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Preparation and characterization of sandwich-structure polyethersulfone membrane with pH sensitivity

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ABSTRACT

In this paper, a novel sandwich-structure polyethersulfone (PES) membrane with pH-sensitivity was developed. The membrane was composed of three layers. The top and bottom layers were made of PES; while the middle layer was prepared by a mixture of cross-linked poly(acrylic acid) (PAA) microgels and PES. The sandwich-structure PES membrane showed evident pH sensitivity and pH reversibility as the pH value changed between 1.0 and 8.8. With the increase of the PAA gel amount added into the membrane, the pH sensitivity increased. The Cu^{2+} ion exchange experiment indicated that the membrane could bind metal ions and could be used to purified water.

Keywords: Polyethersulfone; Poly(acrylic acid); Sub-microgels; Sandwich-structure; Ion exchange; Permeability

1. Introduction

pH sensitivity as a novel and powerful technique has been used in the biotechnology industry for drug delivery systems and advanced separation. Compared with thermosensitivity, it gives more choices both for the materials and applying environment. pH-sensitive hydrogels and microspheres have been intensively investigated [1]. Ni et al. [2] provided a new type of monodisperse hydrogel microsphere, the microspheres were prepared from polyacrylamide (AAm)–methacrylic acid (MAc) cross-linked by *N,N′*-methylene-bis(acrylamide) (MB) in ethanol. The effects of main factors: composition of copolymer, cross-linking degree, and initial total concentration or solid content of the comonomers were investigated, and the microspheres exhibited sharp pH-volume transition.

With respect to the pH-sensitive membranes, there are several researches have been reported. Hydrogels have been used widely for the preparation of membranes with physically or chemically modulated responses, based on anionic polymers such as acrylic or methacrylic acids, which are water-impermeable at low pH [3–8]. Hu and Dickson [9] developed the pore-filled pH sensitive membranes by in situ cross-linking poly(acrylic acid) (PAA) inside poly (vinylidene fluoride) hydrophobic microporous substrate membranes, and found that the membranes show a rapid and reversible response of flux to environmental pH as the pH was changed between 2.5 and 7.4. Young et al. [10] produced pH-sensitive domain in the dense poly(ethylene-*co*-vinyl-alcohol) (EVAL) membrane by blending with a small amount of PAA, and they found that the non-pH-sensitive EVAL membrane prepared at 60 °C could be converted to pH-sensitive by adding a small amount of PAA.

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Polyethersulfone (PES) is one of the most widely used polymeric materials. It is favorable as membrane material for microfiltraiton (MF), ultrafiltration (UF), hemodialysis, protein recovery, plasma separator, water purification, etc. due to its excellent chemical stability, thermal resistance and mechanical properties [11–16]. Many efforts have been made to improve membrane properties, including blending, coating, surface physical treatment, and surface grafting, etc. [17–25]. Our interest is focused on the functionalization of the PES membranes by endowing with pH sensitivity for advanced separation.

PAA as a typical material with hydrophilicity and pH-sensitivity is characterized by its ionizable property. When the environmental pH is higher than the pK_a of PAA, about 4.7, more charge groups (COOH groups) dissociate [26]. The reversibility of this process results in the reversible swelling–shrinking behavior of PAA. When PAA was blended directly with other polymer, the elution of PAA was unavoidable due to the water dissolubility [27].

In the present study, we develop a new method to prepare pH-sensitive sandwich-structure PES membranes by adding cross-linked PAA sub-micrometer scale gels into the middle layer. For the sandwich-structure, PAA gels were well incorporated in the sandwich-structure membranes, and the decrease of the elution of PAA and increase of pH sensitivity were expected. The cross-section morphologies of the membranes were observed by scanning electron microscopy (SEM). The pH-sensitivity and pH-reversibility of the sandwich membrane were investigated by water flux permeation. The ion exchange capacity (IEC) was also investigated, especially the Cu^{2+} ion exchange.

2. Experimental

2.1 Materials

Acrylic acid monomer (AA, Kelong Chemical Reagent Inc., Chengdu, China) was used to synthesize the cross-linked PAA gels. MB (Kelong Chemical Reagent Inc, Chengdu, China) was the cross-linker. Azo-bis-isobutryonitrile (AIBN; Shisihewei Chemical Reagent Inc, Shanghai, China) was the initiator. PES (Ultrason E6020P, CAS Number: 25608-63-3, BASF Aktiengesellschaft) was used to prepare the membranes. Polyethylene glycol (PEG-600, Kelong Chemical Reagent Inc., Chengdu, China) were used as the additive to improve the flux of the membrane. *N,N*-dimethylacetamide (DMAC; Kelong Chemical Reagent Inc., Chengdu, China) was used as the solvent. Copper sulfate ($CuSO_4$; Kelong Chemical Reagent Inc., Chengdu, China) was used for the measurement of IEC.

