Front. Chem. China 2008, 3(4): 432–439
DOI 10.1007/s11458-008-0078-0

RESEARCH ARTICLE

Yanling QIAN, Jianhua WANG, Baoku ZHU, Mei ZHANG, Chunhui DU, Youyi XU

Modification effects of amphiphilic comb-like polysiloxane containing polyether side chains on the PVDF membranes prepared *via* phase inversion process

Abstract Amphiphilic comb-like polysiloxane (ACPS) containing polyether side chains was used as the modification reagent in the preparation of hydrophilic porous poly (vinylidene fluoride) (PVDF) membranes *via* a phase inversion process. The effects of ACPS on morphology, crystallinity, mechanical properties, reservation of ACPS in the phase inversion process, chemical structure, hydrophilicity and filterability performance of porous PVDF membranes were discussed. It was found that the addition of ACPS would result in the delayed demixing which yields "sponge-like" sublayers and longer crystallization time during the membrane formation process. It was revealed that O/F ratios of the bulk membrane were almost the same as those of the corresponding casting solutions which obviously indicated the high reservation of ACPS in the membrane formation process. The fact that the O/F ratios in the membrane surface layers were much higher than those in the bulk membrane proved the enrichment of ACPS on the surface. The filterability experiments and water contact angle testing proved the hydrophilicity of the blend membranes. Through a schematic model, the mechanism relating the membrane structure and performance was interpreted. From the observed results, it can be concluded that ACPS acts as a potential candidate material for preparing PVDF membranes with extraordinary hydrophilicity and filterability.

Keywords poly(vinylidene fluoride), porous membrane, comb-like polysiloxane containing polyether side chains, surface enrichment, hydrophilicity, phase inversion

1 Introduction

As one of the most popular materials for microporous and ultrafiltration membranes, poly(vinylidene fluoride) has earned lots of attention due to its comparatively good mechanical properties, thermal and chemical stability and radiation resistance. However, PVDF membranes also exhibit drawbacks. They are easily fouled by proteins, oil, sewage. In addition, they may need high driving force for water filtration. All these properties are related with the hydrophobicity of PVDF. As a result, modifications to improve the hydrophilicity are urgently required for preparing PVDF membranes with outstanding performance characteristics [1–3]. At present, the main modification methods focus on surface modification [4–7] and blending with hydrophilic components [8–11]. Among the various surface modification methods, smearing glycerol or surfactant has short-term modification effect and may lead to filtrates with high organic concentration. Surface grafting *via* UV, plasma and high-energy particle technologies are complicated processes and entail high production cost. Moreover, they may result in a decrease of rejection and mechanical properties [12]. Thus, they are not very popular in industrial production. Besides, surface modification can deal with the membrane surface layer only [13–16] while fouling exists not only on the surface but also inside the membranes [17].

It was proved by previous researchers that linear hydrophilic polymers such as poly(vinyl pyrrolidone) (PVP) and poly(ethylene glycol) (PEG) can act as pore-inducing components instead of hydrophilicity-improving materials in membranes [18–21] because of the fact that they tend to be washed away both in the membrane forming process and in applications. Recently, comb-like amphiphilic copolymers were introduced to the membrane casting solution for improving the hydrophilicity of membranes [9,22–27]. Principally, the reservation of the copolymer addition in membranes increases remarkably because of the strong attraction between hydrophobic segments of

Translated from *Acta Polymerica Sinica*, 2007, 12: 1168–1175

Yanling QIAN, Jianhua WANG, Baoku ZHU (✉), Mei ZHANG, Chunhui DU, Youyi XU
Institute of Polymer Science, Zhejiang University, Key Laboratory of Macromolecular Synthesis and Functionalization, Ministry of Education, Hangzhou 310027, China
E-mail: zhubk@zju.edu.cn

the amphiphilic copolymer and the hydrophobic matrix (PVDF) while the comb-like hydrophilic segments endow the blend membrane with outstanding hydrophilicity.

Here, the amphiphilic comb-like polysiloxane (ACPS) containing polyether side chains is applied in the PVDF system because of their popularity in industry, their special structures as well as their remarkable properties in aqueous solutions. In this paper, the ACPS containing poly(ethylene oxide)-block-poly(propylene oxide) as side chains was synthesized (ACPS molecular formula is given in Fig. 1). Hydrophilic membranes with remarkable filtration properties and anti-fouling performances were obtained as well.

