

# Swelling Behavior and Pervaporation Properties of New Composite Membrane Systems: Porous Polyethylene Film-Poly(acrylic acid) Hydrogel

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**ABSTRACT:** A new type of composite membrane for pervaporation has been developed. These membranes were prepared by free-radical copolymerization of acrylic acid with a macromolecular polyfunctional crosslinker (allylhydroxyethylcellulose) inside the porous polyethylene (PE) film. It was shown that the porous structure of the PE matrix is filled with poly(acrylic acid) (PAA), and a layer of acid is formed on the film surface. To investigate the effect of the porous matrix on the composite membrane properties, a hydrogel membrane of crosslinked PAA was also prepared without the matrix using the same procedure. PAA in both membranes was in the neutralized form ( $K^+$ ). Swelling behavior of the membranes and their separation characteristics for pervaporation were investigated in water–ethanol solutions depending on the ethanol concentration. All membranes exhibited a high degree of equilibrium swelling ( $Q$

= 20–50 g/g) in dilute ethanol solutions (0–30 vol %), and  $Q$  sharply dropped to 1.5–2 g/g at a EtOH concentration of 30–40 vol % due to collapse of the gel. All membranes under study were highly permeable and selective to water over a wide range of ethanol concentrations in the feed (50–96 vol %), but composite membranes had a higher separation factor due to the restriction effect of the matrix porous structure on swelling of PAA( $K^+$ ) inside the pores. However, composite membranes were characterized by a lower permeation rate, compared to the crosslinked PAA membranes without a matrix, because of their lower effective surface for diffusion. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1461–1465, 2004

**Key words:** membranes; pervaporation; dehydration; hydrogels; poly(acrylic acid); polyethylene porous films

## INTRODUCTION

Separation of water–organic and organic liquids, especially ethanol–water mixtures, by pervaporation is used in industry as an energy-saving process.<sup>1–3</sup> However, new types of membranes with higher characteristics, principally permeation rate ( $P$ ) and separation factor ( $\alpha$ ), are needed to widen the field of application of this method. Mechanical strength and stability of membranes are also extremely important for their exploitation. A membrane containing poly(acrylic acid) (PAA), which is a polyelectrolyte with a high charge density, exhibits very high selectivity and permeability to water.<sup>2,4,5</sup> In our earlier work, a new method of synthesis of highly selective membranes by polymerization of acrylic acid (AA) inside cellulose matrices was suggested.<sup>6,7</sup> It was shown that the formation of an interpenetrating polymer network (IPN) structure leads to a considerable increase in the functional characteristics of membranes. It was also shown that this

method of IPN-membrane preparation makes it possible to achieve an optimum combination of functional properties of all IPN components: high mechanical strength and elasticity of the cellulose matrix and high separating characteristics of the PAA.

In the current work, a new type of membrane containing crosslinked PAA as an active component was prepared by polymerizing AA inside the hydrophobic polyethylene (PE) porous matrix. A strongly developed relief of the polyethylene film surface and through-pores in the film structure<sup>8,9</sup> provide high adhesion of the matrix to PAA, which provides the possibility of efficiently fixing a large amount of PAA inside the matrix and on its surface and thereby forming a new effective hydrophilic–hydrophobic material.

To prepare the membranes, the method of synthesis of highly swelling hydrogels using macromolecular polysaccharide crosslinkers for the formation of a hydrogel network was used.<sup>10–13</sup> Macromolecular crosslinkers, such as allylhydroxyethylcellulose (AHEC), allylcarboxymethylcellulose, and allyldextrane, give the possibility of synthesizing hydrogels with good mechanical characteristics that is very important for composite membrane materials. The hy-

