

# Effect of Surface Modification on Ionic Permeability Across Cellophane Membrane

Ahmad Banihashemi,<sup>1</sup> Mohammad Reza Vakili,<sup>1</sup> Shahrzad Meratian<sup>2</sup>

<sup>1</sup>Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran

<sup>2</sup>ERC of Fars, Shiraz, P.O.Box 71555-414, Iran

Received 5 July 2008; accepted 11 February 2010

DOI 10.1002/app.32244

Published online 12 May 2010 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Cellophane membrane is used for different kinds of membranes and separators because of its advantages. Regenerated cellulose is a hydrophilic membrane; however, it cannot dissolve in water. The operation time of cellophane membrane is short because of the hydrolytic cleavage during the operation. In this study, cellophane membrane was treated by epichlorohydrin. As a result, the surface of the cellophane membrane was changed chemically and morphologically. These changes were investigated by means of FT-IR, scanning electron microscopy, and also the surface properties were studied by contact angle and water absorption. In addition to, hydrolysis

behavior, oxidative resistance, and salt permeability were measured. Meanwhile, thermal stability and tensile strength were done on modified and unmodified membrane. The modified membrane is more resistant against the hydrolytic and oxidative cleavage than the unmodified membrane. Salt permeabilities were increased after treatment. Modification causes to increase thermal stability and tensile strength of the untreated cellophane membrane. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1–6, 2010

**Key words:** cellophane membrane; surface modification; salt permeability; hydrolytic cleavage; epichlorohydrin

## INTRODUCTION

Cellulose and its derivatives provide a very important class of basic material for membranes due to the fact that it is a very hydrophilic polymer but not water-soluble.<sup>1</sup> Regenerated cellulose (cellophane) is used for different purposes of membranes and separators like dialysis membranes. Therefore, cellophane allows the diffusion of ions and low molecular weight solutes but it does not permit the diffusion of proteins or macromolecules of high molecular weight. Also it can be used for electrochemical devices.<sup>2,3</sup> Cellulose, because of its polyhydric alcohol structure, is very sensitive to oxidizing media. Oxidized cellulose is the result of an attack on specific hydroxyls in the molecule by different oxidants. Consequently, one of the disadvantages of cellophane membrane is oxidative and hydrolytic degradation.<sup>4</sup> In this investigation, cellophane dense membrane was modified by epichlorohydrin and the effect of chemical surface modification on ionic permeability, surface properties, chemical and structural changes were studied.

The chemical and structural changes in the membrane were characterized by FT-IR, scanning electron

microscopy (SEM), and contact angle were used in the study of surface modification. Cellophane membrane salt permeability was determined for different electrolytes by the conductometric method.<sup>5</sup> Mechanical properties of membranes were investigated by tensile strength and thermogravimetric analyses were done on modified and unmodified membranes.

## EXPERIMENTAL

### Materials and instruments

Potassium hydroxide, epichlorohydrin, and the other chemicals were purchased from Merck and Fluka chemical company. Dense cellophane membrane sheets POO350 from UBC Company with 28.6 m<sup>2</sup> kg<sup>-1</sup> were used. Fourier transform infrared (FT-IR) spectra were recorded on a FT-IR Bruker tensor 27 fitted with ATR accessory kit. Surface morphology of the modified membrane was studied by using a Cambridge Scanning Electron Microscope S360. Sample spacemen were coated with gold in a sputter coater (E5200, Bio-Rad). The accelerating potential was 20 kV. Conductivities were determined with a Pt-electrode by means of a conductivity meter (OSK 11468C Ogawa Seiki Co.). Thermal gravimetric analysis (TGA) was performed on mettler TA 4000 with a heating rate of 5°C/min in N<sub>2</sub>. All of quantitative measurements have been done at least with 12 specimens and the results have been reported as an average value of measurements. The potassium hydroxide

Correspondence to: M. R. Vakili (mrvakili@gmail.com).

Contract grant sponsors: Shiraz University/ERC of Fars.

solutions which use in this treatment are under stream of nitrogen for 1 h before treatment.