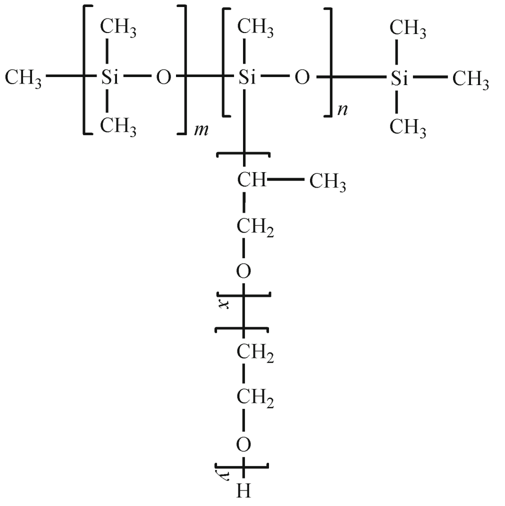

Fig. 1 Structure of amphiphilic comb-like polysiloxane containing polyether side chains

2 Experiments

2.1 Materials

PVDF ($M_w = 1\ 000\ 000$) was purchased from Shanghai 3F New Materials Co., Ltd. *N*, *N*-dimethyl formamide (DMF), bovine serum albumin (BSA) ($M_w = 67\ 000$) and poly (ethylene glycol) (PEG, $M_n = 2\ 000$) were purchased from Sinopharm Chemical Reagent Co., LTD and used as received.

2.2 Synthesis of ACPS

The amphiphilic comb-like polysiloxane was synthesized by a hydrosilylation coupling reaction in the presence of unsaturated diglycidyl ether, terminally unsaturated alkylene oxide polymer, poly(ethylene oxide)-block-poly(propylene oxide) utilizing platinum catalyst with toluene as solvent . The reaction was carried out under nitrogen at 85°C for at least 4–5 h [28]. The molecular weight and composition of ACPS is as follows: $M_n = 25\ 000$, $M_w = 36\ 000$, $n: (n+m) = 0.4$ (as seen in Fig. 1), PPO, PEO composition of 38.7 wt% and 44.0 wt%, respectively, determined by GPC (PL-GPC220, Polymer Laboratories Lid). The measurements were carried out in THF solutions. The NMR (Varian VXR-400) analysis was done in DMSO-*d*6 solutions.

2.3 Preparation of membranes

ACPS/PVDF blend membranes were prepared by the classical phase separation method. PVDF and ACPS were introduced into DMF (the total concentration of PVDF and ACPS was 16 wt%), stirred at 80°C for 48 h until a homogeneous casting solution was obtained. The solution was kept in vacuum at 60°C for 2 h for complete release of the air bubbles. Membranes were cast on glass plates and immersed in pure water at 60°C as coagulation bath for 48 h in order to exchange with DMF completely. Membranes were dried at 60°C in vacuum. The porous membranes using PEG as the additive (the weight ratio of PEG/PVDF was 20/80) were also prepared following the same processes as a reference system.

2.4 Precipitation kinetics and characterization

The precipitation kinetics of membrane formation was characterized by a light transmission instrument (Zhejiang University and Wande photoelectricity Co., LTD) by detecting the light intensity transmitted through the membrane. The micro-morphology was observed using a scanning electronic microscope (SLRI10N SEM, FEI Co., Holland). The water contact angle of membranes was measured by a contact angle goniometer (Dataphysics, OCA20, Germany) to test its surface hydrophilicity. Membrane porosity was measured by a mercury porosimeter (Autopore IV Demo 9500, micromeritics) by determining the corresponding relation between the pressure and mercury permeation and using a mathematical model in which the upper limit pressure was 228 MPa and the lower limit pressure was 0.1–0.2 MPa. The surface and bulk chemical compositions of blend membranes were measured by X-ray photoelectron spectroscopy (XPS, VG Multi lab 2000) and an element analysis instrument (Vario EL, Elementar Co., Germany), respectively. The aggregation and crystallization of PVDF were measured by X-ray diffraction (XRD, D/MAX-RA, Rigaku Co., LTD, Japan) and differential scanning calorimetry (DSC, Perkin Elmer Co., LTD, American). A tensile test machine (RG-7000, Shengzhen Reger Instrument Co., LTD) was used to determine the strength and elongation of PVDF membranes. Filtration experiments were carried out to study the permeability of membranes under a pressure difference of 0.1 MPa. With the buffer of Na_2HPO_4 and KH_2PO_4 solution (PH $\approx$ 7.4), the membrane's rejection (R) to 1 g/L BSA solution was determined. The pertinent equation is

$$R\% = \left(1 - C_p/C_f\right) \times 100\%$$

where C_p and C_f represent the concentrations of filtrate and feed, respectively.

