DuPont, Netherlands. The e-PTFE membranes were purchased from Yeu Ming Tai Co. Ltd., Taiwan. It was produced from the above PTFE fine powder via well-known industrial processes [8,9]. The surface of e-PTFE membrane was then resintering at 260–340°C for 2 min. Methanol, ethanol, *n*-propanol, *t*-butanol and all chemicals were of reagent grade.

2.2. Characterization

Differential scanning calorimetry (DSC) analysis was performed on a Perkin–Elmer DSC-7 differential scanning calorimeter in the flowing nitrogen (60 cm^3/min) at a heating rate of 20°C/min. X-ray diffractograms were recorded with an X-ray diffractometer (Philips Model PW 1710). The membrane surface structures were examined by a Hitachi (Model S570) SEM and an AFM (Digital Instrument, DI 5000) in the tapping mode.

2.3. Pervaporation and vapor permeation measurement

Pervaporation and vapor permeation experiments were performed with an apparatus described previously [10]. In pervaporation, the feed solution is in direct contact with the membrane, whereas in vapor permeation only vapor is supplied to the membrane. The effective area was 10.2 cm^2. The permeation rate was determined by measuring the weight of permeate. The compositions of the feed solution and the permeates were measured by gas chromatography (G.C. China Chromatography 8700 T). The separation factor was calculated from the following equation:

$$\alpha_{A/B} = (Y_A/Y_B)/(X_A/X_B)$$

In pervaporation, X_A and X_B and Y_A and Y_B are the weight fractions of water and alcohol in the feed and permeate, respectively. In vapor permeation, X_A and X_B are the weight fractions of water and alcohol vapors in the feed (A being the more permeative species), and Y_A and Y_B are the weight fractions of the water and alcohol in the permeate.

2.4. Contact angle measurements

The contact angle of water was measured with a face contact angle meter CA-D type (Kyowa Interface Science Co. Ltd.). The contact angle was calculated by the following condition:

$$\text{Contact angle} = 2\tan^{-1}(h/r)$$

where h is the height of the spherical segment and r is the radial of the spherical segment.

3. Results and discussion

3.1. Surface modification of e-PTFE membrane via surface resintering treatment

Surface modification of membranes via heat treatment has been widely used because a higher temperature clearly softens PTFE leading to a smaller specific surface area with a less fine porous structure. For the study of the differently modified e-PTFE membrane surfaces, we used SEM and AFM measuring the membrane surface

