

Preparation of Polyethersulfone Ultrafiltration Tubular Membranes with Superior Properties

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Abstract

Phase inversion via immersion precipitation was employed for PES tubular membrane preparation and using N,N-dimethylacetamide(DMAc) as solvent, PEG-400 as main constant additive. Through the experimental study we obtain a preparation process of PES tubular membrane with superior properties. Ethanol caused an increment in the flux at low coagulation bath temperature relative to the non-ethanol. And the low temperature of coagulation bath also improve membrane's rejection and its influence was most important. Other conditions included that the casting solution temperature must not be too high (15°C was best) and the membrane don't be exposed to atmosphere in long time. The prepared membrane under this condition shows excellent performance on flux and retention. Test results show that the flux can be up to 160 L·m⁻²·h⁻¹ and the rejection can reach more than 97% (for ovalbumin) under this condition. The flux was increased clearly compare to non-ethanol and high temperature.

Keywords: Membrane, Polyethersulfone, Ultrafiltration, Additives

Introduction

Generally, polysulfone (PSF) and polyethersulfone (PES) are widely used for the preparation of microfiltration (MF), ultrafiltration (UF) and gas separation membranes. Besides, they are principally to the favorable characteristics of wide temperature limits, wide pH tolerances, fairly good chlorine resistance, easy to fabricate membranes in a wide variety of configurations and modules, wide range of pore sizes available for UF and MF applications ranging from 10Å to 0.2µm and good chemical resistance to aliphatic hydrocarbons, alcohols and acids.

The common technique for the preparation of asymmetric ultrafiltration membranes is the phase inversion method. Membrane formation occurs in a very short time and involves a great number of elementary steps. However, more likely in some systems, a few or one mechanism is important, so it is worthwhile to look for some consistent correlation between a single parameter and the obtained membrane structure. Several researches have reported the effect of additives such as polyvinylpyrrolidone(PVP) on the performance of an ultrafiltration membrane. This experiment was conducted to study the effect of additives such as PEG-400 and ethanol on the performance of membrane.

Experimental Materials

Polyethersulfone(Ultrason E6020P, Mw=58000 g/mol) provided by BASF Co(Germany). N,N-dimethylacetamide(DMAc) was purchased from Merck (Hohenbrunn, Germany). PEG was purchased from Tianjin Chemical Reagent Co. The molecular weight Mw of PEG was 400 g/mol. Distilled water was used through the experiments. Ethanol was purchased from Tianjin Chemical Reagent Co. Ultraviolet spectrophotometer was purchased from SHIMADZU Co.

Preparation of Membranes

Homogeneous solutions of the polymer dissolved in DM Ac were prepared using PEG additives by stirring and heating at 70°C until the solution is completely dissolved and homogeneous. The resultant polymer solution was kept in a glass bottle and air bubbles in the casting solutions were reduced by ultrasonification process for several hours. The solution was cast on support tube by machine at room temperature.

In order to guarantee a complete phase separation, the membrane was stored in the coagulation bath for 24 h. This allows the water soluble components in the membrane to be leached out.

Flux and Rejection

The performances of the prepared membranes were characterized by using a cross flow system. All filtration experiments were carried out in a cross flow cell. The retentate was circulated by a centrifugal pump. The detail of the experimental set up is shown in Fig.1. Egg albumin was used as the feed for all trials. The retention of protein was investigated for prepared membranes by measuring the amount of protein in the permeate. The

fluxes of each membrane were determined at 15 min with a transmembrane pressure of 0.1MPa. The experiments were carried out at 25°C.

The performance of the prepared membranes were characterized by using a cross flow system. The detail of the experimental set up is shown in Fig.1.

Results and Discussions

Fig.1 shows pure water permeation of prepared membranes cast from 28 wt% PES, 51 wt% DMAc and 10wt%, 14 wt%, 18 wt% and 22wt% PEG. The fluxes of each membrane were determined at 10 min with a transmembrane pressure of 0.1MPa.

UF experimental data are summarized in Fig.1. Using PEG as additive, fluxes of each membrane increases from 47 to 167 l/m²h⁻¹ with an increase of ethanol concentration in the dope solution. The tubular membranes with the dope solution containing 0–25 wt.% ethanol concentration have a dense external surface and different pore sizes in internal surface.

