

PREPARATION OF POLYETHERSULFONE ULTRAFILTRATION MEMBRANES FOR MILK CONCENTRATION AND EFFECTS OF ADDITIVES ON THEIR MORPHOLOGY AND PERFORMANCE

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Abstract Polyethersulfone membranes were prepared from quaternary systems containing *N,N*-dimethylacetamide (DMAc) as solvent, polyvinylpyrrolidone (PVP) as constant additive and acetic acid, acetone and water as variable additives. Phase inversion via immersion precipitation was employed for manufacturing of membranes. The prepared films were immersed in the mixture of pure water and 2-propanol (30/70 vol%) as the non-solvent. Acetic acid caused an increment in the flux at high polymer concentration (16 wt%) and a decline in the flux at low polymer concentrations (10 wt% and 13 wt%). Acetone and water as the solvent in the casting solution declined the flux at any polymer concentration tested. The morphology and performance of the prepared membranes were investigated by scanning electron microscopy and separation experiments using milk as the feed.

Keywords: Membrane; Ultrafiltration; Polyethersulfone; Phase inversion; Milk.

INTRODUCTION

Polymeric membranes have been developed for a variety of industrial applications^[1, 2]. Each application imposes specific requirement on membrane material and structure. There are several ways to prepare polymeric membranes including sintering, stretching, track etching and phase separation. The final morphology of the membrane depends on the properties of the material and the processing conditions. The majority of the membranes are prepared by controlled phase separation of a polymer solution into two phases: one with a high polymer concentration, and one with a low polymer concentration. The concentrate phase solidifies shortly after phase separation, and forms the membrane. The performance of the membranes depends on the morphology formed during phase separation, and subsequent modification. The membranes are formed by polymer precipitation, which occurs as a consequence of concentration variations following diffusive interchange between the solvent and the non-solvent. The role of the polymer precipitation is determined at each point by the progress of the concentration, which is in turn governed by the interchange rate. Depending on the rate of polymer precipitation, the following three types of membranes can be obtained^[3].

- (i) Symmetric, with an almost even porosity across the membrane cross section
 - (ii) Asymmetric, with a selective thin micro-porous upper layer on a thicker macro-porous globular or spongy sublayer
 - (iii) Asymmetric, with large voids and/or finger-like cavities beneath the micro-porous upper layer
- A low precipitation rate leads to type (i) membranes, whereas a high precipitation rate results type (iii) membranes.

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

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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^[4-8]. Boom *et al.* studied the important role of PVP in the phase inversion process^[9, 10]. Findings reveal that the phase inversion mechanisms occur by spinodal decomposition either to form the dense skin layer as well as the micro-porous sub layer. Influence of the concentration of low molecular weight additives such as octanoic acid and carboxylic acid on the flux of polyethersulfone (PES) membrane was studied by Jonsson *et al.*^[11]. Kim *et al.*^[12] studied the effects of ZnCl_2 in the polysulfone casting solution on the formation of membrane structure and performance. The addition of ZnCl_2 induced the intermolecular association of extended polymer chains in the solution and could produce the ultrafiltration membrane having small pores without any significant change in porosity. The effect of sodium dodecyl sulfate (SDS) solutions as a gelation medium on the formation of polyethersulfone membranes was studied by Alsari *et al.*^[13].

At the present time, many cheese manufacturing plants use ultrafiltration membranes for milk concentration. The membranes employed in this huge market may be modified to provide higher flux and rejection. This shows the importance of on-going research in this field. In this study, the effects of additives (acetic acid, acetone and water) in quaternary casting solutions (PES/PVP/DMAc/additive) on morphology and performance of polyethersulfone ultrafiltration membranes have been studied.

EXPERIMENTAL

Materials

Polyethersulfone (PES) Ultrason E6020P ($M_w = 58000$ g/mol, porous flake) provided by BASF Co (Germany), polyvinylpyrrolidone (PVP), acetic acid, acetone and *N,N*-dimethylacetamide (DMAc) from Merck were used for trails. The molecular weight M_w of PVP was 25000 g/mol. Distilled water was used through the experiments.

Scanning Electron Microscopy (SEM)

The cross sections of the prepared membranes were inspected with a scanning electron microscope (SEM, Philips). The samples of the membranes were frozen in liquid nitrogen and fractured. After sputtering with gold, they were viewed with the microscope at 25 kV.