2.2 Synthesis of cross-linked PAA gels

The cross-linking of PAA was carried out by free radical polymerization of AA in DMAC. A mixture of AA (25.29 wt.%), MB (4.71 wt.%), and AIBN (0.3 wt.%) in DMAC were placed in a glass reactor, and bubbled with nitrogen. The polymerization was carried out at 65 °C for 14 h to complete the reaction, and the agitation speed was controlled at 500 rpm. The cross-linked PAA gels were characterized by a Nanozatasizer (Zetasizer Nano ZS model number: ZEN3600, Malvern Instruments, UK) and a SEM (JSM-5900LV, JEOL, Japan). For the SEM observation, aether was added in the gel solution, and then the solution was centrifuged at 8000 rpm, and then was freeze-dried. The gel sample was attached to the sample supports and coated with a gold layer.

2.3 Membrane preparation

The sandwich-structure PES membrane was composed of three layers. The top and bottom layers were made of PES; while the middle layer was prepared by a mixture of cross-linked PAA microgels and PES. To prepare the top and bottom layers, required amount of PES and PEG were dissolved in a mixed solvent containing 5 wt.% water and 95 wt.% DMAC. For the middle layer, required amounts of PAA gels and PEG were dissolved in DMAC. The composition is listed in Table 1.

The bottom layer was prepared by spin coating coupled with a liquid–liquid phase separation technique [28–31] at room temperature. After vacuum degassed, the casting solution for the bottom layer was cast on a glass plate, then the casting solution was immersed in a coagulation bath containing 40 vol.% water and 60 vol.% DMAC for 1 min, and then was transferred into a sufficient volume of double-distilled water for 1 min. After wiping the surface water by filter papers, the de-bubbled mixed polymer solution for the middle layer was cast on the surface of the bottom layer by spin coating, and then immersed in a coagulation bath containing 40 vol.% water and 60 vol.% DMAC for 1 min, and then was transferred into a sufficient volume of double-distilled water for 1 min. The top layer was prepared by casting the PES solution onto the middle layer by spin-coating method. Then the nascent membrane was immersed in the blended solution containing 40 vol.% water and 60 vol.% DMAC for 1 h. For contrast, sandwich-structure membranes without PAA were prepared using the same method. The membranes were rinsed with de-ionized water thoroughly, and stored in double-distilled water till use.

Table 1
Compositions of the polymer solutions used to prepare the sandwich-structure PES membranes

Membranes no.	PES (wt.%)	PAA (wt.%)	PEG (wt.%)	DMAC (wt.%)	Water (wt.%)
M-1					
Bottom layer	12.5	0	4	78.5	5
Middle layer	12.5	0	4	78.5	5
Top layer	13.3	0	4	77.7	5
M-2					
Bottom layer	12.5	0	4	78.5	5
Middle layer	12.5	6.25	4	72.25	5
Top layer	13.3	0	4	77.7	5
M-3					
Bottom layer	12.5	0	4	78.5	5
Middle layer	12.5	12.5	4	66	5
Top layer	13.3	0	4	77.7	5
M-4					
Bottom layer	15	0	4	76	5
Middle layer	15	12.5	4	63.5	5
Top layer	16	0	4	75	5

2.4 Determination of IEC

To measure the IEC, a membrane sample was alternately equilibrated by 0.1 M HCl and 0.1 M NaOH solutions for three times, and washed by double distilled water in between. Afterward, enough NaOH solution permeated through the membrane sample at 80 kPa, using the apparatus as described in Section 2.6, and followed by a thorough washing with double distilled water. Then, the sample was permeated by HCl solution at 80 kPa, with the concentration and the volume were adjusted to contain about twice the HCl required for theoretical IEC, which was calculated according to the AA mass in the sample. The sample was removed from the apparatus and washed by double distilled water. The permeated HCl solution was then titrated with a standard NaOH solution (0.01 M) with the pH meter as the indicator. The IEC is expressed in units of milliequivalents of proton atoms per gram of the dry membrane and was calculated by [32]:

$$\mathrm{IEC(mequiv./g)} = \frac{V_{\mathrm{HCl}}N_{\mathrm{HCl}} - V_{\mathrm{NaOH}}N_{\mathrm{NaOH}}}{m_{\mathrm{c}}} \times 1000 \tag{1}$$

where V_{HCl} and V_{NaOH} are the volumes of the HCl and NaOH solutions, respectively. N_{HCl} and N_{NaOH} are the normalities of the HCl and NaOH solutions, respectively.

2.5 SEM of the membrane section

For the SEM observation, the membrane samples were freeze-dried at their neutral form, and then quenched by liquid nitrogenous gas, attached to the sample supports and coated with a gold layer. A SEM (JSM-5900LV, JEOL, Japan) was used for the morphology observation of the membrane cross-section.

