Studies on syntheses and permeabilities of special polymer membranes.:
15. Permeation characteristics of nylon–12 cellulose acetate blends

Tadashi Uragami, Kazuhito Maekawa, and Mizuho Sugihara
Department of Chemistry, Faculty of Engineering, Kansai University, Suita, Osaka 564, Japan
(Received 6 April 1978)

The permeation characteristics of nylon-12–cellulose acetate polymer blend membranes in the separation of polymers, poly(vinyl alcohols), from their aqueous solutions were investigated under various conditions. The permeation characteristics were influenced markedly by the ratio of nylon-12–cellulose acetate, the feed concentration, the operating pressure and temperature. It was found that the changes of polymer ratio and the concentration of blended polymer were related to the change of microporous structure of the resulting membranes. When the cellulose acetate content was higher, a significant compaction of the membrane occurred under pressure. It was found that there was a concentration polarization of poly(vinyl alcohol) molecules on the membrane surface, whose thickness increased with increase in molecular weight of poly(vinyl alcohol) and in feed concentration. The bursting strength of the polymer blend membranes swollen with water increased considerably as the cellulose acetate content in the blended polymer increased.

INTRODUCTION

A variety of methods has been used to improve the properties of polymeric materials. Typical are polymer blending, copolymerization (block and graft polymerization, etc.), and crosslinking. Blending involves solution, melt, and kneading methods; solution is the simplest. The permeation characteristics of nylon-12 membranes and modified nylon-12 membranes have been reported in earlier papers[1]. For the purpose of improving the permeation characteristics and the bursting strength of the membranes swollen with water, cellulose acetate, which is readily blended with nylon-12, is selected as a copolymer. In this paper, the effects of evaporation time during formation of the membrane, ratio and concentration of blending polymers in the casting solution consisting of nylon-12–cellulose acetate–*m*-cresol, polymer solute in feed, feed concentration, and operating pressure and temperature, on the permeation characteristics are studied using pure water and poly(vinyl alcohol) aqueous solutions as the feeds. The relationships between the permeation characteristics, physical and chemical nature of the resulting membranes and feed are discussed in some detail.

EXPERIMENTAL

Materials

Cellulose acetate (CA) (acetyl content 40%) produced by Wako Pure Chemical Industries Ltd and nylon-12 (N-12) (nylon powder 5001 PWI from Toray Co. Ltd) were used as the membrane substrate. Pure commercial *m*-cresol was employed as the solvent for casting from solution. Three kinds of poly(vinyl alcohol) used as the solutes of feed solutions were PVA 205, PVA 210, and PVA 217 (supplied by Kurary Co. Ltd) with average degree of polymerization ($\overline{DP}$) 550 ± 50, 1250 ± 50, and 1725 ± 25, respectively. Pure commercial solvent grade methyl alcohol was used.

Preparation of membranes

Casting solutions consisted of cellulose acetate, nylon-12, and *m*-cresol and were kept at the casting temperature (6°–7°C) for 24 h. Membranes were made by pouring the casting solution onto an applicator for thin layer chromatography, drawing the blade across a glass plate, allowing exposure of the casting solution at 6°–7°C for a desired period, and immersing the glass plate carrying the solution into a gelation me medium consisting of methyl alcohol/water (70/30 vol %). After immersion for 48 h in a cold gelation medium (6°–7°C), the membranes were removed from the glass plate and boiled in methyl alcohol for 8 h to remove completely any *m*-cresol remaining. These membranes were washed with purified water and treated with water at 40°C for 15 min. They were then pressure treated with water in the normal manner at 6kg/cm^2 for more than 5 min.

Apparatus and measurements

The apparatus used and the experimental procedure have been described in earlier papers[2,3]. The bursting strengths of the membranes swollen with water were measured by means of Tokyo Shikenki Co. bursting strength testing machine, Müllen type 167.

