

# Studies on syntheses and permeabilities of special polymer membranes: 35. Preparation and permeation characteristics of chitin membranes

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## Introduction

Chitin, poly(*N*-acetyl-*D*-glucosamine), is a polysaccharide with a similar chemical structure to cellulose. However, in spite of the fact that their structures are similar, the chemical properties of chitin are markedly different from those of cellulose. In particular, chitin has a better resistance against chemical reagents compared with cellulose. This property of chitin is attributable to a strong micelle structure resulting from hydrogen bonds between the aminoacetyl groups in the chitin molecules<sup>1</sup>.

It is necessary that chitin dissolves easily in certain solvents or chemical reagents in order to be utilized as a fibre and as a membrane, etc. Recently, it was reported that the binary solvents<sup>2</sup> of halogenoacetic acids and organic solvents, the xanthation of alkali chitin by the application of a freezing procedure<sup>3</sup>, and the formic acid-dichloroacetic acid system<sup>4</sup> were suitable for obtaining a viscous chitin solution.

Here, a mixture of *N*-methyl 2-pyrrolidone, *N,N*-dimethyl acetoamide, and lithium chloride was used as a solvent for the dissolution of chitin without degradation of the chitin molecules. The permeation characteristics of chitin membranes prepared from this mixed solvent are discussed from various viewpoints.

## Experimental

Chitin produced by the Sigma Chemical Co. was employed as the membrane substrate. Pure commercial *N,N*-dimethyl acetoamide (DMA) and *N*-methyl 2-pyrrolidone (NMP) were used as solvents for the casting solutions. Lithium chloride (LiCl) was used as additive for dissolution of chitin. Poly(ethylene glycols) (supplied by Sanyo Kasei Co. Ltd.) used as the solutes of feed solutions were PEG 6000 and PEG 20000 whose number average molecular weights were 7800–7900 and 18000–25000, respectively. Poly(vinyl alcohol) (PVA 210, supplied by Kurary Co. Ltd.) was employed as the feed solute.

When chitin powder was added to mixtures of NMP, DMA, and LiCl, no chitin dissolved completely. When the chitin powder was dispersed in mixed solvent of NMP and DMA, then a desired amount of LiCl was added, and this mixed solution was stirred at 25°C for 24 h, chitin was dissolved easily. As can be seen from Table 1, if the added amount of LiCl was small, then the chitin was not completely dissolved. The dissolution mechanism of chitin molecules is due to the severance, by lithium ions, of the hydrogen bonds between the aminoacetyl groups in the chitin molecules, and also was due to the fact that polyamide was dissolved by the addition of salt<sup>5,6</sup>. The solution of chitin was prepared by adding LiCl (2g) giving a viscous solution which was diluted three times with the mixed solvent of NMP and DMA. The membranes were made by pouring this diluted solution of chitin onto a rimmed glass plate, allowing evaporation of the solvent at

the desired temperature for the desired period, and immersing the glass plate together with the membranes into water (25°C). After 24 h in water, the membranes were removed from the glass plate and used for the permeation experiments.

The apparatus, the experimental procedure, and the analysis of feed and membrane-permeated liquid have been reported<sup>7</sup>.

## Results and Discussion

The effect of preparation temperature of the membranes on the permeation characteristics is shown in Figure 1. In general, when the preparation temperature of the membranes becomes higher, the evaporation of solvent in the casting mixture is puffed up and a con-

Table 1 Dissolution of chitin

LiCl (g) *	Dissolution state
1.0	part soluble
1.5	part soluble
2.0	soluble

\* Chitin/NMP/DMA = 0.6/20/20 (g)

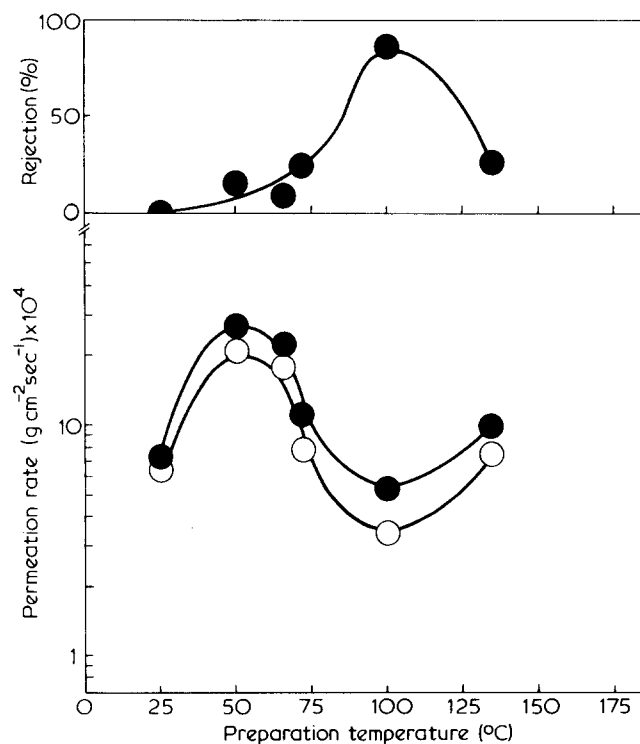


Figure 1 Effect of preparation temperature of membrane on permeation characteristics. Evaporation period, 2 h; feed, (○) pure water, (●) 1% aqueous solution of PEG 6000; operating conditions, 40°C, 1 kg cm<sup>-2</sup>