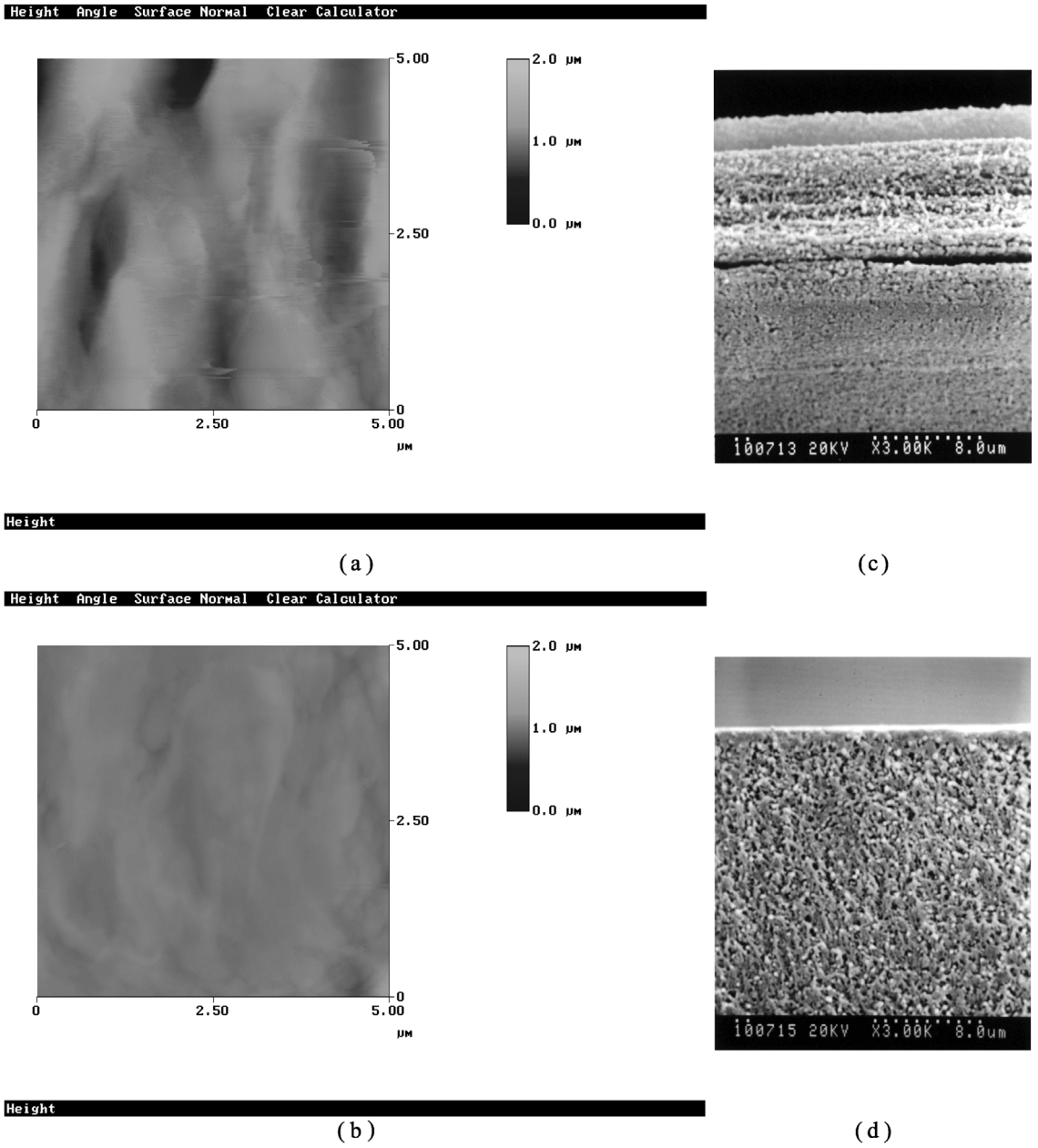

Fig. 1. The effect of surface resintering temperature on the membrane morphology (a,c) surface resintering e-PTFE membrane at 260°C; (b,d) surface resintering e-PTFE membrane at 340°C; (a,b) 2-D image AFM images (c,d) cross-section view SEM photographs.

morphology. The effect of surface resintering temperature on the membrane morphology is shown in Fig. 1. It shows that the structure of the membrane cross-section in Fig. 1(d), i.e., prepared by surface resintering at 340°C, was dense in comparison with that in Fig. 1(c), i.e., prepared by surface resintering at 260°C. In addition, compared with the AFM 2-D image of the e-PTFE membrane with 260°C surface resintering in Fig. 1(a), the 340°C surface resintering e-PTFE membrane becomes denser and smoother in Fig. 1(b). Furthermore, it is known that the heat treatment temperature can influence the polymer physical properties and can therefore be used to control the pervaporation and vapor permeation performances. In our previous work, the temperature of crystal fusion for the surface resintering skiving PTFE (s-PTFE) membrane increases as the

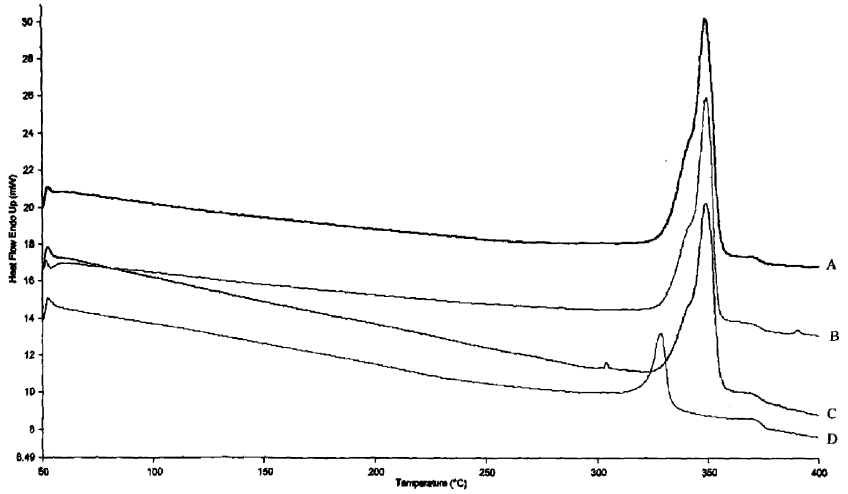

Fig. 2. DSC curves of the e-PTFE membrane: (A) unmodified, (B) 260°C resintering, (C) 300°C resintering, (D) 340°C resintering.