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drogels prepared using polysaccharide crosslinkers have higher strength and elasticity (at similar degrees of swelling) than the hydrogels crosslinked by the frequently used low-molecular-weight crosslinker *N,N'*-methylene-bisacrylamide.<sup>11,12</sup> It was shown in these papers that allyl groups of macrocrosslinker copolymerize effectively with the monomer forming the center of crosslinking. The most effective crosslinking reactions are achieved with synthesis in concentrated solutions of monomer (approximately 30%). Possibly, some portion of the allyl groups does not participate in the copolymerization reaction. It is possible also to suppose that the reactions of degradation chain transfer involving allyl groups do not lead to crosslinking. However, due to the large amount of allyl groups in polymer chains of the crosslinker (AHEC with  $\bar{DP} = 1200$  and with degree of substitution on allyl groups  $DS_A = 0.2$  contains 240 allyl groups) it is not necessary to have a high conversion degree on allyl groups for the realization of effective crosslinking.

In this work we did not vary the conditions of synthesis because the dependencies of hydrogel properties on reagent concentration, temperature, time of reaction, etc. were studied in our previous papers.<sup>10–13</sup> The degree of equilibrium swelling of PAA hydrogels (in  $\text{Na}^+$  or  $\text{K}^+$  form) varied in the range 50–5000 g/g depending on the initial concentration of monomer, macrocrosslinker concentration during synthesis, and its functionality. To synthesize the composite membrane conditions leading to the formation of hydrogels, with minimal swelling degree in the indicated range but with maximal strength and elasticity, were chosen. This choice is conditioned by the fact that increasing equilibrium swelling degree of the membranes with PAA reduces their selectivity.<sup>6</sup> Moreover, it was proved in previous experiments that strongly swollen layers of PAA with a low strength easily exfoliate from the composite membrane surface even during weak mechanical deformations.

In this paper AHEC was chosen as a macromolecular crosslinker. To investigate the effect of the PE porous matrix on the pervaporation properties of composite membranes, the free-standing PAA hydrogel membrane crosslinked by AHEC was also prepared and studied.

## EXPERIMENTAL

Acrylic acid (Aldrich Chemicals) was distilled under vacuum at a pressure of  $\sim 18$  Torr. The fraction with a boiling point of  $47^\circ\text{C}$  was collected.

Water-soluble AHEC, with a degree of substitution on allyl groups  $DS_A = 0.2$ , was prepared by allylation of hydroxyethylcellulose with  $\bar{DP} = 1200$  and a substitution ratio of 2 as described in Ref. 12. Cobalt (III) acetate was prepared by electrolysis of cobalt II acetate

$\{\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}\}$  in 98 wt % acetic acid as described in Ref. 11.

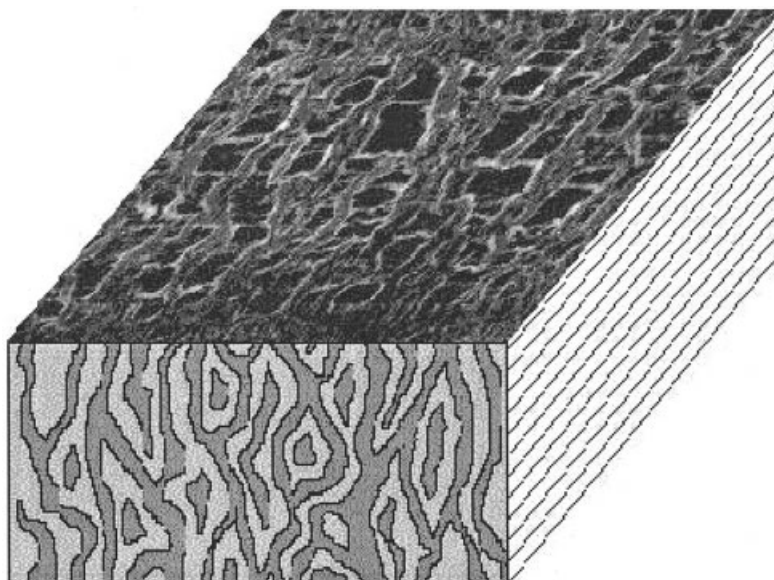
All other reagents of analytical grade were used as received.

