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Preparation of PVDF hollow fiber ultrafiltration membrane via phase inversion/chemical treatment method

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ABSTRACT

Poly(vinylidene fluoride) (PVDF) hollow fiber membranes were prepared via a phase inversion/chemical treatment method, using N,N-dimethylacetamide (DMAc) as solvent, Calcium carbonate as inorganic additive, and water and HCl as coagulation media. Effects of external coagulation bath and bore fluid composition on membrane performance were investigated by using scanning electron microscopy, mechanical properties, porosity, average bubble point pressure, and permeation performance. The results show that: (1) The cross-section morphology of membranes have no significant change, exhibiting a two-layer finger-like structure extended to the middle of the cross-section. (2) The roughness of the external surface increased considerably and the number of the surface pores increased as well when we introduced HCl as the second coagulation. The permeation experiments reveal that acid treatment had no impact on fibers which had precipitated completely. (3) The number and pore size underlying the inner skin layer increased when bore fluid changed from DI water to 10% acetic acid, leading to the decrease of porosity and tensile strength. Moreover, the pure water flux increased from 360 to 580 L/(m^2 h) without the significant change of BSA rejection. The PVDF/$CaCO_3$ membranes prepared from the dope with 10% acetic acid as the bore fluid and 1 mol/L HCl as second coagulation bath had the best ultrafiltration performance.

Keywords: Poly(vinylidene fluoride); Hollow fiber membrane; Calcium carbonate; Chemical treatment; Ultrafiltration

1. Introduction

Ultrafiltration as a separation technology of high efficiency and low energy consumption has widely been applied in the various industrial sector, especially in the wastewater treatment field. The properties of membrane and its porous structure play an important role in the membrane-separation process. A suitable porous membrane should have good hydrophilicity, high permeability, and excellent chemical resistance to the feed streams. In order to obtain high permeability, membranes should have high surface porosity and good pore structures. Polyvinylidene fluoride (PVDF) is one material that can form such

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ideal membranes. The polymer is one of the most extensively applied membrane materials for outstanding antioxidation, superior thermal, and hydrolytic stabilities, as well as good mechanical and membrane forming properties [1,2]. Several studies have reported the developments and applications of PVDF membranes since the 1980s [3,4]. To date, remarkable progress has been made in the fabrications of PVDF membranes with high performance for the applications in wastewater treatment. Nevertheless, fabrication of high performance PVDF membranes remains challenging and it is hard to be achieved.

Currently, much effort is being devoted to improve the performance of PVDF membranes with various techniques, including chemical grafting, physical blending, and surface modification. Among these methods, the addition of inorganic particles to polymer solutions has become one of the attractive methods. Inorganic particles that have been incorporated into PVDF membranes include TiO_2 [5,6], Al_2O_3 [7], ZrO_2 [8], and SiO_2 [9,10]. Recently, researchers have studied the PVDF with $CaCO_3$ for use in orthopaedic surgeries and other applications. Amongst calcium compounds, this work has concentrated only on calcium carbonate, due to its easiness to be found at the market, its low cost, and mainly for its biocompatibility already proven in other areas. Campos et al. studied initial parameters of the structure of PVDF/$CaCO_3$ composite for bony implant applications [11]. Li and Lu observed that the presence of $CaCO_3$ particles hindered the aggregation and the growth of crystal nuclei during polymer crystallization, so that the formation of spherulites was disturbed at the quenching condition [12]. However, there were no previous reports about the effect of reaction between $CaCO_3$ and acidic aqueous coagulation bath and bore fluid on the performance of membranes, during fabricating PVDF/$CaCO_3$ hollow fiber ultrafiltration membranes through phase inversion method.