With the coagulation bath temperature decrease, the flux decline obviously. And in the coagulation bath temperature 30~40°C the flux change greatly. But under 20°C the flux decline slowing. The coagulation bath temperature play an important role in all the factors of film forming.

From Fig.2, it is observed that the influence of different small molecule additive on membrane flux is significant. In the three additives, by adding 3% ethanol the flux obviously is the biggest, and the effect of adding acetone and lithium chloride is weak, which is far less obvious compare to adding ethanol. Coagulation bath at different temperatures show the same rules. The Fig.2 show that adding ethanol in the casting solution can increase the membrane flux.

The picture shows the effect of the ethanol and the coagulation bath temperature on membrane flux. In the diagram, the flux of ethanol is reduced as the additive increases, and the higher coagulation bath temperature increased, the more obvious. When the coagulation bath temperature is low, the effect on the flux is weak. At 11 °C, the flux is almost the same and close to the membrane without ethanol. It is observed that the influence ethanol on membrane flux decreased with coagulation bath temperature decreasing.

The Fig.5 shows that the ethanol content decreased, the rejection rate of tubular membrane changed little. When ethanol content was higher than 3%, the amount of retention was low obviously. This demonstrates that adding very small amounts of ethanol to casting solution don't make rejection rate to decline.

After adding ethanol, the membranes have a greater increase in flux and higher solute rejection as shown in Fig.5 and Fig.6. As ethanol is added to the dope solution, PWP of PES tubular membranes increases from 90 to 165 L/(m²·h⁻¹). Ethanol also was used as additive to improve the separation performance of PES tubular membranes and compare with the separation performance of other non-ethanol. From the two picture, when the coagulation bath temperature was low (under 30°C), the improvement result is more obvious.

Conclusions

Based on the above experimental results, the combining effects of low coagulation bath temperature and small molecule additives do make significant impact on membrane separation performance. At low coagulation bath temperature, PWP of PES tubular membranes has some decrease while it has the higher solute rejection. The addition of ethanol additive in the polymer solution has been shown to play an important method in the development of membrane performance with improved separation.

References

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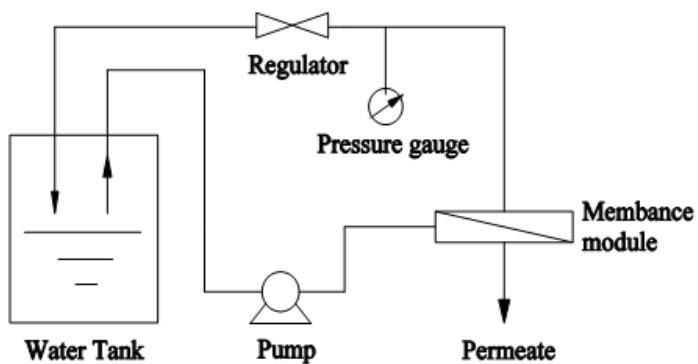


Figure 1. Flowchart of membrane testing

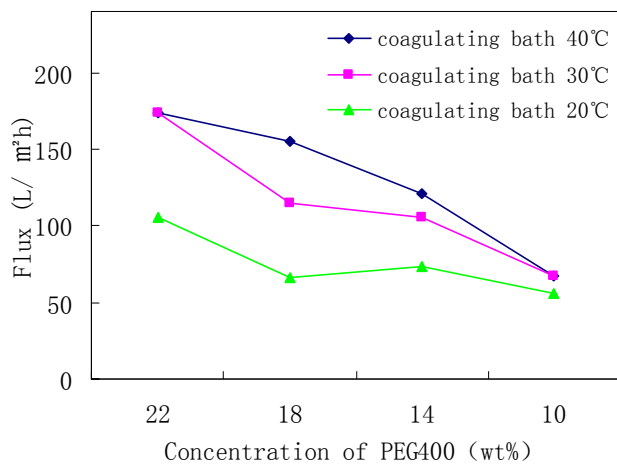


Figure 2. Effects of PEG concentration and coagulation bath temperature on pure water permeation flux

