

Permselectivity of Polyamide Composite Membrane Modified by Solvent

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ABSTRACT: Asymmetric reverse osmosis (RO) polyamide (PA) composite membrane may be modified by means of a solvent-processing technique into pervaporation (PV) membrane for separating organic aqueous solution. Formic acid, acetic acid, phosphoric acid, hydrochloric acid, phenol, and so forth, better solvents for PA, were selected as the modifying agents in this study. The effect of the modifying conditions (type and concentration of the modifying agent, processing time of membrane in liquid medium) on the sorption of modified membranes was investigated. After the PA composite membrane was treated with 8 wt % acetic acid for 1 h, the swelling rate for water (S_w) increased, whereas that for isopropanol (S_{IPA}) decreased, compared with that of the nonmodified membrane. The difference between S_w and S_{IPA} of the membrane treated with acetic acid was greater than that with other modifying agents. The

separation factor and flux of the modified membrane were correspondingly maximal when it was used in a PV separating isopropanol aqueous solution. The contact of solvent molecules in liquid medium with polymer chains in the PA membrane and the intranodular chains in the PA membrane tending to diffuse by reptation toward the solvent molecules were the principal causes leading to a change of structure of asymmetric PA composite membrane. The mechanism of changing membrane structure by means of the solvent-processing technique may better interpret the modification of PA composite RO membrane. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1005–1010, 2004

Key words: polyamides; membranes; reverse osmosis; pervaporation; modification

INTRODUCTION

The development of membrane techniques shows that identical polymer can be prepared in separating membranes with different functions. Cellulose acetate (CA) and polyamide (PA), mass-produced in the polymer industry, have been applied to the preparation of not only reverse osmosis (RO) membranes, nanofiltration (NF) membranes, and ultrafiltration (UF) membranes, but also gas separation (GS) membranes and pervaporation (PV) membranes. Many membrane-making lines for the desalination membrane, especially the RO membrane of CA series and PA series, have been established at home and abroad. These production lines possess perfect membrane-making equipment, mature membrane-making techniques, and produce membranes with stable performance. Developing an asymmetric RO membrane for desalination into a homogeneous membrane for PV separating organics is a recent development of new techniques in membrane production.^{1–4}

An asymmetric RO membrane can be changed by means of a solvent-processing technique into a homogeneous membrane. Researchers carried out the acetone-soaking processing of CTA hollow-fiber RO membrane and CA desalination membrane and achieved the PV membrane with high separation rate and low flux for the separation organic/organic system.^{1–3} The modification for CA series membranes showed that the solvent-processing technique is simple in operation and has an obvious effect of modification.

The supporting layer of composite PA membrane is generally polysulfone (PS) membrane; PA membrane, as the layer of desalination, is asymmetrical, with extremely small thickness. It was deemed of great importance to inquire into the modifying techniques with suitable solvent to change the PA composite RO membrane for desalination of water treatment into the PV membrane for separating organics. In this investigation, both organic acid and inorganic acid, which are good solvents for PA and nonsolvents for PS, were used as the modifying agents. After soaking processing for PA membrane, the adsorption performances of the modified membrane to isopropanol (IPA) and water and its separation of isopropanol aqueous solution were observed, and the modifying mechanism of PA membrane was preliminarily analyzed.

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EXPERIMENTAL

Polymer membrane and chemical reagents

The membrane for this experiment is PA composite RO membrane (made in China or the United States), with the rejection $\geq 95\%$ for tap water of Hangzhou City of China; the supporting layer for the composite membrane was PS porous membrane. The PA composite RO membrane is commercially available and has been used extensively for desalination of water and brackish water.

The chemical reagents for the modifying agent of PA membrane include 88% formic acid, 36% acetic acid, 38.5% phosphoric acid, 36% hydrochloric acid, and phenol (purchased locally in China); the organic reagent for the separating experiment is IPA. These reagents (all made in China) were analytically pure and were used as received in the experiments.

Modifying experiment

Using the same experimental methods as those previously reported¹⁻⁴ for modification of asymmetric membrane of cellulose ester, PA membrane was soaked in the modifying agent at constant temperature of 30°C and for a set time, after which it was removed and cooled to dryness. The concentration of the modifying agent was 10 wt % and the soaking period of PA composite RO membrane in the modifying agent was 1 h, unless otherwise indicated.

Determination of swelling rate of the membrane

At constant 30°C temperature, the membrane slices were soaked in 99% IPA and deionized water, respectively. After swelling equilibrated for one day and night, the slices were removed, rapidly blotted with a piece of filter paper to remove liquid on the membranes' surface, then weighed. The expression formula of the swelling rate of the modified membrane is

$$S_{w,IPA} = \frac{W_s - W_d}{W_d}$$

where S_w and S_{IPA} are the swelling rates of the membrane against water and IPA, respectively; and W_d and W_s represent, respectively, the weight of dry membrane before swelling and that of the swelling membrane after swelling in water or IPA.