2.6 Permeation experiments

An apparatus as described in previous studies [32,33] was used to investigate the membrane solution flux response to pH changing. The effective membrane area of the dead-end UF cell was 4.91 cm^2, and the pressure was supplied by an air compressor. The pH of the feed solution was adjusted by addition of HC1 or NaOH. The test membranes were pre-compacted at 120 kPa by pH 1.0 HCl solution flow at 15 °C until a stable flux was achieved. Afterward, the cell was alternatively fed by pH 8.8 or 1.0 solution at 120 kPa with double-distilled water cleaning in between by opening the cell and washing the membrane surface. The permeated solution was collected over 30 min after 5 min equilibration by the feed flow and weighed. All the flux measurements were conducted at 25 °C.

The flux is related to the applied pressure and the osmotic pressure difference across the membrane. In this study, the applied pressure difference was not significant, and the pressure was controlled at 80 kPa. The pH dependence of the water flux was determined at pH ranging from 1.0 to 8.8, randomly. The water flux was expressed as the hydrodynamic permeability, and calculated by Eq. (2):

$$\mathrm{Flux(mL/m^2\,h\,mmHg)} = \frac{V}{S \cdot t \cdot P} \tag{2}$$

where V is the volume of the permeated solution, S is the effective membrane area, t is the time of the solution collecting, and P is the pressure on the membrane.

2.7 Cu^{2+} ion exchange

To investigate the feasibility of the UF process in copper ion removal, 1 and 100 mmol/L $CuSO_4$ solutions were applied to the membranes using the UF apparatus described above at pressure 80 kPa. The concentration of Cu(II) was determined by an atomic absorption spectrophotometer (Shimadzu SPCA-626D, Japan).

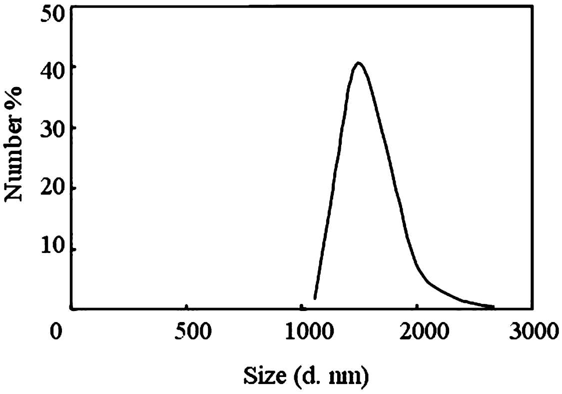


Fig. 1. The size and distribution of the cross-linked PAA gels.

3. Results and discussion

3.1. Cross-linked PAA gels

The cross-linked PAA gels were synthesized through the solution polymerization of AAs in DMAC. When the cross-linker and the initiator were added to AA solution, cross-linked PAA gels can be easily obtained by the free radical polymerization. Fig. 1 shows the size and size distribution of the synthesized particles. The size of the PAA gels ranged from about 1100 to 2500 nm, and the average size was about 1600 nm.

Fig. 2 shows a typical SEM image of the gels. As shown in the figure, the diameter of the gels ranged from about 1 to 3 μm, which was in agreement with the data obtained by the Nano-zatasizer (as shown in Fig. 1). To obtain the dried gels, aether was added to the gel solution, and then phase separation occurred, the uniform gel solution became cloudy, since aether is a non-solvent of PAA. After centrifugation, the gels should be freeze-dried, and then the gels were obtained for the SEM observation.

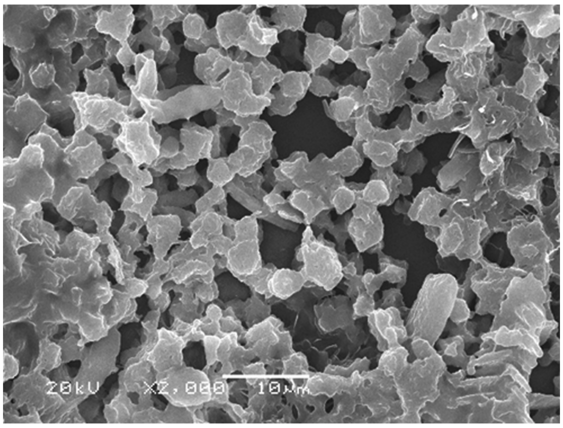


Fig. 2. Typical SEM image of the cross-linked gels.

Furthermore, we found that with the increase of agitation rate, the diameter of the gels increased. It is well-known that with the increase of the agitation speed, the particle size decreased in emulsion polymerization [34]. This was opposite to our result; however, a similar result had been reported in a previous study [2]. Since the initiator, AIBN, was applied in the polymerizations, which dominantly partitioned in the continuous phase, the capture of entities generated in the continuous phase into growing microspheres played an important role in the formation of the microgels [2]. Thus, with the increase of the agitation rate, the capture of the monomer (AA) into the growing gels increased, and the contacting probability of small gels to form large gels in the uniform solution increased.

