

# Effects of the Support-Layer Hydrophilicity on the Active-Layer Formation of Composite Membranes

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**ABSTRACT:** To understand the effects of the hydrophilicity of the support layer on the formation of the active layer and the performance of composite membranes, a support layer was prepared from a polysulfone (PSf) blend with a hydrophilic copolymer, and then its top surface was overcoated with an active layer fabricated by an interfacial reaction of *m*-phenylenediamine (MPDA) with trimesoyl chloride. The time required for impregnating the support layer with an aqueous solution containing MPDA was gradually decreased by increases in the hydrophilicity of the support layer. The required soaking time was

greater than 9 min for the formation of the defect-free active layer when the support layer prepared from PSf was used, whereas it could be reduced about 1 min by the use of the hydrophilic support layer. Furthermore, composite membranes prepared with the PSf/hydrophilic copolymer blend as the support layer always exhibited higher salt rejection and water permeability than those prepared with PSf as the support layer. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1194–1200, 2008

**Key words:** blends; hydrophilic polymers; membranes

## INTRODUCTION

The reverse-osmosis process for obtaining pure water from sea water, brackish water, or wastewater has gained wide attention because of the economics of energy and resources and environmental protection.<sup>1–12</sup> Because a composite membrane composed of a bilayer film has some key advantages with respect to an asymmetric membrane, the former is used in a majority of reverse-osmosis applications. A composite membrane typically consists of a thick, porous, nonselective layer formed in a first process step, which is subsequently overcoated with an ultrathin barrier layer on its top surface in a second process step.<sup>4–10</sup> An anisotropic microporous support layer backed by a woven or nonwoven fabric for handling strength can be optimized for minimum resistance to permeate flow combined with maximum mechanical strength, whereas the barrier layer can be optimized for the desired combination of solute rejection and water permeability. An ultrathin veneer of a composite membrane is often fabricated by an *in situ* method via interfacial polymerization

of reactive monomers on the surface of the support film.<sup>4–9</sup> Crosslinked aromatic polyamides made through the interfacial polymerization of an amine in an aqueous phase and acyl halide in an organic phase are widely used commercially as active barrier layers.<sup>1–5</sup>

For interfacial polymerization, an *m*-phenylenediamine (MPDA) solution in water is coated onto a support layer, which is generally fabricated from polysulfone (PSf), and then is interfacially placed in contact with trimesoyl chloride (TMC) in hexane. Because of this, the hydrophilicity of the support layer influences the active-layer formation and the performance of the composite membrane. PSf is widely used as the support layer of composite membranes. However, its hydrophobicity prolongs the time required for soaking in an aqueous solution containing MPDA and deters the formation of the active layer. Enhancement of the hydrophilicity of the support layer is essential in the fabrication of composite membranes. Poly(1-vinylpyrrolidone) (PVP), which is a water-soluble polymer, is often added to the casting solution to improve the hydrophilicity of the support layer and to aid in the formation of micropores. Hydrophilicity enhancement of the support layer with PVP is limited because most PVP is washed out during the solvent exchange process for the support-layer formation.<sup>13,14</sup>

Even though the hydrophilicity of the support layer influences the performance of the composite membrane, its effects have not been intensively

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investigated. In this study, a hydrophilic copolymer, which was not water-soluble, was added to the casting solution to fabricate support layers exhibiting further enhanced hydrophilicity. The active layer was formed on the support layer prepared here by the interfacial reaction of MPDA and TMC. Performance changes of the composite membranes with the hydrophilicity of the support layer and soaking time of the support layer in an aqueous solution of MPDA were explored.

## EXPERIMENTAL

### Materials

Commercially available PSf (weight-average molecular weight = 69,000; grade Udel P-3500) and PVP (weight-average molecular weight = 55,000) were purchased from Amoco Performance Products, Inc. (Alpharetta, GA), and Aldrich Chemical Co. (Milwaukee, WI), respectively. TMC and MPDA were also purchased from Aldrich Chemical. Poly(1-vinylpyrrolidone-*co*-acrylonitrile) [P(VP-AN)], used as a water-insoluble hydrophilic copolymer, was synthesized in our laboratory. Details for the synthesis of P(VP-AN) copolymers were described previously.<sup>15</sup>

