Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Effect of Film Aging on the Pervaporation Properties of Latex Membranes

Yi Wei[a]; Robert Y. M. Huang[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF WATERLOO, WATERLOO, ONTARIO, CANADA

To cite this Article Wei, Yi and Huang, Robert Y. M.(1995) 'Effect of Film Aging on the Pervaporation Properties of Latex Membranes', Separation Science and Technology, 30: 6, 981 — 992

To link to this Article: DOI: 10.1080/01496399508015411

URL: http://dx.doi.org/10.1080/01496399508015411

SEPARATION SCIENCE AND TECHNOLOGY, 30(6), pp. 981–992, 1995

Effect of Film Aging on the Pervaporation Properties of Latex Membranes

YI WEI and ROBERT Y. M. HUANG
DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF WATERLOO
WATERLOO, ONTARIO N2L 3G1, CANADA

ABSTRACT

Latex membranes have recently been investigated for their application in pervaporation separation processes. Acrylonitrile–butyl acrylate copolymer latex membrane showed selective permeation to water in pervaporation with water–ethanol mixtures. Different from solvent-cast membranes, the pervaporation properties of latex membranes were found to change with the membrane aging time or under different aging conditions. It is shown that aging leads to better membrane fusion, thus decreasing the permeation rate and increasing the separation factor. Aging the membrane in a medium which keeps the latex particle from good fusion would cause a high permeation rate but a low separation factor. Based on our observations, a comprehensive transport mechanism of the permeant through latex membranes during pervaporation is proposed.

INTRODUCTION

As an efficient and energy-saving separation method, pervaporation membrane separation is receiving increasing interests. More and more polymers are being tested for better separation performance. However, most of the current pervaporation membranes are prepared from casting of a polymer solution. Recently, efforts are made to prepare pervaporation membranes from direct casting of polymer emulsions (1–3). Termed *latex membranes*, the membranes thus prepared show preferential permeation toward water when used to separate ethanol–water mixtures by pervaporation, and they are potentially useful for dehydration of alcohols. Compared with the solvent casting method, the casting of latex causes much less pollution since no organic solvent is involved.

In a previous paper (1) it was shown how a latex membrane formed by coalescence of latex particles. Similar to other latex films, the degree of film fusion of a latex membrane is affected by film aging. Therefore, the separation properties of latex membranes during pervaporation are affected by film aging. Such an aging effect, however, is not significant for solvent-cast membranes (4).

It has long been observed that the properties of a polymer material will change, more or less, with time; the material is said to undergo aging (5). However, the aging effect for a latex film is somewhat different from that of other materials. In this case the packing of latex particles, rather than molecules or other units, changes significantly with time. So a discussion of latex membrane aging is mainly concerned with how close the latex particles are packed and what changes significantly in properties are related to the degree of particle packing (degree of film fusion), with time.

Aging of latex films has long received attention, and a number of proposals have been made to rationalize this phenomenon (6–8). The most widely accepted idea is the so-called *further gradual coalescence* or *autohesion*. It describes the mutual interdiffusion of polymer chain ends across the particle–particle interface, which tends to make the film achieve a higher degree of fusion, i.e., become more homogeneous. However, it has been demonstrated that a latex film may not become as perfectly uniform as can be achieved by a solvent-cast film (6). Our observations on the structure of latex membranes also showed a possible two-phase structure, i.e., the polymer bulk region and the particle–particle boundary region (1), which agrees with the observation of other researchers (4).

Since no latex membranes have been prepared for the pervaporation separation process before, the effect of membrane aging on permeation and separation behaviors during pervaporation remains unclear. This paper reports our observations about the effect of latex membrane aging on the pervaporation of ethanol–water mixtures, from which a comprehensive transport mechanism is proposed.

Pervaporation separation performance is characterized by permeation rate J (g/m^2·h) and separation factor α. The latter is defined as

$$\alpha = \frac{Y_i/Y_j}{X_i/X_j} = \frac{Y_i/X_i}{Y_j/X_j} \qquad (1)$$

where X and Y are the weight fraction in feed and permeate, respectively, and i and j are the permeating species water and ethanol, respectively.