In the swelling experiment, only the change of the adsorption quantity of PA membrane as composite layer was investigated. Because the reagent for the modifying experiment was not a good solvent of PS, it may be hypothesized that there are no obvious influences of PS membrane and the composite membrane

support layer on the adsorption quantity of swelling agent.

PV separation experiment

The PV experiment was performed with the same device used in previous experiments.^{1,2} The feed, operating temperature, and the downstream pressure were 87 wt % IPA aqueous solution, 25°C, and 1000 Pa, respectively. The PV permeate was collected by liquid N₂; the constituents of the feed and permeate were determined with a gas chromatograph (GC, Model 3420; Beijing Analytic Instrument Factory) with a thermal conductivity detector. The GC conditions were as follows: column temperature: 150°C; injector temperature: 120°C; detector temperature: 150°C; filament temperature: 250°C; carrier air flow: 20 mL/min; correction factor: 1.8294051. The separation performance of the membrane by PV was expressed with permeate flux J and separating factor α .

RESULTS AND DISCUSSION

Performances of PA and its composite membrane

The structural formula of PA, [CORNH]_{*m*} or [NHR₁NHCOR₂CO]_{*n*}, consists of methylene and amide bond. Because hydrogen bonds can be formed between polymer chains, constituting a hydrogen bond net to cause orderly aggregation of macromolecules, PA thus possesses higher crystallinity. Whereas the ratio of amide/methylene in PA (i.e., the concentration of amide in the PA) macromolecular chains increases, the polarity of PA increases, and the hydroscopicity also increases. If PA membrane would be applied to the separation of an organic mixture, such as an alcohol/water system, the PA membrane would preferentially adsorb water, and the water in the organic mixture would preferentially permeate through the membrane.

The PA composite membranes for water treatment, such as RO membrane for desalination and NF membrane for water softening, were all prepared into an asymmetrical separating membrane with PA composite layer on the PS membrane that is resistant to inorganic acid, organic acid, and phenol. The PA chains in the composite layer are densely packed inside the nodules. The internodular chain segment displacement represents high porosity of the membrane⁵; thus, PA composite RO membrane possesses high water permeability.

Modification of PA membrane

Choice of modifying agent

PA is a good membrane material for separating organic mixture because it is indissoluble in alcohol,

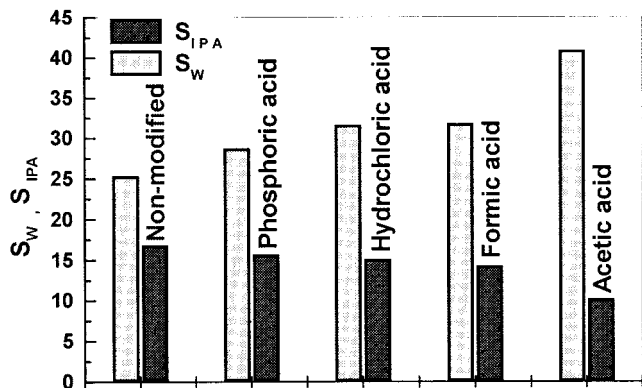


Figure 1 Relationship between different modifying agents and swelling rate of PA composite membrane.

acetone, ethyl acetate, and common hydrocarbon group solvents, but dissolvable in phenol, sulfuric acid, formic acid, acetic acid, and some inorganic salts. Thus, a good solvent for PA was used as the modifying agent in the experiment. The PA composite membrane was soaked for treatment in a series of modifying agents at low concentration. Then, the swelling rates of the modified membrane against pure water (S_w) and IPA (S_{IPA}) were determined and the results are shown in Figure 1.

As shown in Figure 1, the swelling rate of PA non-modified membrane against water is greater than that against IPA. After the PA membrane was treated with phosphoric acid, hydrochloric acid, formic acid, and acetic acid, respectively, the swelling rates of PA modified membrane against IPA were less than those of PA nonmodified membrane and decreased successively, although its swelling rates against water were all greater than those of PA nonmodified membrane and increased successively. Obviously, all modifying agents chosen in the experiment, regardless of organic acid solution or inorganic acid solution, obviously increased the hydrophilicity. Compared with the swelling rate of PA nonmodified membrane, it can be seen that PA composite RO membrane modified with good solvent for PA would increase the permselectivity of the membrane against IPA aqueous solution.