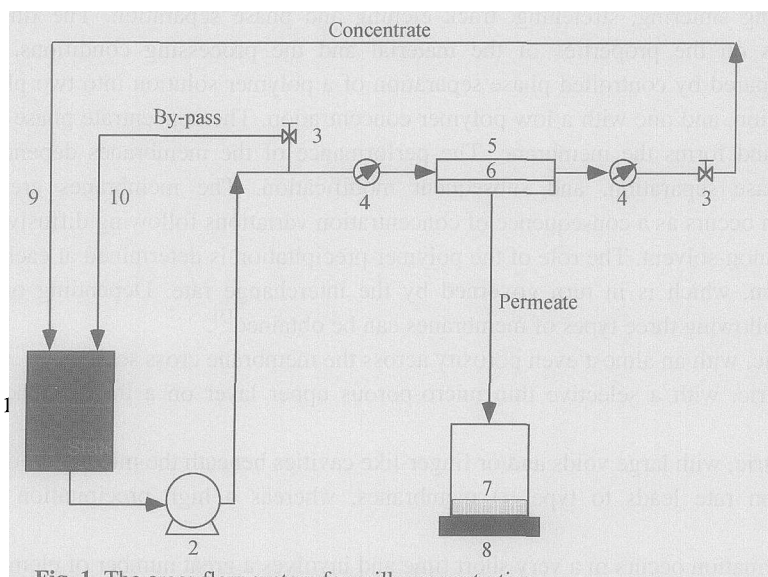


Fig. 1 The cross flow system for milk concentration

1) Feed tank; 2) Pump; 3) Valve; 4) Pressure gauge; 5) Crossflow cell
6) Membrane; 7) Permeate; 8) Balance; 9) Concentrate; 10) By-pass

Flux and Retention

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. Milk was used as the feed for all trails. The retention of protein was investigated for prepared membranes by measuring the amount of protein in the permeate using the standard Brathford method^[14]. The fluxes of each membrane were determined at 15 min with a transmembrane pressure of 200, 400 and 600 kPa, respectively. The experiments were carried out at 20°C.

Preparation of Membranes

Homogeneous solutions of the polymer dissolved in DMAc were prepared using various additives by stirring. The solution was cast on a smooth glass plate by film applicator at room temperature. The membrane thickness was maintained at 100 μm . The film was immediately immersed in the coagulation bath containing a mixture of distilled water and 2-propanol (30/70 vol%) 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. As the final stage, the membrane was dried by placing between two sheets of filter paper for 24 h at room temperature. The different compositions of casting solutions are listed in Table 1.

Table 1. Compositions of casting solutions

PES (wt%)	(DMAc) (wt%)	Acetic acid (wt%)	Acetone (wt%)	Water (wt%)	PVP (wt%)
16	80	2	—	—	2
16	78	4	—	—	2
16	76	6	—	—	2
13	83	2	—	—	2
13	81	4	—	—	2
13	79	6	—	—	2
10	86	2	—	—	2
10	84	4	—	—	2
10	82	6	—	—	2
16	80	—	2	—	2
16	78	—	4	—	2
16	76	—	6	—	2
13	83	—	2	—	2
13	81	—	4	—	2
13	79	—	6	—	2
10	86	—	2	—	2
10	84	—	4	—	2
10	82	—	6	—	2
16	80	—	—	2	2
16	78	—	—	4	2
16	76	—	—	6	2
13	83	—	—	2	2
13	81	—	—	4	2
13	79	—	—	6	2
10	86	—	—	2	2
10	84	—	—	4	2
10	82	—	—	6	2

RESULTS AND DISCUSSIONS

Membrane Morphology

Effect of acetic acid

Figures 2 and 3 show micrographs of cross sections of membranes cast from 16 wt% and 13 wt% PES, 2 wt% PVP and 2 wt%, 4 wt% and 6 wt% acetic acid. DMAc was used as the solvent and mixture of water and 2-propanol (30/70 vol%) was employed as the non-solvent. The flat membranes obtained from 16 wt% PES exhibit a highly heterogeneous structure owing to the presence of large voids and cavities of different sizes and shapes beneath the upper layer. The membrane with 13 wt% PES (without acetic acid) demonstrate a structure, which looks like channels or large open pores from the top to the bottom of the membrane. This morphology is named the channel like structure^[15].