### Surface modification of cellophane membrane and salt diffusion

Initially, a piece of cellophane sheet was weighted and, soaked in 40% potassium hydroxide solution for 6 h under nitrogen stream and very fast shaking at  $30^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ . Then, the membrane was immersed and shaken in pure epichlorohydrin at  $25^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$  for 80 min. Finally, the surface of the membrane was hydrolyzed by 40% potassium hydroxide solution under nitrogen gas at  $25^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$  and shaking, after that, it was washed with distilled water and immersed in distilled water for 24 h and then it was dried and weighted. All of solutions were prepared by deionized water.

The salt diffusion measuring cell consisted of two-half cells. The membrane was tightly clamped between two glass half-cells by using rubber rings.<sup>6</sup> A magnetic stirrer was placed at the bottom of each half-cell to minimize concentration—polarization at the membrane surfaces the measurements were carried out at a stirring rate of 500 rpm.

### Water absorption, hydrolysis, and oxidation study

To estimate hydrophilicity, the membranes were immersed in distilled water for 24 h at  $25^{\circ}\text{C}$ . An increase in weight of the membrane was recorded and the results were expressed as a percentage of water absorption.

The membranes, modified and unmodified, were immersed in potassium hydroxide solution (40%), and an aqueous solution with different pH (2 and 4). A decrease in the weight of membranes was calculated after 2 weeks.

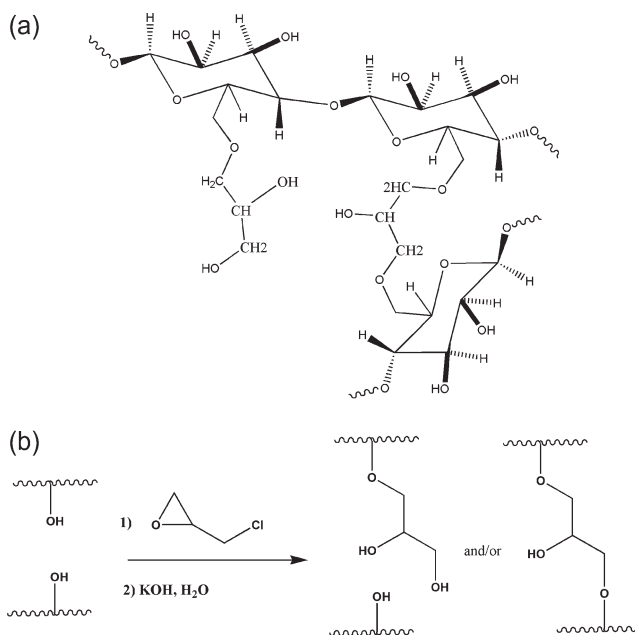
Weighted and dried samples were placed in a beaker containing solution of 35% KOH and 5%  $\text{KMnO}_4$  at  $25^{\circ}\text{C}$ , the membranes were washed by distilled water for 30 s and then, dried and weighted.<sup>7</sup>

### Contact angle

Contact angle measurements were made with a Krüss G40. The averages of the contact angles of the modified and unmodified membranes were measured by drops of diiodomethane.

### Tensile strength

The tensile properties of the samples in wet states were measured at room temperature with a tensile rate 5 mm/min according to ASTM D882. Six measurements were carried out for each sample. The wet



**Figure 1** The modified cellulosic membrane (a) and the surface modification of cellophane membrane (b).

membranes were measured immediately after soaking in water for 30 min.

## RESULTS AND DISCUSSION

A piece of cellophane membrane was swelled in a potassium hydroxide solution. Then, the swelled membrane was immersed in epichlorohydrin. As a result, the cellophane surface was modified chemically to protect the surface and end cap hydroxyl groups. Therefore, ether linkages were made in this reaction. The rest of the epoxy groups were hydrolyzed by a potassium hydroxide solution in the last step. Controlled conditions are very important for this treatment, because they affect the membrane properties. Concentration of potassium hydroxide, temperature control, fast shaking, and time of swelling in the first step of treatment are important factors to create pores and appropriate conditions for the main reaction. In the second step of modification, the reaction time and reaction temperature are prominent to make a flexible modified membrane.

