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Preparation and Characterization of Hydrophilic PVDF Hollow Fiber Ultrafiltration Membrane

Liguo Wang[1,a], Xiuju Wang[2,b], Aimin Wang[3,c], Wenjuan Liu[1,d]
Shiqi Guo[1,e], Siquan Liu[2,f*]

[1]College of Resources and Environmental Sciences, University of Jinan, Jinan, China

[2]School of Chemistry and Chemical Engineering, University of Jinan, Jinan, China

[3]Shandong Zhaojin Motian Co., Ltd., Zhaoyuan, China

[a]lgwang666@163.com, [b]chm_wangxj@ujn.edu.cn, [c]wam@chinamotian.com
[d]liuwenjuan0901@163.com, [e]scyaalice@126.com, [f]chm_liusq@ujn.edu.cn

*Corresponding Author Tel. 13698613168 Fax. +86-531-82767367

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Abstract. Hydrophilic Polyvinylidene fluoride (PVDF) hollow fiber ultrafiltration membranes were prepared by wet-spinning method. The effects of technical parameters of acrylic acid grafted onto PVDF on the performance of hydrophilic PVDF membranes were investigated via orthogonal test, the technical parameters of preparation of hydrophilic PVDF membranes were determined, and hydrophilic PVDF membranes were prepared. Then hydrophilic PVDF membranes were characterized in terms of breaking strength, breaking elongation, rupture pressure, pure water flux and rejection. The fouling properties and the conditions of acrylic acid grafted onto PVDF were also examined. The results showed that acrylic acid had been grafted onto PVDF, the breaking strength and rupture pressure improved greatly, and the fouling properties were better than PS hollow fiber UF membrane.

Introduction

Polyvinylidene fluoride (PVDF) has been widely used as one of the membrane materials, well-known for its excellent chemical resistance and thermal stability. PVDF membranes are usually prepared by using thermal induced phase separation and solution phase inversion methods [1–4]. These advantageous properties, coupled with its intrinsic hydrophobicity, make it an outstanding membrane material particularly for industrial waste treatment applications involving oily emulsion [5], organic/water separations [6, 7], membrane distillation [8, 9] and ultrafiltration [10]. PVDF membranes have been reported to be highly organic selective [11], and they have the ability to withstand prolonged exposure to high temperatures of 366K [12]. PVDF membrane can be autoclaved for specific applications.

However, PVDF membranes are easily fouled and their permeation flux reduces rapidly because of the intrinsic hydrophobicity of PVDF. The pure water flux and antifouling property are important performances of the separation membranes. The separation performance is strongly retained when membrane surfaces are hydrophobic, but its pure water flux reduces rapidly. In order to expand the application areas of membranes, PVDF membrane need Hydrophilic treatment. The hydrophobic faces of membranes can become more hydrophilic through mixing the hydrophilic polymers or inorganic materials in PVDF dope solutions, grafting hydrophilic branches and depositing hydrophilic film on the base hydrophobic membranes, as reported by Ochoa et al. [13]. Domestic scientists have done a lot of researches about modification of PVDF membrane [14-18], which indicates that Graft Modification and blending of membrane materials are the main direction of future development of hydrophilic membrane.

In this study, acrylic acid was grafted onto PVDF in PVDF/N, N-dimethylacetamide (DMAc) solution systems for the development of hydrophilic hollow fiber membranes. The factors that affected the performance of PVDF membranes were studied, the technical parameters were made certain, and then hydrophilic PVDF hollow fiber ultrafiltration membrane was prepared, and its performance were also analysed.

Experimental

Reagents and Chemicals. Polyvinylidene fluoride (PVDF) used was purchased from Shanghai 3F new material Co., Ltd., China. N,N-dimethylacetamide (DMAc,≥99.6%) was used as solvent, purchased from Shanghai Jingwei Chemical Reagent Corporation, China. polyethylene glycol (PEG, AR, 400MW),Tween-8 (medical grade), acrylic acid monomers (AR), Ammonium persulphate (AR), glycerin (medical grade), Bovine serum albumin (BSA, medical grade), Ovalbumin (medical grade), polyvinylpyrrolidone (PVP, K30), were purchased from domestic companies. All the water used in this work was deionized water.