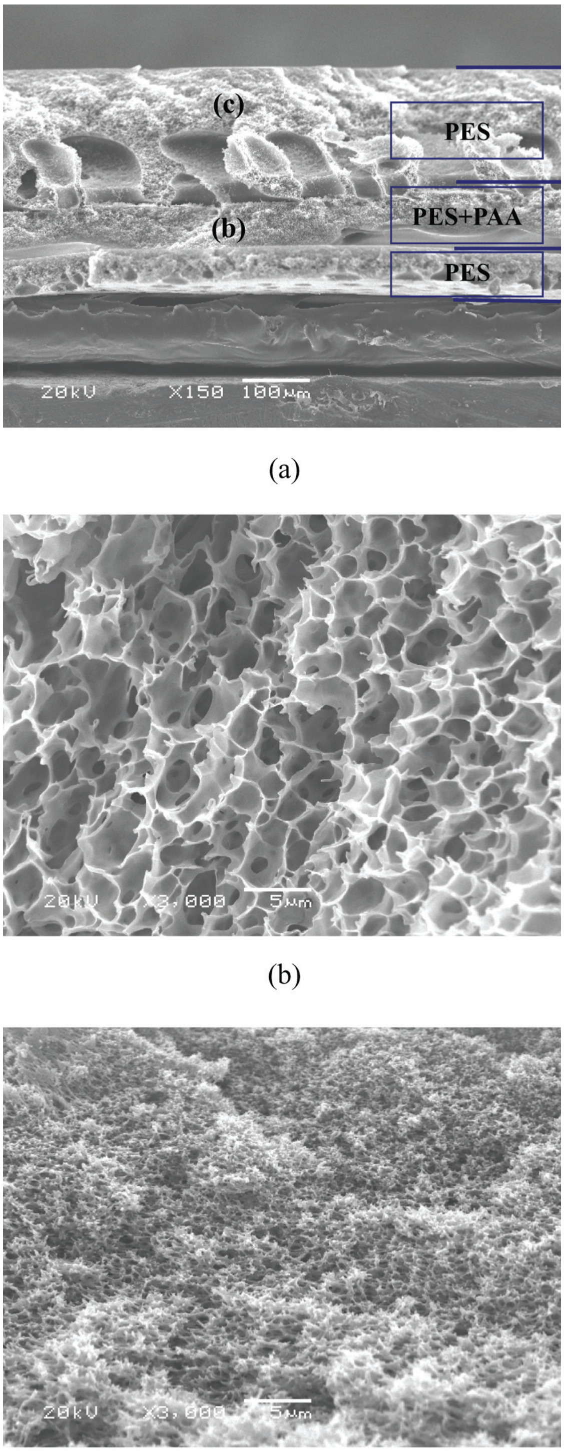
3.2. Preparation of sandwich-structure membrane

Macroscopically, the cross-section of the membranes was monolayer. Microscopically, the sandwich-structure of the membrane (M-3) was evidently shown under the observable detection sensitivity of the SEM, as indicated in Fig. 3a. The SEM picture for the middle layer is shown in Fig. 3b, while that for the top layer is shown in Fig. 3c. As shown in Fig. 3b, the structure of the middle layer has been substantially altered by the blending of PAA gels, and no finger-like structure was found, which indicated that the PAA gels are well incorporated in the membrane. The cross-linked micro PAA gels suppressed the macrovoid formation, and might affect the phase-separation process [35], thus no finger-like structure was found.

The thickness of the fabricated membranes were measured by a digital micrometer after that the membranes were rinsed and dried. Statistically, the thickness of the membrane M-1, M-2 and M-3 were 250 ± 10 μm, while that was 330 ± 10 μm for membrane M-4. These indicated that with the increase of the PES concentration, the thickness of the membranes increased; while there was no visible increase in the thickness when the PAA content increased. In another study, the effect of the spinning speed on the membrane thickness was investigated, and there was no significant difference was observed.

3.3. IEC

The membrane IEC was carried out to investigate the charge property. The membranes (M-1, M-2, and M-3) with different blending ratios of the PAA gels in the middle layer were studied, as shown in Fig. 4. As can be seen from the figure, all the titrated IECs are smaller than the calculated IECs based on the



(a)

(b)

(c)

Fig. 3. SEM images of the cross-section views of the membranes prepared with the mass fraction of PAA 24.6% (M-3). Magnification: (a) 150×; (b) 3000×; and (c) 3000×.