**TABLE I**  
Hydrolysis Effects on the Membranes

Membrane	Weight loss percentage <sup>a</sup>		
	pH 2	pH 4	KOH 40%
Modified	3.75%	3.50%	3.81%
Unmodified	4.76%	4.00%	4.20%

<sup>a</sup> The average of weight loss percentages were measured after 2 weeks at  $25^{\circ}\text{C}$  in aqueous solution.

**TABLE II**  
**Thermal Properties of Membranes**

Membrane	$T_{10\%}$ ( $^{\circ}\text{C}$ ) <sup>a</sup>	Char yield (%) <sup>b</sup>
Modified	234	20
Unmodified	176	12

<sup>a</sup> Temperature at 10% mass loss determined by TGA in nitrogen at a heating rate of  $5^{\circ}\text{C min}^{-1}$ .

<sup>b</sup> Char yield percent at  $700^{\circ}\text{C}$ , obtained from TGA.

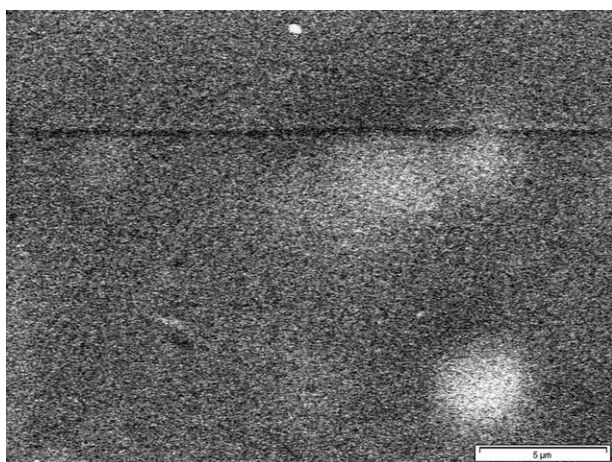
The modified cellophane membranes will be brittle in high temperature and long reaction time.

The reaction of modification has been shown in Figure 1. This reaction consists of two competitive reactions: grafting and cross linking reactions. Increasing reaction time and temperature cause to make a brittle membrane due to increasing cross linkage bonds. The final step of treatment is hydrolysis of remain epoxy rings on the membrane which increases the grafting reaction.

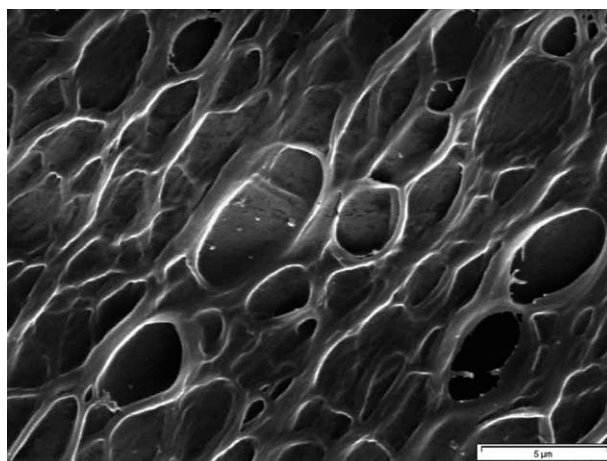
The solution of KOH that was used in this modification was under stream of nitrogen to prevent of oxygen exposure. However, the study of tensile strength of the membranes shows that tensile strength of modified membrane improves by this treatment. The averages of tensile strength of unmodified and modified membranes are 21.7 and 24.9 MPa, respectively. Consequently, this result approve that not only oxygen exposure has not been degraded cellophane membrane significantly, but also modification causes to increase tensile strength because of cross linking between cellulose chains.