Membranes were repeatedly washed at 60°C to investigate the stability of ACPS polymers in blend membranes.

3 Results and discussion

3.1 Forming kinetics and morphology of membranes

Different ACPS/PVDF mass ratios of 0:100, 5:95, 10:90, 20:80 and 30:70 were used for membrane preparation. Light transmission and delayed precipitation time are presented in Fig. 2. t represents the length of time needed for a liquid membrane to exhibit a sharp decrease of light transmission in the coagulation bath. It was found that when the ACPS content increased, the delayed precipitation time increased too and this indicates that the phase separation process of the casting solution shifts from instantaneous demixing to delayed demixing. At the same time, the coagulation and precipitation rate decrease. Combining these results with membrane micro-morphology in Fig. 3, it could be concluded that instantaneous demixing results in the formation of "finger-like" macrovoids in the sublayer whereas delayed demixing yields "sponge-like" sublayers and decreases the mean diameter of the membrane pores. There are no significant changes on the membrane surface. The porosity of membranes is listed in Table 1. A decrease in membrane porosity is observed when the ACPS concentration increases (see SEM photograph).

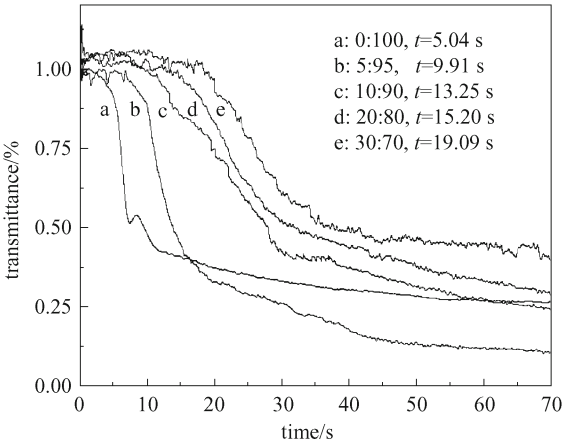

Fig. 2 Light transmission during the precipitation of casting solutions with different ACPS/PVDF ratios 0/100; b) 5/95; c) 10/90; d) 20/80; e) 30/70

The PEG/PVDF system followed the same phase inversion behavior as the ACPS/PVDF system showing delayed precipitation in the membrane forming process, too. However, there are some differences between the two systems. The PEG/PVDF system shows high porosity, larger "finger-like" pores and much more spherical crystals on the membrane surface layer. All of these result in the poorer mechanical properties of PEG/PVDF membranes as compared with that of ACPS/PVDF membranes.

3.2 Crystallization and mechanical properties

There are five crystal phases for PVDF – α (II), b (I), γ (III), δ (IV) and ε [29] – according to the XRD results. Among the five, the α (II) phase is the most popular one having trans-chain form with atoms H and F alternating on the two sides of the main chain. Usually, α (II) PVDF is obtained in the membranes prepared *via* the P-S process. Table 2 presents the crystallinity data from XRD and DSC corresponding to the surface layer crystallinity and bulk crystallinity (total crystallinity), respectively. There are two characteristics in these data. First, the bulk crystallinity is much higher than the surface layer crystallinity and second, both increase when the ACPS content increases.

The reason for a lower surface layer crystallinity is given as follows. When a liquid membrane meets the coagulation liquid, the demixing of casting solutions in the surface layer occurs instantaneously leaving no time for PVDF to crystallize in this region. At the same time, the formation of a crystalline surface layer may prevent the exchange of the solvent in the sublayer of the membrane and the non-solvent of the coagulation bath. As a result, the precipitation and phase inversion of the sublayer casting solution are much slower than those in the surface layer and PVDF molecules in the sublayer may have sufficient time to adjust their conformation for crystallization. The crystallinity trend of the blend membranes is presented in Fig. 2 where it can be seen that the delayed precipitation time increases when the ACPS content increases.

Compared with ACPS/PVDF systems, membranes prepared from the PEG/PVDF system have higher crystallinity of PVDF both in the surface layer and the sublayer. This might be related with the longer delayed precipitation time for PEG system or, some special depression effect of linear PEG chains on PVDF crystallization.

Table 2 also lists the mechanical properties of blend PVDF membranes in detail. In principle, membranes with "sponge-like" pores have better mechanical properties than membranes with "finger-like" pores. The addition of ACPS increases the mechanical properties because of the control of "fingerlike" pores and development of "sponge-like" pores as shown in Fig. 3. In addition, the higher bulk crystallinity contributes to the increase of membrane strength.