Instrumentation. FT-IR type Infrared spectrometer (AVATAR 360, 4000～400cm-1), purchased from Nicolet Company, America. 7520 type UV-Vis spectrophotometer, purchased from Changfang Optical Instrument Co., Ltd., Shanghai. Analytical Balance (TG328A/S, 0.1mg) and Electronic Balance (YP2001N, 0.1g) were purchased from Shanghai Jingmi Scientific Instrument Co., Ltd. Membrane performance evaluation equipments and other equipments were purchased from domestic companies.

Preparation of hydrophilic PVDF membrane. Firstly, Required amount of DMAc, predried PVDF Polymer, PEG and surfactant were placed in a reaction task, and .stirred at a certain temperature for several hours until all polymer chips was dissolved. Secondly, Dope temperature was maintained, required amount of ammonium persulphate was added, then acrylic acid monomers was added slowly, and they were stirred and reacted at the PVDF dissolved temperature for several hours. Thirdly, the fully dissolved and reacted polymer solution was allowed to stand and degassed for 12 hrs at reaction temperature. Finally, PVDF hollow fibre membranes were spun via a dry-wet phase inversion method.

Characterization of hydrophilic PVDF Membrane. Pure water flux and rejection were measured in accordance with HY/T062-2002 Hollow fiber ultrafiltration module. Contact angles of PVDF membranes were measured by contact angle meter (Dataphysics Model OCA40, Germany). The breaking strength and breaking elongation were measured by Electronic single fiber strength tester (YG061FQ, China), and the rupture pressure of hollow fiber membranes was measured with homemade testing equipment. Infrared spectra of PVDF hollow fiber membrane was obtained by FT-IR Spectrometer (BROKER Model TENSOR27, Germany). The fouling properties of PVDF hollow fiber membrane was tested with homemade testing equipment.

Results and discussion

Determination of the experimental factors. In the process of preparation of hollow fiber membrane, there are many factors affecting membrane structure, mainly including: 1) the choice of the casting solvent, the concentration and temperature of casting solution; 2) the height of air gap; 3) the membrane preparation environmental conditions, such as temperature, humidity, air convection state; 4) the speed of casting solution extruded from the spinneret; 5) the nonsolvent selection, composition and temperature of inside and outside coagulation bath; 6) the existence of solvent additives or macromolecular additives in casting solution. These factors and technical parameters of membrane preparation affect the membrane performance. For this test of PVDF hollow fiber ultrafiltration membrane preparation, process parameters and factors which influence membrane structure and performance are as followed: spinning solution technical parameters (including the content of PVDF, additive type and concentration, acrylic acid monomers quantity used for grafting

polymerization and amount of initiator, reaction temperature and time), process conditions (include casting speed, core fluid flow velocity and the height of air gap, casting solution temperature and coagulation bath temperature) and the environmental conditions (including environmental temperature and humidity).
Based on the results of single factor analysis of the factors affecting the structure and properties of PVDF hollow fiber membrane, together with our previous research achievements, four main factors of the test were selected and determined: PVDF concentration, acrylic acid content, reaction temperature and time. According to the analysis, the orthogonal table $L_9\,(3^4)$ was arranged for four three-level factors, and the factors were arranged. It shows in Table 1 below.

Table 1 The Levels and Factors

Factors	Content of PVDF (%)	Content of acrylic acid (%)	Reaction temperature (℃)	Reaction time (hr)
1	15	0.5	70	2
2	17	1.0	80	4
3	19	2.0	90	6

The analysis of the influence factors of membrane performance with orthogonal table. Based on the selected element bit-level table of the test, using orthogonal table L_9 (3^4) arranged and determine the experiment program, PVDF hollow fiber ultrafiltration membranes were prepared according to the experimental program, and the pure water flux, bovine serum albumin(BSA) rejection and the fracture pressure of PVDF hollow fiber membranes were tested.
In this experiment, three indicators were used to measure the effect of this experiment. The composite score of each experiment was obtained according to the comprehensive assessment of the indicators, and was calculated by orthogonal table. Three indicators were graded one by one, then added them and obtained the comprehensive test scores. Specific rating criteria were as follows:

The rupture pressure of hollow fiber membrane (P): $P \geq 0.60$MPa,100; $0.55 \leq P < 0.60$MPa,90; $0.50 < P < 0.55$MPa,80; $P \leq 0.50$MPa,60.