### Preparation of polyethylene matrix

Microporous PE films were prepared, as described earlier,<sup>8</sup> from a commercial linear high-density PE ( $M_w = 1.4 \times 10^5$ ,  $M_w/M_n = 6–8$ , melting point  $T_m = 132^\circ\text{C}$ ) by melt extrusion at  $200^\circ\text{C}$  and subsequent annealing for 30 min at  $130^\circ\text{C}$ . The porous structure was produced by uniaxial extension of annealed films at room temperature followed by thermal fixation at  $110^\circ\text{C}$  for 30 min. These microporous PE membranes were 10–15  $\mu\text{m}$  thick and contained through flow channels with an average size of 200–250 nm. Overall porosity of the films was 40%. A schematic representation of the film crosssection (Fig. 1) demonstrates the open-cell structure and through-pores in the porous film. A relief-like character of the film surface is presented in Figure 1 by its electron microscopic image.

### Synthesis of membranes

To synthesize the composite membranes, the polyethylene film was immersed in an aqueous reaction solution containing AA (30 wt %) and AHEC (2 wt %). To initiate the free-radical polymerization cobalt (III) acetate, as proposed by us previously,<sup>10,11</sup> was used at a concentration of  $0.5 \times 10^{-3}$  M. The matrix was allowed to soak for 10 min in the reaction solution and was placed between two glass plates, pressed with clamps, and thermostated at  $50^\circ\text{C}$ . Free-radical polymerization started after an induction period of 10–15 min and was completed in 2 h (this time is sufficient to reach the degree of monomer conversion 98%<sup>10</sup>). Crosslinked PAA hydrogel membrane was synthesized between two glass plates under the same conditions but without any type of matrix. Subsequently, the membranes were washed with 0.1 M HCl for 3 days to remove low-molecular-weight impurities and dried to constant weight. The membrane thickness was 50 and 90  $\mu\text{m}$  for crosslinked PAA and composite PE–PAA membranes, respectively. The content of PAA in the composite membranes was 86 wt %. This value was determined gravimetrically by comparing weights of dry composite membrane and polyethylene porous matrix, which was used for synthesis. Before the degree of membrane swelling and their pervaporation characteristics were measured, carboxyl groups were transformed into the salt ( $\text{K}^+$ ) form. For this purpose membranes were placed for 1 h in water–ethanol (70% wt % ethanol) solution containing 0.2 M KOH with periodic stirring, and then they were put in 70% ethanol for 1 h. The degree of membrane equilibrium swelling ( $Q$ ) in water and in EtOH– $\text{H}_2\text{O}$  mix-



**Figure 1** Model of porous film structure: surface and crosssection. The upper plane on the scheme is the electron microscopic image of the film surface, and the front vertical plane is the computer-generated model of the crosssection. It is possible to see the closed, opened, and through-pores in the scheme of the crosssection.

tures was estimated at  $Q = (W_s - W_d) / W_d$ , where  $W_s$  and  $W_d$  are the weights of swollen and dry membranes, respectively.

### Pervaporation

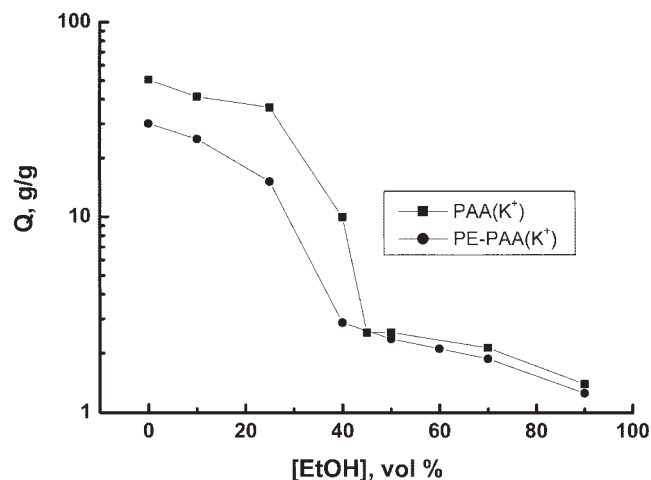
Experiments on pervaporation were carried out in a flange-type cell similar to that used in Ref. 6,7 The feed mixture temperature was kept constant (50°C) with the aid of a liquid thermostat. The permeate was collected in a trap cooled with liquid nitrogen, weighed, and analyzed using a chromatograph with a column 1 m long packed with Porapak Q and heated to 140°C. Helium was used as the carrier gas. The permeation rate of membranes was normalized for the membrane thickness of 25  $\mu\text{m}$ . The value of  $\alpha$  was calculated as  $\alpha = (y_a / y_b) / (x_c / x_d)$ , where  $y_a$  and  $y_b$  are the weight fractions of water and ethanol in the permeate, and  $x_c$  and  $x_d$  are the weight fractions of water and ethanol in the feed mixture, respectively.