centrated polymer layer in the surface of the casting mixture is formed. Consequently, the permeation rate for liquid becomes smaller and the rejection for solute in the feed increases. However, as can be seen from Figure 1, the permeation characteristics are significantly changed by the preparation temperature of the membranes. The result implies that the structures of the resulting membranes are dependent on the preparation temperature of the membranes. At the 25°C preparation temperature, the evaporation loss of NMP and DMA are small because the boiling points of these solvents are relatively high. However, these solvents have higher hygroscopicity and LiCl is a deliquescent salt. Therefore, water molecules are absorbed by the casting mixture from the atmosphere during the evaporation step of the membrane formation process. Since the water molecules are a strong non-solvent for chitin, the chitin molecules are aggregated heterogeneously as soon as the water molecules are absorbed into the casting mixture and a rough membrane is formed. The fact that the rejection of PEG 6000 for the membrane prepared at 25°C is small, is attributed to the above phenomenon. The membrane thickness obtained at this preparation temperature is considerably higher. Consequently, the small permeation rate is caused mainly by permeation resistance.

When the preparation conditions of the membrane are at 50°C for 2 h, no NMP and DMA in the casting mixture evaporate completely and the casting mixture is in the solution state. If, under such a state the casting mixture is immersed into water (gelation medium), dense membranes are not formed. The thickness of the resulting membrane at 50°C is thinner than that at 25°C. Therefore, the permeation rate of the membrane obtained at 50°C is greater.

The decrease of permeation rate from 50°C to 100°C is due to the formation of a denser membrane with an increase in the amount of evaporation of the casting solvent. This is suggested by the fact that the rejection for PEG 6000 increases with a rise in preparation temperature of the membrane. In the membrane prepared at 135°C the permeation rate increases again and the rejection for PEG 6000 decreases markedly. These permeation characteristics are attributed to a decrease in the entanglements between the chitin molecules based on thermal decomposition of the chitin molecules.

Figure 2 shows the permeation characteristics when the operating pressure is changed and aqueous solutions of PEG 20000 and PVA 210 are used as feed solutions. The arrows in Figure 2 indicate the direction of pressure change in each operation. Change of the permeation rate for an aqueous solution of PEG 20000 with the operating pressure is similar to that for pure water permeability. Namely, when the operating pressure rises from a lower pressure to a higher pressure, the permeation rates for pure water and aqueous solution of PEG 20000 increase with an increase in operating pressure. Conversely, as the operating pressure lowers from higher pressure to lower pressure, the permeation rates decrease accordingly. In addition, the permeation rates in the system of decreasing the operating pressure are smaller than those in the system of increasing the operating pressure. However, the rejection for PEG 20000 decreases with the operating pressure at lower pressure, the rejection for PEG 20000

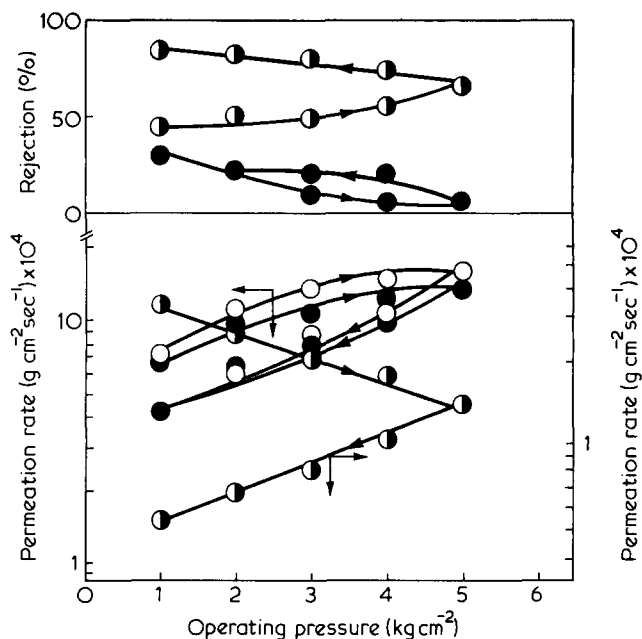


Figure 2 Effect of operating pressure on permeation characteristics. Preparation conditions of membrane, 25°C, 1 h; feed, (○) pure water, (●) 1% PEG 20000, (◐) 1% PVA 210, aqueous solutions; operating temperature, 40°C

becomes higher than the rejection at the same pressure under the system of increasing the operating pressure. These phenomena are dependent mainly on a compaction of the membrane under pressure rather than the effects of blocking pores of PEG molecules in the membrane and concentration polarization of PEG molecules onto the membrane surface<sup>7,8</sup>. The above permeation characteristics for aqueous solutions of PEG 20000 are explained by a decrease of the pore number and pore size based on the compaction of the membrane under pressure.

However, when an aqueous solution of PVA 210 is used as the feed solution, the permeation rate increases and the rejection decreases with an increase in the operating pressure. When the operating pressure lowers from a higher pressure to a lower pressure, even if the operating pressure is the same, the permeation rate is remarkably smaller and the rejection is higher than those rates in the system of an increased operating pressure. These phenomena are attributed to the compaction of the membrane under pressure, in addition the concentration polarization of PVA 210 molecules onto the membrane surface and the blocking of the pores of PVA 210 molecules in the membrane.

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