EXPERIMENTAL

Latex and Membrane Preparation

Poly(acrylonitrile-*co*-butyl acrylate) [P(AN-BuA)] latexes were synthesized by emulsion polymerization as described in a previous paper (1). The polymerization recipe is

Reactor charge:	
Distilled water	387 g
Sodium dodecyl sulfate	1.5 g
Monomer mixture:	
Acrylonitrile	33.4 g
Butyl acrylate	64.8 g
Initiator:	
Potassium persulfate (in 1.5 wt% aqueous solution)	0.2 g

The latex obtained from the polymerization was cast directly onto a glass plate after being filtered through a nylon screen. The membrane thickness was 95 μm. Latex films were aged in a temperature-controlled vacuum oven for a desired time period.

To prepare the solvent-cast membrane from a polymer chemically identical to the latex membrane, the same polymer emulsion was first coagulated by 5 wt% NaCl aqueous solution under continuous stirring, and then the coagulates were washed with large amounts of deionized water to remove any residual latex and emulsifier. The solid polymer obtained was dried under vacuum at 40°C for 72 hours, then dissolved in dimethylformamide (DMF) to form a viscous solution of 7.5 wt% solids. This solution was then cast onto a glass plate with a Gardener casting knife to adjust the membrane thickness. The thickness of solvent-cast membranes was 80 μm.

Pervaporation

A schematic diagram of the pervaporation apparatus is shown in Fig. 1. Pervaporation was initiated by switching on the feed and vacuum pumps; the pressure at the permeate side was maintained below 3 mmHg. The permeate was collected by one of the glass traps immersed in liquid nitrogen after reaching steady state. The trap filled with permeate was warmed to ambient temperature, weighed, and analyzed for permeate composition. Pervaporation was carried out with ethanol–water mixtures with 95 wt% ethanol. Pervaporation was conducted at temperatures of 25

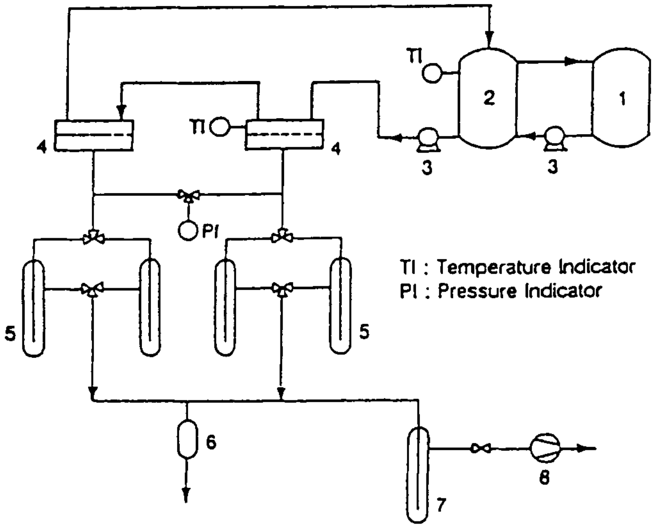

FIG. 1 Schematic diagram of the pervaporation separation apparatus: (1) water bath, (2) feed tank, (3) circulation pump, (4) membrane cells, (5) permeant collection traps, (6) vent to atmosphere, (7) cold trap, (8) vacuum pump.

and 35°C. The permeate composition was analyzed by a Perkin-Elmer 8310 Gas Chromatograph. The column used was a 8′ × 1/8″ SS packed with Hayesep P 60/80 mesh. Nitrogen was used as the carrier gas with a flow rate of 20 mL/min.

RESULTS AND DISCUSSION

Effect of Aging on Pervaporation of Latex Membrane

Figure 2 shows the pervaporation properties of the latex membrane as a function of aging time. As can be seen from this figure, both separation factor and permeation rate change with membrane aging time. The permeation rate (Fig. 2b) decreases initially with aging time, then reaches a relatively stable value. The same observation was made by Chainey and Willkinson with the permeation of helium through a poly(*n*-butyl methacrylate) latex film (4).