Dry/wet spinning technology was used to prepare PVDF/$CaCO_3$ hollow fiber membrane, which has been described elsewhere [13,14]. The fabrication of PVDF hollow fiber membranes with desirable properties could be achieved by controlling the dope composition, rheology, and coagulation composition and temperature, which determine the resultant membrane morphology and mechanical properties. Deshmukh and Li studied the effects of coagulation medium, ethanol (10 ± 50%) in water, and PVP as a pore-forming additive on the morphology of the PVDF hollow fiber membranes [15]. Cheng studied the effect of coagulation bath temperature on PVDF membrane morphology [16]. By changing the coagulation bath temperature from 25 to 65℃, the morphology of PVDF membranes changed from a symmetric structure composed of spherical crystallites to an asymmetric one with dense top surface accompanied by a cellular structure mixed with spherical particles. In addition, Wang et al. observed a similar effect of coagulation bath temperature on the crystallinity [17]. In this work, organic–inorganic PVDF/$CaCO_3$ composite hollow fiber membranes were prepared by phase inversion/chemical treatment method. The objective of this work was to systematically reveal the morphology, mechanical properties, and permeability of the PVDF/$CaCO_3$ composite hollow fiber membranes after acid treatment or not during fabrication process.

2. Experimental

2.1. Materials

PVDF (Solef®6020) was purchased from the Solvay Advanced Polymers, L.L.C. Calcium carbonate ($CaCO_3$, analytical grade) was purchased from the Shanghai FengXianFengCheng Reagent Company. Lithium Choride (LiCl, analytical grade) was purchased from the Tianjin Kermel Chemical Reagent Co. Ltd., Polyvinyl Pyrrolidone (PVP) was purchased from the BASF chemical company, Germany. N,N-dimethylactamide (DMAc; >99%) was obtained from the Tianjin FuCheng Reagent Company. Hydrochloric acid (HCl, 36–38%) was of analytical grade (from the Beijing Chemical Works) and used as received. Bovine serum albumin (BSA) ($M_w = 67{,}000$) was purchased from the Shanghai Lanji Co. Ltd.

2.2. Hollow fiber membrane and membrane module preparation

The additives (3 wt% $CaCO_3$, by weight of the solution; and 8 wt% PVP, by weight of the solution) were added to the dope of DMAc containing 16%wt PVDF with constant stirring at 60℃ for 24 h to get a homogenous dope for spinning. The scheme of the spinning apparatus for PVDF/$CaCO_3$ hollow fiber membranes is shown in Fig. 1.

In this study, coagulation with high temperature (60℃) was chosen, in order to obtain the asymmetric hollow fiber membranes consisting finger-like voids structures. In this process, water, hydrochloric acid (HCl), and ethylic acid were used as the internal coagulation. Tap water was used as the first external coagulation and HCl as the second external coagulation. The spinning conditions have been summarized in Table 1 for a quick reference. The fabricated hollow fiber membranes were kept in the water bath for 24 h to remove the residual solvents, and then immersed in a tank containing 25 wt% glycerol aqueous solution for

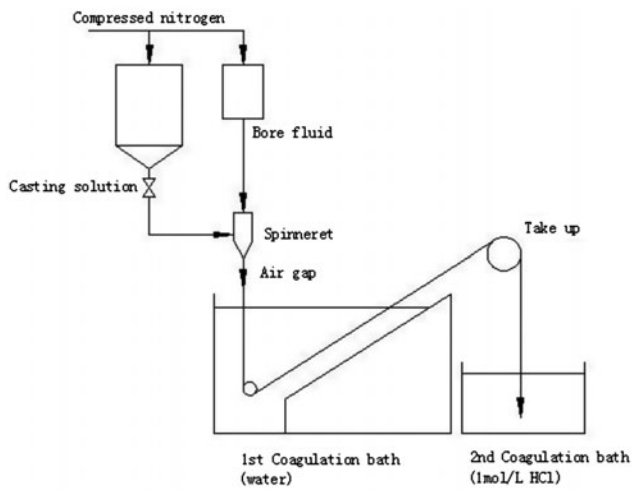


Fig. 1. Schematic diagram of the spinning apparatus for PVDF/$CaCO_3$ hollow fiber membrane.