Pure water flux (J): $J \geq 200$L/m^2·hr·0.1MPa,100; $180 < J < 200$L/m^2·hr·0.1MPa,80; $J \leq 180$L/m^2·hr·0.1MPa,60.

Rejection of BSA (R): $R \geq 90\%$,100; $R < 90\%$,80.

According to the determinate specific rating criteria, the test results were analyzed by variance analysis, and the calculated results were shown in table 2.

Table 2 The variance analysis of orthogonal experimental results of the performance of PVDF UF membrane

	The content of PVDF (%) 1	The content of acrylic acid (%) 2	Reaction temperature (℃) 3	Reaction time (hr) 4	Pure water flux (L/m^2·hr)	Rejection of BSA (%)	Breaking pressure of hollow fiber (MPa)	composite score
1	1（15）	1（0.5）	3（90）	2（4）	166.4	83.7	0.40	200
2	2（17）	1	1（70）	1（2）	149.3	93.2	0.53	240
3	3（19）	1	2（80）	3（6）	134.6	95.4	0.56	250
4	1	2（1.0）	2	1	193.1	85.9	0.49	220
5	2	2	3	3	232.7	92.3	0.62	300
6	3	2	1	2	167.5	94.5	0.59	250
7	1	3（2.0）	1	3	215.8	85.3	0.54	260
8	2	3	2	2	239.4	93.6	0.65	300
9	3	3	3	1	178.3	96.1	0.61	260
Ⅰ	680	690	750	720				2280
Ⅱ	840	770	770	750				
Ⅲ	760	820	760	810				
R	180	130	20	90				

Table 2 showed the content of PVDF and the content of acrylic acid affecting the performance of hydrophilic PVDF hollow fiber membrane maximally, grafting time had a lower effect, and the grafting temperature has little effect on the performance of PVDF hollow fiber membrane. Finally, the technical parameters of membrane preparation were made certain, those were:

Casting solution composition: omitted

Casting solution temperature: 80℃

Coagulation bath composition: deionized water

Coagulation bath temperature: 40～45℃

Flow velocity of Casting solution: 7.5～8.0mL/min

Flow velocity of inside Coagulation bath: 12.0～12.8mL/min

The other technical parameters of preparation of hydrophilic PVDF membrane were the same as that of conventional hollow fiber membrane.

The performance of the prepared PVDF hollow fiber membrane. Hydrophilic PVDF hollow fiber ultrafiltration membranes were prepared according to the technical parameters of membrane preparation determined before. The performance of hydrophilic PVDF HFUF membranes prepared in this experiment was compared with commercial PVDF HF membrane and PVDF HF membrane prepared before in our laboratory. The results were shown in table 3.

Table 3 Performance comparison of PVDF hollow fiber membranes

	Commercial PVDF HF membrane	Membrane prepared before	Membrane prepared in this experiment
Pure water Flux （$L/m^2 \cdot hr \cdot 0.1MPa$）	58～110	120	≥230
Rejection of BSA（%）	95	≥90	≥90
Breaking strength（cN）	370	310	≥870
Breaking elongation（%）	210	63	183～217
Rupture pressure（MPa）	0.45	0.35	≥0.55

As shown in table 3, the pure water flux, breaking strength and rupture pressure of the membrane prepared in this experiment were all improved greatly, the rejection of BSA and breaking elongation were close to those of the commercial PVDF HF membrane. This shows that the membrane modification method is effective in hydrophilic membrane preparation.

FT-IR Spectrum(ATR). Hydrophilic PVDF hollow fiber membranes were detected with FT-IR, and the asymmetry stretching vibration and symmetry stretching vibration absorption peak appear at $1719cm^{-1}$ and $1401cm^{-1}$, which suggests that acrylic acid monomer has been grafted onto the molecular chain of PVDF, shown in fig. 1. This can be proved by the improvement of pure water flux.