### Membrane preparation

Composite membranes for the reverse-osmosis process were formed by a two-step process. The membranes consisted of a thick, porous layer formed in the first process step, which was subsequently overcoated with an ultrathin barrier layer on its top surface in the second process step. A flat-sheet, asymmetric support layer was prepared via solution casting from *N*-methyl-2-pyrrolidone (NMP) onto nonwoven polyester fabrics.<sup>16,17</sup> The total fraction of solids in the casting solution was held constant at 22 wt %. The casting solution, consisting of 22 wt % polymers and 78 wt % NMP, was cast with a doctor blade with a thickness of 0.15 mm. The cast film was immediately immersed in a water bath and kept in it for 24 h until most of the solvent was removed. The active skin layer of the composite membrane was prepared with an *in situ* interfacial polymerization technique. The support was immersed in a deionized water solution containing 1 wt % MPDA. Excess reagent was squeezed off with a soft rubber roller. The PSf support, impregnated with an amine solution, was then immediately reacted with a hexane solution containing 1 wt % TMC. After the removal of the hexane solution, the coated substrate was washed with pure water before drying at room temperature.

### Membrane characterization

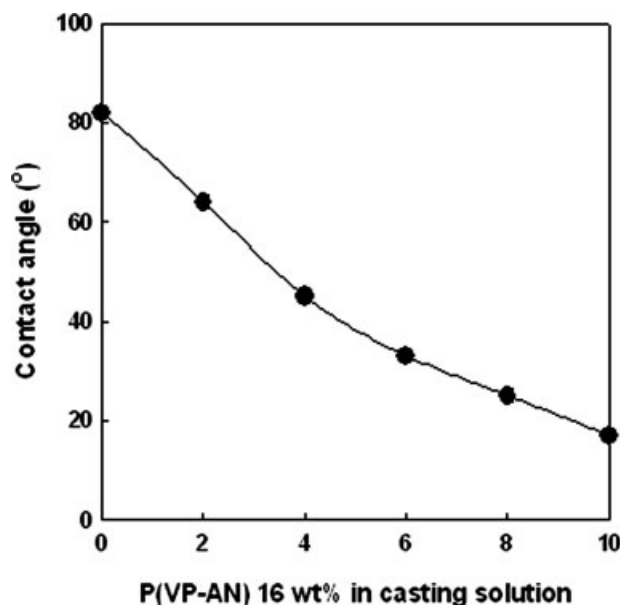
An aqueous solution containing 1000 ppm poly(ethylene glycol) with a weight-average molecular weight of 20,000 (PEG 20,000; polydispersity index = 1.03) was used as the feed solution for the performance test of the support layer. The permeate flux was measured at 3 bar, a flow rate of 2.5 L/min, and 30°C. The solute concentration of the permeate was measured with a high-performance liquid chromatograph equipped with a refractometer.<sup>15</sup> The performance of the composite membranes was examined with homemade continuous-type test equipment for the reverse-osmosis process at a testing pressure of 30 kg/cm<sup>2</sup> with a 2000 ppm NaCl solution. A circular membrane with a diameter of 70 mm was placed in the test cell with the skin layer facing the incoming feed. The membrane was supported on a porous stainless steel plate. A rubber o-ring was used to seal the membrane and to ensure leak-free operation. The effective membrane area was kept at 19.6 cm<sup>2</sup>. The salt concentrations of the feed water and the product water were measured with a standardized digital conductivity meter (model 32, YSI Co., Yellow Springs, OH). Every experiment described here was performed at a stirrer speed of 1000 rpm to minimize concentration polarization. Five specimens of each membrane were prepared for the examination of the water permeability and rejection ability.

For evaluation of the membrane hydrophilicity, the contact angle between water and the membrane surface was determined. The contact angle between the water and membrane surface was directly measured with a contact-angle goniometer [model 100-00-(115/220)-S, Rame-Hart, Netlong, NJ].<sup>18</sup> To minimize experimental error, the contact angle was measured 10 times for each sample and then averaged. An atomic force microscope (AFM CP, Park Scientific Instruments, Sunnyvale, CA) was used to investigate the surface morphology of the membranes. Membranes were fractured under a liquid nitrogen condition to observe the cross-sectional morphology with a scanning electron microscope (JSM-6700F, JEOL, Tokyo, Japan).