0032–3861/78/121437–04$02.00
© 1978 IPC Business Press

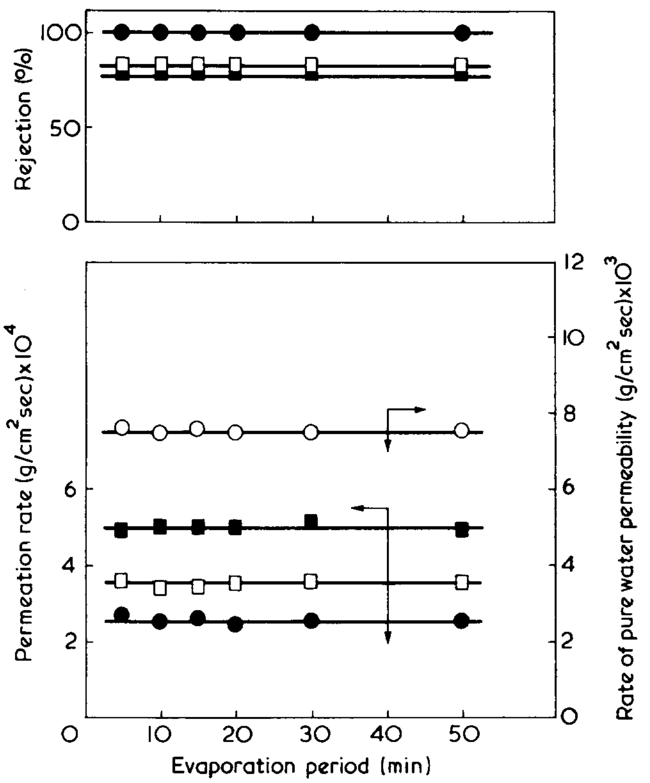

Figure 1 Effect of evaporation period on permeation characteristics. Casting solution: N-12/CA/m-cresol = 11.25/3.75/85 (wt-%); heat treatment: 40°C, 15 min; feed: (○) pure water, (□) 1% PVA205, (■) 1% PVA 210, (●) 1% PVA 217 aqueous solutions; operating condition: 40°C, 5 kg/cm^2

RESULTS AND DISCUSSION

Effect of evaporation period

The effect of the evaporation exposure period on the permeation characteristics of nylon-12–cellulose acetate blend polymer membranes is shown in *Figure 1*. The rate of pure water permeability, the permeation rate, and the rejection are constant, regardless of the evaporation period. The permeation characteristics of nylon-12 membranes of an exposure of 5 min showed similar results to those in our earlier paper[1]. This phenomenon is attributed to the fact that the evaporation loss of *m*-cresol, which is the casting solvent, and of water absorbed into the casting solution during the exposure process, under ambient conditions (temperature 6°–7°C, humidity 80–90%), attain equilibrium. It is presumed from *Figure 1* that there is not a great difference in the fine structures of the resulting membranes. The formation mechanism of these membranes and the fine structure of the resulting membranes may differ from those of Loeb–Sorirajan[4] and Manjikian[5] type porous asymmetric membranes which are formed by phase separation in the casting solution with the evaporation of good solvent from the membrane substrate during the evaporation process. The permeation rates and the rejections for aqueous solutions of poly(vinyl alcohol) differ for three different cases. The rejection for aqueous solution of PVA 217 is 100%. Therefore, only water molecules are permeated. However, this permeation rate is smaller than those for PVA 205 and PVA 210, which have lower rejections. If the permeation phenomenon is normal, the permeation rate in order of lower rejection should be higher. These results support the theory that the concentration polarization (refs 1, 2, 6 and 7) of poly(vinyl alcohol) molecules occurs on the membrane surface. The layer of the concentration polarization for PVA 217 is the thickest. This layer may play a role in permeation resistance. The osmotic pressure of the feed bulk solution at the membrane interface is markedly increased by this layer, and consequently the effective driving pressure is decreased. The permeation characteristics for aqueous solutions of poly(vinyl alcohol) are influenced by these factors.

