

Influence of Post-treatments on the Properties of Porous Poly(vinyl alcohol) Membranes

Yan-Li Wang, Hu Yang, Zhen-Liang Xu

Chemical Engineering Research Center, East China University of Science and Technology, China 200237

Received 6 April 2006; accepted 15 May 2006

DOI 10.1002/app.24712

Published online 12 October 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Porous poly(vinyl alcohol) (PVA) membranes were prepared by a phase-inversion method. The influence of chemical crosslinking and heat treatments on the swelling degree, resistance to compaction, mechanical strength, and morphology of porous PVA membranes was extensively studied. The crosslinking degree and crystallinity of the membranes, calculated from IR spectra, increased with the treatment time. The porosity, calculated on the basis of swelling experiments, showed a decreasing trend for heat-treated membranes but remained almost at a constant value for crosslinked membranes. Such a change was further proved with scanning electron microscopy pictures. The behavior was explained by the rearrangement of PVA chains during the heat-treatment process, which led to morphological

changes in the membranes. The mechanical properties of the porous membranes in dry and wet states were measured, and a great difference was observed between crosslinked and heat-treated membranes in the dry and wet states. The cross-linked membranes showed good mechanical properties in the dry state but became fragile in the wet state. On the contrary, the heat-treated membranes were more flexible in the wet state than in the dry state. This change was explained by the turnaround of inner stress in the systems during the swelling process. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1423–1429, 2008

Key words: mechanical properties; membranes; morphology; poly(vinyl ethers)

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a nontoxic, water-soluble, synthetic polymer. Its low protein adsorption makes it widely used as a coating for ultrafiltration (UF) and microfiltration (MF) membranes^{1,2} because it can reduce fouling phenomena. In the past few years, some researchers have prepared porous membranes directly with a PVA matrix. Mostly, PVA hydrogels have been used as UF membranes,^{3–5} and more recently, the phase-inversion method has been applied to prepare PVA membranes with a porous structure.⁶ Because PVA is soluble in water, the stability of its porous structure is a big problem or challenge. Furthermore, for applications, a stable structure and good mechanical properties in water are basic requirements for membranes used in aqueous systems. Crosslinking and heat treatments are two posttreatment methods used to improve the water-proofing and mechanical properties of PVA films. In principle, a crosslinking reaction can use chemical crosslinking agents such as aldehyde,⁷ carbonyl groups,⁸ electron beams,⁹ γ irradiation,¹⁰ and ultra-

violet irradiation.¹¹ Yu et al.¹² summarized the most popular chemical crosslinking reagents (Table I). Heat treatments^{13,14} are used to increase the crystallinity of PVA, which acts as physical crosslinking in a system.

The influence of posttreatments on dense PVA films has been extensively studied in the literature, which provides much information that should be helpful for the same treatment with porous PVA membranes. Surely some new differences will emerge as well, including possible changes in the structure/morphology and mechanical properties of porous PVA. It is believable that the morphology of porous PVA membranes may change because of chain movement during the post-treatment. From the point of view of process control, it is necessary to understand the structural changes of membranes during the posttreatment, which may help to control the structure of the final product membrane because the separation properties are tightly related to the morphology of the membrane.

In this study, porous PVA membranes prepared by the phase-inversion method were treated by chemical crosslinking with glutaraldehyde and heating. Their properties were extensively studied with permeation, scanning electron microscopy (SEM), IR, and mechanical measurements. The different behaviors of the membranes caused by the posttreatments were explained.

Correspondence to: H. Yang (yang_hu@etang.com).

Contract grant sponsor: National Fund for the 973 Project; contract grant number: 2003CB615705.

TABLE I
Chemical-Crosslinking Reagents Used
for PVA in the Literature^{12,17}

Polymer	Crosslinking reagent
PVA	Poly(acrylic acid)
PVA	Glutaraldehyde, acetone, and HCl
PVA	Citric acid and maleic acid
PVA <i>N</i> -methylol nylon 6	Formic acid
PVA	Amic acid
Carboxymethylated PVA	Glutaraldehyde
PVA	Sulfur-succinic acid
PVA	Formaldehyde, glutaraldehyde, and HCl

EXPERIMENTAL

Materials

All reagents used in the experiments were reagent-grade unless otherwise noted. PVA (polymerization degree = 1750, saponification degree = 99%) and poly(ethylene glycol) (PEG; molecular weight = 10,000) were purchased from Shanghai Chemical Reagent Co. (Shanghai, China). Glutaraldehyde (25% aqueous solution), sodium sulfate, sulfuric acid, and other agents were from Shanghai Lianqiao Chemical Co. (Shanghai, China). Water was double-distilled and deionized before use.