The aging effect for latex membranes is due to film structure and morphology changes with time. As previously discussed, latex membranes show different structures in the amorphous matrix, i.e., the bulk polymer and the boundary regions (1). Upon aging, the film becomes more uniform

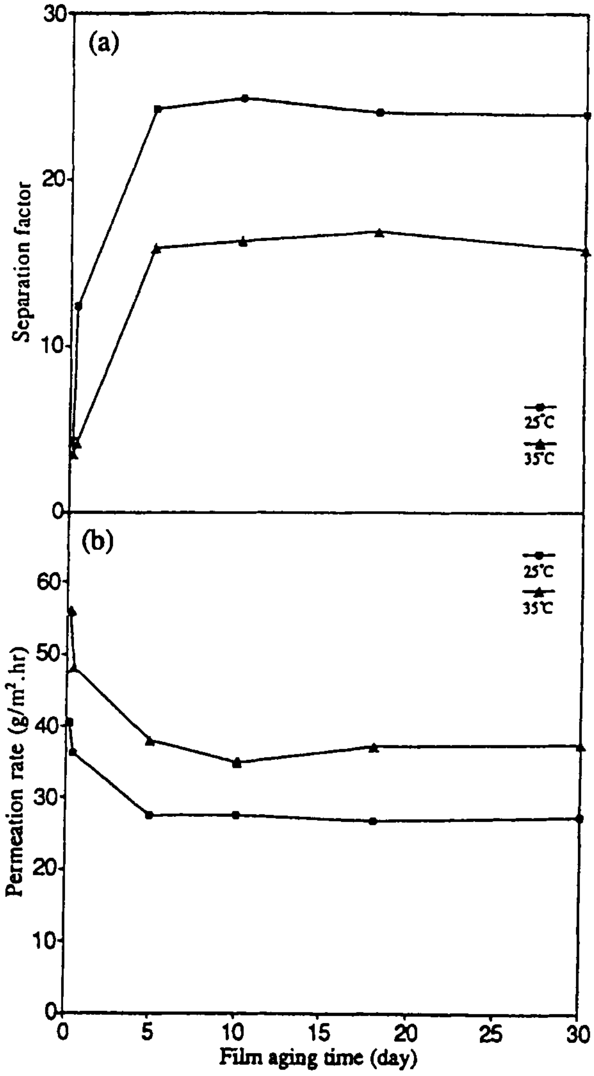

FIG. 2 Pervaporation properties of the latex membrane as a function of membrane aging time: (a) separation factor, (b) permeation rate.

in structure, and perhaps some microvoids inside the membrane are also eliminated. However, this homogenizing process between the hydrophilic boundary regions and the bulk polymer phase is limited by their interactions and miscibility, so that a kind of balance between the two opposite effects is reached within a certain time period rather than the creation of a perfectly fused film.

It is therefore believed that liquid permeation through a latex membrane during pervaporation, similar to gas permeation, is composed of permeation through the bulk polymer and through the boundary regions. In other words, permeation in the polymer bulk and in the boundary region takes place simultaneously, and both contribute to the total permeation. Since the permeant's diffusivity in the polymer bulk does not change significantly with time, as indicated by solvent-cast membranes, and if we assume the pervaporation process is diffusion controlled (2), then the decease in permeation rate (J), shown in Fig. 2(b), can be attributed to the decrease in boundary region permeation (J_b) as a function of aging time. J_b continues to decrease until the latex membrane has aged for a certain period of time and has reached a certain degree of film fusion where no significant further gradual coalescence is occurring and remains relatively constant.

The pervaporation separation factor (Fig. 2a), however, increases with increasing aging time. This can be comprehended based on the above discussions, because in a well-fused film there are less voids or loose structure, particularly within the boundary regions, which makes the diffusion process more selective.

To further elucidate the boundary region permeation, the membranes were aged in water, after which their pervaporation properties were tested. In this experiment, 6 hours after the membrane was cast (at this time the film was visually dry), the membrane was removed from the plate and immersed in water and aged for different time periods. The results are given in Fig. 3. Again, a similar aging effect is observed.

Aging a latex membrane in water may have two possible consequences.

1. The hydrophilic components, such as chain ends and functional groups, accumulate on the particle surface by migrating toward the aqueous phase, making the boundary region (and/or the membrane surface) more hydrophilic; meanwhile, the further gradual coalescence of particles is hindered.
2. The leaching of certain water-soluble ingredients, such as surfactant molecules, residual monomers, or even very low molecular weight polymer fractions.