For the PEG/PVDF membrane, strength at break increases because of the "sponge-like" pores and higher

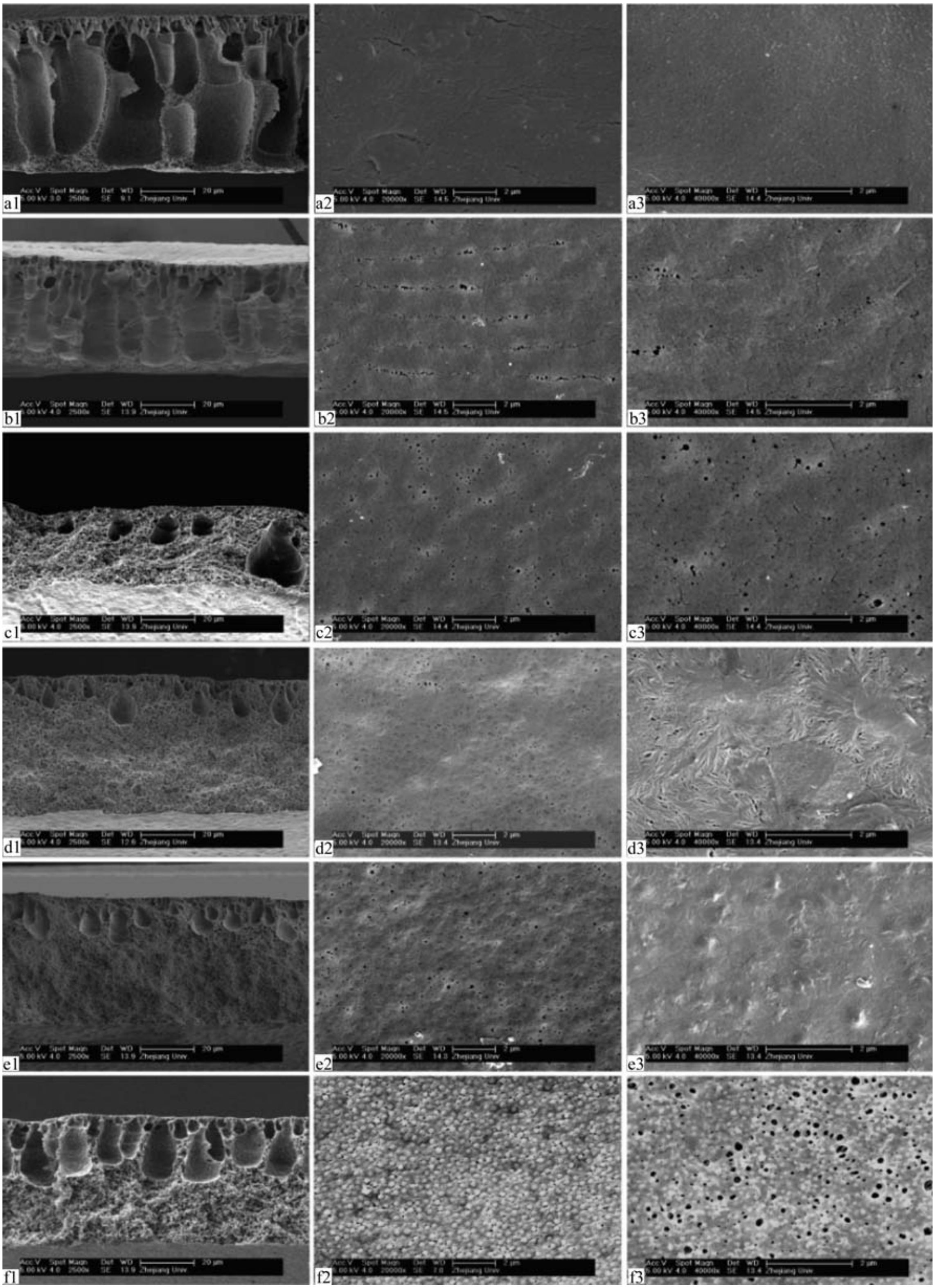

Fig. 3 SEM images of membranes prepared from the casting solutions with ACPS/PVDF mass ratios of (a) 0/100, (b) 5/95, (c) 10/90, (d) 20/80 and (e) 30/70, and from the reference solution of (f) PEG/PVDF (20/80)
(1) Cross section, (2) top surface, (3) bottom surface

Table 1 Porosity of blend membranes prepared from different casting solutions

casting solution	mass ratio of ACPS/PVDF					reference with PEG/PVDF = 20/80
	0/100	5/95	10/90	20/80	30/70	
Porosity/%	73	68.2	68.3	60.7	58.5	69.0