Influence of treating conditions for modification

Figures 2–5 indicate the relationship between swelling rate of PA composite membrane and the concentration of different modifying solvents. It may be observed from these figures that, after treating with the modifying agents, whether inorganic acid or organic acid, and processing time, whether 1 or 5 h, all S_w values of modified membrane against water are greater than S_{IPA} values of modified membrane against IPA; more-

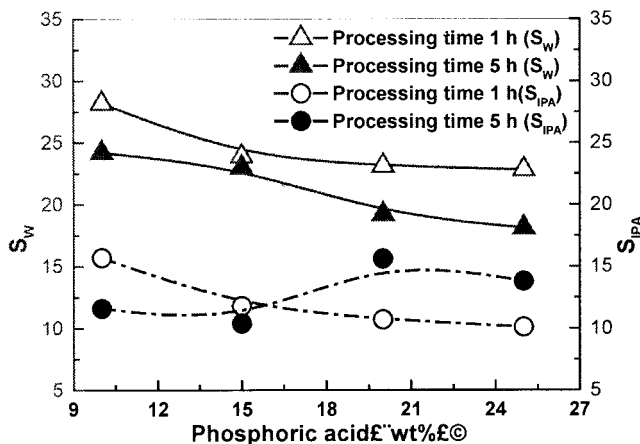


Figure 2 Effect of phosphoric acid concentration on modified membrane.

over, as the concentration of modifying agent increases, S_w and S_{IPA} values show different changes.

Figure 2 shows that S_w values of the membrane treated with phosphoric acid are substantially lower, whereas, contrarily, S_{IPA} values after the membrane was treated with over 15 wt % phosphoric acid for 5 h are higher than those after being treated for 1 h. Correspondingly, S_w values decrease even more dramatically, attributed to the over 15 wt % concentration of phosphoric acid, as the concentration increases; the S_w values of the membrane treated for 5 h gradually approximated to S_{IPA} values, showing that, although the preferential adsorbing ability of the membrane against water decreased, the preferential adsorbing ability of the membrane against IPA increased. Figure 3 shows that there is no obvious influence of the concentration of hydrochloric acid on the S_w value of the modified membrane, and S_{IPA} values decrease with the increase of the concentration of hydrochloric

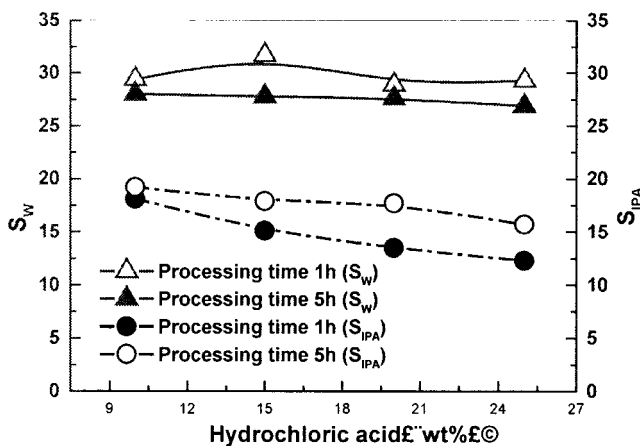


Figure 3 Effect of hydrochloric acid concentration on modified membrane.

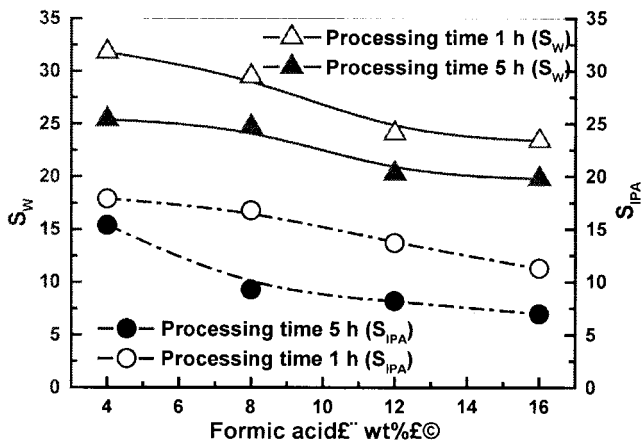


Figure 4 Effect of formic acid concentration on modified membrane.

acid in liquid medium. Figure 4 shows that all S_w and S_{IPA} values of the modified membrane decrease with the increases of formic acid concentration. Figure 5 shows that, as the concentration of acetic acid increases, the S_w values of the membrane being treated for 1 h begin to increase and when its concentration reaches the maximum value at 8 wt %, they gradually decrease; the S_{IPA} values also undergo a similar change, but the changing trend of S_w and S_{IPA} values of the membrane being treated for 5 h is in conformity with that for 1 h.