## RESULTS AND DISCUSSION

### Characteristics of the support layers

A membrane prepared from a PSf/NMP (22/78) casting solution was used as a control support layer. The polymer content of all casting solutions was kept at 22 wt %. Support layers were also prepared from the casting solutions containing PSf and various amounts of P(VP-AN). A hydrophilic copolymer that is added to the casting solution for the fabrica-



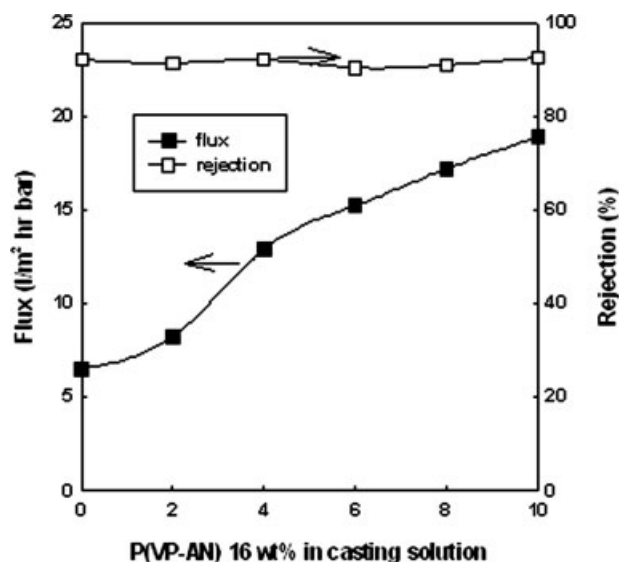
**Figure 1** Contact angles of the support layers as a function of the P(VP-AN) 16 content in the casting solution. The total polymer content of the casting solution was fixed at 22 wt %.

tion of the hydrophilic support layer has to satisfy the following two conditions. First, a hydrophilic copolymer should be water-insoluble to control the hydrophilicity of the support layer. P(VP-AN) copolymers containing less than 10 wt % acrylonitrile (AN) are water-soluble.<sup>15</sup> As described previously, membranes prepared from miscible PSf blends with P(VP-AN) copolymers have the proper membrane structure as a support layer.<sup>15</sup> P(VP-AN) copolymers containing 2–16 wt % AN formed miscible blends with PSf.<sup>15</sup> Because of this, P(VP-AN) 16 (the numerical value included as part of the code for the copolymers indicates the weight percentage of AN) was used as a hydrophilic copolymer. The contact-angle studies were conducted to assess changes in the hydrophilicity as the P(VP-AN) 16 copolymer was incorporated into the membrane. Figure 1 shows the contact-angle values of various membranes. A decline in the contact angle was observed with increasing P(VP-AN) 16 copolymer content.