24 h to prevent the collapse of porous structures, which were to be used for making test modules [18].

Membrane modules were prepared to test hollow fiber separation performance in terms of pure water permeation flux and solute rejection quantitatively. Eight fibers with a length of about 20 mm were assembled into a glass tube. Then, the two ends of the bundles were sealed with an epoxy resin. To eliminate the effect of the residual glycerol on module performance, each module was immersed in water for 24 h and run in the test system for 30 min under the pressure of 0.15 MPa before any sample collection.

2.3. Membrane morphology observation

The morphologies of the cross-section and the inner and external surface of hollow fiber membranes were observed with a scanning electron microscope (SEM; JSM5800, JEOL, Japan). The fibers were immersed into liquid nitrogen for a few minutes and then coated with gold under vacuum before test.

2.4. Mechanical properties, porosity, and bubble point pressure measurement

Mechanical properties of hollow fiber membranes were measured by a test machine at a loading velocity of 500 mm/min. The report values were measured three times for each sample and then averaged.

The membrane porosity ε (vol.%) was defined as the volume of the pores was divided by the total volume of the porous membranes. It could be determined by gravimetric method, determining the weight of liquid (here pure water) contained in the membrane pores [19]. The inner and outer diameters of the sample (10 pieces of hollow fibers) were measured under a microscope to obtain the bulk volume (V_b). The porosity (ε) of the sample was calculated according to Eq. (1):

$$\varepsilon = \frac{(w_1 - w_2)/d_w}{V_b} \times 100\% \tag{1}$$

where w_1 was the weight of the wet membranes (g), w_2 was the weight of the dry membranes (g), d_w was the pure water density (0.998 g/cm^3), and V_b was the bulk volume.

The pore density distribution of fabricated fibers was determined by bubble point pressure test. The average bubble point pressure was measured by the bubble point instrument (Surway FILGUARD-311, Shanghai), using N_2 as the test gas with operating pressure in 0.4 MPa and alcohol as wetting liquid.

2.5. Membrane performance measurement

The permeation flux and rejection of the hollow fiber membranes were measured by a self-prepared

Table 1
Spinning conditions of the fabricated PVDF/$CaCO_3$ hollow fiber membranes

	Fiber-A				Fiber-B			
	A-1	A-2	A-3	A-4	B-1	B-2	B-3	B-4
Bore fluid	DI water				DI water	1% HAc	0.1 mol/L HCl	10% HAc
First external coagulation	Water				Water			
Second external coagulation	Water	1 mol/L HCl (20 min)	1 mol/L HCl (2 h)	Water	1 mol/L HCl (2 h)			
Post-treatment	None	None	None	1 mol/L HCl (24 h)	None			
The length of air gap	3 cm							

UF experimental equipment. Deionized water was used to measure the pure water flux, and 1 g/L BSA aqueous solution was performed for the solution rejection of each membrane module. Three modules were parallel tested, and the average of their performance was reported.

The newly membranes were pre-pressured at 0.15 MPa for 30 min. The pure water and the rejection of BSA were measured at 0.1 MPa and room temperature, respectively. At a constant pressure of 0.1 MPa, deionized water was fed from inner lumen to the outer surface of hollow fiber membranes and then was collected and measured. Pure water flux (J_w) was obtained by Eq. (2):

$$J_w = \frac{Q}{A\Delta T} \tag{2}$$

where Q is the total volume of the permeation water during experiment, A is the effective membrane area of the module, and ΔT denotes the measuring time.

The rejection of membrane was determined with an aqueous solution containing 1 g/L BSA, which was fed at constant flow from the lumen to the outer surface of the membranes. The membrane solution rejection R (%) was calculated by Eq. (3):

$$R(\%) = \left(1 - \frac{2C_p}{C_f + C_r}\right) \times 100 \tag{3}$$

where C_p, C_f, and C_r are the concentration in permeate, feed, and remaining solution in mg/L, respectively. The concentrations of BSA in permeate and feed were determined by a UV-sepctrophotometer (UNIC UV-2100, USA) at a wave length of 280 nm.