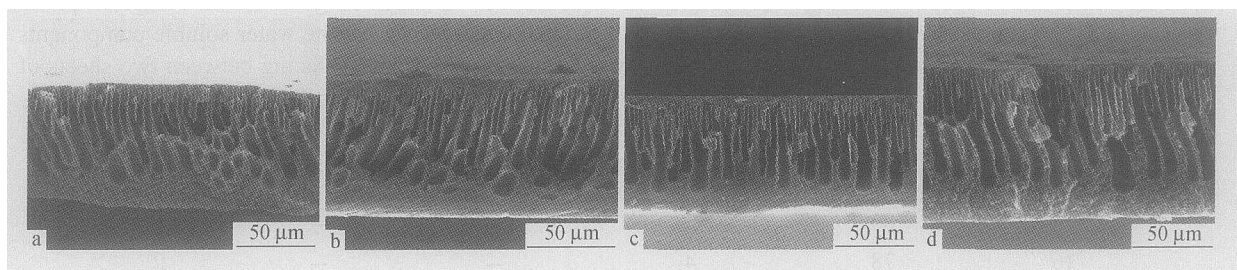


Fig. 2 SEM micrographs of cross sections of membranes prepared from PES/PVP/DMAc/acetic acid/water+2-propanol (30/70 vol%) casting solutions of different compositions
a) 16 wt% PES, 2 wt% PVP; b) 16 wt% PES, 2 wt% PVP and 2 wt% acetic acid;
c) 16 wt% PES, 2 wt% PVP and 4 wt% acetic acid; d) 16 wt% PES, 2 wt% PVP and 6 wt% acetic acid

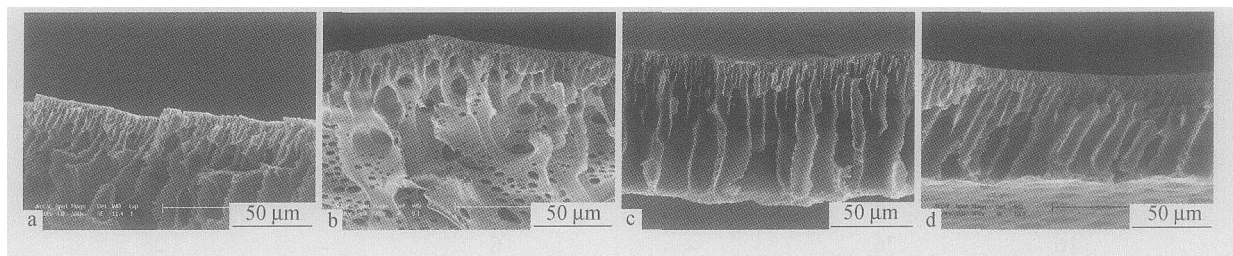


Fig. 3 SEM micrographs of cross sections of membranes prepared from PES/PVP/DMAc/acetic acid/water+2-propanol (30/70 vol%) casting solutions of different compositions
a) 13 wt% PES, 2 wt% PVP; b) 13 wt% PES, 2 wt% PVP and 2 wt% acetic acid;
c) 13 wt% PES, 2 wt% PVP and 4 wt% acetic acid; d) 13 wt% PES, 2 wt% PVP and 6 wt% acetic acid

The porosity of the membranes increases with the addition of acetic acid in the casting solution at high PES concentration (16 wt%). Addition of acetic acid in the casting solution causes a fast exchange rate between the solvent and the non-solvent in the coagulation bath. This leads to an increment in the number and the size of the cavities in the sublayer. Adversely, addition of acetic acid in the casting solution at low PES concentration (13 wt%) causes the channel-like structure turns to figure-like configuration.

Effect of acetone

Figures 4 and 5 demonstrate SEM images of cross sections of membranes cast from 16 wt% and 13 wt% PES, 2 wt% PVP and 2 wt%, 4 wt% and 6 wt% acetone. DMAc was used as the solvent, and mixture of water and 2-propanol (30/70 vol%) was employed as the non-solvent. These figures show that the addition of acetone in the casting solution decreases the size and the number of finger-like pores in the sublayer. Acetone is lost by evaporation from the film surface before the wet phase separation. However, the addition of acetone in the casting solution results in a low exchange rate between the solvent and the non-solvent in the coagulation bath. This means higher polymer concentration in the upper layer of the membrane forming film and a denser sublayer with smaller pores in the final membrane^[16].

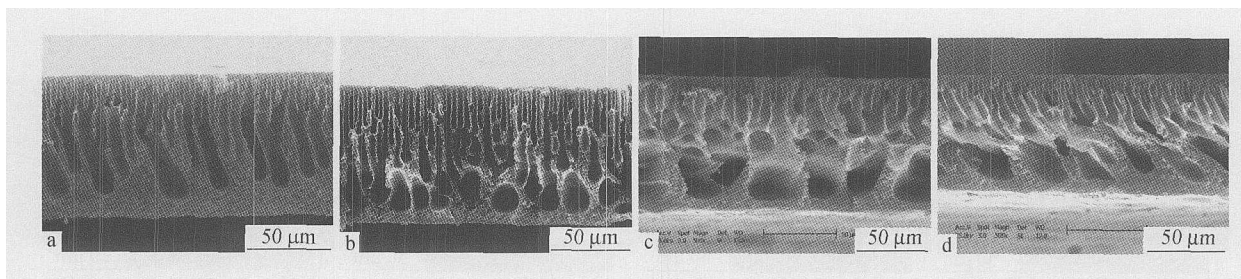


Fig. 4 SEM micrographs of cross sections of membranes prepared from PES/PVP/DMAc/acetone/water+2-propanol (30/70 vol%) casting solutions of different compositions