Effect of polymer blend ratio

The rates of pure water permeability of polymer blend membranes are shown in *Figure 2* where the concentrations of polymer blend in the casting solution are kept constant at 10 and 15 wt% and the ratio of nylon-12–cellulose acetate is changed. As can be seen from *Figure 2*, the rate of pure water permeability decreases with increasing cellulose acetate concentration in the polymer blend. In particular, this decrease is large when the concentration of blend polymer is 10 wt %. When discussing the permeability of the polymer membrane, the physical and chemical natures of the membrane must be considered. If pure water permeability is evaluated from the standpoint of the chemical nature of polymer membrane, the rate of pure water permeability should increase when the content of cellulose acetate, which is more hydrophilic than nylon-12, is higher because water 'clustering' causes deformation due to an hydrophilicity of polymer membrane. However, from the results in *Figure 2*, it is found that increase of hydrophilic property of polymer membrane is unfavourable for water permeability. This finding implies that the balance between hydrophilic and hydrophobic properties in the polymer membrane is an important factor in the water permeability of polymer membrane. When the concentration of cellulose acetate in the polymer blend and the operating pressure increase, the differences between the rates of pure

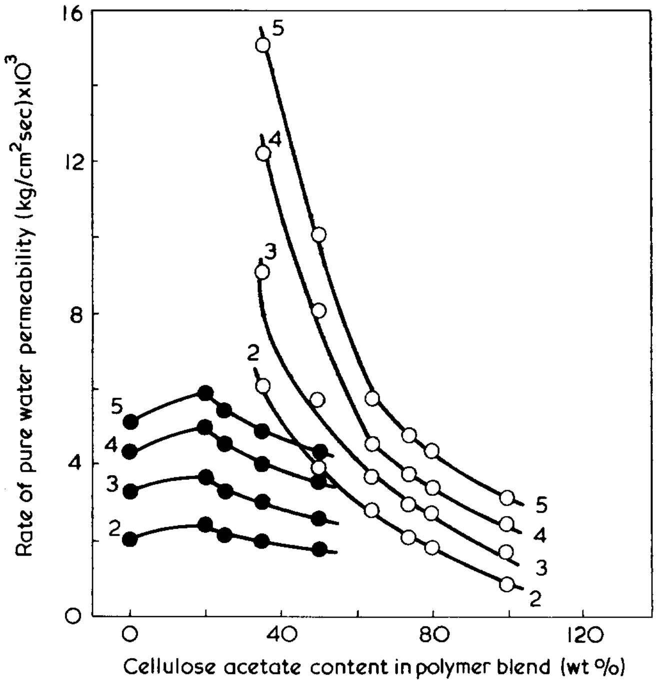

Figure 2 Effect of cellulose acetate content in polymer blend on pure water permeability. Concentration of blend polymer: (○) 10 wt-%, (●) 15 wt-%; heat treatment: 40°C, 15 min; feed: pure water; operating temperature: 40°C; numbers in figure represent operating pressure (kg/cm^2)

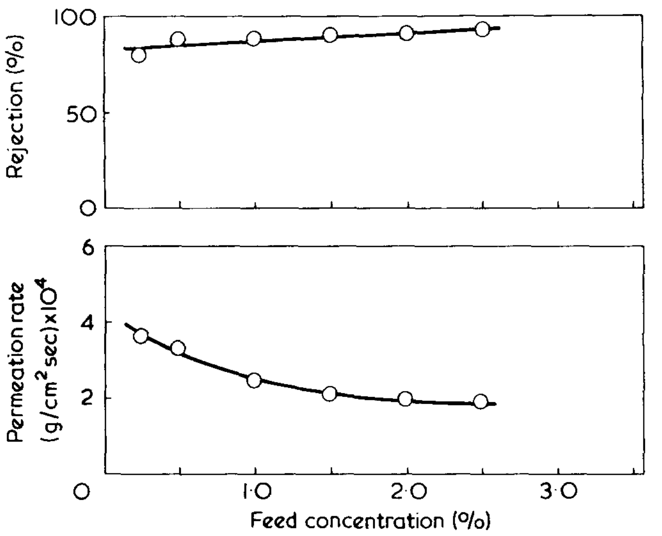

Figure 3 Effect of feed concentration on permeation characteristics. Casting solution: N-12/CA/m-cresol = 7.5/2.5/90 (wt-%); heat treatment: 40° C, 15 min; feed: aqueous solutions of PVA 205; operating condition: 40° C, 2 kg/cm^2