Table 1
Effect of surface resintering temperature on the heat of crystal fusion of e-PTFE membrane

Surface resintering temperature (°C)	Heat of crystal fusion (J/g)
Unmodified	46.2
260	72.7
300	61.2
340	26.2

surface resintering temperature increases. However, an opposite trend was observed in this article. The DSC analysis curves for the surface resintering e-PTFE membrane heated at 20°C/min in nitrogen is shown in Fig. 2. It shows that the temperature of crystal fusion for the surface resintering e-PTFE membrane decreases as the surface resintering temperature increases from 260°C to 340°C. The heat of crystal fusion for the surface resintering and unmodified s-PTFE membranes are shown in Table 1. The heat of crystal fusion decreases with the surface sintering temperature increases. This implies that the crystallinity of the e-PTFE membrane decreases with increasing the surface resintering temperature. To investigate the effect of the surface resintering temperature on the structure transition of the e-PTFE membrane, X-ray diffraction studies were made and are shown in Fig. 3. This phenomenon might be due to the fact that the orientation of polymer chains during the uniaxial expanded procedure results the high crystallinity. Nevertheless, the higher resintering temperature clearly softens the e-PTFE leading to a polymer chain contraction resulting in a relaxation structure of the e-PTFE membrane.

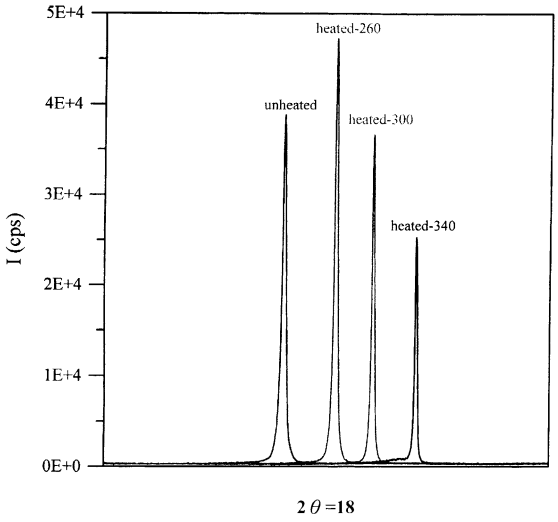

Fig. 3. X-ray diffraction patterns of the e-PTFE membranes: (a) unmodified, (b) 260°C resintering, (c) 300°C resintering, (d) 340°C resintering.

3.2. Influence of the surface modification condition on the pervaporation and vapor permeation performance

The effect of surface resintering temperature on the pervaporation and vapor permeation performance of 90 wt.% aqueous ethanol solutions through the e-PTFE membranes are shown in Table 2. Total permeation rate decreases and separation factor increases with increasing surface resintering temperature. These results can be explained from the viewpoint of the surface density and the surface roughness of the e-PTFE membrane. Firstly,

Table 2
Effect of surface resintering temperature on the pervaporation and vapor permeation performance of 90 wt.% aqueous ethanol solutions through e-PTFE membranes

Surface resintering temperature (°C)	Vapor permeation		Pervaporation	
	Permeation rate (g/m^2 h)	H_2O in permeate (wt.%)	Permeation rate (g/m^2 h)	H_2O in permeate (wt.%)
Unmodified	2047	40	1580	37
260	1115	43	841	40
300	983	74	547	68
340	417	99	282	93