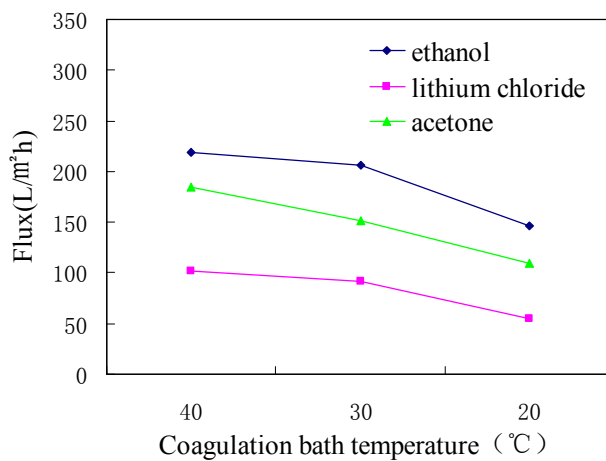


Figure 3. The effect of different small molecule additive on Flux

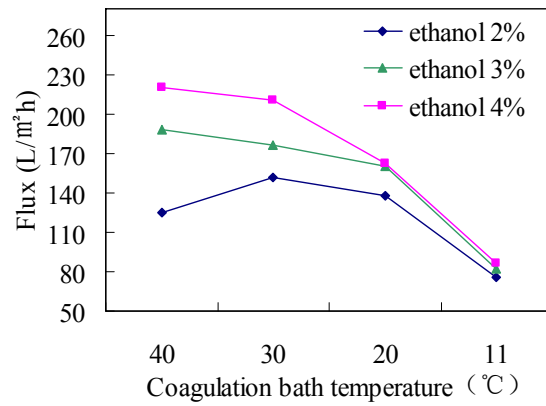


Figure 4. The effect of the ethanol and the coagulation bath temperature on membrane flux

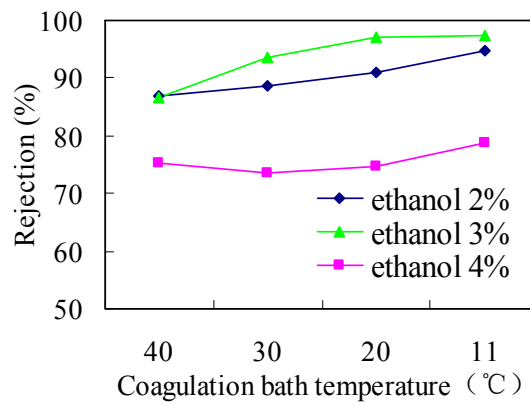


Figure 5. The effect of the ethanol and the coagulation bath temperature on membrane Rejection

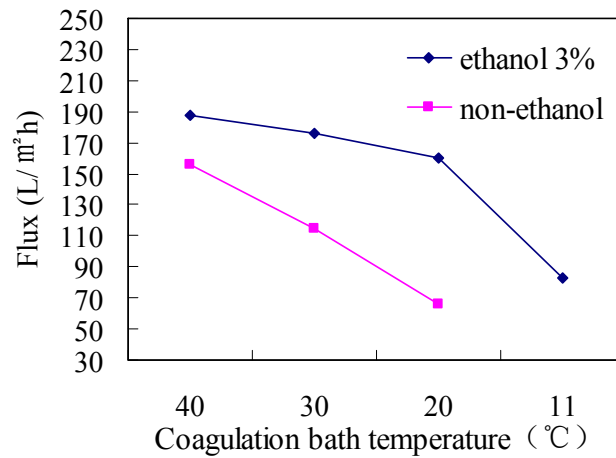


Figure 6. The change of membrane Flux with addition of ethanol

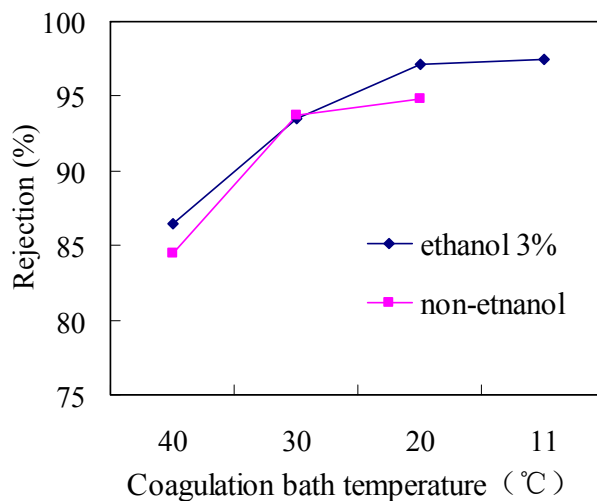


Figure 7. The change of membrane Rejection with addition of ethanol