Membrane preparation

Porous PVA membranes were prepared by the phase-inversion technique, which has been described widely in the literature. In brief, an aqueous solution containing 10 wt % PVA and 0.5 wt % PEG was prepared as the casting solution. After being kept at 50°C for 12 h to remove air bubbles, the solution was cast onto a glass plate at 20°C with a glass tube wrapped with wire at the two ends. The nascent membrane was immersed immediately into the coagulation bath to form an asymmetric structure; here acetone was used as a coagulant. After coagulation for 30 min, the membrane was ready for the post-treatment. The following procedure was adopted to get a quick-drying membrane: the membrane was placed in acetone to replace the solvent and then dried in a vacuum oven at 25°C for 1 h. The thickness of the membranes was about 100 μm .

Posttreatment

For the chemical-crosslinking process, a saturated sodium sulfate solution (27.5%, 1 g/100 g) mass ratio percent was used in place of water to weaken the swelling of the PVA membranes and to prevent the deformation of their pore structure. Glutaraldehyde and sulfuric acid were used as the crosslinking agent

and catalyst, respectively. The solution was prepared by their dissolution in a saturated sodium sulfate solution, and their concentrations were 3 and 5 wt %, respectively. PVA membranes were immersed into the crosslinking solution at 25°C for different times, washed with deionized water, and dried with acetone. Finally, crosslinked PVA membranes were dried in a vacuum oven at 25°C and kept in a desiccator before use. For the heat-treatment process, dry PVA membranes were kept in an oven at 120°C for different times. Moreover, before and after the posttreatment, no obvious size change in the membranes was found.

Swelling experiments

Circular membranes were dried in an oven at 50°C for 24 h to achieve a constant weight. Their weight and size were recorded with an electronic balance and ruler, respectively. Dry membranes were put in deionized water and kept there for 24 h to reach the swelling balance. Filter paper was used to blot surface water before the wet membranes were weighed. The swelling degree was calculated with the size change and weight change:

$$\text{Dimensional swelling degree} = \frac{d_1 - d_0}{d_0} \times 100\% \quad (1)$$

$$\text{Weight swelling degree} = \frac{w_1 - w_0}{w_0} \times 100\% \quad (2)$$

where subscript 1 represents the wet state, subscript 0 represents the dry state, d is the diameter of the membrane, and w is the weight of the membrane.

Permeation experiments

A cross flow UF apparatus was used to carry out permeation experiments. The effective membrane surface was 28.26 cm^2 , and the operating pressure was 0.2 MPa. Membranes were prepressed under 0.3 MPa for 1 h before the measurements.

IR spectra

The IR spectra of the membranes were recorded with a Nicolet 5DX Fourier transform infrared spectrometer (Waltham, MA) in the range of 400–4000 cm^{-1} , and attenuated total reflection was used. The spectra were obtained through the averaging of 32 scans at a 2- cm^{-1} resolution.

SEM

The morphology of the membranes was measured with SEM (JSM-5600LV, JEOL, Japan, Tokyo). The membrane specimens were frozen in liquid nitrogen,

TABLE II
Posttreated PVA Membrane Samples and Their Relative Crosslinking Degree, Crystallinity, and Porosity Data

Sample	Posttreatment method	Treatment time	H_{3310}/H_{2920}	Crystallinity (%)	Porosity
M-C1	Crosslinking	5 min	2.36	—	0.65
M-C2	Crosslinking	15 min	2.27	—	0.61
M-C3	Crosslinking	30 min	2.26	—	0.65
M-H1	Heat treatment	1 h	—	18.7	0.48
M-H2	Heat treatment	2 h	—	27.9	0.42
M-H3	Heat treatment	3 h	—	48.9	0.39

broken to obtain cross sections, and coated with gold for SEM observations. The SEM photographs were observed at 10 kV.

Mechanical measurements

The tensile behavior of the PVA membranes was determined with an Instron 5567 at a strain rate of 5 mm/min. The tensile strength was calculated by the division of the force at break across the cross-sectional area of the specimens. For wet specimens, membranes were immersed in water for 30 min, and then the water was wiped off with filter paper.

