Properties of Cellulose/PAN Blend Membrane

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ABSTRACT: The water flux of a cellulose/PAN blend membrane increased with the PAN content, while retention to glucosan T40 decreased. The water flux decreased and the retention increased with the whole solid content. The membrane obtained had a high ability to remove creatinine and urea. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 3105–3111, 2002; DOI 10.1002/app.10021

Key words: cellulose; polyacrylonitrile; blend membrane

INTRODUCTION

Interest in polymer blends has been increasing in recent years. In fact, since it is very costly to develop new homopolymers, and as it is well known that when two different polymers are mixed, the result is often a multiphase system and presents a nonlinear cooperative effect, resulting in materials possessing various properties. However, there have been few detailed studies dealing with polymer blends where one component was unmodified cellulose. This is probably due to certain disadvantages inherent in the preparation of cellulose blends with polymers: For example, cellulose cannot melt and no convenient organic solvent has been available until recently. In recent years, a variety of solvents for cellulose have been described.[1–20]

The paraformaldehyde/dimethyl sulfoxide (PF/DMSO) system seems to be a favorable one. Since cellulose and polyacrylonitrile (PAN) are membrane materials with different advantages, for example, cellulose is abundant and can regener-

ate[21] and PAN is a synthetic polymer which has the property of excellent chemical stability to endure acid and alkali, bacterium, light and climate, and heat,[22,23] it is of great importance to investigate the properties of the cellulose/PAN blend membrane. Since PAN is also soluble in DMSO, the PF/DMSO system was chosen as a cosolvent for the cellulose/PAN blend.

EXPERIMENTAL

Materials and Reagents

The cellulose sample employed was cotton linters with a degree of polymerization (DP) of 495, heated at 105°C to a constant weight and kept over fresh phosphorus pentoxide in a desiccator before use. Reagent-grade DMSO, paraformaldehyde, urea, creatinine, ammonium chloride, sodium hydroxide, dimethylaminobenzaldehyde, picric acid, and oil of vitriol were supplied by the Shanghai Feida Chemical Co. (Shanghai, China). PF was ground into powders and dried over fresh phosphorus pentoxide in a desiccator before use. The number-average molecular weight of PAN (Jinshan Chemical Co., China) was 51,000. Special-class anthrone (Shanghai Chemical Reagent

Plant, Shanghai, China) acted as color-producing reagent for ultrafiltration. The weight-average molecular weight of analysis-grade glucosan T40 (Pharmacia Co., Sweden) was 41,500, which acted as base material for ultrafiltration.

Preparation of Blend Solution

The cellulose, PAN, PF, and DMSO (cellulose and PF had the same weight) were put into a 500-mL flask; the mixture was heated to 60°C under mechanical stirring for 30 min and then heated to 115–120°C for 1 h, at which time cellulose would dissolve. After being kept under a vacuum for 5 min to remove the remaining PF and then filtered, homogeneous blend solutions with various compositions were obtained. The concentrations of the solutions ranged from 5 to 9%.

Membrane Preparation

Membranes were cast from the blend solutions with various ratios through the phase-inversion procedure: The solution was cast onto a dry and smooth glass plate by employing a laboratory caster to form a homogeneous liquid layer with a certain thickness, which was dipped into the water solution of DMSO to be solidified after a certain time of evaporation in air. When the membrane was taken off the glass plate, all membranes were washed by distilled water until solvent free and kept in distilled water for use.

Measurement of Membrane Property

Measurement of Water Flux

Water flux was measured under a pressure of 0.1 MPa at 25°C on a ultrafiltration device from Sartorius Co. The equation was

$$\text{water flux} = \frac{\text{water flow volume (L)}}{\text{membrane area (m}^2) \times \text{time (h)}}$$

Measurement of Retention to Glucosan T40

Retention to T40 was measured at a 620-nm wavelength on a 751G spectrophotometer (Shanghai No. 1 Analysis Instrument Co., China). From the values of the absorption of the glucosan solution before and after ultrafiltration, we can obtain the corresponding glusocan concentrations and calculate the retention as follows:

$$\text{Retention} = \left(1 - \frac{2 \times c_1}{c_0 + c_2}\right) \times 100\%$$

where c_1 and c_2 refer to the concentration of the flow solution and the remaining solution after ultrafiltration separately. c_0 refers to the primary concentration before filtration.