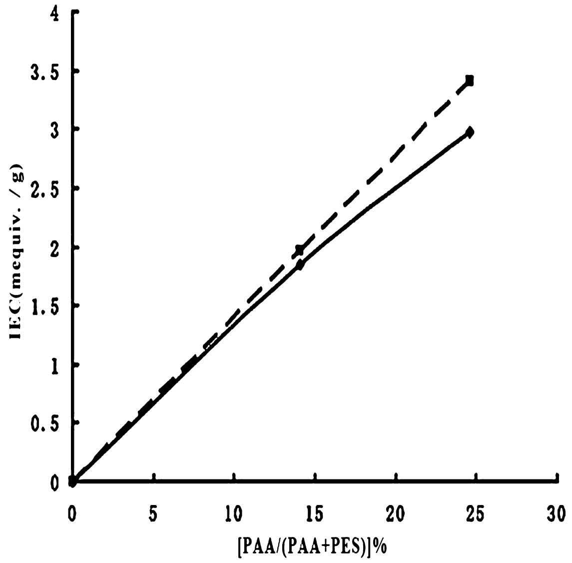


Fig. 4. Titrated and calculated IECs as a function of the initial blend composition [PAA/(PAA + PES)] in the casting dope. The line is the titrated IEC; the broken line is the calculated IEC.

theoretical AA mass in the swatches. Furthermore, the difference increased with the PAA mass fraction increased. This indicated that the PAA gels might be eluted from the sandwich-membrane matrix, since PAA gels might go in to the water when phase inversion occurred during the membrane preparation as they were hydrophilic. However, the tendency of the hydrophilic PAA gels elution from the membranes was suppressed by the sandwich-structure of the membrane, as the PAA gels were only added into the middle layer, while the PES layers existed on both sides of PAA gels.

In addition, when the membranes were equilibrated in the NaOH solution, the tendency of carboxyl groups ionized was suppressed by their around ionized carboxyl groups. Therefore, carboxyl groups could not be ionized hundred-percent, resulting in the difference of IEC. The more polyelectrolyte incorporated, the smaller the space between the carboxyl groups, which resulted in a lower degree of dissociation and the increase in the IEC difference [9].

At the same time, this impact of neighboring polyelectrolyte was weakened in virtue of the structure of the sandwich-structure membranes. When phase inversion occurred during the membrane preparation, the eluted PAA gels from the middle layer might go into the PES layers on both the sides which could change the structure of the bottom layer and the top layer. This suggests that, there were more carboxyl groups exist in sandwich-structure membrane than monolayer membrane. And with the decrease of polyelectrolyte densities, the space between the carboxyl groups increased, which result in the higher extent of polyelectrolyte ionization and the decreased difference of IEC.

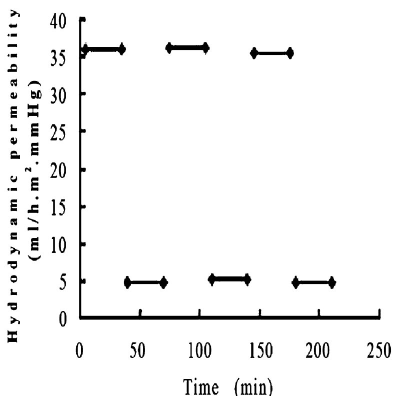


Fig. 5. Hydrodynamic permeability for the M-3 at 80 kPa as the feed was exchanged between pH 2.0 and 8.0 with 5 min equilibration flow followed by 30 min sample collecting (three times collection).

3.4. Membrane pH reversibility

The pH reversibility of the membrane M-3 was evaluated by the solution flux at pH 2.0 and 8.0 to investigate the membrane flux as a function of environmental pH. The solution was collected in 30 followed 5 min equilibration in the solution flow in each experiment. The hydrodynamic permeability is reversible between 36 and 5 mL/m^2 h mmHg as the solution was alternated, as shown in Fig. 5.

As shown in Fig. 5, the flux is fully reversible for the sandwich-structure membranes, and the flux alternation was about seven times. For the membrane M-2, the flux alternation was only two times (data not shown in the figure). The PAA gels were dispersed in the PES matrix, and the pores were only partially closed by the PAA gels at higher pH value.

3.5. Membrane water flux as a function of pH value

The flux performance of the membranes at different pH values has been utilized to verify the concept of pH-sensitive sandwich-structure membrane provided by the PAA gels. The membranes without pH-sensitive are expected exhibit a horizontal line. Any deviation from the line would suggest that the membrane structure has been altered. The pH-sensitivity of the membrane was carried out using the sandwich-structure membranes with different amount of PAA gels, and the result is shown in Fig. 6.

The effect of pH changing from 1.0 to 8.8 on water flux through three membranes (M-1, M-2, and M-3) was studied. The PES amount for the three membranes is the same, but the contents of the PAA gels are different. From the figure, the membrane performance has been permanently altered by the PAA gels. The water flux of the membranes (M-2 and M-3) containing PAA gels was higher than that for M-1 (without PAA) at low pH value.