RESULTS AND DISCUSSION

Degree of crosslinking and crystallinity

A list of the posttreated PVA membranes and their properties and preparation conditions are shown in Table II. Half were prepared by chemical crosslinking, and half were prepared by a heat treatment.

The related crosslinking degree and crystallinity of the membranes, calculated from IR spectra (see Fig. 1), are shown in Table II as well. In the literature, IR spectra are used to characterize the crosslinking degree^{15,16} and

crystallinity of PVA,^{17,18} the absorbance ratio of a functional group to a reference peak is calculated to quantitatively or half-quantitatively analyze structural changes of PVA. Briefly, in the spectra of PVA, the C—H stretching vibration at 2920 cm^{-1} is taken as the reference peak, and the hydroxyl group at 3310 cm^{-1} is taken as the functional group. During the chemical-crosslinking process, the number of hydroxyl groups decreases, whereas the number of C—H groups increases, so the change in the peak height ratio of two peaks at 3310 cm^{-1} and 2920 cm^{-1} (H_{3310}/H_{2920}) reflects the different crosslinking degrees of PVA.

For crystallized PVA, the peak at 1141 cm^{-1} is crystallinity-sensitive, whereas the peak at 1425 cm^{-1} is quite stable, so the height of these two peaks (h_{1425} and h_{1141}) can be used to calculate the crystallinity (X) of PVA:¹⁷

$$X(\%) = a \times \frac{h_{1425}}{h_{1141}} - b \quad (3)$$

where $a = 102.6$ and $b = 63.6$ are constants.

In Figure 1, no peak at 1140 cm^{-1} is present for crosslinked membranes, and this means that they are almost amorphous. The results calculated from the IR spectra are in Table II. With the crosslinking

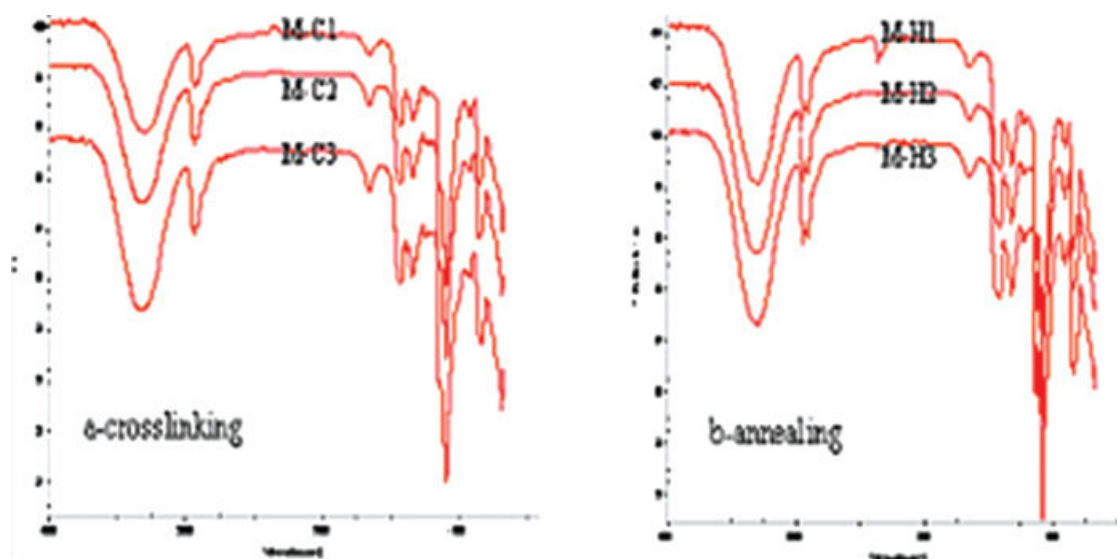


Figure 1 IR spectra of porous PVA membranes with different treatments. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