- a) 16 wt% PES, 2 wt% PVP; b) 16 wt% PES, 2 wt% PVP and 2 wt% acetone;
c) 16 wt% PES, 2 wt% PVP and 4 wt% acetone; d) 16 wt% PES, 2 wt% PVP and 6 wt% acetone

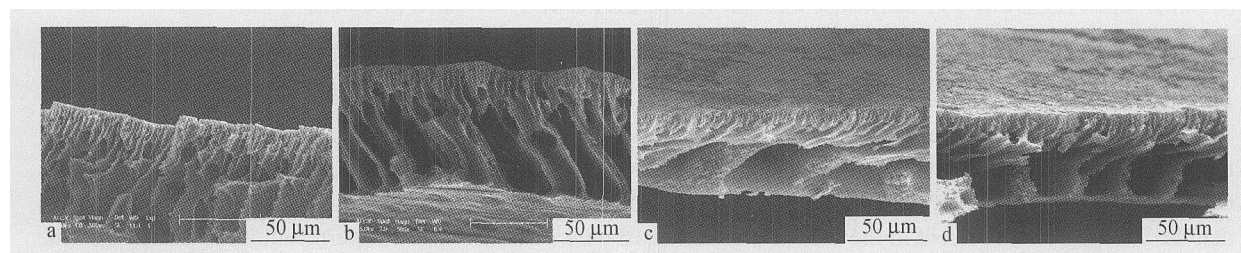


Fig. 5 SEM micrographs of cross sections of membranes prepared from PES/PVP/DMAc/acetone/water+2-propanol (30/70 vol%) casting solutions of different compositions

- a) 13 wt% PES, 2 wt% PVP; b) 13 wt% PES, 2 wt% PVP and 2 wt% acetone;
c) 13 wt% PES, 2 wt% PVP and 4 wt% acetone; d) 13 wt% PES, 2 wt% PVP and 6 wt% acetone

Effect of water

The SEM micrographs of membranes prepared by addition of 2 wt%, 4 wt% and 6 wt% water in the casting solutions (16 wt% and 13 wt% PES and 2 wt% PVP) are represented in Figs. 6 and 7. DMAc was used as the solvent, and mixture of water and 2-propanol (30/70 vol%) was employed as the non-solvent. Addition of water in a ternary system (PES/PVP/DMAc) causes a delay demixing for immersed film in the coagulation bath. Two distinct types of membrane preparation processes can be distinguished: instantaneous demixing and delay demixing. Generally, instantaneous demixing results in membranes of asymmetric porous structure, and delayed demixing — membranes with symmetry in the porous part. The type of top layer (porous or dense) and the presence of macro voids depend on the delay time. Delayed demixing is often associated with the formation of a dense layer. However, delayed demixing structures do not always contain a dense top layer, but in all cases an almost symmetric porous structure in the sublayer is generated. Delayed demixing can only be linked to the formation of a dense top layer under certain conditions: the generation of a high polymer concentration at the interface between polymer solution and coagulation bath^[17]. An increase in water concentration causes the formation of a membrane with a dense top layer.

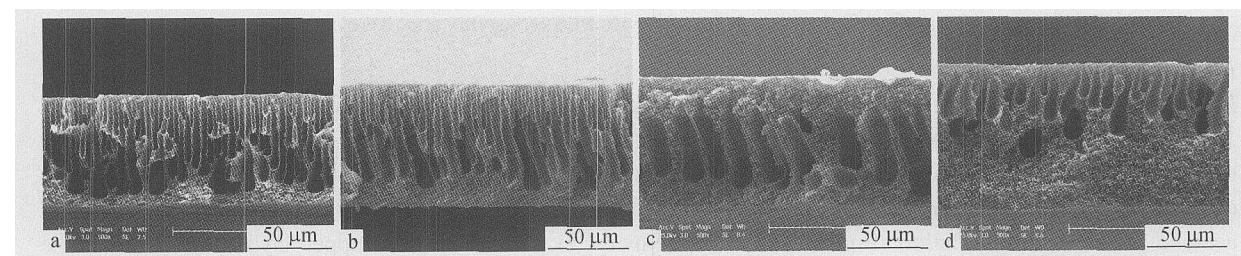


Fig. 6 SEM micrographs of cross sections of membranes prepared from PES/PVP/DMAc/water/water+2-propanol (30/70 vol%) casting solutions of different compositions