Measurement of Elimination of Urea and Creatinine on Cellulose Concentration

Elimination of urea and creatinine was measured at 430 and 510 nm separately on the 751G spectrophotometer. From the values of the absorption of the solution before and after ultrafiltration, we can obtain the corresponding concentrations and calculate the elimination of urea and creatinine. The solution for ultrafiltration was prepared as follows: Urea, 300 mg, was dissolved in a small amount of distilled water and 20 mg creatinine was dissolved in a small amount of ammonium chloride. Both solutions were mixed together into a 2000-mL flask, diluted to the scale of 200 mL by water, and then kept in a refrigerator for use. The color agent for urea was prepared by mixing 5 mL of a 10% sodium hydroxide with 25 mL saturated picric acid. The color agent for creatinine was prepared as follows: *p*-Dimethylaminobenzaldehyde, 2.5 g, was dissolved in 50 mL alcohol in a 100-mL flask, 5 mL oil of vitriol was added into it, and then it was distilled to the scale of 100 mL by alcohol. The volume ratios of the solutions to color agents were 2:1. The equation used was

$$\text{Elimination} = \frac{2 \times c_1}{c_0 + c_2} \times 100\%$$

where c_0, c_1, and c_2 have the same meaning as described above.

Cross-section Morphology of the Membrane

A Comscan-Series-4 scanning electron microscope was used to study the cross-section morphology of the membranes. The membranes were dried at room temperature and fractured in liquid nitrogen, then sprayed with gold for testing.

RESULTS AND DISCUSSION

Dependence of Water Flux and Retention to Glucosan on Blend Ratio

Water flux showed an increasing tendency with the content of PAN (Figs. 1 and 2). [The concen-
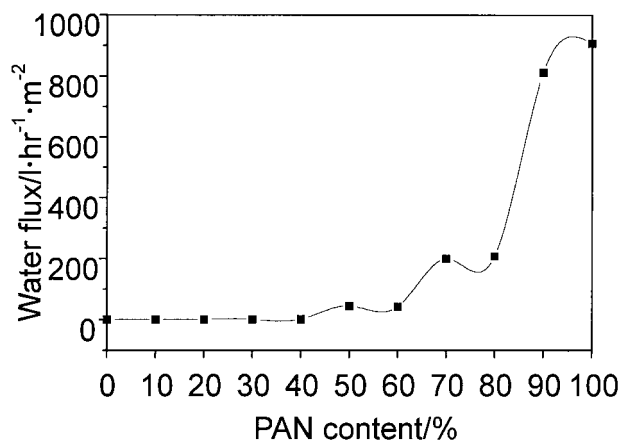
Figure 1   Dependence of water flux on blend ratio.

trations of the solution were all 9% (wt.).] According to our research,[24] cellulose and PAN macromolecules may be thermodynamically incompatible at the crystal region. The tendency of self-aggregation of both macromolecules increased with the content of PAN, and the dimension of the domain and the pores formed between two kinds of domains also increased. Phase separation became worse, which led to an increase of the water flux and a decrease of the retention of the blend membrane.

SEM photographs (Fig. 3) of the blend membranes with different blend ratios show that the cross sections were all divided into three parts: the thin layer surface, the middle transferring layer, and the underneath support layer; the support layer became more asymmetric with the content of PAN. The form of the pores was transferred from the sponge pore to the needle pore, then to the finger pore, the aperture increased, and the structure loosened. The pore of the cellulose membrane was a typical dense sponge pore, that of the PAN membrane was a typical loose finger pore, that of membrane with the blend ratio 7:3 was stratified through a number of little pores, and a finger pore emerged from the membrane with the blend ratio 6:4. The aperture increased from the outer to the inner layer.

Dependence of Water Flux and Retention on Concentration of Blend Solution

The concentration discussed below ranged from 5 to 9% and the blend ratio was 9:1. Cellulose and PAN macromolecules existed in the casting solution in two states, that is, the macromolecular

network was formed by a certain number of macromolecules through intermolecular interaction and macromolecular entanglement; the other was micelle aggregate (microcell) formed through the macromolecular approach and macromolecular entanglement and aggregation. So, there existed two kinds of pores on the skin-layer surface of the membrane formed by macromolecules corresponding to the two aggregating states: One was a network pore formed by the chain-segment network with a smaller dimension and a larger number; the other was a microcell pore with a larger dimension and smaller number. As concentration increased, not only did the density of the macromolecules increase, which led to a density increase of the macromolecular network, but also the macromolecular entanglement among neighboring microcells increased and the average aperture of both kinds of pores decreased, which led to a decrease of the pore ratio and appeared as a decrease of the water flux and an increase of retention macroscopically. In addition, the wall of network pores formed from a casting solution of higher concentration was thicker, which led to an increase of resistance when water passed through; the rate of water penetration decreased and water flux decreased (Fig. 4).