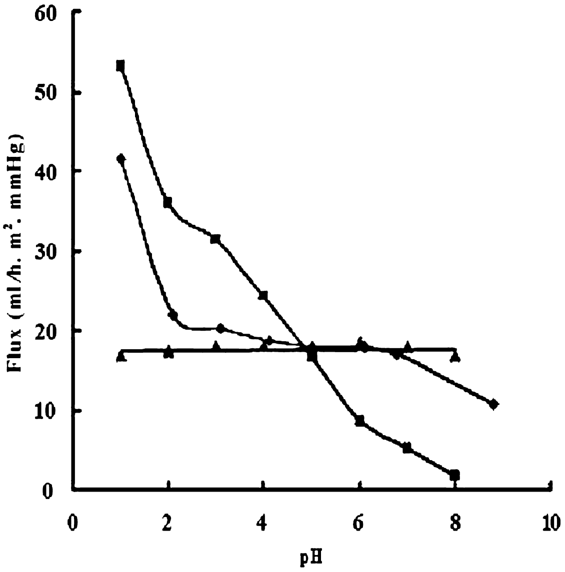


Fig. 6. Water flux as a function of pH for the membranes M-1 (▲, the PAA/(PAA + PES) was 0%); M-2 (□, the PAA/(PAA+PES) was 14.1%); and the membrane M-3 (■, the PAA/(PAA + PES) was 24.6%) at 25 °C, 80 kPa. Duplicate experiments showed similar results.

As can be seen from Fig. 6, a variation of water flux of the two membranes with PAA gels was observed. For M-2, the flux changed from 41 at pH 1 to 11 mL/m^2 h mmHg at pH 8.8; and that changed from 53 to 2 mL/m^2 h mmHg for M-3. Most of carboxyl groups were in their unionized state at low pH value, conducing PAA segments coiled down. At high pH value, the dissociated and extended carboxyl groups resulted in opening-pores decrease and lower flux. Furthermore, with the increase of the PAA gel amount in the membranes, the flux change increased with the pH changing. Based on the flux performance of M-2 and M-3 and the general assumptions, the sandwich-structure membrane with PAA is hypersensitive to pH value.

In addition, the water flux for the membranes with the higher amount of PAA gels was larger at low pH value, due to the increased hydrophilicity of the membrane surface. At the pH value of about 4.7 (the pK_a of PAA), there was no difference in the flux for all the three membranes. At higher pH value larger than 4.7, more charge groups (COOH groups) dissociate, and the pore sizes of the membranes decreased, which resulted in the decrease of the water flux.

For membrane M-4, the water flux was too small under the experimental conditions due to the high PES concentration (data not shown in the figure). The variation of PES concentration in the matrix remarkably affects the microstructure of the membrane and water flux. With the increase of the PES concentration, the water flux decreased [36].

About 1 mmol/L Asp or Lys solutions were also applied to the membrane M-3 to study the permeability. The pH of solution was 3.2 for Asp, and 9.4 for Lys. The flux of acidic amino acid Asp was 29.2 mL/m^2 h mmHg; while that for the basic amino acid Lys was 1.9 ml/m^2 h mmHg. The result is consistent with the water flux for the membrane M-3 as shown in Fig. 6.

3.6. Cu^{2+} ion exchange

The sandwich-structure membrane can be used for the removal of metal ions. PES is a hydrophobic material with negligible interactions with ions, whereas PAA is a hydrophilic material whose carboxylic groups have both ion exchange and complexation abilities. As a counter-ion, Cu(II) could bind to the negatively charged PAA by the electrostatic long-range interactions, but the adsorption rate decreased with the decrease of the concentration of Cu(II) [37].

In this study, deficient $CuSO_4$ solution (1 mmol/L) and excessive $CuSO_4$ solution (100 mmol/L) were applied to the membrane M-3. For the 1 mmol/L $CuSO_4$ solution, the retention ratio of Cu(II) was about 65% in the experimental conditions. The 100 mmol/L $CuSO_4$ solution could be used to test the maximum retention quantity of Cu(II) as the Cu(II) was excessive. The Cu(II) ions adsorption amount was 1.58 mmol/g, which was 92.7% of the theoretical adsorption amount calculated from the IEC. These results indicated that the prepared sandwich-structure membranes could bind and remove Cu(II), and could be used to purify water.

4. Conclusion

In the present study, a new method for the preparation of pH-sensitive and ion exchange sandwich-structure PES membranes has been successfully accomplished by adding required mounts of cross-linked micro PAA gels into the middle layer. The PAA gels are well dispersed in the PES sandwich-structure matrix, and the PAA plays an important role on the pH sensitivity and pH reversibility of the membrane. The sandwich-structure membranes exhibited higher sensitivity to pH value due to the decrease of the PAA elution from the membranes and the increase of the space between the carboxyl groups, which were resulted by the special sandwich-structure. The results of Cu^{2+} ion exchange indicated that the sandwich-structure membranes could be used for the removal of metal ions as ion exchange membranes.