- a) 16 wt% PES, 2 wt% PVP; b) 16 wt% PES, 2 wt% PVP and 2 wt% water;
c) 16 wt% PES, 2 wt% PVP and 4 wt% water; d) 16 wt% PES, 2 wt% PVP and 6 wt% water

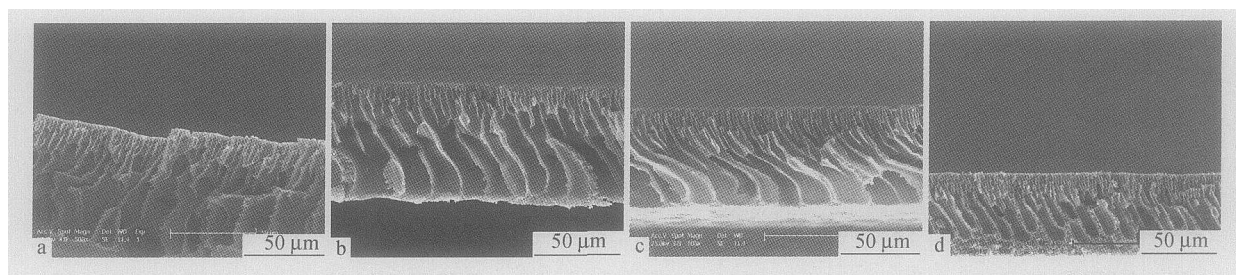


Fig. 7 SEM micrographs of cross sections of membranes prepared from PES/PVP/DMAc/water/water+2-propanol (30/70 vol%) casting solutions of different compositions

a) 13 wt% PES, 2 wt% PVP; b) 13 wt% PES, 2 wt% PVP and 2 wt% water; c) 13 wt% PES, 2 wt% PVP and 4 wt% water; d) 13 wt% PES, 2 wt% PVP and 6 wt% water

Membrane Performance

Effect of acetic acid

The influences of the presence of acetic acid in the casting solution on the flux and retention of prepared membranes at 16 wt%, 13 wt% and 10 wt% of PES are presented in Figs. 8–10, respectively. DMAc was used as the solvent and mixture of water and 2-propanol (30/70 vol%) was employed as the non-solvent. Figure 8 shows that the addition of acetic acid in the casting solution at 16 wt% PES increases the permeability and decreases the selectivity of the membrane. As investigated in the morphology section, the porosity of the PES membranes at high concentrations increases with the addition of acetic acid in the casting solution. Figures 9 and 10 illustrate that the addition of acetic acid in the casting solution at 13 wt% and 10 wt% PES results in lower flux and higher rejection. The membrane performance is a reflection of membrane morphology. Addition of acetic acid in the casting solution at low PES concentrations causes turns from the channel-like structure to a finger-like configuration. This structure is responsible for the flux decline in low PES concentrations.

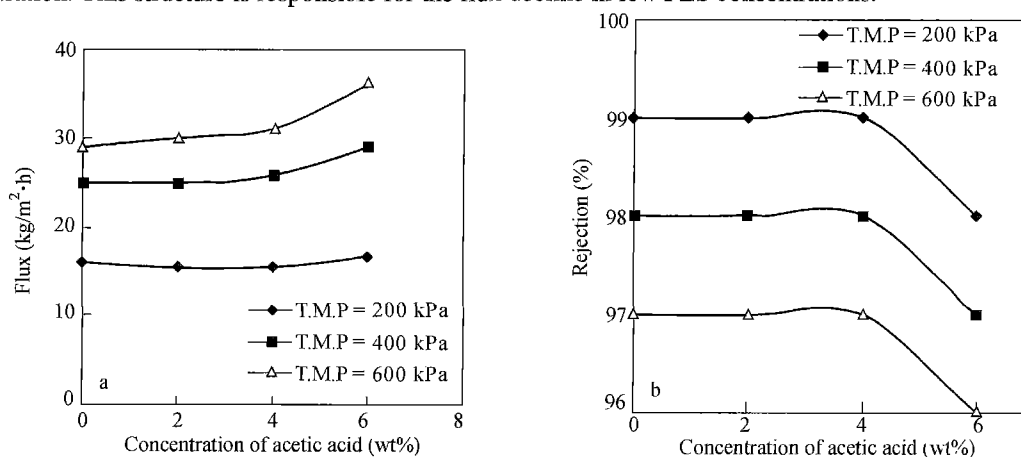


Fig. 8 Effects of acetic acid concentration at 16 wt% PES on (a) flux and (b) rejection of protein

Effect of acetone

Figures 11–13 demonstrate the influence of addition of acetone in the casting solutions of 16 wt%, 13 wt% and 10 wt% PES, respectively. DMAc was used as the solvent and mixture of water and 2-propanol (30/70 vol%) was employed as the non-solvent. In all tested PES concentrations the presence of acetone in the casting solution causes a decline in flux of prepared membranes and an improvement in the retention of membranes. Addition of acetone in the casting solution results in higher polymer concentration in the upper layer of the membrane forming films and a denser layer with smaller pores in the final membranes. This is due to the low exchange rate between the solvent and the non-solvent in the coagulation bath^[16].