## RESULTS AND DISCUSSION

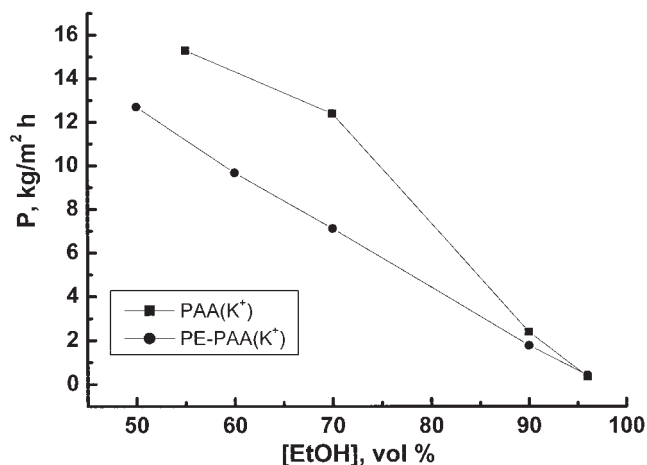
As a result of the hydrogel formation, the opaque milk-white PE porous film became transparent due to the filling of pores with PAA. No splitting or exfoliation of hydrophilic PAA from the hydrophobic PE matrix was observed. Because of the through porous structure, the hydrogel is located inside the pores and also on the film surface, which results in the formation of a space-continuous phase of PAA with the PE matrix inside the PAA hydrogel.

Figure 2 demonstrates the dependence of equilibrium swelling degree on ethanol concentration in mixtures of ethanol–water for PAA(K<sup>+</sup>) and PE-PAA(K<sup>+</sup>) membranes. The behavior of the curves is typical of swelling polyelectrolyte hydrogel in the solvent–non-solvent mixture. For these systems, sharp changes in  $Q$ , by one or two orders of magnitude resulting from phase transition,<sup>14</sup> are observed at a definite concentration of nonsolvent.

The  $Q$ –[EtOH] curve for the composite membranes shows that swelling of PAA(K<sup>+</sup>) takes place mainly in the surface layer, while the swelling inside the matrix is restricted by pore size. As a result, the composite



**Figure 2** Effect of ethanol concentration on the swelling of membranes in water–ethanol mixtures.



**Figure 3** Permeation rate of membranes at 50°C versus EtOH concentration in the feed.

membranes have lower  $Q$  compared with hydrogel membranes in the entire range of ethanol concentrations. At high ethanol concentrations ( $[\text{EtOH}] = 96\text{--}50$  vol %), the values of  $Q$  for both membranes are not high, and the hydrogel layer is firmly fixed on the PE matrix.

At lower ethanol concentrations ( $[\text{EtOH}] = 40\text{--}0$  vol %) at high degrees of swelling the hydrogel layer forms loops extending above the matrix surface, which is caused by the strongly developed matrix relief. Mechanical deformations of these systems, which can occur during membrane testing or use, lead to some exfoliation of the hydrogel layer. The pervaporation properties of the membranes were investigated at moderate swelling degrees at  $[\text{EtOH}] = 50\text{--}96$  vol %, when the composite membranes were mechanically stable.