for the reduction in free volume of membrane accompanying the shrinkage that takes place during the surface modification, heat treatment temperature is probably partially responsible. Thus, the surface density of the e-PTFE membrane decreases with the surface resintering temperature increases, resulting in the vapor permeation rate decreases. The results from the SEM and AFM photographs (Fig. 1) corresponds well with the above mentioned observation (Table 2). According to the SEM and AFM analyses discussed above, it is known that, when the surface resintering temperature increases, the membrane surface becomes denser and smoother (roughness decreases). Therefore, it is reasonable to expect that the vapor permeation and pervaporation performances would be influenced by the resintering temperature. Secondly, in order to further evaluate the effect of surface resintering temperature on the surface roughness of the e-PTFE membranes, an AFM was used to examine the membrane surface structure. The values of surface roughness and AFM photographs are shown in Table 3 and Figs. 4 and 5, respectively. It can be seen that the membrane surface roughness for the surface resintering e-PTFE membranes are different, which might be responsible for the difference in the pervaporation and vapor permeation performances presented in Table 2. It shows that the surface roughness of the e-PTFE membrane decreased with the surface resintering temperature increased. As a result, the effective pervaporation and vapor permeation membrane area decreases with decreasing the membrane roughness. These results agree well with the results mentioned above, as indicated in Table 2. In addition, the product of total permeation rate and separation factor has been defined as the pervaporation separation index (PSI), which is a measure of the separation ability of the membrane. Table 4 shows the effect of the surface resintering temperature on the PSI value for the 90 wt.% aqueous ethanol solution through the e-PTFE membranes. The optimum vapor permeation results were obtained by the e-PTFE membrane with 340°C surface resintering treatment, giving a separation factor of 891, permeation rate 417 g/m^2 h, and 37.1×10^4 PSI value. In addition, Table 2 also shows that the permeation rate of vapor permeation is higher than that of the pervaporation. These phenomena might be due to the fact that the ethanol concentration in the vapor phase is higher than that of the liquid phase at the vapor–liquid equilibrium. The experimental of vapor permeation was carried out by using the same apparatus as pervaporation, except that the feed solution is not in contact with the membrane. The feed solution was vaporized first and then permeated through the membrane. Thus, the plasticizing effect of ethanol results the permeation rate of vapor permeation higher than that of the pervaporation.

Table 3
Effect of surface resintering temperature on the surface roughness of e-PTFE membrane

Surface resintering temperature (°C)	R_a	R_{MS}
Unmodified	9.5	12.1
260	125.5	161.1
300	56.2	71.6
340	28.9	37.1

R_a: average plane roughness; R_{MS}: square mean plane roughness.

3.3. Pervaporation and vapor permeation properties of the e-PTFE membrane for different aqueous alcohol mixtures

The dependence of both the permeation rate and the separation factor on the molecular size of the permeating species for the 340°C surface resintering e-PTFE membranes are shown in Table 5. It is observed that an increase of the number of carbon atoms in alcohol molecule results in an increase of the separation factor but a decrease of the permeation rate. These phenomena can be explained by the molecular size of the alcohol. The molecular length of methanol, ethanol, and *n*-propanol are 2.9, 4.2, and 5.4 respectively. The separation factor was found to depend on the molecular length for the linear alcohol system, and it was also found that the permeation rate increased as the molecular length decreased. In addition, the interaction between permeants and polymer membranes can be used to further explain the above phenomena. The contact angle and the difference in the solubility parameters between the polymer membrane and alcohol for different alcohols are