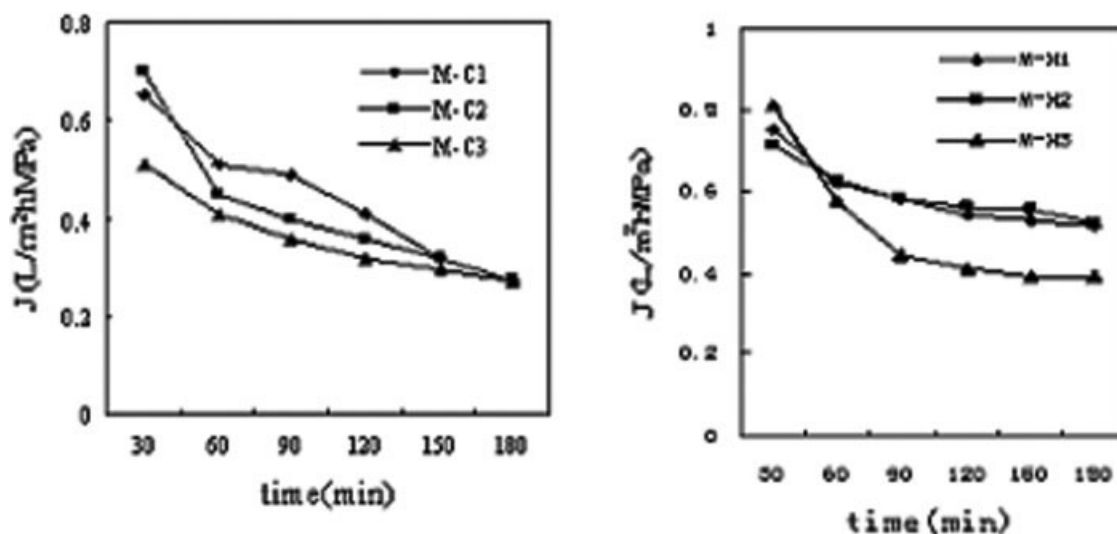


Figure 2 Water flux (J) of PVA membranes at 25°C and 0.2 MPa: (a) crosslinked membranes and (b) heat-treated membranes.

time increasing, the peak height ratio decreases, whereas at a longer crosslinking time, the ratio changes little beyond the testing error (ca. 1%). This means that it is not easy to precisely determine a higher crosslinking degree of a porous PVA membrane with IR spectra. The reason may be that water molecules in air influence the peak intensity of 3310 cm^{-1} during the measurement, whereas the porous structure of the PVA membrane shows a higher affinity to water molecules than a dense film. For heat-treated PVA membranes, the crystallinity increases with the treatment time. This means that PVA chains are rearranged to form a crystal region during the heat treatment. All this is in agreement with the results obtained for PVA films.

Pure water permeation

The pure water fluxes of porous PVA membranes are shown in Figure 2. Basically, these membranes are asymmetric UF membranes, and their molecular weight cutoff is less than 680,000 Da. In Figure 2, a similar trend can be observed for all membranes: the water flux decreases with time. Especially for crosslinked membranes, the curves show no sign of stopping at the testing time. Decreases in the water permeation flux are often observed in water UF by UF/MF membranes for various reasons: changes in the surface tension of the membrane pores, fouling by colloidal matter, and changes in the membrane morphological structure. In our case, pure deionized water was used, and PVA is a highly hydrophilic polymer, so the main reason for such a change should be morphological changes in the membranes. This can be explained as follows: during a water permeation experiment, water molecules will swell a

PVA membrane and thus weaken its mechanical properties; at the same time, the membrane has to endure the transmembrane pressure. These two factors play together and lead to the deformation of the membrane. Such a change is virtually irreversible; repeating the experiment with the same membrane will cause a very low water flux.

According to Figure 2, the results show that heat-treated membranes have better anticompaction properties than crosslinked membranes. The reason should be as follows. For crosslinked membranes, chains are connected by glutaraldehyde through acetal bands at crosslinking points, and these points are not strong enough to act as supporters to resist the transmembrane pressure. For heat-treated membranes, the crystal regions act as supporters. They have a better anticompaction effect than crosslinking points, as shown in Figure 3. After the water permeation experiments, virtually all the membranes had shrunk. For cross-