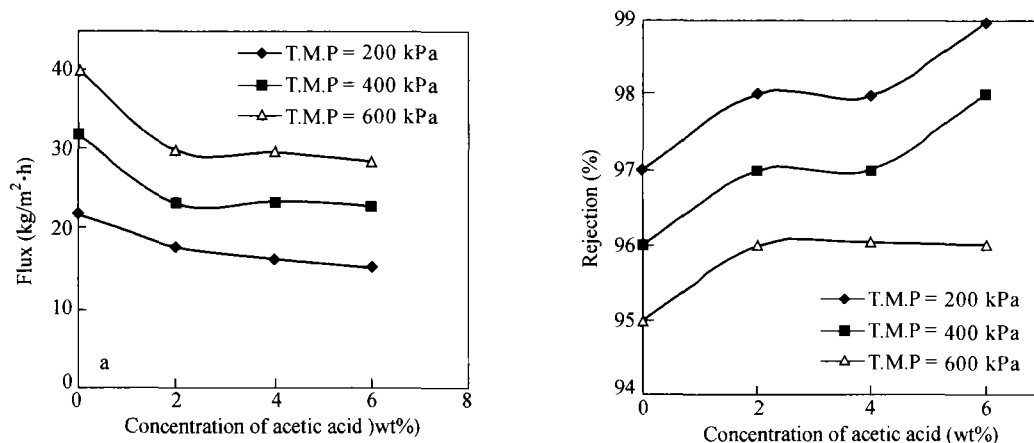


Fig. 9 Effects of acetic acid concentration at 13 wt% PES on (a) flux and (b) rejection of protein

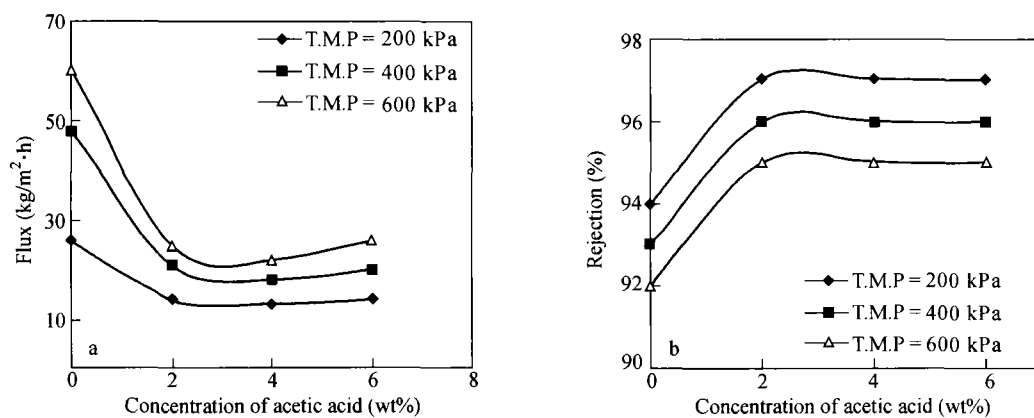


Fig. 10 Effects of acetic acid concentration at 10 wt% PES on (a) flux and (b) rejection of protein

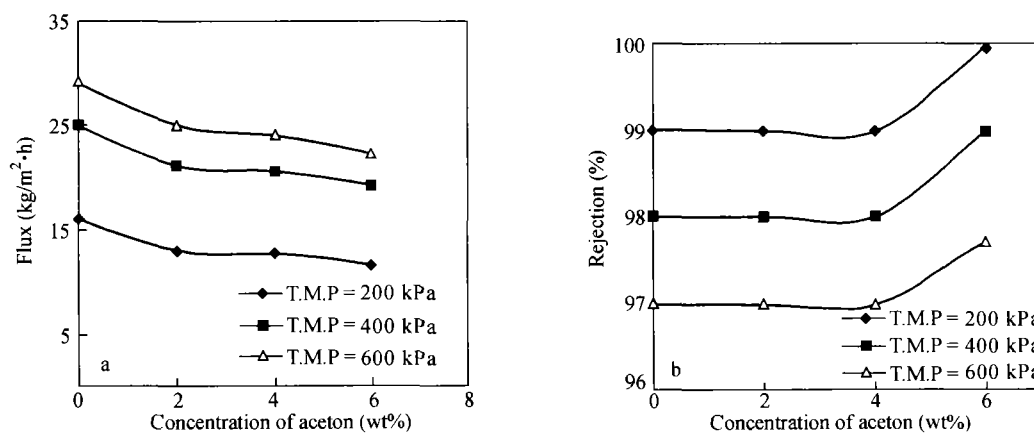


Fig. 11 Effects of acetone concentration at 16 wt % PES on (a) flux and (b) rejection of protein