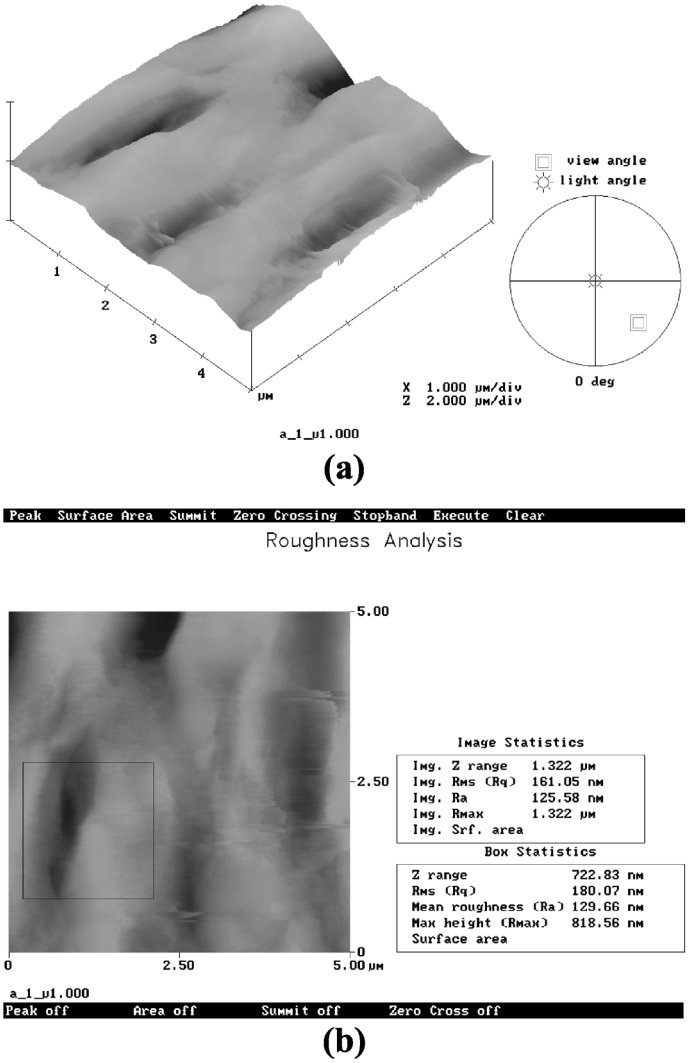

Fig. 4. AFM images of the surface of the s-PTFE (260°C resintering) membrane: (a) 3-D image, (b) 2-D image.

summarized in Table 6. The difference in solubility parameters between the polymer membrane and alcohols follows the order of methanol > ethanol > *n*-propanol. That is, the larger-size alcohol has higher affinity for the membrane than the smaller-size alcohol. Thus, the contact angle of the former is lower than that of the latter. Consequently, the solubility of alcohols for the surface resintering e-PTFE membrane is higher than that of water, but the diffusivity of water across the membrane is much higher than that of the alcohols.

3.4. Effect of feed composition on the vapor permeation performance

Fig. 6 shows the influence of the feed ethanol concentration on the permeation rate and the separation factor for the 340°C surface resintering e-PTFE membrane. The permeation rate decreases with increasing ethanol concentration. The affinity between the permeates and the surface resintering e-PTFE membrane can illustrate the above phenomenon. The difference of solubility parameter between the alcohol and the surface resintering e-PTFE membrane ($\delta_{\text{s-PTFE}} - \delta_{\text{EtOH}} = 7.3$ $(\text{cal/cm}^3)^{1/2}$) is lower than that of the water and the surface resintering e-PTFE membrane ($\delta_{\text{s-PTFE}} - \delta_{\text{H}_2\text{O}} =$ 16.1 $(\text{cal/cm}^3)^{1/2}$). That is, the interaction between the ethanol and the surface resintering e-PTFE membrane is higher than that of the water. Once the ethanol molecules are incorporated into the surface resintering e-PTFE membrane, they are difficult to diffuse through the membrane. Thus, lower water content of the higher feed ethanol concentration results in a decreasing per-