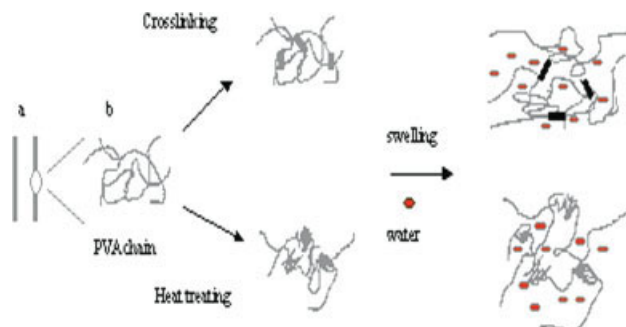


Figure 3 Schematic illustration of the structural changes of PVA chains in membranes through chemical-crosslinking and heat-treatment methods and the swelling process in water: (a) membrane channel and (b) membrane wall. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

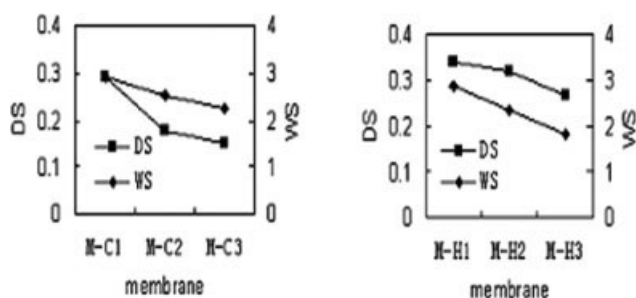


Figure 4 Dimensional swelling degree (DS) and weight swelling degree (WS) of porous PVA membranes.

linked membranes, the shrinkage was about 10%, and for heat-treated membranes, it was 9%.

Swelling degree and porosity

The dimensional swelling degree and weight swelling degree of PVA membranes are shown in Fig-

ure 4. The swelling degree of all membranes decreases with an increasing crosslinking degree or crystallinity. This phenomenon can be explained by the physical or chemical crosslinking function, which changes the swelling behavior of PVA chains.

The membrane porosity was further calculated from the swelling degree, which is listed in Table II. If the volume occupied by PVA chains in a porous membrane is assumed to be constant, the density change caused by the treatment can be neglected. The density is set at 1.26 g/cm³ for amorphous PVA, and it is 1.30 g/cm³ for crystallized PVA. Table II shows that for crosslinked membranes, the porosity almost remains constant at different treatment times, whereas for heat-treated membranes, the porosity decreases with the treatment times. The change in the porosity means that the micromorphology of the membranes has changed, and this is also reflected in the SEM pictures.

