THE EFFECT OF ADDITIVE TO THE NYLON 4 DIALYSIS MEMBRANES

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The effect of adding certain inorganic salts mainly containing transition metal chlorides (hexahydrate) to the casting solutions of nylon 4 is to swell the nylon 4 membranes and to improve the permeability of NaCl solute for the nylon 4 dialysis membranes. Swelling is affected by the formation of complexes involving the inorganic salts and the amide group of the nylon 4 polymer substrate. The morphologies using scanning electron microscopy (SEM) were studied. The permeability of NaCl and the water content evaluated as a function of the amount of inorganic salts: FeCl$_3$·6H$_2$O, CoCl$_2$·6H$_2$O, NiCl$_2$·6H$_2$O, CuCl$_2$·6H$_2$O and AlCl$_3$·6H$_2$O added. Especially, the best permeability of NaCl is the nylon 4 membrane by adding the different amount of aluminum chloride. The nylon 4 membranes were analyzed by UV-Visible and FT-IR spectroscopy, to investigate the formation of complexes between the salts and the nylon 4 polymer substrate.

INTRODUCTION

The glass-transition temperature, the melting peak point and the hydrophilicity of nylon 4 are better than those of aliphatic polyamide, so the poly (pyrrolidone) polymer is suitable for dialysis membranes. Previous works on nylon 4 membranes have been devoted to improve the performance of nylon 4 membranes reported by Huang et al. To improve the performance of nylon 4 membranes, Lai et al. used Co-60 irradiation which induced hydrophilic vinyl monomers to be grafted onto nylon 4 membranes for reverse osmosis desalination purpose. Jong et al. used a chemical method to graft different hydrophilic monomers onto nylon 4 membranes for reverse osmosis, ultrafiltration, and electrodialysis.

Since the addition of inorganic salts to casting solutions was proven very useful in making cellulose acetate with higher overall performance. As reviewed by Kraus et al., the performance of aromatic polyamide membrane is affected by adding low molecular weight additives in the casting solution. Bottino and co-workers reported the high performance of ultrafiltration polyvinylidene fluoride based membranes cast from LiCl doped solutions.

The present study is to improve the permeability of NaCl solute and the water content of nylon 4 membranes by adding certain inorganic salts mainly containing transition metal chlorides (hexahydrate) to the casting solutions. The formation of complexes involving the inorganic salts and the amide group of the nylon 4 was studied by UV-Visible and FT-IR spectroscopy.

EXPERIMENT

Polymer Synthesis

Nylon 4 was synthesized by CO$_2$-initiated polymerization of 2-pyrrolidone using potassium 2-pyrrolidonate as a catalyst. The molecular weights of samples, measured by a Cannon-Fensake viscometer with m-cresol as a solvent at 25°C, were about
Membrane Preparation

The nylon 4-formic acid solution comprises 10 wt% nylon 4 and 90 wt% mixture of 4 : 1 (V/V) 90% formic acid solution and n-ProH. Then, the solution doped with the amount of 5~20 wt % inorganic salts : FeCl₃·6H₂O, CoCl₂·6H₂O, NiCl₂·6H₂O, CuCl₂·6H₂O, and AlCl₃·6H₂O were stirred at 25°C for 96 hrs, the stable maturation time for the mixture solution. The mixture solution was casted on a clean glass plate. The membrane casted on the glass plate was immersed in a water bath for 10 min. after the membrane on the glass plate was heated in an oven at 30°C. Finally, the film was removed from the bath and leached under running water until additive salts were removed from the membrane.

Dialysis Permeability

A stainless cell consisting of two compartments (171 cm³ each) was used. A membrane was clamped between two compartments using suitably supporting and sealing devices. One of the compartments was filled with distilled water ; the other with testing solution of 0.8 NaCl wt%. The solution in the compartments were stirred during measuring their permeabilities and kept in water bath at 37.0 ± 0.5 °C.