Dependence of Water Flux and Retention on Temperature of Casting Solution

The concentration values of solutions discussed below were all 7% (wt) except as specially indicated (Fig. 5). Water flux decreased and retention
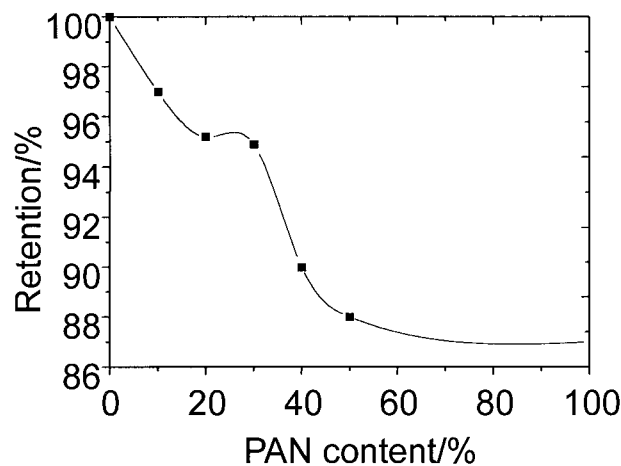

Figure 2   Dependence of retention to T40 on blend ratio.
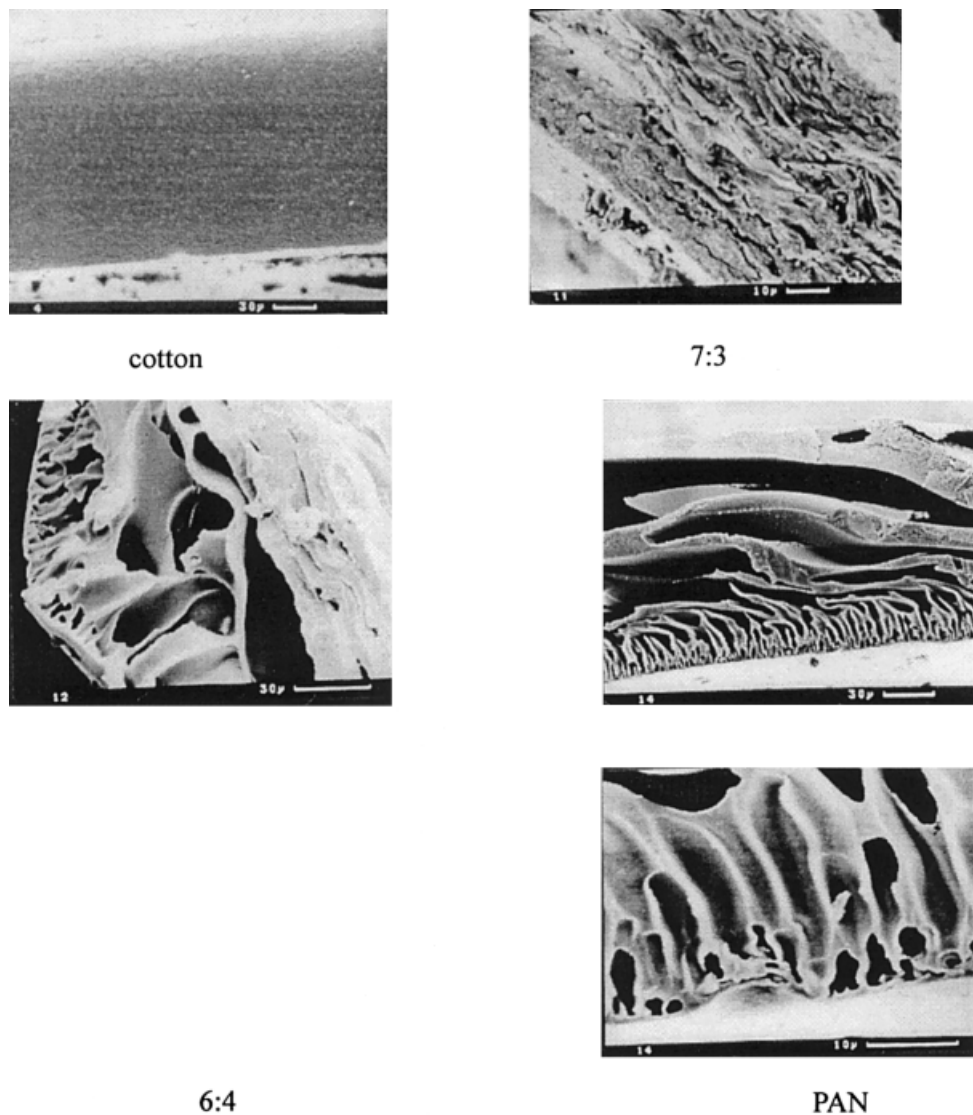
cotton