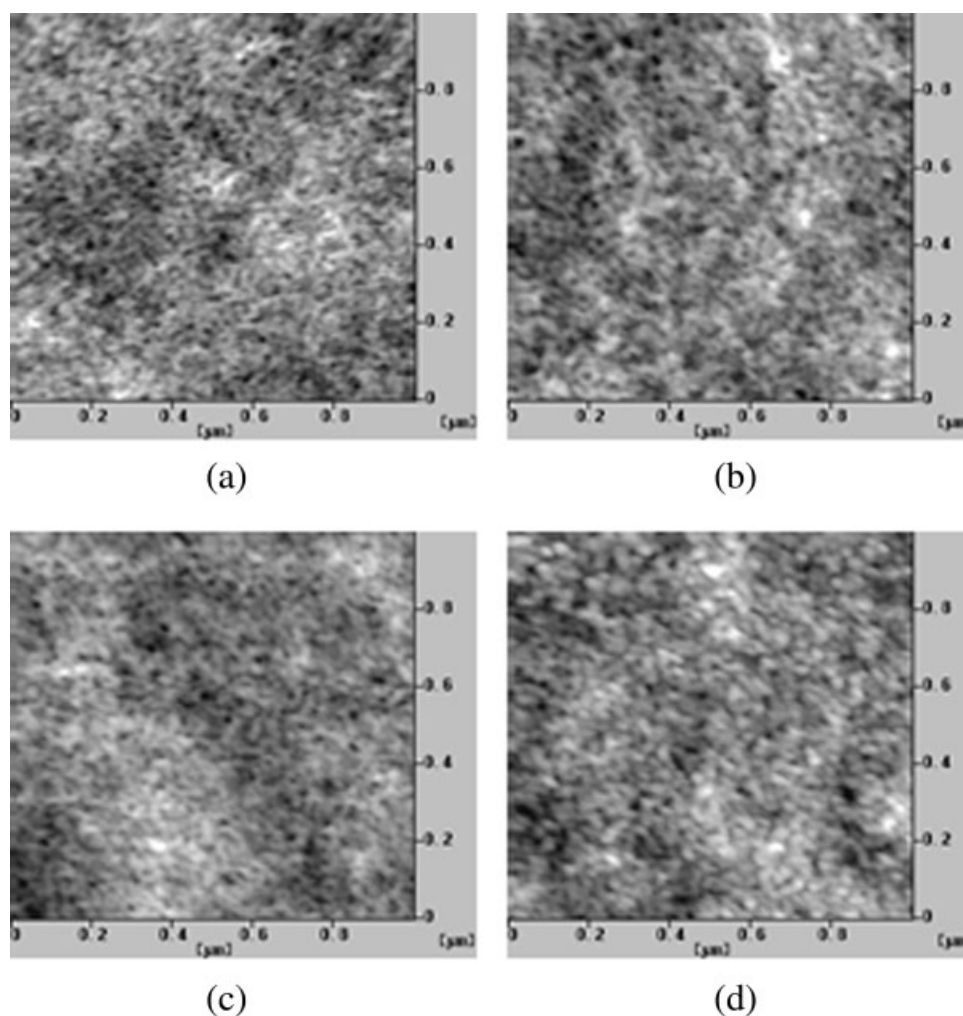
The performance of membranes prepared from miscible blends of PSf and P(VP-AN) 16 was examined through changes in the blend composition of the casting solution. Figure 2 shows the water permeability and rejection of PEG 20,000 examined with six different membranes. The solute rejection of the blend membranes was similar to that of the PSf membrane, whereas the water flux increased with the P(VP-AN) 16 content of the casting solution. These results suggested that the pore sizes existing on the surfaces of both membranes were

similar, and the better water permeability of PSf/P(VP-AN) 16 membranes versus that of PSf stemmed from hydrophilic properties of the membranes provided by the P(VP-AN) 16 copolymer. A membrane prepared from a 17/5/78 PSf/PVP/NMP casting solution had lower solute rejection (86.2%) than a PSf membrane, whereas the water flux (7.2 L/m<sup>2</sup> h bar) was increased. Enlargement of the pores existing on the surface due to PVP dissolving during the phase-inversion process might have induced high water flux and reduction of solute rejection. A membrane prepared from a blend of PSf and PVP also showed a slightly reduced contact angle (73°). PVP remaining in the membrane matrix might also give some help in increasing the water permeability and decreasing the contact angle.<sup>13,14</sup>

Figure 3 shows the surface morphologies of various membranes observed with atomic force microscopy. Changes in the surface morphologies were subtle, regardless of the kinds of casting solutions used for membrane formation. However, changes in the cross-sectional morphologies with the casting solution were observed, as shown in Figure 4. The prepared membranes exhibited the typical asymmetric structure, having fully developed macrovoids. A membrane prepared from PSf consisted of a dense top layer and a fingerlike macrovoid. Membranes prepared from PSf/P(VP-AN) 16 blends exhibited a different cross-sectional morphology. The asymmetric structure of these membranes consisted of a dense top layer, a microporous sublayer that was occupied by closed cells, and a fingerlike macrovoid. With increasing P(VP-AN) 16 content, the microporous sublayer



**Figure 2** Performance of support layers prepared from the PSf/P(VP-AN) 16 blends. The total polymer content of the casting solution was fixed at 22 wt %.