Table 2 Crystallization and mechanical properties of the blend membranes prepared from different casting solutions

casting solution	mass ratio of ACPS/PVDF					reference with PEG/PVDF = 20/80
	0/100	5/95	10/90	20/80	30/70	
crystallinity (DSC, %)	37.2	42.5	44.3	43.1	43.0	46.3
crystallinity (XRD, %)	16.9	16.3	19.8	19.8	20.0	25.9
strength at break/MPa	10.1	12.6	11.3	13.9	15.6	11.9
elongation/%	210	294	293	297	300	181

crystallinity but the elongation is smaller than that of the ACPS/PVDF membrane and even the pure PVDF membrane. So, ACPS is more effective than linear PEG in improving the mechanical properties of PVDF membranes.

3.3 Chemical composition and hydrophilicity of membrane matrix/surface

ACPS is water soluble and can be lost from the blend system in the membrane-forming process. So, the ACPS content in solid membranes is not clear. The bulk composition of membranes was characterized by elemental analysis. It is revealed that the O/F ratio of bulk membrane (O/F = 0.25 for ACPS/PVDF = 30:70 membrane) was almost the same as that of the corresponding casting solution (O/F = 0.27 for corresponding system) indicating a rather good reservation of ACPS in the membrane forming process. This reservation should come from the intense entanglement between polysiloxane segments and PVDF segments.

Table 3 Comparison of O/F atomic ratio on the surface and bulk of the membranes prepared from the casting solution with ACPS/PVDF ratio of 30/70

	O/F ratio		
	casting solution[a]	membrane matrix[b]	membrane surface[c]
pure PVDF membrane	0	0	0
blend membrane	0.27	0.25	0.34

Calculated from ACPS/PVDF ratio in casting solution; [b] Elemental analysis; [c] XPS

On the other hand, membrane performance is affected greatly by the chemical composition of the membrane surface. The instability of surface composition should be seriously considered. XPS data (Fig. 4), which measured the surface element composition, showed major emission peaks at 284.7 eV for C (1s), 685.3 eV for F (1s), 534.2 eV for O (1s) and 101.3 eV for Si (2p), respectively. From the peak integral, the O/F ratio is calculated as 0.34, larger than that of the the bulk (0.25) or the casting solution (0.27). This indicates the enrichment of ACPS on the surface.

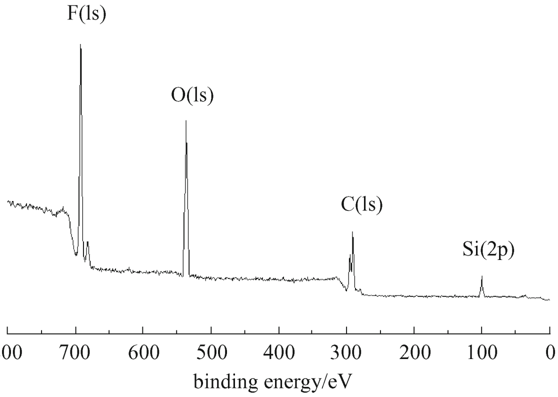

Fig. 4 XPS curve of membrane prepared from casting solution with ACPS/PVDF ratio of 30/70

In the phase inversion process, hydrophilic poly(ethylene oxide) segments move to the interface of the membrane and extend outwards to the coagulation bath while the polysiloxane bone chains twist with the PVDF chains resulting in difficulty in separating ACPS molecules from the PVDF membrane into coagulation bath. Thus, the membranes have a hydrophilic surface (not only the membrane surface but also the inside-wall of pores) due to the enrichment of PEO segments. Water soluble PEG or linear amphiphilic polymers have difficulty forming structures as shown in Fig. 5 and this provides the surface improved hydrophilicity modification through

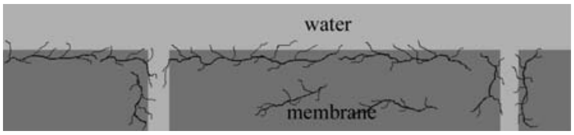

Fig. 5 Schematic illustration of ACPS in the membranes

blending with comb-like ACPS. The modification effect is directly expressed in the results of contact angle measurements given in Fig. 6.