According to eq. (1), the average of modified membrane weight increased 12.1% of the membrane weight. The average value is related to 12 specimens:

$$\% \text{ Weight gain} = \frac{W_{\text{modified}} - W_{\text{unmodified}}}{W_{\text{unmodified}}} \times 100 \quad (1)$$

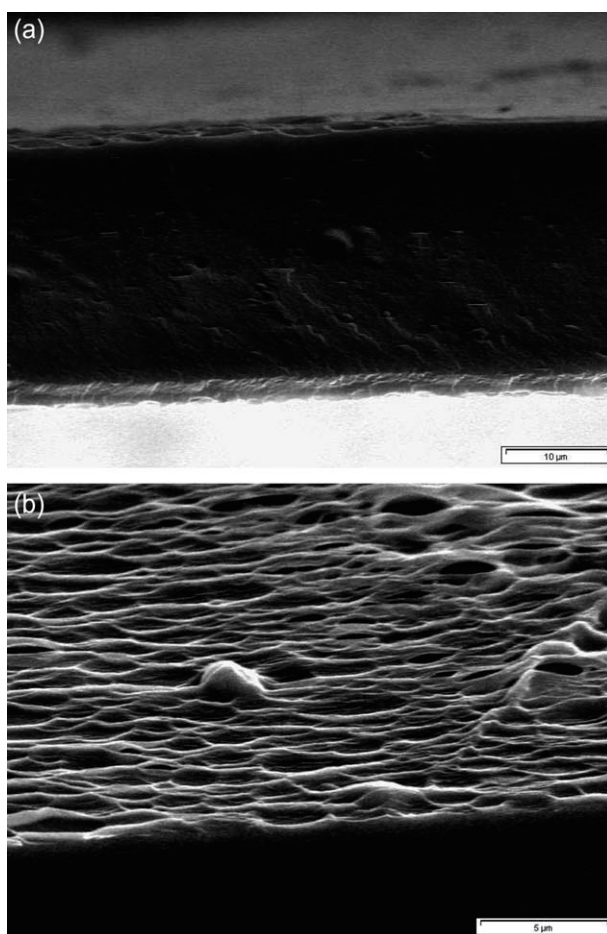


**Figure 2** Scanning electron micrograph of the unmodified surface membrane.



**Figure 3** Scanning electron micrograph of the modified surface membrane.

Surface hydrophilicity was evaluated by contact angle and water absorption.<sup>8,9</sup> The average of contact angles of the unmodified and the modified cellophane were found to be  $39.4^{\circ}$  and  $37.1^{\circ}$ , respectively, by drops of diiodomethane. The average value is related to 12 pieces of membrane. It shows that changes of