7:3

6:4

PAN

Figure 3 SEM photos of blend membrane cross section with different ratio.

increased with the temperature of the casting solution, mainly because the evaporation rate of the solvent increased with the temperature of the casting solution, which controlled the interdiffusion between water and the solvent. The casting solution was concentrated, which led to a decrease of the water flux and an increase of the retention.

Dependence of Water Flux and Retention on Preevaporation Time

Water flux reached a maximum and retention reached a minimum when the preevaporation time reached 3 min, which may be concerned mainly with the character of the preevaporation

process (Fig. 6). As DMSO is a strong hydrophilic solvent, there existed an interdiffusion between the water and the solvent during preevaporation. The entrance of the water into the surface of the casting solution controlled the diffusion during the initial stage of the preevaporation process (<3 min). Water was a nonsolvent to the blending system and its surface tension was rather strong, which helped the formation of a rather loose membrane-layer structure with large pores, so water flux increased and retention decreased. When the preevaporation time reached 3 min, the evaporation of the solvent and the entrance of the water was balanced; water flux was maximum. With further preevaporation, the evaporation of
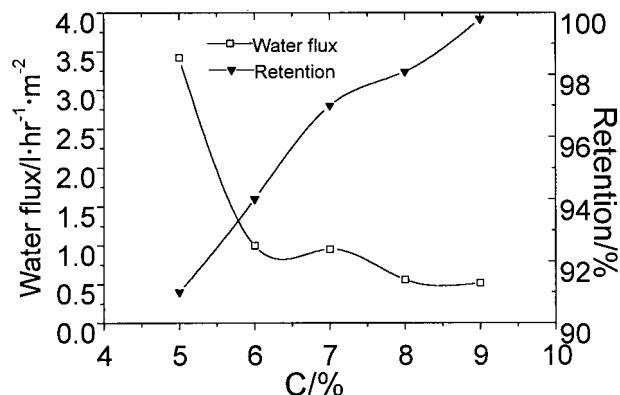
Figure 4 Dependence of water flux and retention on concentration.

Figure 6 Dependence of water flux and retention on preevaporation time.

the solvent controlled the process, which led to the concentration increase of macromolecules in the casting solution and a rather dense skin layer formed. The retention increased and water flux decreased.

Dependence of Water Flux and Retention on Preevaporation Temperature

Figure 7 shows that the membrane property fluctuated during the invested preevaporation temperature range. The needed membrane property can be obtained through control of the preevaporation temperature.

Dependence of Elimination of Urea and Creatinine on Blend Ratio

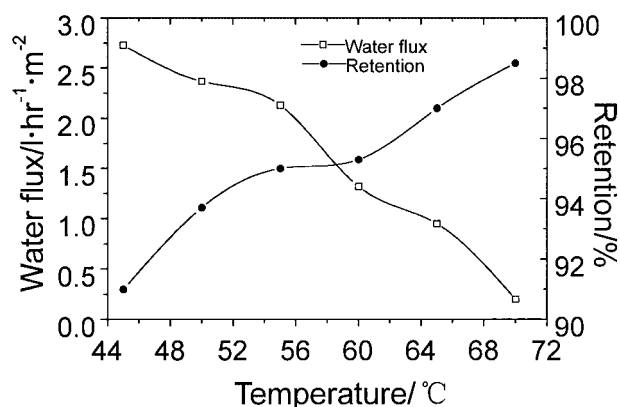The concentration values discussed below were 9% (wt). Figure 8 shows that the blend membrane

had a rather high ability to eliminate creatinine and urea at the same level as that of pure cellulose membrane[25] and the PAN membrane due to dialysis,[26,27] which may be of use for blood hemodialysis.