3. Results and discussion

3.1. Effect of external coagulation bath on membrane morphology and permeability

The SEM images of a typical cross-section structure are shown in Fig. 2. All the fibers fabricated in the present work have this similar structure, exhibiting a two-layer finger-like structure extended to the middle of the cross-section. There was no appreciable cross-section morphological variation under different conditions. At 60˚C, the crystallization of PVDF was suppressed, favouring liquid–liquid demixing as the dominating phase inversion mechanism. The dense inner and outer skins with the underlying finger-like morphology are typical for the rapid phase separation and the liquid–liquid demixing mechanism. This was also suggested by Yeow et al. [20]. Moreover, some finger-like pores near the inner surface grow more completely. The reason could be that the external layer of nascent fiber entered into the external coagulation bath after passing through a short air gap distance, led to the delayed onset of demixing. While the inner surface would contact bore fluid first, an instantaneous liquid–liquid demixing occurred immediately.

The external surface morphologies of the Fiber-A series (A-1, A-2) with and without acid treatment are shown in Fig. 3. It can be observed from A-1 that when coagulation (such as water) was used for fabrication of the membranes, dense surface with no obvious pores formed. However, when HCl was introduced to the coagulation, the roughness of the membrane surface increased considerably. This phenomenon could be interpreted as follows: for the PVDF/$CaCO_3$-DMAc-water system, the solution may go through rapid phase separation and thus produce a rough dense surface. However, in the case of PVDF/$CaCO_3$–DMAc–water/HCl system, as HCl diffused from the external coagulation into the nascent fiber, the release of carbon dioxide caused by the reaction of HCl and calcium carbonate resulted in the convex surface.

Water permeability and BSA rejection are also significant characteristics of a filtration membrane. BSA was used as a model protein to investigate the separation performance. Fig. 4 shows the water permeability and BSA rejection of Fiber-A series membranes. The water permeability was remarkably improved from

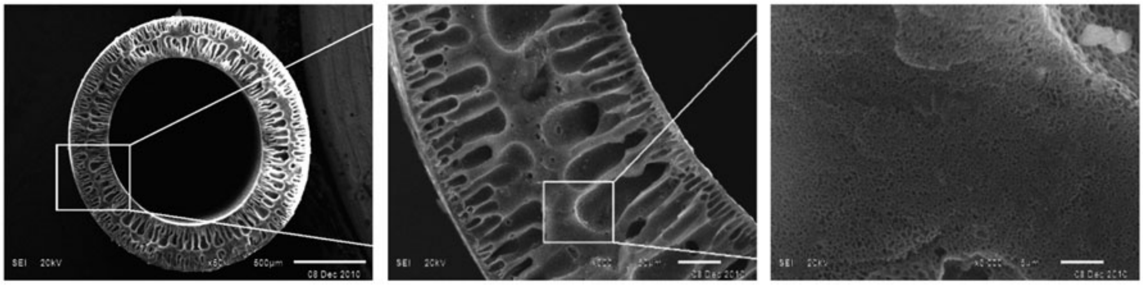
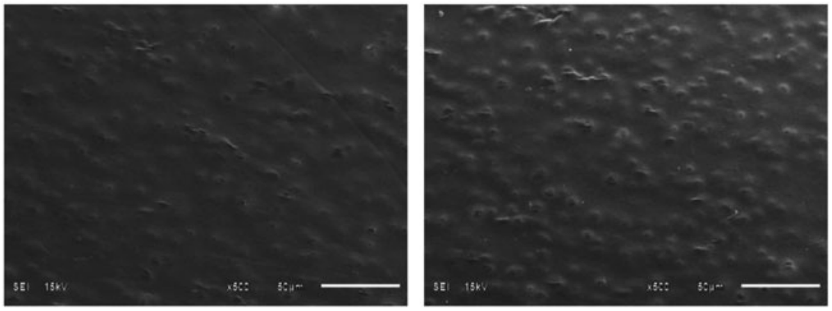


Fig. 2. SEM image of showing a typical morphology of PVDF/$CaCO_3$ hollow fiber membranes.