**Figure 4** Cross section of the modified membrane.

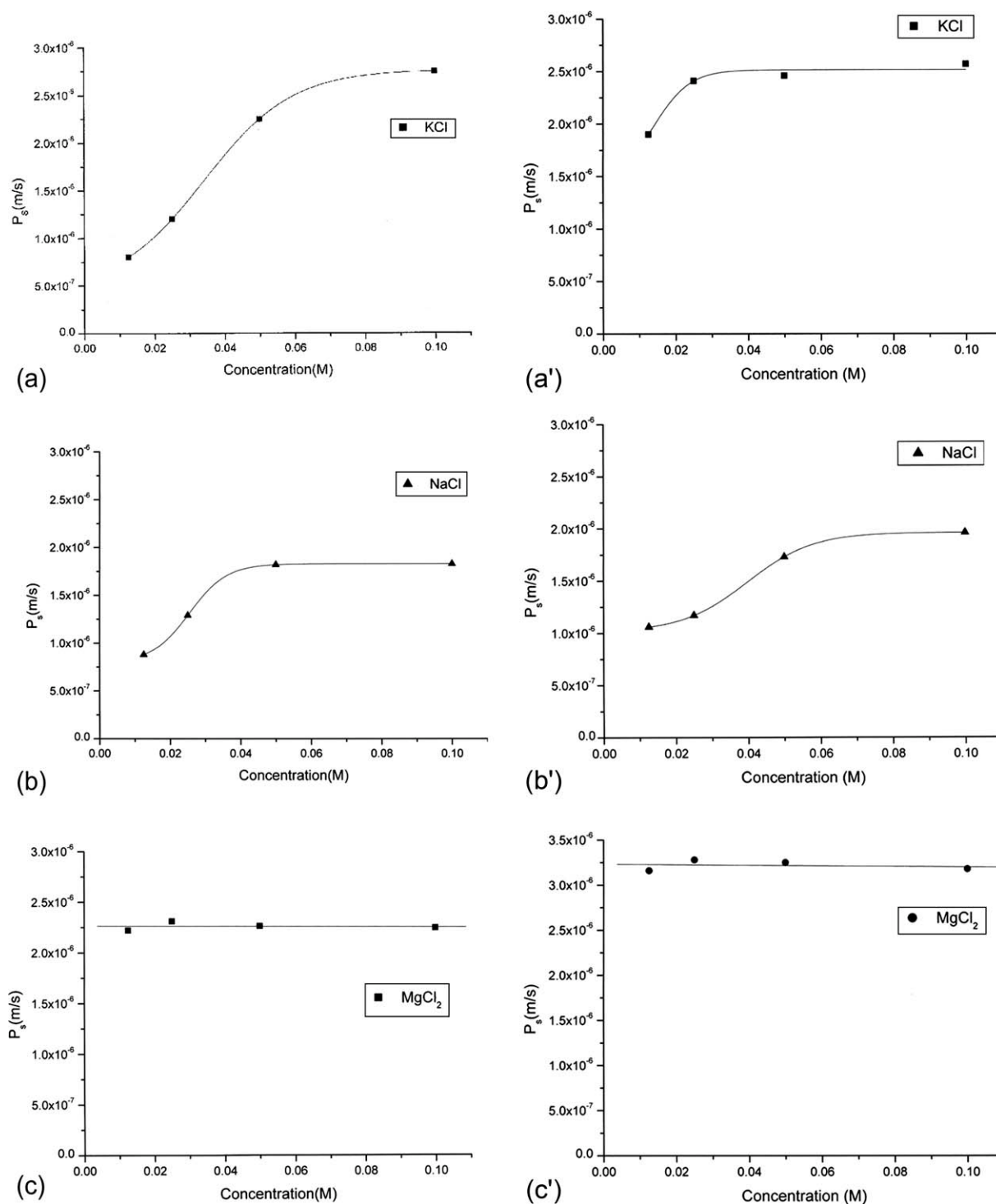


Figure 5 Unmodified membrane (a–c) and modified membrane (a'–c').

surface tension after treatment are little. The average of water absorption of unmodified and modified membranes was 66.0% and 65.0%, respectively, it was carried out for 16 specimens of each membrane. These results indicated that hydrophilicity of the membrane decreased very little after modification.

As can be seen in Table I, hydrolysis causes the average of membranes weight loss in different pH,

as modified membranes are more resistant against hydrolysis than unmodified membranes. Because, surface cross linking protects the surface of modified membrane.

Thermogravimetric analysis indicated that the treatment enhanced thermal stability of the membrane due to partially cross linking on the surface of the modified membrane, as shown in Table II. The

treated membrane had excellent oxidative stability. The modified membrane gained 16.0% in weight due to  $\text{MnO}_2$  precipitation on the membrane. There are some cracks on the membrane after the oxidation test. However, an unmodified membrane was degraded completely. The reason for these stabilities is probably surface cross linking after treatment.

Figure 2 shows scanning electron micrograph of the untreated cellophane dense membrane, and Figure 3 shows scanning electron micrograph of the treated cellophane membrane with blind pores, which have an average diameter of 2.17 microns. The cross section of the membrane shown in the Figure 4 indicates that the penetration of surface modification is 1.5 microns on each side. The picture of unmodified cellophane membrane shows no pore in the surface. The role of Condition in the first step of modification is determined to make the surface pores, temperature control with shaking and appropriate time are necessary to create this kind of blind pore. In the second step, epichlorohydrin reacts with the cellophane chains on the surface and fixed the separated chains of cellophane with cross linking reaction on the surface. Although the surface cross linking reaction can reduce salt permeability, the surface morphology changes possibly to improve salt permeability.