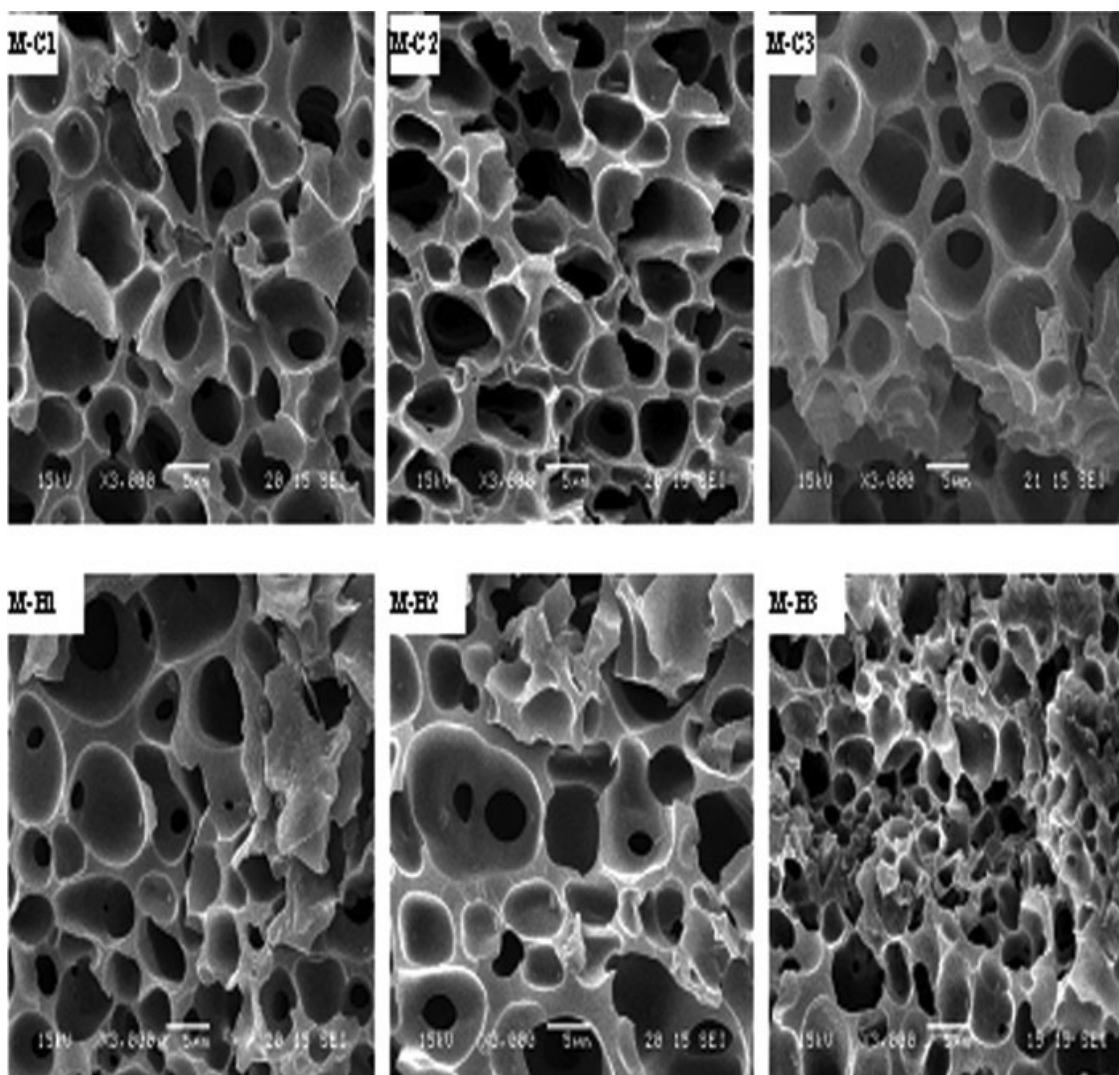


Figure 5 SEM pictures of the cross sections of porous PVA membranes.

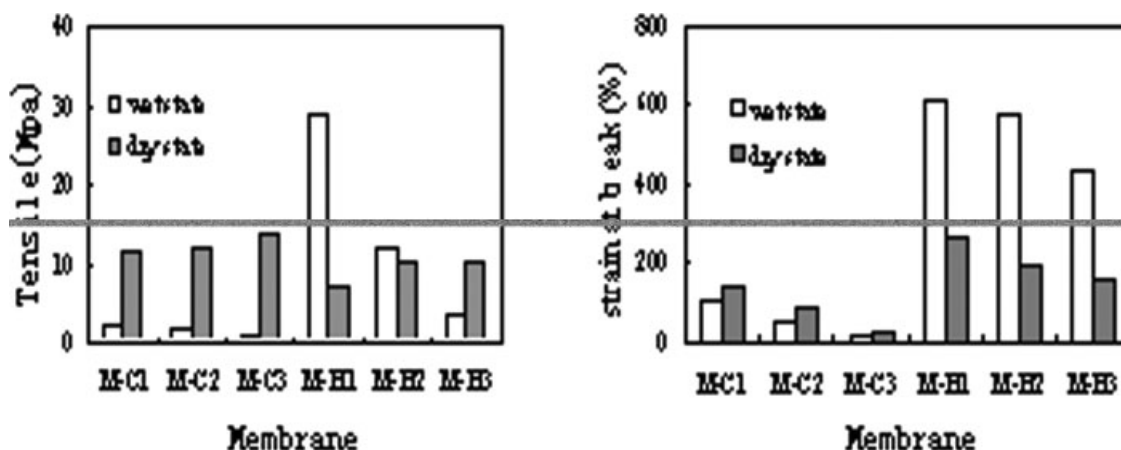


Figure 6 Mechanical properties of porous PVA membranes in the wet and dry states.

Membrane morphology

The porous PVA membranes prepared in this study were typical asymmetrical membranes similar to those reported in the literature.⁶ Here, for simplification of the discussion, only pictures of cross sections of membranes are shown (Fig. 5). We mainly discuss the morphological changes of membranes caused by the posttreatment. For heat-treated PVA membranes, the morphology changes greatly. The pore structure shrinks obviously when the membrane is heat-treated for 2 h (M-H3). With a longer treatment time, the membrane pore size decreases, whereas for crosslinked PVA membranes, no obvious morphological change can be observed. This result is in agreement with the porosity changes of membranes calculated from the swelling experiment. In the crosslinking process, polymer chains are fixed by a crosslinking agent, whereas in the heat-treatment process, polymer chains obtain enough energy to rearrange and form a new structure, and this leads to the morphological changes in the membranes, as well as the pore structure.