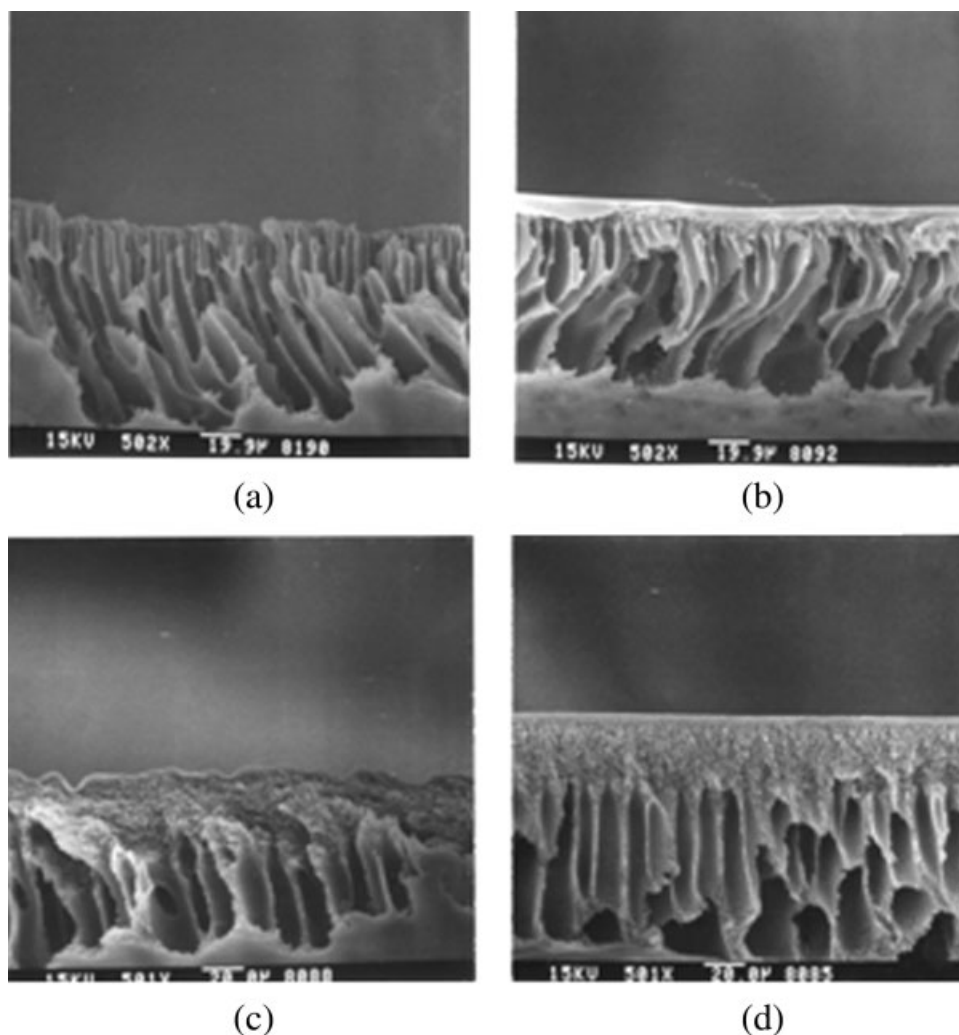
**Figure 3** Surface morphologies of various support layers observed with atomic force microscopy: (a) 22/78 PSf/NMP, (b) 18/4/78 PSf/P(VP-AN) 16/NMP, (c) 14/8/78 PSf/P(VP-AN) 16/NMP, and (d) 12/10/78 PSf/P(VP-AN) 16/NMP.

was thickened. The formation of an asymmetric membrane depends on kinetic parameters such as the exchange rate between the solvent and nonsolvent and the kinetics of phase separation and on thermodynamic parameters such as the phase diagram, polymer–solvent interaction, solvent–nonsolvent interaction, and interfacial stability.<sup>13,14,19,20</sup> Thus, the material selection of, for example, polymers, solvents, and nonsolvents is very important for the control of membrane morphology. It is known that the kinetics of phase separation are retarded and the microporous sublayer is thicker when the casting solution contains more hydrophilic polymers.<sup>14,19,20</sup> Membranes prepared here from the casting solutions containing PSf and P(VP-AN) 16 exhibited results similar to those of the membranes prepared from the casting solutions containing other hydrophilic polymers. A microporous sublayer existing in the support layer provides mechanical strength for the support layer and reduces the defects existing on the dense top

layer. The reduction of the defects on the dense top layer might result in an even coating of the active layer.