The permeability P (in cm²·min⁻¹), under the assumption of neglecting liquid film resistance of both side of membrane, was calculated from:

\[
\ln \frac{C'' - C'}{C'' - C' - 2C(t)} = \frac{2PA}{\delta V(t)} t
\]

where \( V(t) \) is the volume of the solution at time \( t \), \( A \), the effective membrane area (24.28 cm²), \( \delta \), the membrane thickness, \( C'' \) and \( C' \), the concentration of the concentrate and diluent compartments at initiation, respectively, \( C(t) \), the concentration of diluent compartments at time \( t \). Concentration of NaCl was determined by a Conductivity Meter Model SC-15 (Suntex).

Water Content

Clean and dried membranes with known weights were immersed in distilled water at room temperature overnight to reach equilibrium swelling. The membranes were removed and quickly blotted with absorbent paper to remove surface liquid and weighed quickly. The degree of water content was calculated by the following equation:

\[
\text{Water Content} (%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%
\]

where \( W_{wet}, W_{dry} \), represent the weights of wet, dry membranes, respectively.

Spectrophotometry Analysis

Visible and UV absorption spectral data of the polyamide membranes adding varied inorganic salts were obtained by using a Milton Roy Type 1201 spectrophotometer. FT-IR spectra of the polyamide membranes ranging from 4000 cm⁻¹ to 500
cm\(^{-1}\) were obtained by using the Bomen DA 3002 FT-IR spectrophotometer.

**SEM Photograph**

The surfaces of cryofracture samples coated with gold film of 150A thickness, were measured a Hitachi Co. Type S-570 scanning electron microscopy (SEM).

**RESULTS AND DISCUSSION**

**Effect of Salts Content upon the Permeability and Water Content of the Nylon 4 Membranes**

The effect of inorganic salt: FeCl\(_3\)·6H\(_2\)O, CoCl\(_2\)·6H\(_2\)O.
6H₂O, NiCl₂•6H₂O, CuCl₂•6H₂O, and AlCl₃•6H₂O in the nylon 4 dialysis membranes indicates that the permeability of NaCl solute increases with increasing the concentration of the salts content, as shown in Figure 1. Then, the best permeability of NaCl solute for dialysis is the nylon 4 membranes by adding the different amount of aluminum chloride. It shows that the effect of adding aluminum chloride salt to the casting solutions swells the resultant membranes well. Furthermore, from Figure 1, the permeability of NaCl reaches a maximum at 15 wt% FeCl₃•6H₂O for the nylon 4 membrane; however, the additional amount of 20 wt% FeCl₃•6H₂O into the casting solution of nylon 4 polymer made a supersaturated solution. Since inorganic salts added to the casting solution became neither integral parts of the membrane structure nor chemical changes in the polymer matrix but did themselves swell. Therefore, the permeability of NaCl solute for the nylon 4 dialysis membranes is a function of the additional amount of the salts: FeCl₃•6H₂O, CoCl₂•6H₂O, NiCl₂•6H₂O, CuCl₂•6H₂O and AlCl₃•6H₂O. On the other hand, Table 1 shows that the water contents for the nylon 4 membrane increase with increasing the concentration of the salts content. It also indicates that the effect of adding aluminum chloride salt to the casting solutions is to largely increase the water contents of nylon 4 membranes.

**Figure 5** SEM of cross section:
(a) Nylon 4
(b) 5 wt% FeCl₃•6H₂O-Nylon 4 membrane.
(c) 10 wt% FeCl₃•6H₂O-Nylon 4 membrane.
(d) 15 wt% FeCl₃•6H₂O-Nylon 4 membrane.