Acknowledgements

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References

[1] Y. Kamijo, K. Fujimoto, H. Kawaguchi, Y. Yuguchi, H. Urakawa and K. Kajiwara, Preparation and structural characterization of hydrogel microspheres, Polymer, 28 (1996) 309-316.
[2] H. Ni, H. Kawaguchi and T. Endo, Characteristics of pH-sensitive hydrogel microsphere of poly(acrylamide-*co*-methacrylic acid) with sharp pH–volume transition, Colloid Polym. Sci., 285 (2007) 873-879.
[3] E.O. Akala, P. Kopeckova and J. Kopecek, Novel pH-sensitive hydrogels with adjustable swelling kinetics, Biomaterials, 19 (1998) 1037-1047.
[4] M.D. Blanco, O. Garcia, R.M. Trigo, J.M. Teijon and I. Katime, 5-Fluorouracil release from copolymeric hydrogels of itaconic acidmonoester, Biomaterials, 17 (1996) 1061-1068.
[5] H. Brondsted, C. Andersen and L. Hovgaard, Crosslinked dextran—a new capsule material for colon targeting of drugs, J. Control. Release, 53 (1998) 7-13.
[6] M. Changez, K. Burugapalli, V. Koul and V. Choudhary, The effect of composition of poly (acrylic acid)-gelatin hydrogel on gentamicin sulphate release: in vitro, Biomaterials, 24 (2003) 527-536.
[7] M.J. Shieh, P.S. Lai and T.H. Young, 5-Aminosalicylic acid permeability enhancement by a pH-sensitive EVAL membrane, J. Membr. Sci., 204 (2002) 237-246.
[8] B. Vazquez, M. Gurruchaga, I. Goni, E. Narvarte and J.S. Roman, A pH-sensitive hydrogel based on poly (ethoxy triethylene glycol monomethacrylate), Polymer, 36 (1995) 3327-3333.
[9] K. Hu and J.M. Dickson, Development and characterization of poly(vinylidene fluoride)–poly(acrylic acid) pore-filled pH-sensitive membranes, J. Membr. Sci., 301 (2007) 19-28.
[10] P.S. Lai, M.J. Shieh, C.L. Pai, C.Y. Wang and T.H. Young, A pH-sensitive EVAL membrane by blending with PAA, J. Membr. Sci., 275 (2006) 89-96.
[11] N. Kim, C.S. Kim and Y.T. Lee, Preparation and characterization of polyethersulfone membranes with p-toluenesulfonic acid and polyvinylpyrrolidone additives, Desalination, 223 (2008) 218-226.
[12] J.J. Qin, M.H. Oo and Y. Li, Development of high flux polyethersulfone hollow fiber ultrafiltration membranes from a low critical solution temperature dope via hypochlorite treatment, J. Membr. Sci., 247 (2005) 137-142.
[13] J.H. Kim and C.K. Kim, Ultrafiltration membranes prepared from blends of polyethersulfone and poly (1-vinylpyrrolidone-*co*-styrene) copolymers, J. Membr. Sci., 262 (2005) 60-68.
[14] M. Ulbricht, O. Schuster, W. Ansorge, M. Ruetering and P. Steiger, Influence of the strongly anisotropic cross-section morphology of a novel polyethersulfone microfiltration membrane on filtration performance, Sep. Purif. Technol., 57 (2007) 63-73.

[15] C.S. Zhao, T. Liu, Z.P. Lu, L.P. Chen and J. Huang, Evaluation of polyethersulfone hollow fiber plasma separator by animal experiments, Artif. Organs., 25 (2001) 60-63.

[16] S. David, D. Gerra, C. De Nitti, B. Bussolati, U. Teatini, G.R. Longhena, C. Guastoni, N. Bellotti, F. Combarnous and C. Tetta, Hemodiafiltration and high-flux hemodialysis with polyethersulfone membranes, Contrib. Nephrol., 2003 (138) 43-54.

[17] M. Ulbricht and G. Belfort, Surface modifications of ultrafiltration membranes by low temperature plasma. II. Graft polymerization onto polyacrylonitrile and polysulfone, J. Membr. Sci., 111 (1996) 193-215.

[18] Y. Wang, T. Wang, Y. Su, F. Peng, H. Wu and Z. Jiang, Remarkable reduction of irreversible fouling and improvement of the permeation properties of poly(ether sulfone) ultrafiltration membranes by blending with Pluronic F127, Langmuir, 21 (2005) 11856-11862.

[19] A.V.R. Reddy, D.J. Mohan, A. Bhattacharya, V.J. Shah and P.K. Ghosh, Surface modification of ultrafiltration membranes by preadsorption of a negatively charged polymer: I. Permeation of water soluble polymers and inorganic salt solutions and fouling resistance properties, J. Membr. Sci., 214 (2003) 211-221.