Both consequences lead to a more distinct boundary region, which causes

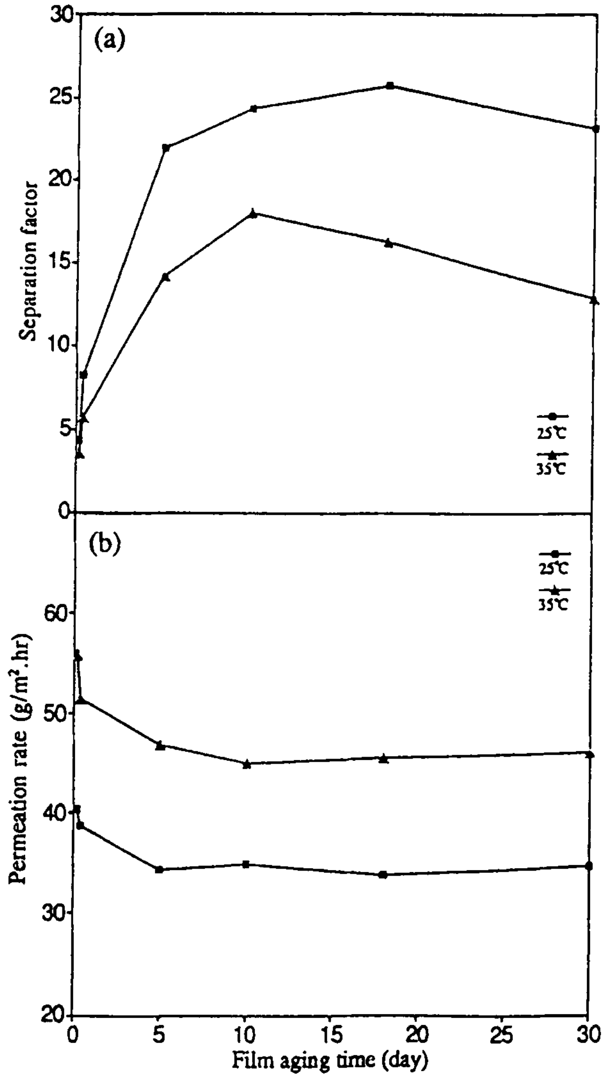

FIG. 3 Pervaporation properties of the latex membrane aged in water as a function of membrane aging time: (a) separation factor, (b) permeation rate.

a high permeation rate J_b; or lead to a more hydrophilic boundary region, which may increase the selectivity toward water (3). This argument is supported by the experimental data, which indicates that a latex membrane aged in water has a higher permeation rate (Fig. 3b) than a membrane aged in air (Fig. 2b). Although a less well fused film results when a membrane is aged in water, its selectively toward water increases with aging time because a more hydrophilic interface/surface favors the transport of water (3).

The effect of aging on solvent-cast membranes was shown to be insignificant, and permeability reduction with aging time is usually not observed (4). For better comparison, solvent-cast membranes having the same composition as the latex membrane were prepared, as described in the Experimental Section. From the pervaporation data in Table 1, it is apparent that the aging effect is not significant for these solvent-cast membranes.

The decrease in J with aging time can be explained on a molecular level according to the free volume concept. This is because the transport mobility of molecules in a closely packed system, e.g., a latex membrane, is primarily determined by the degree of packing of the system or by its inverse measure, viz., the free volume. Aging usually decreases the free volume of the system, implying closer packing, and thus a decrease in permeability is observed.

Transport through Latex Membranes

It was shown that solvent-cast membranes are formed by the piling up of polymer molecules dissolved in the solvent. The primary film formation unit in a solvent-cast membrane is the macromolecule (linear or grafted), and the films thus formed usually have a homogeneous structure (1). However, the primary film formation unit in a latex membrane is the polymer particle. These particles coalesce to form the film, and film morphology changes with aging time or thermal treatment. Although the particle contours become less and less distinguishable with aging, this particle–parti-

TABLE 1
Aging Effect on Pervaporation Properties of Solvent-Cast Membrane

Feed temperature (°C)	Aging time (hours)	Permeation rate (g/m^2·h)	Separation factor
25	24	26.3	27.80
25	240	27.4	29.16
35	24	39.2	18.16
35	240	37.3	18.87

cle interface (or boundary layer) may never be, on a microscopic level, exactly identical to the polymer bulk. Consequently, latex membranes are usually not as homogeneous as solvent-cast membranes (4).