Figure 5 also shows clearly that the S_{IPA} value after 5 h of soaking is greater than that after 1 h of soaking, resulting in the increasing difference of S_w value and S_{IPA} value after 1 h soaking. The obvious difference from the swelling performance of the membrane being treated with other modifying agents is that the difference between S_w values and S_{IPA} values of PA composite membrane being treated with acetic acid for 5 h

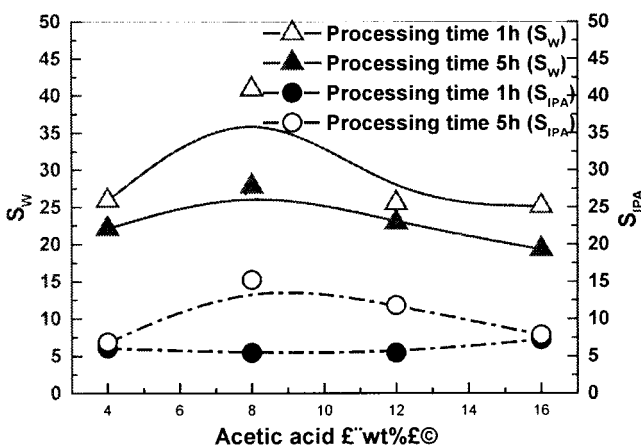


Figure 5 Effect of acetic acid concentration on modified membrane.

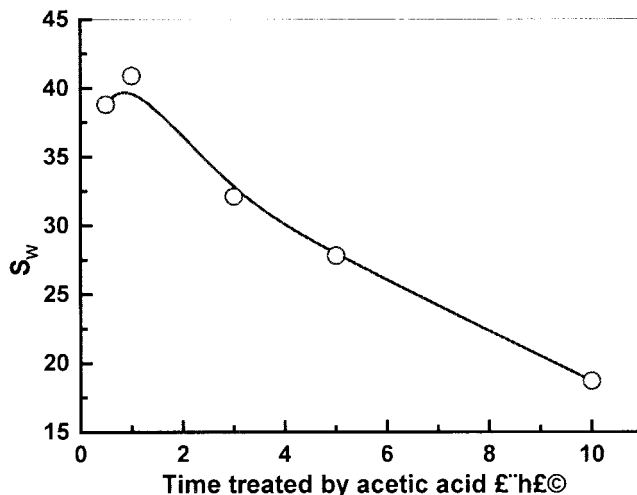


Figure 6 Relationship between swelling rates of modified composite membrane and treating time with acetic acid.

is smaller than that for 1 h with the increases of the concentration of acetic acid; that is, permselectivity for water in the membrane modified with acetic acid after 1 h of soaking is superior. It shows that as the treatment time with acetic acid decreases, the performance of preferential adsorption against water of the modified membrane decreases. The relationship between swelling rate of the modified membrane against water and the treatment time with acetic acid of concentration 8 wt % can be clearly seen from Figure 6.

The obvious difference of preferential adsorption performance of the membrane against IPA and water can be attributed to different changes of the structure of asymmetric porous RO membrane modified with solvent processing.

Separating performance of PA composite membrane modified

Table I lists the PV separating performance of PA composite membrane modified with solvents. Table I shows that, after being modified with acids and phenol, the PA composite membrane possesses better PV performance for separating IPA aqueous solution compared with other modifying agents, and its regularity of changing separation performance is in conformity with the swelling rate of the membrane modified. That is, when the modified membrane with the greatest swelling rate against water and the lowest swelling rate against IPA is used for separating IPA aqueous solution, the separating factor is maximum and the permeate flux is also maximum. In the experiment, phenol, a good solvent for PA, was used as the modifying agent; the PA composite membrane treated with phenol aqueous solution at low concentration showed better PV separation performance.

TABLE I
Separating Performance of PA Composite Membrane Modified

Property	Modifying agent				
	Phosphoric acid	Hydrochloric acid	Formic acid	Acetic acid	Phenol
Concentration, processing time	15 wt %, 1 h	15 wt %, 1 h	8 wt %, 1 h	8 wt %, 1 h	0.05 wt %, 3 h
Separation factor, α	174	189	207	276	264
Flux, J ($\text{g m}^{-2} \text{h}^{-1}$)	286	298	306	307	308