[20] M.L. Steen, A.C. Jordan and E.R. Fisher, Hydrophilic modification of polymeric membranes by low temperature H_2O plasma treatment, J. Membr. Sci., 204 (2002) 341.

[21] R.M. Boom, T. van den Boomgard and C.A. Smolders, Mass transfer and thermodynamics during immersion precipitation for a two-polymer system: evaluation with the system PES–PVP–NMP–water, J. Membr. Sci., 90 (1994) 231-249.

[22] D. Rana, T. Matsuura, R.M. Narbaitz and C. Feng, Development and characterization of novel hydrophilic surface modifying macromolecule for polymeric membranes, J. Membr. Sci., 249 (2005) 103-112.

[23] H. Yamagishi, J. Crivello and G. Belfort, Development of a novel photochemical technique for modifying poly (arylsulfone) ultrafiltration membranes, J. Membr. Sci., 105 (1995) 237-247.

[24] M. Ulbricht, M. Riedel and U. Marx, Novel photochemical surface functionalization of polysulfone ultrafiltration membranes for covalent immobilization of biomolecules, J. Membr. Sci., 120 (1996) 239-259.

[25] L. Zhang, G. Chowdhury, C. Feng, T. Matsuura and R. Narbaitz, Effect of surface-modifying macromolecules and membrane morphology on fouling of polyethersulfone ultrafiltration membranes, J. Appl. Polym. Sci., 88 (2003) 3132-3138.

[26] J. Hendri, A. Hiroki, Y. Maekawa, M. Yoshida and R. Katakai, Permeability control of metal ions using temperature- and pH-sensitive gel membranes, Radiat. Phys. Chem., 60 (2001) 617-624.

[27] C.O. M'Bareck, Q.T. Nguyen, S. Alexandre and I. Zimmerlin, Fabrication of ion-exchange ultrafiltration membranes for water treatment: I. Semi-interpenetrating polymer networks of polysulfone and poly (acrylic acid), J. Membr. Sci., 278 (2006) 10-18.

[28] K.J. Baik, J.Y. Kim, H.K. Lee and S.C. Kim, Liquid–liquid phase separation in polysulfone/polyethersulfone/*n*-methyl-2-pyrrolidone/water quaternary system, J. Appl. Polym. Sci., 74 (1999) 2113-2123.

[29] H. Matsuyama, M. Nishiguchi and Y. Kitamura, Phase separation mechanism during membrane formation by dry–cast process, J. Appl. Polym. Sci., 77 (2000) 776-783.

[30] C.A Smolders, A.J. Reuvers, R.M. Boom and I.M. Wienk, Microstructures in phase-inversion membranes. I. Formation of macrovoids, J. Membr. Sci., 63 (1992) 259-275.

[31] B.H. Fang, Q.Y. Ling, W.F. Zhao, Y.L. Ma, P.L. Bai, Q. Wei, H.F. Li and C.S. Zhao, Modification of polyethersulfone membrane by grafting bovine serum albumin on the surface of polyethersulfone/poly (acrylonitrile-*co*-acrylic acid) blended membrane. J. Membr. Sci., in press.

[32] A.M. Mika, R.F. Childs, J.M. Dickson, B.E. McCarry and D.R. Gagnon, A new class of polyelectrolyte-filled microfiltration membranes with environmentally controlled porosity, J. Membr. Sci., 108 (1995) 37-56.

[33] S. Suryanarayan, A.M. Mika and R.F. Childs, The effect of gel layer thickness on the salt rejection performance of polyelectrolyte gel-filled nanofiltration membranes, J. Membr. Sci., 290 (2007) 196-206.

[34] H.M. Ni, Y.Z. Du, G.H. Ma, M. Nagai and S. Omi, Mechanism of soap-free emulsion polymerization of styrene and 4-vinylpyridine: characteristics of reaction in the monomer phase, aqueous phase, and their interface, Macromolecules, 34 (2001) 6577-6585.

[35] R.M. Boom, I.M. Wienk, Th. van den Boomgaard and C.A. Smolders, Microstructures in phase inversion membranes. Part 2. The role of a polymeric additive, J. Membr. Sci., 73 (1992) 277-292.

[36] Y.J. Zhang, Q. Wei, C.B. Yi, C.Y. Hu, W.F. Zhao and C.S. Zhao, Preparation of polyethersulfone-alginate microcapsules for controlled release, J. Appl. Polym. Sci., 111 (2009) 651-657.

[37] A. Alpatova, S. Verbych, M. Bryk, R. Nigmatullin and N. Hilal, Ultrafiltration of water containing natural organic matter: heavy metal removing in the hybrid complexation–ultrafiltration process, Sep. Purif. Technol., 40 (2004) 155-162.