If the solution-diffusion mechanism (9) is adopted to describe permeate transport through a latex membrane during pervaporation, it is expected that the diffusion process be different from that of a solvent-cast homogeneous membrane, because of the existence of the boundary region in latex membranes. For example, assume a permeant molecule at a certain point within the polymer bulk is diffusing toward the permeate side. It has to diffuse through the interface of the particles, i.e., through the boundary region. Once it moves into the boundary region, it can diffuse further along the boundary region or enter the adjacent particles (polymer bulk). It may also diffuse within the boundary region for a certain time before entering the polymer bulk. This process continues until the molecule reaches the permeate side. In this case, the penetrating molecules have a high degree of freedom in the diffusion process, and diffusion takes place in both the boundary region and the polymer bulk randomly. Because the permeant has a different diffusivity in the two different structures, and its diffusion within the membrane is completely random, it is difficult to apply the existing mathematical models developed for solvent-cast membranes to accurately predict the pervaporation properties of latex membranes.

A schematic representation of permeant transport through a latex membrane during pervaporation is given in Fig. 4. In this figure the permeation

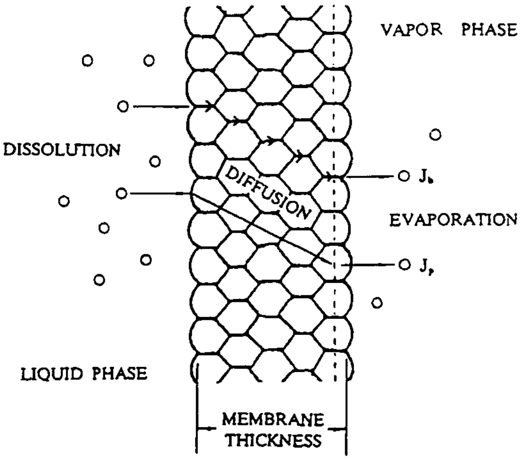

FIG. 4 Schematic transport mechanism through a latex membrane.

process is a combination of dissolution, diffusion, and desorption. Separation is achieved by selective sorption and selective diffusion. Different from the transport in a homogeneous solvent-cast membrane, the diffusion in the boundary region and in the polymer bulk both contribute to the diffusion process. For simplicity, the permeation of liquid through a latex membrane can be qualitatively described in a way similar to gas permeation. In this approach, as illustrated in Fig. 4, the total permeation rate (J) through a latex membrane is broken into two parts: the permeation rate through the polymer bulk (J_p) and the permeation rate through the boundary (hydrophilic) region (J_b). Thus:

$$J = J_p + J_b \tag{2}$$

where for any component i, the permeation rate is given by

$$J_i = J_{i,p} + J_{i,b} \tag{3}$$

As usually assumed in the solution-diffusion mechanism, diffusion is the rate-determining step during pervaporation. For Fickian diffusion,

$$J_i = -\left[(v_p)(D_{i,p})\frac{\partial c_{i,p}}{\partial x} + (v_b)(D_{i,b})\frac{\partial c_{i,b}}{\partial x}\right] \tag{4}$$

where v_p is the volume fraction of the polymer bulk, v_b is the volume fraction of the boundary region, and D is the diffusivity of permeant i in different regions. Subscripts "p" and "b" represent the polymer bulk and the boundary region, respectively.

Equation (4) can be analyzed by addressing some simple cases.

1. If the diffusivities in both regions are relatively close to each other, the pervaporation properties of the latex membrane are generally determined by diffusion through the polymer bulk since its volume fraction is much higher than that of the boundary region. However, the contribution from boundary region diffusion may become significant when the latex particle size is decreased, i.e., the boundary region volume fraction is increased.
2. If the permeant diffusivity in the two membrane structures differs, which is a common situation, and if the particle size and size distribution are fixed, pervaporation properties are governed by the nature of the polymer bulk and the boundary region. The contribution from the boundary region is significant in this case. Latex membranes fall into this case when functional groups, especially hydrophilic groups, are incorporated. It is also true when the degree of film fusion is low.