Figures 3 and 4 present the dependencies of permeation rate  $P$  and separation factor  $\alpha$  on ethanol concentration in the feed. The curves are similar to those for the cellulose–PAA IPN-membranes obtained in our earlier work, i.e., the permeation rate decreases and the separation factor increases with increasing ethanol concentration.<sup>6,7</sup> This behavior can be explained by a decrease in the swelling degree and, hence, increase in the volume fraction of polymer in the membrane. It has been shown in our work<sup>6</sup> that the permeation rate for different types of cellulose–PAA IPN-membranes is proportional to their swelling degree: it reduces with decreasing  $Q$ . At the same time, it is known that a high selectivity of the membranes based on PAA at separation of water–organic mixtures is related to the high chemical affinity of the PAA functional groups to water. At high degrees of swelling, the volume fraction of water in the membranes is much higher than that of the polymer, and both components of the ethanol–water mixture can freely diffuse through the zones filled with water.

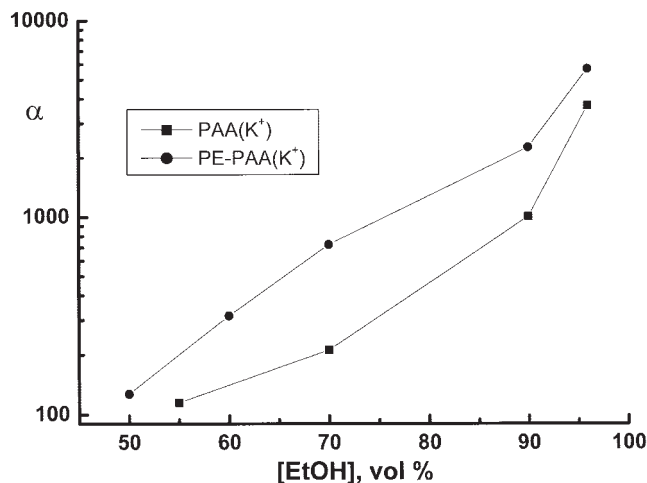
These highly swollen membranes are characterized by very low selectivity. As the volume fraction of the polymer component grows, the degree of interaction between the components of the ethanol–water mixture and polymer plays a more and more important role.

The hydrogel PAA(K<sup>+</sup>) membranes have a higher permeation rate at  $[\text{EtOH}] = 50\text{--}90$  vol % compared to composite PE–PAA(K<sup>+</sup>) membranes (Fig. 3) because of a smaller effective surface of the composite membrane available for penetration of the mixture components. However, the separation factor for the composite membranes is higher than for the hydrogel PAA(K<sup>+</sup>) membranes. This effect is attributable to the restriction of the PAA(K<sup>+</sup>) swelling inside the PE matrix and, hence, increase in the effective density of PAA(K<sup>+</sup>) in the composite. Thus, the composite PE–PAA(K<sup>+</sup>) membranes have an advantage over one-component PAA(K<sup>+</sup>) samples due to not only their higher mechanical stability but also their higher selectivity.

## CONCLUSION

The procedure of synthesis of a new type of highly efficient composite hydrophobic–hydrophilic PE–PAA membranes for separation of ethanol–water mixtures in a wide range of ethanol concentration (50–96 vol %) has been elaborated.

It has been shown that the composite PE–PAA(K<sup>+</sup>) membranes are mechanically stable in this ethanol concentration range. As the ethanol concentration decreases to 50 vol %, the degree of swelling sharply increases, both for free-standing one-component PAA(K<sup>+</sup>) and for composite membranes. However, under these conditions the mechanical stability of the two types of membranes is low.



**Figure 4** Separation factor of membranes at 50°C versus EtOH concentration in the feed.

It has been established that the separation factor of the composite membranes is considerably higher than that of the one-component PAA(K<sup>+</sup>) membranes due to the effect of restriction of the PAA(K<sup>+</sup>) swelling degree inside the porous PE matrix.

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