#### Characteristics of the composite membranes

The active layer of the most successful commercial product (FT-30) is composed of a crosslinked aromatic polyamide, which is produced by the interfacial polymerization of MPDA and TMC. In this study, the active layers of the composite membranes were also fabricated from MPDA and TMC onto various support layers prepared here. The performance of the membranes prepared here was compared with that of the commercially available FT-30 membrane. The latter exhibits 98.3% salt rejection and 0.45 L/m<sup>2</sup> h bar water permeability. Figure 5 shows changes in the membrane performance with the soaking time of the support layer in an aqueous solution of MPDA when a PSf support layer was used. Salt rejection of the composite membranes was rapidly increased

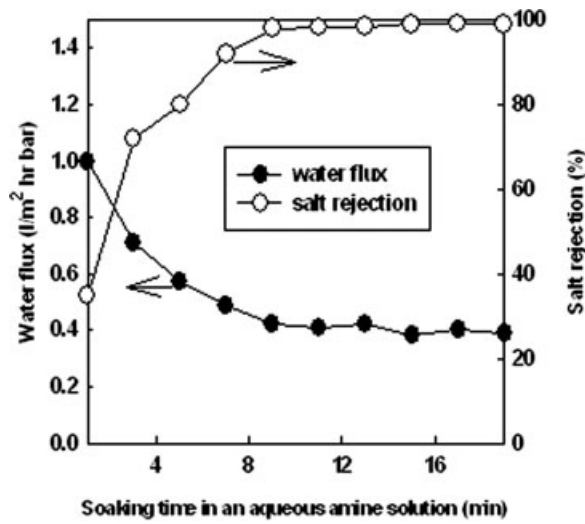


**Figure 4** Cross-sectional morphologies of various support layers observed with scanning electron microscopy: (a) 22/78 PSf/NMP, (b) 18/4/78 PSf/P(VP-AN) 16/NMP, (c) 14/8/78 PSf/P(VP-AN) 16/NMP, and (d) 12/10/78 PSf/P(VP-AN) 16/NMP.

with the soaking time and then leveled off asymptotically. Salt rejection rapidly increased up to about 80% during the first 5 min and then gradually increased with the soaking time. Water permeability exhibited trends opposite to those of salt rejection. The composite membrane showed a performance nearly equivalent to that of the FT-30 membrane when the soaking time was greater than about 9 min (salt rejection: 98.6%; water permeability: 0.42 L/m<sup>2</sup> h bar). This means that a defect-free active layer of the composite membrane is formed on the PSf support layer when the soaking time is greater than 9 min.

Figure 6 shows changes in the salt rejection of the composite membranes fabricated with various PSf/P(VP-AN) support layers with the soaking time. With the increase in the soaking time, salt rejection rapidly increased and then leveled off at a fixed value. As shown in Figure 7, the soaking time

required for the fabrication of the composite membranes that exhibited nearly equivalent salt rejection with FT-30 (or better salt rejection than FT-30) was gradually reduced with the increase in the P(VP-AN) 16 content in the casting solution. When the casting solution contained about 10 wt % P(VP-AN) 16, the required soaking time was about 1 min. Membranes prepared with the PSf/P(VP-AN) blend as a support layer always exhibited higher salt rejection and water permeability than that prepared with PSf as a support layer. The composite membranes prepared with the PSf/P(VP-AN) blend as a support layer exhibited 99.2% salt rejection, regardless of the P(VP-AN) content. As shown in Figure 8, the water permeability gradually increased with the increase in the P(VP-AN) 16 content in the casting solution. The water permeability of the composite membrane was 0.58 L/m<sup>2</sup> h bar when the support layer prepared from the casting solution containing 10 wt %

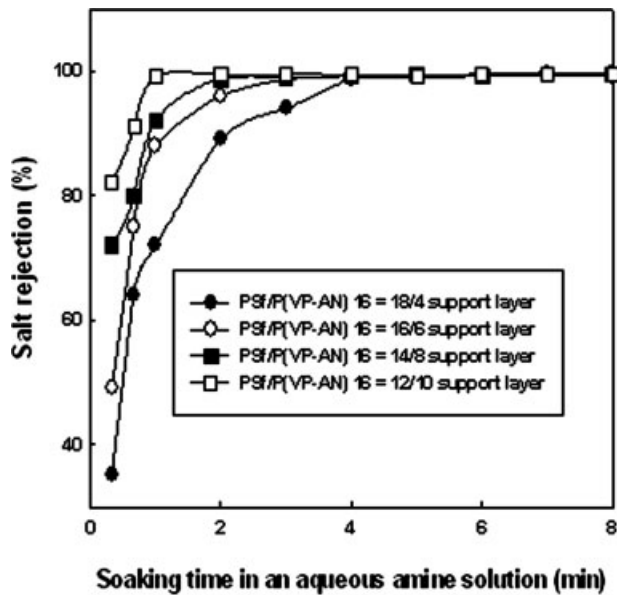


**Figure 5** Performance changes of the composite membrane with the soaking time in an aqueous solution of MPDA. A support layer prepared from a casting solution containing PSf was used.