In Eq. (4) the volume fractions can change with film aging, and they thus are hard to predict or measure. The diffusivities are also difficult to determine. Obviously the concentration gradients in the two regions are not the same, and thus they are also hard to calculate. Nevertheless, if we do not consider multiregion diffusions and simply treat the latex membrane as a homogeneous system, an overall diffusion coefficient for component i ($D_{i,\mathrm{o}}$) can be defined. If Fick's law is also applied, then

$$J_i = -D_{i,\mathrm{o}} \frac{\partial c_i}{\partial x} \tag{5}$$

Recognizing that the difference in pervaporation with latex membranes and solvent-cast membranes is caused by the difference in their film structures, a structural factor k can be defined to describe this difference. If we assume the diffusivity of one component in the polymer bulk of a latex membrane is the same as its corresponding solvent-cast membrane, i.e., $D_{i,\mathrm{p}} = D_i$, then

$$k = \frac{D_{i,\mathrm{o}}}{D_{i,\mathrm{p}}} = \frac{D_{i,\mathrm{o}}}{D_i} \tag{6}$$

and

$$J_i = -D_{i,\mathrm{p}} k \frac{\partial c_i}{\partial x} = -D_i k \frac{\partial c_i}{\partial x} \tag{7}$$

Apparently a larger k value indicates a greater difference between the latex membrane and its corresponding solvent-cast membrane. In other words, the value of k can be used to measure the significance of diffusion through the boundary region. It should be noted here that for membranes of the same polymer composition but which are cast from different solvents or under different conditions, the pervaporation properties vary a lot, and therefore the information carried by k is only correct for the specific system being compared.

CONCLUSIONS

Film aging is an important aspect which largely affects the pervaporation properties of latex membranes. Aging causes a further gradual coalescence which makes the particle–particle interface less distinguishable and achieves a better film fusion. The permeation rate decreases with increasing membrane aging time, and tends to reach a relatively stable value when fully aged. The medium in which the membrane is aged may influence the membrane performance significantly.

Based on a comprehensive transport model for pervaporation through a latex membrane, selective diffusion is a combination of diffusion through the polymer bulk and through the boundary region. This comprehensive mechanism provides a qualitative explanation for the aging effect of the latex membrane as well as other effects during pervaporation (10).

ACKNOWLEDGMENTS

The authors wish to thank the Natural Science and Engineering Research Council of Canada (NSERC) for their financial support of this research. Thanks are due to Dr. C. K. Yoem for his suggestive criticisms.

REFERENCES

1. Y. Wei and R. Y. M. Huang, *J. Membr. Sci.*, *82*, 27 (1993).
2. R. Y. M. Huang and Y. Wei, *Ibid.*, *87*, 257 (1994).
3. R. Y. M. Huang and Y. Wei, *Ibid.*, *89*, 9 (1994).
4. M. Chainey and M. C. Willkinson, *J. Polym. Sci., Polym. Chem. Ed.*, *23*, 2947 (1985).
5. I. C. E. Struik, *Physical Aging in Amorphous Polymers and Other Materials*, Elsevier, Amsterdam, 1978.
6. E. B. Brandford and J. W. Vanderhoff, *J. Macromol. Chem.*, *1*(2), 335 (1966).
7. E. B. Brandford and J. W. Vanderhoff, *J. Macromol. Sci.—Phys.*, *B6*(4), 671 (1972).
8. S. S. Voyustkii, *Polymer Reviews, Vol. 4, Autohesion and Adhesion of High Polymers*, Interscience, New York, 1963.
9. R. Y. M. Huang (Ed.), *Pervaporation Separation Processes*, Elsevier Science Publishers, Amsterdam, 1990.
10. Y. Wei and R. Y. M. Huang, *Sep. Sci. Technol.*, *30*(5), 697 (1995).

Received by editor June 17, 1994
Revised July 12, 1994