water permeability in *Figure 2* become smaller. On the other hand, from the standpoint of the physical nature of the polymer membrane, a microphase separation between the cellulose acetate molecules and the nylon-12 molecules must be considered. Since the structures of these two kinds of polymer in the casting solution differ as the polymer blend ratio is changed, different microphase separations occur during the evaporation process. Consequently, the fine structure of the resulting membranes changes. The results in *Figure 2* suggest that the physical and chemical nature of the membranes have a complex relation to the permeation characteristics.

Effects of feed concentration and operating pressure

The effect of feed concentration on the permeation rate and the rejection by the polymer blend membrane of an aqueous solution of poly(vinyl alcohol) is shown in *Figure 3* where the total concentration of the polymer blend is 15 wt % and the cellulose acetate–nylon-12 ratio is 1/3. The permeation rate decreases and the amount of rejection increases slightly with an increase in feed concentration. The former effect may be due mainly to an increase of viscosity of the feed solution and of the thickness of the concentration polarization layer of poly(vinyl alcohol) molecules onto the membrane surface with an increase in feed concentration. This effect also depends on an increase in osmotic pressure occurring with it under a given operating pressure, and hence a decrease in effective driving pressure for fluid flow, as well. The latter effect may be attributed to increase of apparent molecular size of solute based on entanglement between poly(vinyl alcohol) molecules and of the thickness of the concentration polarization layer with an increase in feed concentration.

Figure 4 shows the effect of operating pressure on the permeation rate and the rejection by the polymer blend membrane for an aqueous solution of PVA 217. The rate of pure water permeability and the permeation rate increase and the rejection is constant. The extent of increase in the permeation rate is much smaller than that of the rate of pure water permeability with an increase in operating pressure. This difference is dependent on the rejection of poly(vinyl alcohol) molecules. At a given feed concentration, since the effective driving pressure increases with an increase in operating pressure, the permeation rate is increased with it. *Figure 4* also includes the permeation rate and the rejection of aqueous PVA 217 by nylon-12 and cellulose acetate membranes. The permeation rates and the rejections by those membranes are constant regardless of the operating pressure. This phenomenon is attributed to the increase of the membrane compaction under pressure and of the degree of concentration polarization[1,2]. These permeation rates are also smaller than that of the polymer blend membrane. From these results it is inferred that the permeation characteristics in the concentration of aqueous polymer solutions are significantly influenced by the membrane structure and the concentration polarization layer.

When the concentration of cellulose acetate in the polymer blend was larger, it was found in *Figure 2* that the membrane compaction under pressure was greater. In order to investigate this result from a different direction, the permeation characteristics for aqueous solution of PVA 205 with the change of operating pressure were measured. The result obtained is shown in *Figure 5*. When the cellulose acetate content in the polymer blend is higher, the rejection increases as the operating pressure increases. In the case of relatively higher nylon-12 content, the rejection is constant. On the other hand, the extent of increasing the permeation rate for the system of higher cellulose acetate content is smaller than that for higher nylon-12. These phenomena suggest that the compaction under pressure of those membranes having higher cellulose acetate content is larger.

Effect of operating temperature

The effect of operating temperature on the permeation rate and the rejection is shown in *Figure 6*. The permeation