A-1 (×500) A-2 (×500)

Fig. 3. SEM images of A-1 and A-2 external surface.

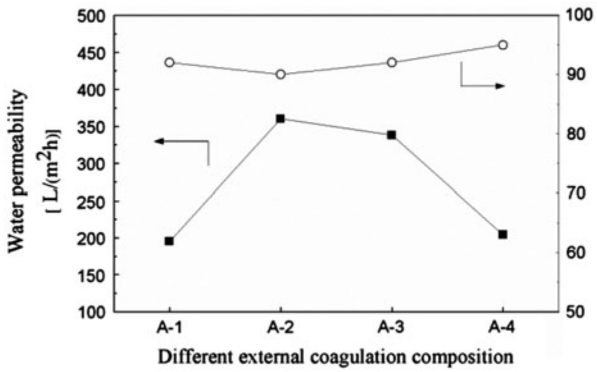


Fig. 4. Effect of different external coagulation composition on water permeability and BSA rejection of PVDF/$CaCO_3$ hollow fiber membranes.

195 L/m^2 h (A-1) to 360 L/m^2 h (A-2) when HCl was introduced as the second external coagulation. However, the BSA rejection was not affected evidently by the change of external coagulation. The reasons will be discussed below. It also could be seen that the pure water flux of A-3 was 338 L/m^2 h. That is to say, for fibers which had precipitated completely, acid treatment had no impact because HCl cannot diffuse from the external coagulation into the fibers. And the reaction between HCl and $CaCO_3$ had been finished within 20 min. Therefore, compared with A-1, the pure water flux of A-4 (204 L/m^2 h) had no significant change.

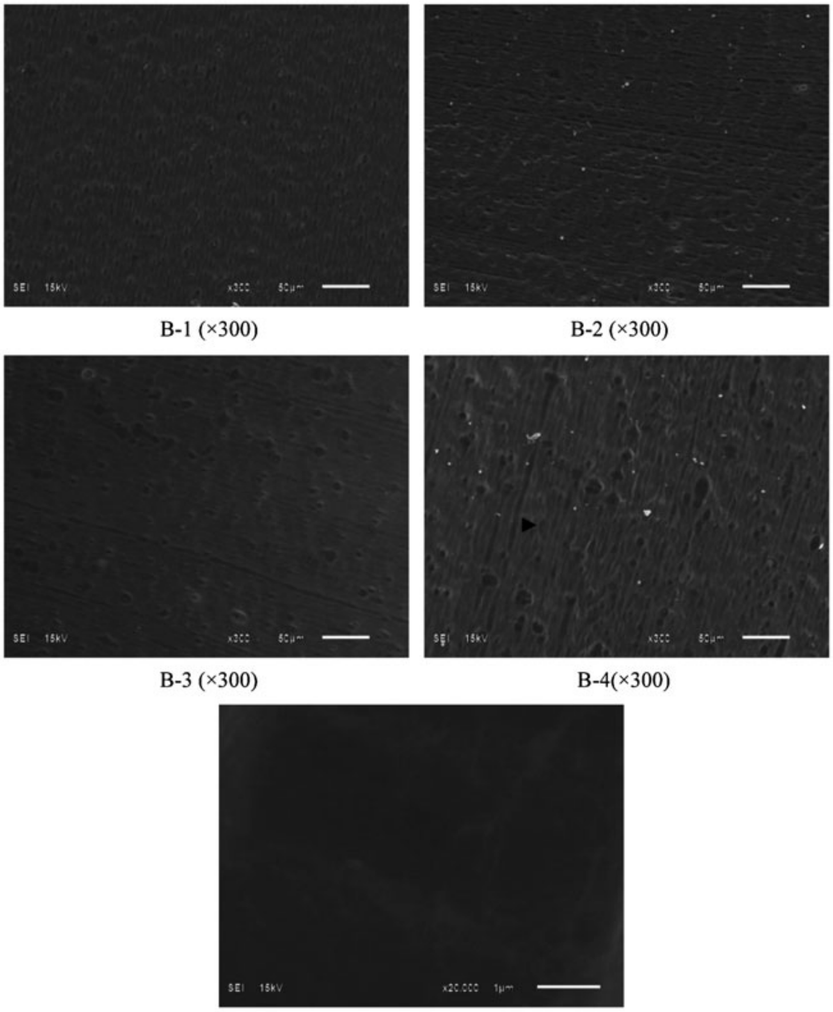
The fibers prepared through acid treatment showed higher water permeability in the present work. Therefore, in order to obtain a high permeability of the PVDF hollow fibers, water and HCl were adopted as the first and second coagulation, respectively, in the next work.