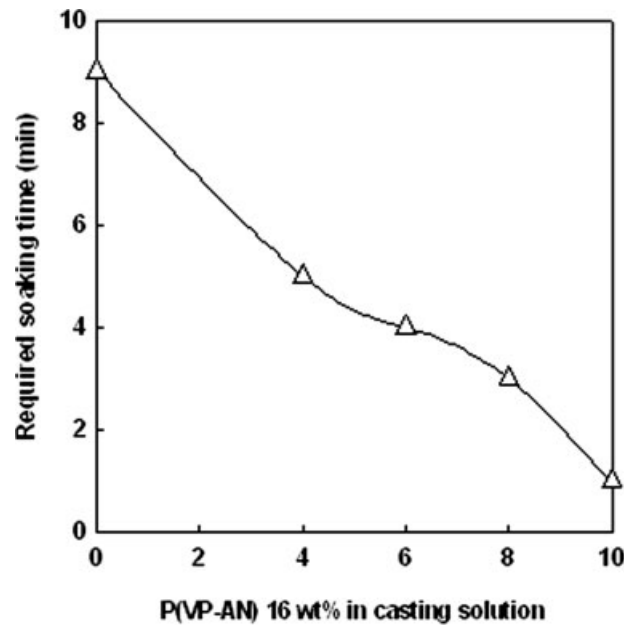
P(VP-AN) 16 was used. These results indicate that the defect-free active layer is easily formed by the enhancement of the hydrophilicity of the support layer.

### CONCLUSIONS

The active layer of the composite membrane, which was prepared by an interfacial reaction of MPDA

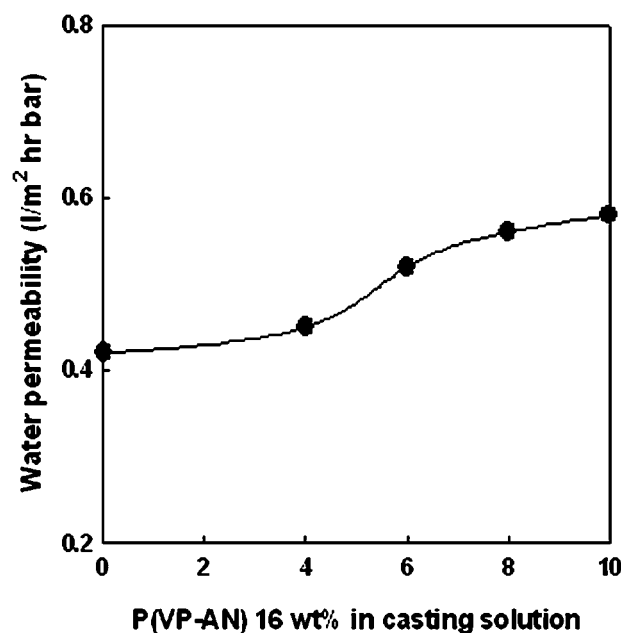


**Figure 6** Changes in the salt rejection of the composite membrane with the soaking time in an aqueous solution of amine. The support layers were prepared from casting solutions containing PSf and various amounts of the P(VP-AN) 16 copolymer.



**Figure 7** Required soaking time in an aqueous solution of MPDA for the formation of defect-free composite membranes as a function of the P(VP-AN) 16 copolymer content in the casting solutions.

with TMC, was overcoated onto support layers with different hydrophilicities. The hydrophilicity of the support layer was controlled by changes in the P(VP-AN) 16 content in the casting solution. With the increase of the hydrophilicity of the support layer, the water permeability of the support layer was continuously increased, whereas changes in the



**Figure 8** Changes in the water permeability of the composite membrane with the P(VP-AN) 16 content in the casting solution.

solute rejection were negligible. The required soaking time in an aqueous solution containing MPDA was gradually decreased by an increase in the hydrophilicity of the support layer. The required soaking time was greater than 9 min for the formation of the defect-free active layer when the PSf support layer was used. The required soaking time could be reduced about 1 min with the hydrophilic support layer. Composite membranes prepared with the PSf/P(VP-AN) 16 blend as a support layer always exhibited higher salt rejection and water permeability than that prepared with PSf as a support layer.

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