**UV-Visible and FT-IR Spectral Analysis**

The formation of polyamide-metal chelate had
been identified from UV-Visible and IR spectra by Yen et al.\textsuperscript{13}. The effect of the additional amount of the salts to the casting solutions of nylon 4 membranes is observed by UV-Visible, as shown in Figures 2–3, and FT-IR spectra in Figure 4. The UV-Visible spectral bands of the 0.001 wt\%, 0.01 wt\% and 0.1 wt\% FeCl$_3$·6H$_2$O in formic acid solution all appear at 255 nm, as shown in Figure 2, when the different amount of FeCl$_3$·6H$_2$O–HCOOH solutions are added to the nylon 4-formic acid solution, stirred for 96 hrs, the stable maturation time for the mixture solution\textsuperscript{12}. The mixture solutions are casted into the membranes which show that the UV-Visible spectral bands different amount of FeCl$_3$·6H$_2$O in the nylon 4 membrane UV-Visible spectral bands are all shifted to a shorter wavelength, about 237 nm, as shown in Figure 3.

These phenomena are also appear in the other inorganic salts: CoCl$_2$·6H$_2$O, NiCl$_2$·6H$_2$O, CuCl$_2$·6H$_2$O, and AlCl$_3$·6H$_2$O added to the casting solution. It was postulated that any complex formations between the inorganic salts and the nylon 4 polymer substrate would involve the cationic portion of the salt and the amide group of the nylon 4 polymer. The formation of complexes can swell the nylon 4 polymer substrate.

The formation of complexes was studied by FT-IR spectroscopy. The FT-IR spectrum for the nylon 4 membrane with 5–15 wt\% FeCl$_3$·6H$_2$O are shown in Figure 4. It shows that a narrowing of the C = O stretching band at 1645 cm$^{-1}$ shifts to
shorter frequency side with increasing the concentration of FeCl$_3$·6H$_2$O.

Another peak due to the C-NH stretching band shifts to longer frequency side with increasing the concentration of FeCl$_3$·6H$_2$O. It is also found that a peak due to the N-H stretching band at 3290 cm$^{-1}$ shifts to a lower frequency with increasing the concentration of FeCl$_3$·6H$_2$O. From these results, it may be confirmed that the formation of complexes involving the inorganic salts and the amide group of the nylon 4 polymer substrate.

**SEM Morphology**

The cross section morphologies of cryofracture surfaces of nylon 4 membranes containing FeCl$_3$·6H$_2$O less than 10 wt% show homogenous, as shown in Figure 5 (A) and (B). At the concentration of 10 wt% FeCl$_3$·6H$_2$O, the asymmetry cavities disperses in the nylon 4 matrix, as shown in Figure 5 (C). When the concentration of FeCl$_3$·6H$_2$O reaches 15 wt% for the nylon 4 dialysis membrane, the number of asymmetry cavities increase and the size of each cavity becomes big, as shown in Figure 5 (D). The results agree with the observations of the additional amount of AlCl$_3$·6H$_2$O in the nylon 4 dialysis membrane, as shown in Figure 6. Thus, the number and size of asymmetry cavities for the nylon 4 membrane increase with increasing amount of the inorganic salts. Qualitatively, these results are in agreement with those of the permeability of NaCl solute investigations because of the swelling effect of the salts for the nylon 4 polymer.

**CONCLUSION**

The permeability of NaCl and the water content for nylon 4 dialysis membranes is a function of the addition amount of the inorganic salts mainly containing transition metal chlorides (hexahydrate): FeCl$_3$·6H$_2$O, CoCl$_2$·6H$_2$O, NiCl$_2$·6H$_2$O, CuCl$_2$·6H$_2$O and AlCl$_3$·6H$_2$O. It assumes that any complexes formation between the inorganic salts and the nylon 4 polymer substrate would involve the cationic portion of the salt and the amide group of the nylon 4 polymer substrate. The number and size of asymmetry cavities for the nylon 4 membrane increase with increasing amount of the inorganic salts because the salts can swell the nylon 4 polymer substrate.

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**References**


9) M. A. Kraus, M. A. Frommor, M. Nemas, and