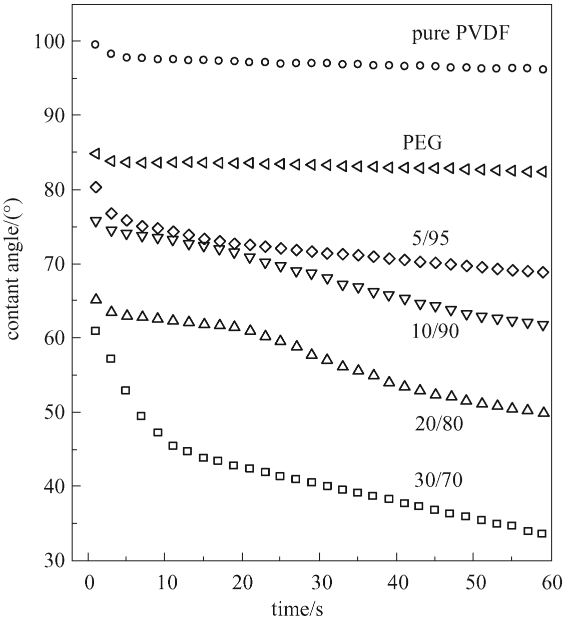

Fig. 6 Water contact angles for the blend membrane prepared from casting solutions with different ACPS/PVDF ratios

The hydrophilicity of blend membranes increases sharply *via* blending with ACPS as indicated by measurement of the surface contact angle. The sample with ACPS/PVDF ratio of 30/70 can be wetted thoroughly in a very short time while linear PEG hardly influence the original contact angle or osmosis indicating little effect on hydrophilicity modification. This is due to bad reservation in membranes during the membrane forming process and later applications [18–19,30]. These results show the rationality of ACPS modification while the feasibility should be proved by filtration properties and performance stability as discussed below.

3.4 Membrane filtration property and its stability

Pure water flux and BSA rejection were tested to study the filtration and rejection properties. PVDF membranes and PEG/PVDF membranes with similar surfaces allowed no water to pass through under a pressure difference of 0.1 MPa indicating the total hydrophobicity of both membranes. Their water flux increased to 12.5 and 31.4 L/h·m^2, respectively, after ethanol treatment while the BSA rejection of both membranes was 90% and 81.7%, respectively. Nevertheless, the water flux of PVDF membranes modified with ACPS increased with increasing ACPS content. The data, shown in Fig. 7, illustrates the effect of ACPS modification on membrane hydrophilicity and filtration. ACPS/PVDF membranes exhibited consistently high rejection to BSA (greater than 90%). All of the results reveal good separation performance of ACPS/PVDF blending membranes and the rationality of using ACPS for preparation of PVDF membranes with super hydrophilicity *via* a one step P-S process is demonstrated.

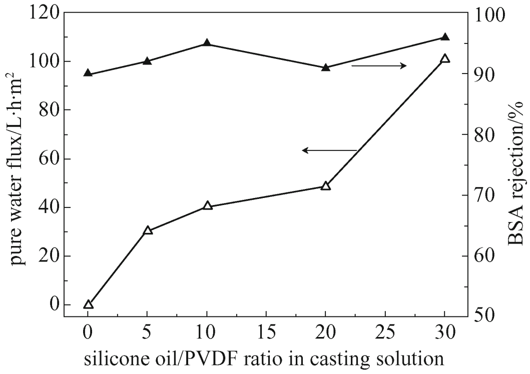

Fig. 7 Pure water flux and BSA rejection of the blend membranes prepared from the casting solutions with different ACPS/PVDF ratios

The rejection of pure PVDF membrane was measured after treatment with alcohol.

Stability of application properties over a long time period is crucial to all of the membranes but this aspect is easily neglected by most of the researchers. In this paper, various blend membranes were immersed and repeatedly washed in water at 60°C (a more rough condition for application) to investigate the performance stability of membranes. Original water contact angle and water flux data of membranes with ACPS/PVDF ratio of 30/70 after experiments are listed in Fig. 8. Unlike in the linear modification system [31–34], the hydrophilicity of ACPS/PVDF blend membranes increases and then stabilizes at a certain level. These data indicate the enrichment of PEO segments on membrane surface during the washing process. The water flux increases during the experiment,

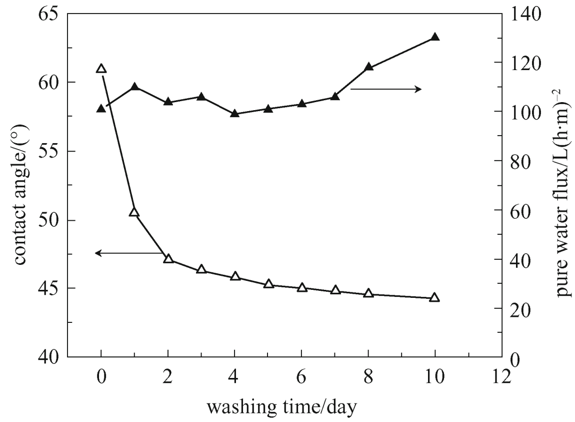

Fig. 8 Changes of pure water flux and initial contact angle with leaching time for the blend membrane prepared from the casting solution with ACPS/PVDF ratio of 30:70

responding to the surface enrichment of PEO segments and the hydrophilicity increase of membranes.