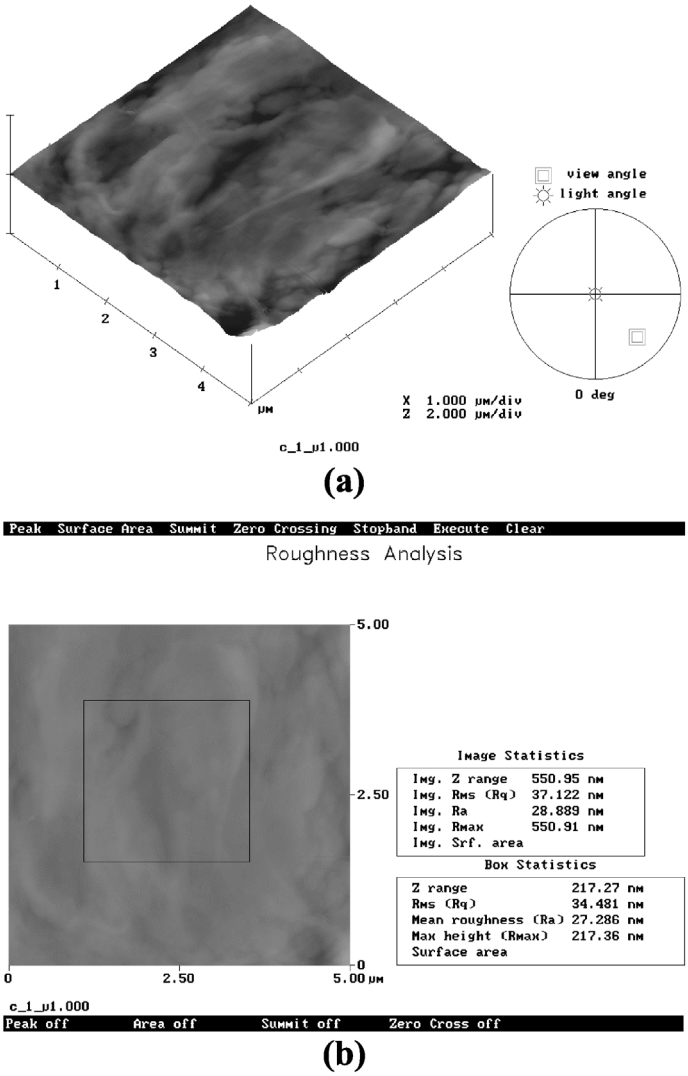

Fig. 5. AFM images of the surface of the s-PTFE (340°C resintering) membrane: (a) 3-D image, (b) 2-D image.

meation rate. Moreover, compared with the pervaporation, vapor permeation effectively increases the permeation rate. These phenomena might be due to the fact that the ethanol concentration in the vapor phase is higher than that of the liquid phase at the vapor–liquid equilibrium. The plasticizing effect of ethanol results the permeation rate of vapor permeation higher than that of the pervaporation.

Table 4
Effect of the surface resintering temperature on the PSI value for the 90 wt.% aqueous ethanol solution through the e-PTFE membranes

Surface resintering temperature (°C)	PSI × 10^4
Unmodified	1.2
260	0.8
300	2.5
340	37.1

4. Conclusion

The membranes porosity is too high to obtain a highly selectivity for the membranes prepared via stretching methods. Thus, surface modification of membranes via heat treatment has been used in this article. The crystallinity of the e-PTFE membrane decreases with increasing the surface resintering temperature. The optimum vapor permeation results were obtained by the

Table 5
Effect of feed alcohol solutions on pervaporation and vapor permeation performances through the 340°C surface resintering e-PTFE membranes

Feed mixtures	Vapor permeation		Pervaporation	
	Permeation rate (g/m^2 h)	Separation factor	Permeation rate (g/m^2 h)	Separation factor
Methanol	534	367	421	103
Ethanol	417	891	282	119
n-propanol	344	–[a]	166	683

[a] 100 wt.% H_2O in the permeate.

Table 6
Contact angle and the solubility parameter difference between the 340°C surface resintering e-PTFE membrane and alcohols

Permeating molecule	Contact angle	δ (cal/cm^3)$^{1/2}$	$\delta_{\text{e-PTFE}} - \delta_{\text{alcohol}}$
Water	104	23.4	16.1
Methanol	51	14.5	7.2
Ethanol	41	12.7	5.4
n-propanol	35	11.9	4.6

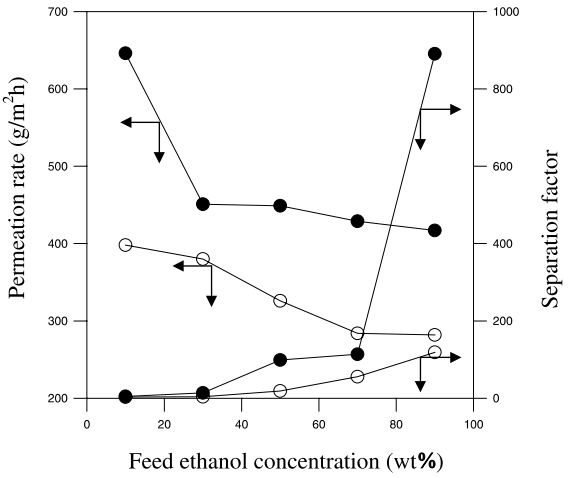

Fig. 6. Influence of the feed ethanol concentration on the permeation rate and the separation factor for the 340°C surface resintering e-PTFE membrane. (●) vapor permeation; (○) pervaporation.

e-PTFE membrane with 340°C surface resintering treatment, giving a separation factor of 891, permeation rate 417 g/m^2 h, and 37.1×10^4 PSI value. It was found that both the interaction between permeant and membrane and the plasticizing effect of permeant on membrane could significantly alter the permeation and separation properties of the prepared membranes. The plasticizing effect of ethanol results the permeation rate of vapor permeation higher than that of the pervaporation.

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