3.2. Effect of bore fluid composition on membrane morphology and permeability

Among the spinning parameters, the bore fluid composition can be easily changed during the spinning process. Therefore, the effects of the bore fluid composition were investigated, with different acidity solutions being used as bore fluid to control the solvent/non-solvent exchange rate and the reaction rate between $CaCO_3$ and acid, which reveal the effects of bore fluid composition on the membranes performance.

Fig. 5 shows the inner surface structure of hollow fibers from the casting solution with different bore fluid composition (Fiber B-1 to –Fiber B-4). As may be observed from the partial magnified pictures of B-4-PM (20,000×), a dense and smooth surface with no obvious pore was formed. The macrovoids under the inner surface can be seen clearly. That is to say, the dense skin layer is very thin. The other fibers have the similar structure as well. It also can be seen that the pore size and the number of macrovoids under the inner surface increased considerably when bore fluid changed from DI water to 10% acetic acid (B-1 to B-4). The reasons for this are not yet fully understood, but this is probably as follows: the space of $CaCO_3$ became pores in the membrane and the release of CO_2 promoted the formation of macrovoids. With the increase of the acid concentration, the reaction rate between $CaCO_3$ and bore fluid increased. The PH of 10% acetic acid was higher than that of 0.1 mol/L HCl, but acetic acid had a better compatibility with DMAc because acetic acid was organic acid. Thus, the HAc–DMAc exchange rate was faster, leading to the formation of more macrovoids.

The separation performance of hollow fiber is largely determined by the membrane structure. The skin layer, which contains an effective separating layer, is one of the key factors determining the membrane selectivity. The wall structure affects more on the permeability than on the selectivity [21]. As shown in Fig. 6, the permeability increased greatly when bore fluid changed from DI water to 10% acetic acid.



B-1 (×300) B-2 (×300)

B-3 (×300) B-4(×300)

B-4-PM (×20000)

Fig. 5. The inner surface morphology of Fiber-B series membranes with different bore fluid composition (PM: partial magnified).

However, the BSA rejection was not affected evidently by the change of bore fluid. The results agree with the results of the morphology change of membranes in Fig. 5. Moreover, higher pure water flux suggests a higher porosity. This will be indicated by the porosity (as shown in Fig. 7) of the wall structure of the hollow fibers in the next section.

3.3. Mechanical properties of hollow fiber membrane

The results of mechanical properties test including tensile strength and breaking elongation were listed in Table 2. It was clear that the tensile strength of membranes declined when bore fluid changed from DI water to 10% acetic acid (B-1 to B-4). Because of a bore fluid with a lower PH, the reaction rate between $CaCO_3$ and bore fluid increased, which led to the increase in the microdefects. Moreover, a higher polar of bore fluid increased the exchange rate of solvent and bore fluid, thus resulted in a thin dense structure and hence a lower strength. This agrees with the observation shown in Fig. 5.