Dependence of Water Retention on Blend Ratio

The hydrophobic nature of PAN provides ease of care, while the hydrophilic nature of cellulose provides the moisture transmission behavior necessary for comfort. As the cellulose/PAN blend is not only used for membranes but also for fiber, comfort is necessary and water retention is an important value. The value of water retention of the blend showed a decreasing tendency with the PAN content except in the range of 40–60%, where there was a maximum (Fig. 9). Since cellulose and PAN were incompatible at the crystal
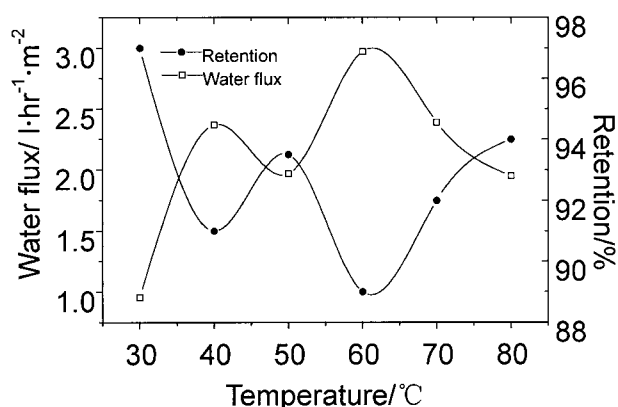

Figure 5 Dependence of water flux and retention on temperature of casting solution.

Figure 7 Dependence of water flux and retention on preevaporation temperature.

region[24] and the water retention of PAN was lower than that of cellulose, the value of the water retention of the blend membrane decreased with the content of PAN. When the content of PAN reached 50%, which formed a certain distracting action on the cellulose macromolecules, the inter-action among cellulose macromolecules lessened, hydrogen bonds decreased, and free hydroxyl groups increased, which resulted in increase of their adsorption on the water molecules.

From the above study, it was seen that the cellulose/PAN blend membrane had a high ability to eliminate creatinine and urea. The membrane structure changed from dense to loose with the blend ratio and different kinds of membranes may be prepared according to different needs and may be used in the preparation of artificial internal organs.

CONCLUSIONS

1. Water flux increased and retention decreased with the content of PAN.
2. Water flux decreased and retention increased with the concentration and temperature of the blend solution.
3. The property of the membrane could be controlled by membrane-making conditions, that is, preevaporation temperature and time and the blend ratio.
4. The blend membrane had a high ability to eliminate urea and creatinine during the blend range.
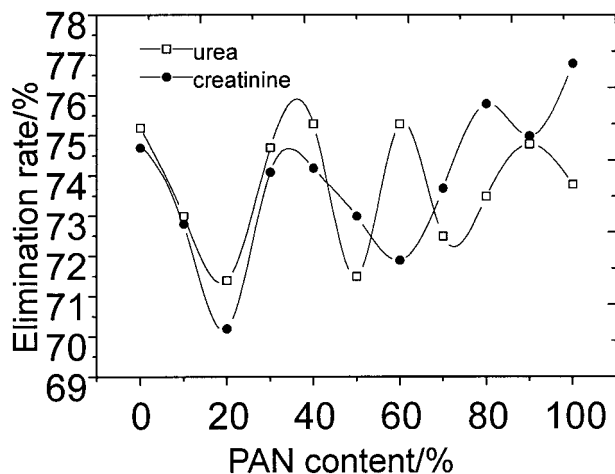

Figure 8 Dependence of elimination of urea and creatinine on blend ratio.
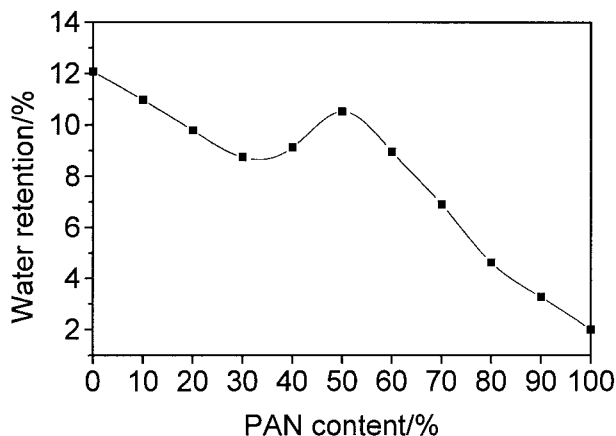

Figure 9 Dependence of water retention on blend ratio.

5. Water retention showed a decreasing tendency with PAN content except in the range of 40–60%, where there was a maximum.

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