Ionic transport behaviors through cellophane membranes, which are used in electrochemical systems are important. In this study, the permeability of potassium chloride, sodium chloride, and magnesium chloride through the modified and unmodified membranes with different concentration of these salts have been investigated.

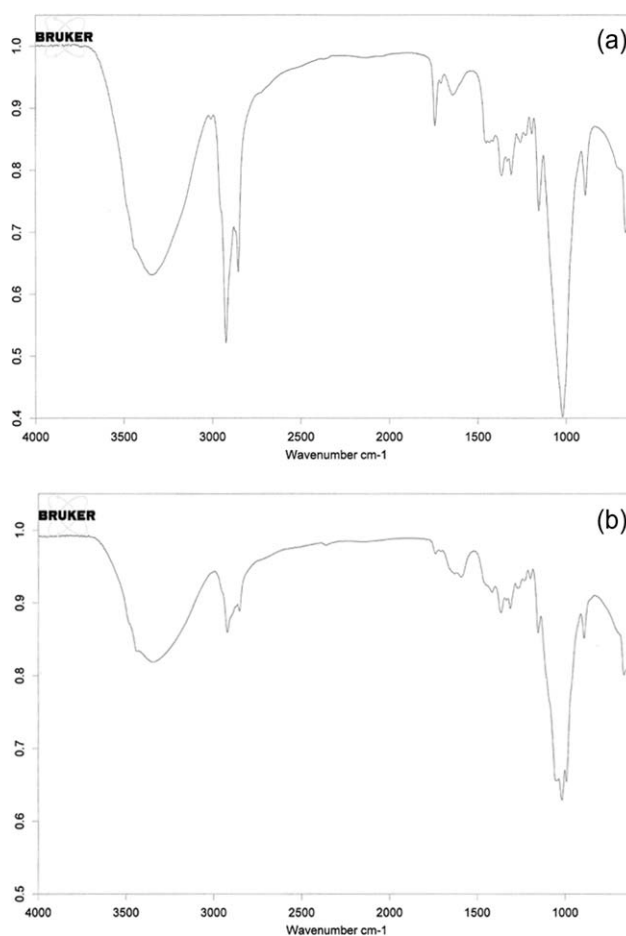
Salt permeability through a membrane can be determined from salt diffusion measurements by taking into account Fick's first law. The salt flux through a membrane (for a quasi-steady state) can be written as:

$$J_s = P_s(c_1 - c_2) = P_s \Delta c = \left( \frac{1}{S_m} \right) \left( \frac{dn}{dt} \right) = \left( \frac{V_0}{S_m} \right) \left( \frac{dc_2}{dt} \right) \quad (2)$$

where  $J_s$  is the diffusive salt flux,  $P_s$  the salt permeability in the membrane,  $c_1$  and  $c_2$  the external concentrations,  $V_0$  the volume of the solution at the side of concentration  $c_2$  and  $S_m$  represents the membrane area. From eq. (2), the following expression is obtained (assuming that  $c_1$  is constant):

$$\frac{d\sigma_2}{dt} = \left( \frac{S}{V_0} \right) \left( \frac{d\sigma}{dc} \right)_e P_s \Delta c \quad (3)$$

where  $\sigma_2$  represents the conductivity of the solution  $c_2$ ,  $(d\sigma/dc)_e$  being an electrolyte characteristic param-