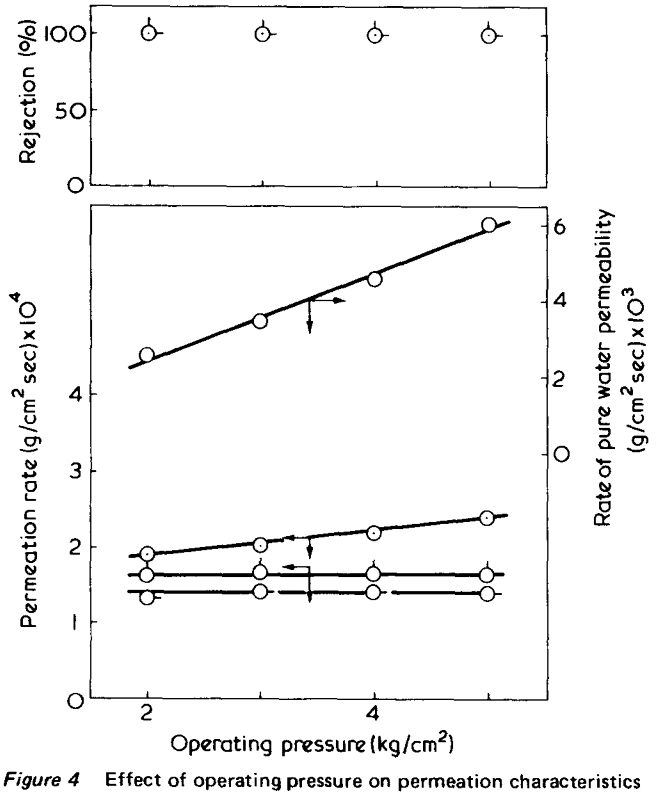

Figure 4 Effect of operating pressure on permeation characteristics for aqueous solution of PVA 217. Casting solution, N-12/CA/m-cresole = 7.5/7.5/85 (wt-%); heat treatment, 40° C, 15 min; feed, (O) pure water, (⊙) 1% aqueous solution of PVA 127; permeation characteristics for nylon-12 and cellulose acetate membranes are represented (Ó) and (O-), respectively; operating temperature, 40° C

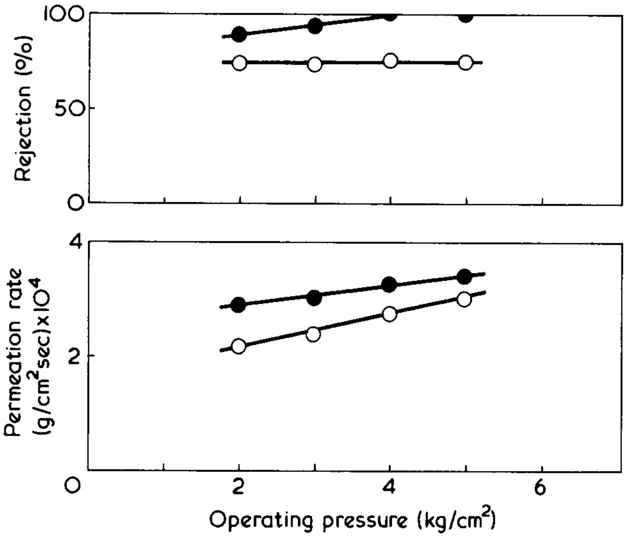

Figure 5 Effect of operating pressure on permeation characteristics for aqueous solution of PVA 205. Casting solution: (○) N-12/CA/m-cresole = 6.7/3.3/90 (wt-%), (●) N-12/CA/m-cresole = 2.0/8.0/90 (wt %); heat treatment: 40°C, 15 min; feed: 1% aqueous solution of PVA 205; operating temperature: 40°C