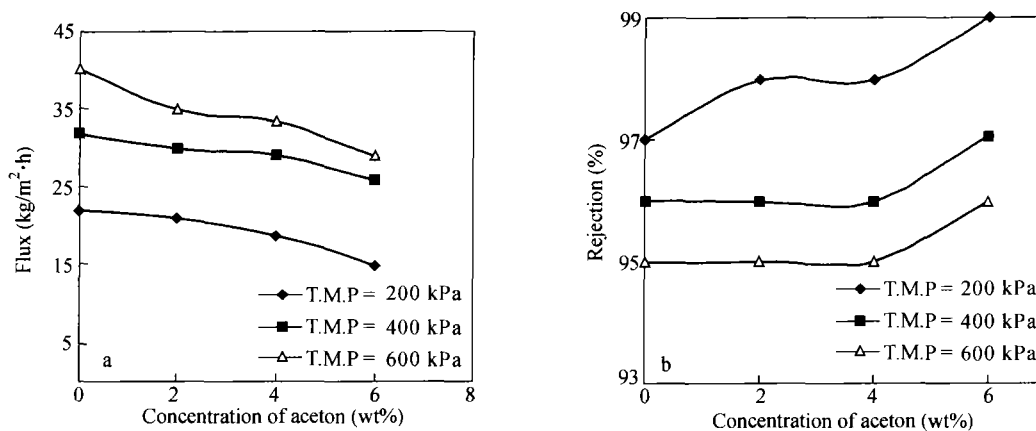


Fig. 12 Effects of acetone concentration at 13wt% PES on (a) flux and (b) rejection of protein

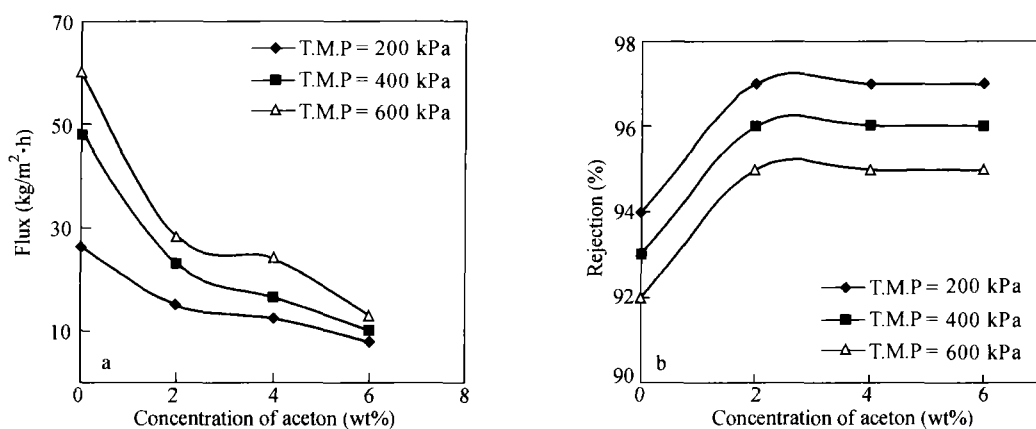


Fig. 13 Effects of acetone concentration at 10 wt % PES on (a) flux and (b) rejection of protein

Effect of water

Figures 14–16 illustrate the influence of addition of 2 wt%, 4 wt% and 6 wt% water in the casting solutions of 16 wt%, 13 wt% and 10 wt% PES concentrations, respectively. DMAc was used as the solvent and mixture of water and 2-propanol (30/70 vol%) was employed as the non-solvent. The data indicate that the addition of water causes flux decline and retention improvement. The presence of water as an additive in the casting solution results in formation of membranes with lower porosity in the sublayer and small pores in the skin layer. This leads to lower flux and higher retention.