Mechanical properties

The mechanical properties of porous PVA membranes in both dry and wet states were measured, as shown in Figure 6. In the dry state, with an increasing crosslinking degree or crystallinity, the tensile strength of the membranes increases. This is in agreement with the normal results of crosslinking. Moreover, crosslinked membranes have a higher tensile strength and a lower strain ratio than heat-treated membranes.

However, in the wet state, the membrane behaviors are completely different. Crosslinked membranes become fragile, and their tensile strength and strain ratio decrease in the wet state versus those in the dry state. For heat-treated membranes, both the

tensile strength and strain ratio increase, and this means that those membranes are very flexible. Furthermore, the tendency for change with the crosslinking or heat treatment is in contrast to that in the dry state. Heat-treated membranes show better elasticity than chemically crosslinked membranes. This may be explained by the inner stress in the system during the swelling process. When water molecules are absorbed into a membrane, polymer chains tend to extend themselves by an affinity force from water molecules (see Fig. 3). However, such behavior is confined by chemical-crosslinking bonds or a crystal region, so with the crystallinity or crosslinking degree increasing, the inner stress in the system becomes stronger and stronger, and thus the mechanical properties of the membrane deteriorate.

CONCLUSIONS

A study of the influence of posttreatments on the water permeation flux, morphology, and mechanical properties of porous PVA membranes has been carried out. Chemical crosslinking has no significant influence on morphological changes in membranes, whereas heat treatments increase the crystallinity of membranes and thus change their morphology. For mechanical performance, great diversity exists among membranes in dry and wet states. Cross-linked membranes show good mechanical properties in the dry state, whereas they become fragile in the wet state. On the contrary, the mechanical properties of heat-treated membranes are better in the wet state than in the dry state, and this can be explained by the inner stress in the system produced by the swelling process.

References

- Li, N.; Liu, Z. Z.; Xu, S. G. *J Membr Sci* 2000, 169, 17.

2. Li, R. H.; Barbari, T. A. *J Membr Sci* 1995, 105, 71.
3. Dai, W. S.; Barbari, T. A. *J Membr Sci* 1999, 156, 67.
4. Amanda, A.; Kulprathipanja, A.; Toennesen, M.; Mallapragada, S. K. *J Membr Sci* 2000, 176, 87.
5. Djennad, M.; Benachour, D.; Berger, H.; Schomäcker, R. *Eng Life Sci* 2003, 11, 446.
6. Chuang, W. Y.; Young, T. H.; Chiu, W. Y.; Lin, C. Y. *Polym J* 2000, 41, 5633.
7. Hassan, C. M.; Peppas, N. A. *Adv Polym Sci* 2000, 153, 37.
8. Gimenez, V.; Mantecon, A.; Ronda, J. C.; Cadiz, V. *J Appl Polym Sci* 1997, 65, 1643.
9. Bray, J. C.; Merrill, E. W. *J Appl Polym Sci* 1973, 17, 3779.
10. Muhlebach, A.; Müller, B.; Pharisa, C.; Hofmann, M.; Seiferling, B.; Guerry, D. *J Polym Part A: Polym Chem* 1997, 35, 3603.
11. Miranda, T. M. R.; Goncalves, A. R.; Amorim, M. T. P. *Polym Int* 2001, 50, 1068.
12. Yu, J.; Lee, C. H.; Hong, W. H. *Chem Eng Prog* 2002, 41, 693.
13. Peppas, N. A.; Merrill, E. W. *J Polym Sci Polym Chem Ed* 1976, 14, 441.
14. Krkumova, M.; Lopez, D.; Benavente, R.; Mijangos, C. J. M.; Perena, J. M. *Polym J* 2000, 41, 9265.
15. Kim, K. J.; Lee, S. B.; Han, N. W. *Polym J* 1993, 12, 1295.
16. Yeom, C. K.; Lee, K. H. *J Membr Sci* 1996, 109, 257.
17. Peppas, N. A. *Makromol Chem* 1977, 178, 595.
18. Peppas, N. A.; Hansen, P. J. *J Appl Polym Sci* 1982, 27, 4787.