**Figure 6** IR spectra of unmodified cellophane membrane (a) and modified cellophane membrane (b).

eter. Straight lines were obtained for the different studied samples when  $\sigma_2$  versus time were represented. According to eq. (3), salt permeability through the membrane can be determined from the slopes of these straight lines.<sup>10</sup> A comparison of the values obtained for untreated membrane and the treated sample shows variations in  $P_s$  values depending on the treatment. Variation of  $P_s$  values with the constant concentrations for both membrane samples and the different electrolytes were studied. The fitting by a nonlinear program of experimental values are shown in Figure 5, as can be observed for 1 : 1 electrolytes, both membranes present the same kind of behavior. Salt permeability strongly increases for the concentration interval between 0.005M and 0.02M, but a practically constant value is reached for  $C \geq 0.02M$ , in agreement with that reported in the literature for different dense cellulosic membrane. However, for 2 : 1 electrolyte,  $P_s$  values are practically independent of salt concentration.<sup>11</sup> Salt permeability of the membrane increased after treatment, especially in lower concentrations. The higher the charge density the lower salt permeability in the low concentration range.<sup>12</sup> These results show that salt

permeability of the modified membrane is suitable for ions with different size and different mobility. It is a valuable behavior for this type of membrane to use in electrochemical systems and batteries.

Figure 6 shows a comparison of the infrared spectra for the treated and untreated samples of membrane. In this treatment, the surface of cellophane membrane chemically is changed. ATR FT-IR spectra were used for investigating surface chemical changes. According to Figure 6, new functional groups like hydroxyl groups and ether linkages have been created but the new hydroxyl groups overlap with the hydroxyl groups of cellophane membrane. As a result, starching of the new hydroxyl groups absorption is not observed in the IR spectrum of modified membrane. The chemical changes are approved by the new stretching peaks of ether linkage after modification. From the vibrational point of view, structural information was assessed by the creation of the new peaks at 993 and 1050  $\text{cm}^{-1}$  after modification due to new C—O bonds formation and also, analyzing the other changes in peak position and relative intensity of the infrared band. These changes in the IR spectrum of modified membrane prove chemically changes during the modification.<sup>4,13</sup>

### CONCLUSIONS

The effect of chemical surface treatment on a cellophane membrane has been determined by chemical and structural changes. The modified membrane

showed good thermal, hydrolytic, and oxidative stability. The salt permeability was increased by treatment and also, the modified membrane had enough hydrophilicity. The FT-IR spectra of the membranes indicated some new peaks and changes. It approved chemical changes on the membrane after treatment.

The authors thank Prof. Dr. B. Tamami and Prof. Dr. M.E. Bahrololoom for their valuable contributions in this study.

### References

1. Vazquez, M. I.; Benavente, J. *J Membr Sci* 2003, 219, 59.
2. Sakai, K. *J Membr Sci* 1994, 96, 91.
3. Arora, P.; Zhang, Z. *Chem Rev* 2004, 104, 4419.
4. Klemm, D.; Philipp, B.; Heinze, T.; Heinze, U.; Wagenknecht, W. *Comprehensive Cellulose Chemistry, Vol. 1: Fundamentals and Analytical Methods*; Wiley-VCH: Weinheim, 1998; pp 187–190.
5. Vazquez, M. I.; de Lara, R.; Galan, P.; Benavente, J. *J Membr Sci* 2005, 256, 202.
6. Benavente, J.; Munoz, A.; Heredia, A. *J Membr Sci* 1998, 139, 147.
7. Degen, P. J.; Lee, J. U.S. Pat. 5,318,866 (1994).
8. Hosseinpour, D.; Mohammadi, N.; Moradian, S. *Polym Test* 2003, 22, 727.
9. Majumdar, S.; Adhikari, B. *Anal Chim Acta* 2005, 554, 105.
10. Vazquez, M. I.; Galan, P.; Casado, J.; Ariza, M. J.; Benavente, J. *Appl Surf Sci* 2004, 238, 415.
11. Vazquez, M. I.; Milano, C.; de Lara, R.; Guerrero, O.; Herrera, C.; Benavente, J. *Desalination* 2006, 200, 15.
12. Kimura, Y.; Lim, H. J.; Iijima, T. *Die Angew Makromol Chem* 1986, 138, 151.
13. Dawy, M.; Nada, A. A. M. *Polym Plast Technol Eng* 2003, 42, 643.