Analysis of modifying mechanism of PA composite membrane

It has been pointed out^{4,5} that the separating layer of polymeric membranes consists of closely packed nodules, and the internodular spaces are loosely filled with chain segments that bridge the spaces between the adjacent nodules. Thus, the permselectivity of the membrane is more or less governed by the transport through these micropores relative to that through the bulk of the nodules. We can imagine that the effect of these micropores, attributed to the “defects” on the asymmetric membrane in PV, disappears in RO. The micropores in the asymmetric RO membrane can be reptated by means of a solvent-processing technique into free defects and homogeneous membrane of high permselectivity in PV.¹⁻⁴

When PA membrane is soaked in liquid medium, the solvent molecules come into contact with the PA membrane, and can interact relatively strongly with the polymer chains. The polymer chains are subjected to a thermodynamic driving force of enthalpic nature that tends to mix them together, and thus the solvent molecules penetrate easily into the spaces between the adjacent nodules, and come into contact with PA chains in internodules because of the tendency of these chains to diffuse by reptation through the mesh of surrounding chains toward the solvent molecules. The PA chains that occupy the internodular spaces during the contact with the modifying agent in liquid medium are vitrified in the space after removal of the solvent. This change process⁴ is shown in Figure 7,

from which it may be noted that the modification of the membrane structure in solvent processing undergoes three steps: (1) the solvent molecules come into contact with the PA membrane; (2) the solvent molecules penetrate the spaces between the nodules and the PA chains tend to diffuse toward the solvent molecules; and (3) the PA chains that occupy the internodules are vitrified in the space after solvent removal. The process results in a decrease in the size of the nodule, the space in the internodule is changed into a denser polymer phase, the “defects” of the surface of PA membrane in PV disappear, and the asymmetric membrane is changed into a denser and more homogeneous membrane. It is quite evident that the second step in solvent processing is critical in changing the structure of PA membrane.

The type and concentration of the modifying agent and processing time in liquid medium lead to a different structure of the modified membrane because of the interaction of solvents in liquid medium with polymer chains in the PA membrane. When the concentration of acetic acid in the liquid medium is less than 10 wt %, as shown Figure 5, the higher the content of modifying agent in the liquid medium is and the faster the structure modification is. The time scale of the change in permselectivity is compatible with the required time for reptation of PA chains in the membrane. The experimental results depicted in Figures 2–6 show that the permselectivity of the modified membrane is worse with a decrease of the adsorption performances for water and IPA when the PA

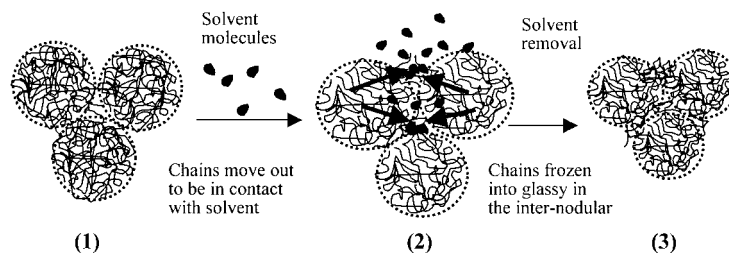


Figure 7 Schematic representation of mechanism of skin structure change of PA membrane in solvent processing: (1) the solvent molecules come into contact with the PA membrane; (2) the solvent molecules penetrate the spaces between the nodules and the PA chains tend to diffuse toward the solvent molecules; (3) the PA chains that occupy the internodules are vitrified in the space after solvent removal.

composite RO membrane was treated in the liquid medium of high concentration of modifying agent. It is noteworthy that there is a risk of deterioration of the PA composite membrane when the PA membrane has been processed by good solvent for PA.

CONCLUSIONS

A PA composite membrane used in RO desalination can be modified by means of solvent-processing technique into PV membrane of separating organic aqueous solution. The swelling rates of the modified membrane treated under conditions of various kinds of modifying agents were different. The S_w increased and S_{IPA} decreased, whether inorganic acid or organic acid was used to treat the PA membrane, compared with the nonmodified membrane. The difference between S_w and S_{IPA} of the modified membrane treated with 8 wt % acetic acid for 1 h was the greatest among those with other modifying agents. The separation factor and flux of the modified membrane were correspondingly maximal when the membrane was used to PV separate isopropanol aqueous solution.

The structural change of PA composite RO membrane in solvent processing undergoes three steps. In the second step—that is, the solvent molecules penetrate into the space between the nodules and the PA chains tend to diffuse toward the solvent mole-

cules—is critical in the modification of PA membrane structure. Because of interaction of solvent molecules with polymer chains, the size of nodules in the asymmetric membrane decreases and the internodular spaces can be filled by the polymer chains arising from between adjacent nodules. The PA composite RO membrane was transformed into a denser and more homogeneous membrane. The mechanism of changing membrane structure by means of a solvent-processing technique may better interpret the modification of PA composite RO membrane.

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