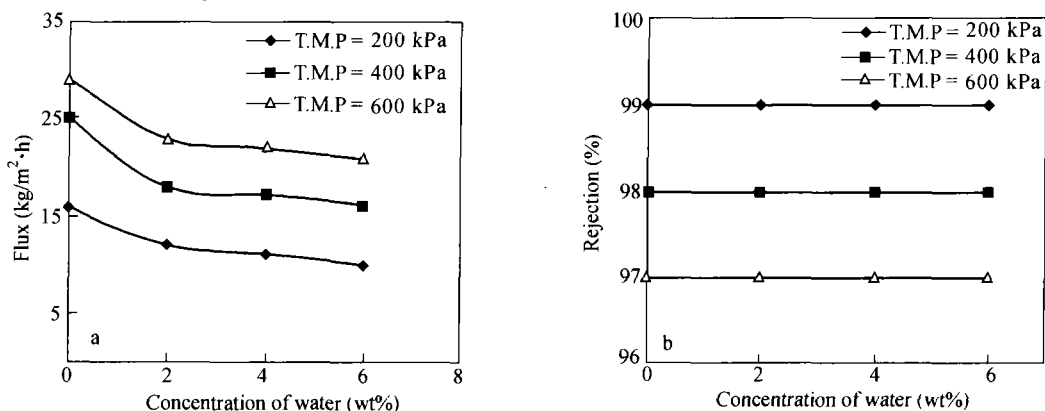


Fig. 14 Effects of water concentration at 16wt % PES on (a) flux and (b) rejection of protein

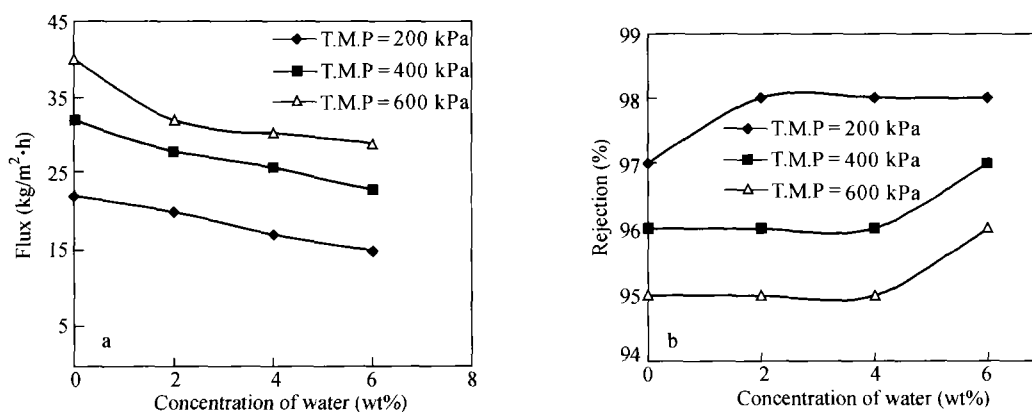


Fig. 15 Effects of water concentration at 13 wt % PES on (a) flux and (b) rejection of protein

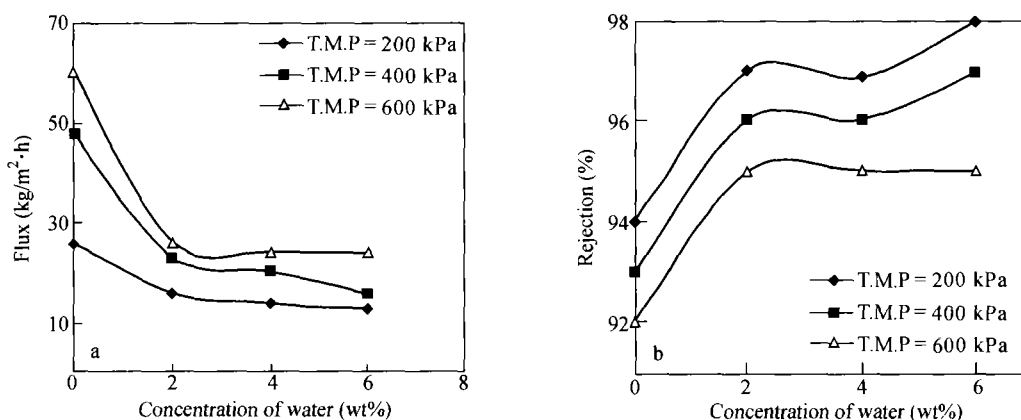


Fig. 16 Effects of water concentration at 10 wt % PES on (a) flux and (b) rejection of protein

CONCLUSIONS

The influences of additives in the casting solution on the membrane structure and performance were investigated. The membranes were prepared by quaternary casting solution systems PES/PVP/solvent/additives. The phase inversion with immersion precipitation was employed for the preparation of membranes. Structure and properties of the membranes are governed by several parameters. Addition of acetic acid at a high polymer concentration (16 wt%) in the casting solution, increases the porosity and results in higher flux. Addition of acetic acid in low polymer concentrations, acetone and water at all tested concentrations of PES in the casting solutions results in the formation of a dense upper coating and a decline in the size and number of finger-like pores in the sublayer. This provides a lower flux and a higher retention of protein.

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