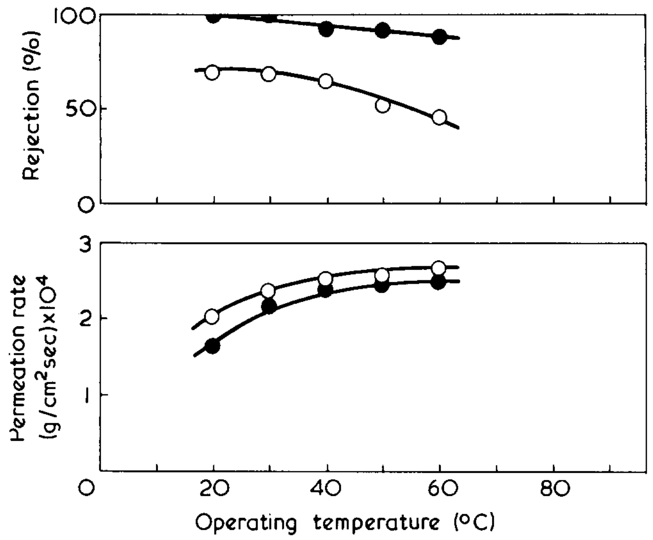

Figure 6 Effect of operating temperature on permeation characteristics. Casting solution: (○) N-12/CA/m-cresol = 7.5/2.5/90 (wt-%), (●) N-12/CA/m-cresole = 11.25/3.75/85 (wt-%); heat treatment: 60°C, 15 min; feed: 1% aqueous solution of PVA 205; operating pressure: 2 kg/cm².

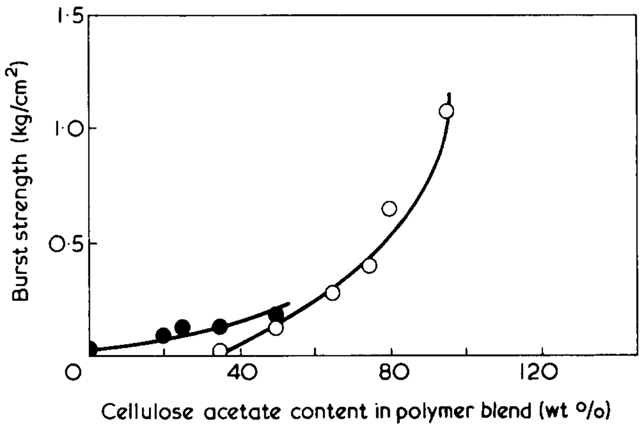

Figure 7 Relationship between cellulose content in blend polymer and bursting strength of polymer blend membrane swollen with water. Concentration of polymer blend: (○) 10 wt-%, (●) 15 wt-%

rate increases and the rejection decreases as the operating temperature increases. These results depend on a decrease in the feed viscosity and an increase in the molecular movement of the membrane substrate with an increase in operating pressure. When the concentration of polymer blend is 15 wt %, the permeation rates are smaller than those where the polymer blend is 10 wt % and the rejections are greater at all operating temperatures. It is reported that the magnitude of the average pore radius in the membranes consisting only of cellulose acetate decreases with an increase in concentration of cellulose acetate[6,8]. The results in *Figure 6* suggest that the former membrane (15 wt %) is denser than the latter (10 wt %).

Bursting strength of polymer blend membranes

Figure 7 shows the relationship between the cellulose acetate content of the polymer blend and the strength of the blend membranes swollen with water. The strength of the blend membrane increases markedly as the cellulose acetate content in the blend increases. The strength of a nylon-12 membrane at a nylon-12 concentration of 20 wt % is less than 0.05 kg/cm² (ref 1) but that of a cellulose acetate membrane although only 10 wt % has the extremely high value of 1.1 kg/cm². It is seen that the bursting strength of nylon-12 membrane is improved by blending with cellulose acetate.

REFERENCES

1 Uragami, T., Maekawa, K. and Sugihara, M. *Kobunshi Ronbunshu* 1977, **34**, 691; *J. Membr. Biol.* submitted for publication
2 Uragami, T., Fujino, K. and Sugihara, M. *Angew. Makromol. Chem.* 1976, **55**, 29
3 Uragami, T., Tamura, M. and Sugihara, M. *Angew. Makromol. Chem.* 1976, **55**, 59
4 Loeb, S. and Sourirajan, S. *Adv. Chem. Ser.* 1963, **38**, 110
5 Manjikian, S. *Ind. Eng. Chem. (Prod. Res. Dev.)* 1967, **6**, 23
6 Uragami, T., Fujino, K. and Sugihara, M. *Angew. Makromol. Chem.* in press
7 Uragami, T., Fujino, K. and Sugihara, M. *Angew. Makromol. Chem.* submitted for publication
8 Kleman, K. and Friedman, L. *J. Am. Chem. Soc.* 1932, **54**, 2637