4 Conclusion

It is possible to introduce amphiphilic comb-like polysiloxane to prepare PVDF membranes with ultra-hydrophilic, anti-fouling and high flux properties *via* phase inversion process. The addition of ACPS would lead to the delayed demixing between casting solution and coagulating water during the phase inversion process. The instantaneous demixing resulted in the formation of membranes with "finger-like" macrovoids in the sublayer, whereas the delayed demixing yielded membrane structures containing a "sponge-like" pore sublayer. Solidified PVDF membranes with larger pore size were obtained with increasing PVDF content of the casting solution. The introduction of ACPS into the membrane system increased the PVDF crystallinity due to the delayed demixing. The O/F ratio of bulk membrane was almost the same as that of the corresponding casting solution indicating high reservation of ACPS in the membrane formation process. The fact that the O/F ratio in membrane surface layer was much higher than that in the bulk membrane proved the enrichment of ACPS on the surface. Such enrichment was fully proven by measurements of the water contact angle. As the ACPS molecules were tightly entangled with the PVDF chains, ACPS could be reserved in the membrane stably and thus, resulted in the reliable hydrophilic stability for PVDF membranes. This stability was also proved through continuous shake tests (in 60°C water) simulating the application process.

References

1. Ochoa N A, Masuelli M, Marchese J. Effect of hydrophilicity on fouling of an emulsified oil wastewater with PVDF/PMMA membranes. J Membr Sci, 2003, 226(1-2): 203–211
2. Liu F, Zhu B K, Xu Y Y. Improving the hydrophilicity of poly (vinylidene fluoride) porous membranes by electron beam initiated surface grafting of AA/SSS binary monomers. Appl Surf Sci, 2006, 253: 2096–2101
3. Ying L, Kang E T, Neoh K G. Covalent immobilization of glucose oxidase on microporous membranes prepared from poly(vinylidene fluoride) with grafted poly(acrylic acid) side chains J Membr Sci, 2002, 208: 361–374
4. Park Y W, Inagaki N. Surface modification of poly(vinylidene fluoride) film by remote Ar, H_2, and O_2 plasmas. Polymer, 2003, 44: 1569–1575
5. Clochard M C, Bègue J, Lafon A, Caldemaison D, Bittencourt C, Pireaux J J, Betz N. Tailoring bulk and surface grafting of poly(acrylic acid) in electron-irradiated PVDF. Polymer, 2004, 45: 8683–8694
6. Klee D, Ademovic Z, Bosserhoff A, Hoecker H, Maziolis G, Erli H J. Surface modification of poly(vinylidenefluoride) to improve the osteoblast adhesion. Biomaterials, 2003, 24: 3663–3670
7. Han S, Choi W K, Yoon K H, Koh S K. Surface reaction on polyvinylidenefluoride (PVDF) irradiated by low energy ion beam in reactive gas environment. J Appl Polym Sci, 1999, 72: 41–47
8. Enrica F, Johannes C J, Alessandra C, Efrem C, Enrico D. Effect of additives in the casting solution on the formation of PVDF membranes. Desalination, 2006, 192: 190–197
9. Wang Y Q, Wang T, Su Y L, Peng F B, Wu H, Jiang Z Y. Remarkable Reduction of Irreversible Fouling and Improvement of the Permeation Properties of Poly(ether sulfone) Ultrafiltration Membranes by Blending with Pluronic F127. Langmuir, 2005, 21: 11856–11862
10. Yeow M L, Liu Y, Li K. Preparation of porous PVDF hollow fiber membrane *via* a phase inversion method using lithium perchlorate (LiClO4) as an additive. J Membr Sci, 2005, 258: 16–22
11. LU Y, CHEN H L, LI B G. Influence of Additives on Phase Separation Process of PVDF Solution and Membrane Morphology. Acta Polymerica Sinica, 2002, 5: 656–661 (in Chinese)
12. Lu X F, Bian X K. Surface modification of ultrafiltration membrane and its application. Membr Sci & Technol, 2003, 23: 97–115 (in Chinese)
13. Chen H, Belfort G. Surface modification of poly(ether sulfone) ultrafiltration membranes by low-temperature plasma-induced graft polymerization. J Appl Polym Sci, 1999, 72: 1699–1711
14. Pieracci J, Crivello J V, Belfort G. Photochemical modification of 10 kDa polyethersulfone ultrafiltration membranes for reduction of biofouling. J Membr Sci, 1999, 156: 223–240
15. Nunes S P, Sforca M L, Peinemann K V. Dense hydrophilic composite membranes for ultrafiltration. J Membr Sci, 1995, 106: 49–56
16. LI B, CHEN W G, WANG X G, ZHOU Q X. PNIPAAm-Grafted Layers on Polypropylene Films II. Surface Properties and Temperature Sensitivity Study. Acta Polymerica Sinica, 2003, 1: 7–12 (in Chinese)
17. Kelly S T, Zydney A L. Mechanisms for BSA fouling during microfiltration. J Membr Sci, 1995, 107: 115–127
18. Kim J H, Lee K H. Effect of PEG additive on membrane formation by phase inversion. J Appl Polym Sci, 1998, 138: 153–163
19. Kim I C, Lee K H. Effect of poly(ethylene glycol) 200 on the formation of a polyetherimide asymmetric membrane and its performance in aqueous solvent mixture permeation. J Membr Sci, 2004, 230: 183–188
20. Chen N P, Hong L. Surface phase morphology and composition of the casting films of PVDF–PVP blend. Polymer, 2002, 43: 1429–1436
21. Qin J J, Wong F S, Li Y, Liu Y T. A high flux ultrafiltration membrane spun from PSU/PVP (K90)/DMF/1,2-propanediol. J Membr Sci, 2003, 211: 139–147
22. Park J Y, Acar M H, Ariya A, William K, Mayes A M. Polysulfone-graft-poly(ethylene glycol) graft copolymers for surface modification of polysulfone membranes. Biomaterials, 2006, 27: 856–865
23. Ma X L, Su Y L, Sun Q, Wang Y Q, Jiang Z Y. Preparation of protein-adsorption-resistant polyethersulfone ultrafiltration membranes through surface segregation of amphiphilic comb copolymer. J Membr Sci, 2007, 292: 116–124
24. Hester J F, Banerjee P, Won Y Y, Akthakul A, Acar M H, Mayes A M. ATRP of Amphiphilic Graft Copolymers Based on PVDF and Their Use as Membrane Additives. Macromolecules, 2002, 35: 7652–7661
25. Hester J F, Mayes A M. Design and performance of foul-resistant poly(vinylidene fluoride) membranes prepared in a