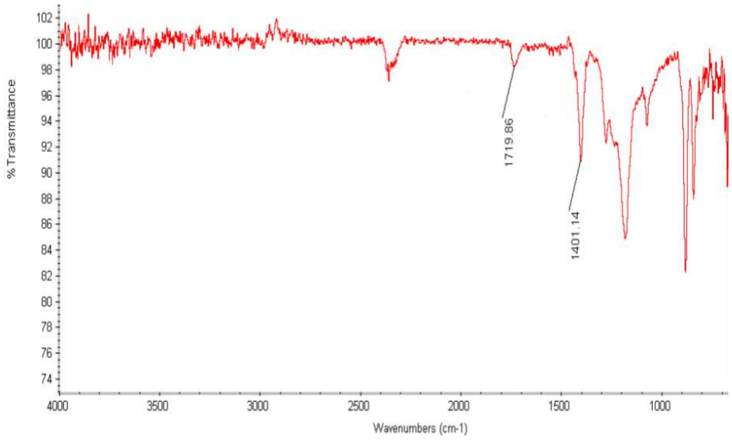

Fig. 1 FT-IR spectrum(ATR) of PVDF hollow fiber membrane

Antifouling ability of Hydrophilic PVDF HFUF membranes. The antifouling ability of PVDF HFUF membranes was investigated with filtration of ovalbumin solution. The running mode: the hollow fiber membrane module ran by cross-flow filtration for 10 minutes, and rinsed with deionized water for 3 minutes, determined its pure water flux. Then, continued to run by cross-flow filtration for 10 minutes, determined its pure water flux after rinse. Repeated the same process, and determined the change of pure water flux of PS UF membrane and PVDF UF membrane with the change of operating time.

Compared with polysulfone(PS) UF membrane, PVDF membrane has larger water flux, which decrease slowly with operating time. It had nice antifouling ability, and its original water flux can be renewed after being rinsed, shown in fig. 2. This also can be proved from the change of its contact angle. The angle of hydrophilic membrane in this experiment was 62.3°, and that of the commercial PVDF HF membrane was 84.3°.

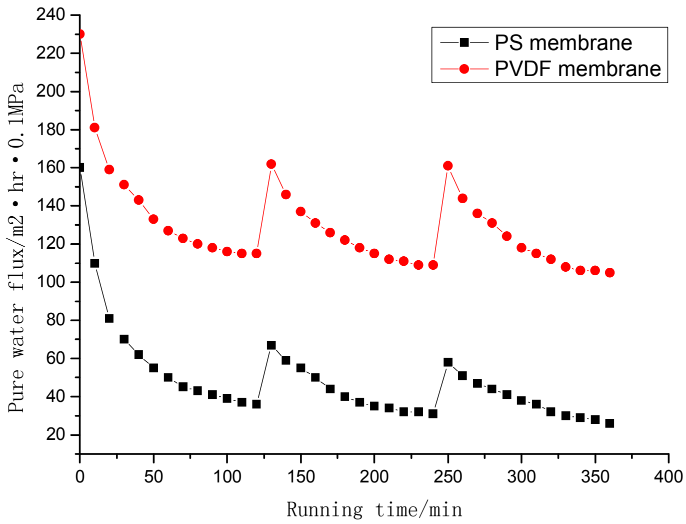

Fig. 2 Water flux of PS UF membrane and PVDF UF membrane vs operating time

Summary

1) Acrylic acid monomers were grafted onto PVDF to form PVDF membrane casting solution for the first time, the factors that affected the performance of PVDF membrane were investigated via orthogonal table, and then the technical parameters were made certain, hydrophilic PVDF hollow fiber ultrafiltration membranes were prepared successfully.

2) PVDF hollow fiber membranes have been detected with FT-IR, and the asymmetry stretching vibration and symmetry stretching vibration absorption peak appear at 1719cm^{-1} and 1401cm^{-1}, which suggests that acrylic acid monomers have been grafted onto the molecular chain of PVDF.

3) Compared with polysulfone(PS) UF membrane, PVDF membrane has larger water flux, which decrease slowly with operating time. It has nice antifouling ability, and its original water flux can be renewed after being rinsed.

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