Table 2 also showed that the breaking elongation was high and had no significant change for Fiber-B membranes. The elongation is mainly the deformation of the amorphous regions. The bore fluids and coagulation bath are all strong non-solvent, the demixing rate was fast, and the molecular chains were frozen in a less ordered form. Under tensile stress, the molecules can be stretched more to rearrange into a more ordered form. Therefore, the breaking elongation would be high.

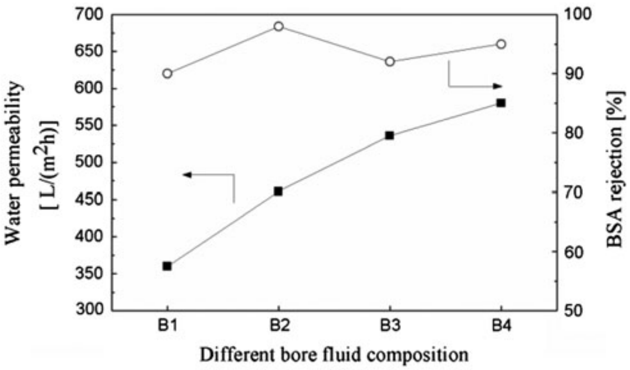


Fig. 6. Effect of different bore fluid composition on water permeability and BSA rejection of PVDF/$CaCO_3$ hollow fiber membranes.

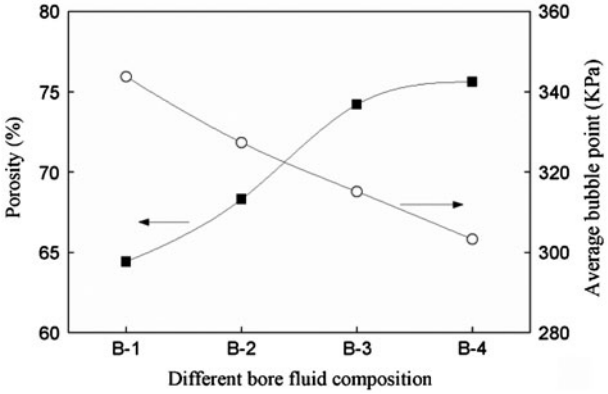


Fig. 7. Measurement of porosity and average bubble point pressure of hollow fiber membranes.

Table 2
The mechanical properties of PVDF hollow fibers spun with various bore fluid composition

Fiber	Tensile strength (MPa)	Breaking elongation (%)
B-1	3.51	131.95
B-2	3.47	131.75
B-3	3.24	124.79
B-4	3.01	126.89

3.4. *Porosity and average bubble point pressure of hollow fiber membranes*

The porosity and average bubble point pressure of the Fiber-B series are shown in Fig. 7. All the prepared membranes showed a good porosity in the range of 64.4–75.6%. The average bubble point decreased and the porosity of membranes increased when bore fluid changed from DI water to 10% acetic acid (B-1 to B-4), indicating that higher the value of porosity is, the worse the average bubble point pressure of membranes will be. In other words, the porosity and average bubble point pressure are affected by the reaction rate between $CaCO_3$ and bore fluid. The results in Fig. 7 agree with the results of mechanical properties.

4. Conclusions

The PVDF/$CaCO_3$ hollow fiber membranes were successfully prepared by phase inversion/chemical treatment and characterized as filtration membranes. The obtained hollow fiber membranes exhibited a very high pure water permeability and good separation performance as an ultrafiltration membrane. Various membranes were prepared by varying the external coagulation and bore fluid. Especially, the membrane prepared with 10% acetic acid as the bore fluid and 1 mol/L HCl as second external coagulation showed permeability of 580 L/(m^2 h) and 92% in BSA rejection. Based on these investigations, we concluded that these PVDF hollow fiber membranes have a good prospect.

Acknowledgments

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