single-step by surface segregation. J Membr Sci, 2002, 202: 119–135

26. Irvine D J, Mayes A M. Nanoscale Clustering of RGD peptides at surfaces using comb polymers. 1. synthesis and characterization of comb thin films. Biomacromolecules, 2001, 2: 85–94
27. Hester J F, Banerjee P, Mayes A M. Preparation of protein-resistant surfaces on poly(vinylidene fluoride) membranes *via* surface segregation. Macromolecules, 1999, 32: 1643–1650
28. Legrow G E, Buese M A. Alkylmethylsiloxane dimethylsiloxane polyalkylene oxide copolymers. Eur Patent, EP. 1149872A2. 2001-10-31
29. Lovinger A J. Annealing of Poly (vinylidene fluoride) and formation of a fifth phase. Macromolecules, 1982, 15: 40–44
30. Zheng Q Z, Wang P, Yang Y N. Rheological and thermodynamic variation in polysulfone solution by PEG introduction and its effect on kinetics of membrane formation *via* phase-inversion process. J Membr Sci, 2006, 279: 230–237
31. Nardin C, Meier W. Hybrid materials from amphiphilic block copolymers and membrane proteins. Molecular Biotechnology, 2002, 90: 17–26
32. Callewaert M, Gohy J F, Dupont-Gillain C C, Laurence B P and Rouxhet P G. Surface morphology and wetting properties of surfaces coated with an amphiphilic diblock copolymer. Surf Sci, 2005, 575: 125–135
33. Yuan J Y, Wei G Y, Wang Y M, Pan G Y. Syntheses and Characterization of ABA Type Amphiphilic Block Copolymer. Acta Polymerica Sinica, 2001, 5: 625–628 (in Chinese)
34. Gao B J, Yang Y F, Jiu H F, Ge Z. Synthesis of Water-Solution Amphiphilic Acrylamide-Styrene Block Polymer Using Microemulsion Method. Acta Polymerica Sinica, 2001, 5: 608–612 (in Chinese)