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Fabrication and properties of recycled poly (vinylidene fluoride) (PVDF) hollow fiber membranes

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ABSTRACT

The structure and performance of waste PVDF hollow fiber membranes were investigated by shear viscosity and melt flow index (MFI) and the effect of running time on the properties of waste PVDF hollow fiber membranes was discussed. In addition, the recycled PVDF hollow fiber membranes were fabricated via dry-wet spinning method. The obtained results showed that the PVDF molecular weight decreased with the increase of the running time. The decrease of PVDF molecular weight also led recycled PVDF hollow fiber membranes to have higher porosity and better permeability. However, the mechanical properties and BSA rejection were lower. Moreover, the wettability of recycled PVDF hollow fiber membranes was similar to original PVDF hollow fiber membrane which was prepared from PVDF powder.

Keywords: Waste PVDF hollow fiber membrane; Molecular weight; Recycled PVDF hollow fiber membrane; Structure and performance

1. Introduction

With the increase in water demand, membrane separation technology has attracted more and more researchers' attention. Membrane separation technology is an emerging technology which applies membrane in the processes of water treatment, separation and concentration of the mixtures [1]. In the previous literature, the frequently-used materials for MBR has been reported, including polysulfone (PSF) [2], polyvinylidene fluoride (PVDF) [3], polyethersulfone (PES) [4], polyethylene (PE) [5], polytetrafluoroethylene (PTFE) [6] and so on. Among these membrane materials, PVDF is a semi-crystalline polymer which has attracted much attention because of its excellent physical and chemical properties [7]. Nowadays, a majority of commercial microfiltration and ultrafiltration membranes are PVDF membranes [8]. Moreover, PVDF hollow fiber membrane has been widely applied in water treatment, especially for MBR applications [9].

In general, membrane fouling is the most major factor that limits the cost effectiveness of their use for water and wastewater treatment in membrane technology [10]. For example, the membrane fouling limits the stable water flux, reduces the sustainability of operation and the lifetime of the membrane, etc. [11]. The pollutants can be classified into reversible fouling and irreversible fouling. And the latter causing perpetual degradation in the membrane performance [12]. After used for a period of time, the membranes have to be cleaned to ensure the membranes' separation performance [13]. Therefore, membrane cleaning aims to reduce the influence of pollutants on the structure and properties of recycled PVDF hollow fiber membrane. The pollutants that are deposited on the membrane surface can be removed effectively only via physical methods, such as hydraulic cleaning, mechanical cleaning and ultrasonic cleaning [14–16]. While physical cleaning cannot remove the pollutants that are adsorbed into the membrane layer [17]. Strugholtz et al. [18] investigated that NaOCl and NaOH is often used reagents for chemical cleaning which can be able to remove most of the irreversible fouling on

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the membranes. Nevertheless, continuous contact with this cleaning agent induced ageing process [19]. For example, the chemical groups and physical structures of membrane changed. Moreover, the hydraulic performances and mechanical properties reduced [20,21].

When the pollutants cannot be cleaned only via physical methods and the ageing process was induced via chemical method, the separation performance of PVDF hollow fiber membranes won't be ensured for a long running time. Therefore, a large number of waste PVDF membranes are produced and result in resources waste, environmental pollution and high operating cost. Currently, the recycling of polymer is focused on the bottles, toys, plastic tarps, pipes, tire and so on [22]. So far, few studies have appropriately investigated the regeneration of PVDF hollow fiber membranes. Therefore, the regeneration of waste PVDF hollow fiber membrane has attracted many researchers' attention. In this work, the waste PVDF hollow fiber membranes are produced during drinking water treatment. The pollutants are mainly composed of biofouling and inorganic fouling [23]. And the main pollutants can be removed via physical cleaning [24].

Compared to previous reports, this research illustrates that the decay of PVDF hollow fiber membranes' separation performance is mainly due to mechanical and chemical degradation. Moreover, this paper introduces a new method of fabrication of recycled PVDF hollow fiber membranes from the waste membranes. This method is helpful to reuse of resources and reduction of environmental pollution and production costs.

2. Experimental

2.1. Materials

Three types of waste PVDF hollow fiber membrane which had been used in MBR for 1-3-5 years (named F1-F2-F3) were friendly provided by TEDA New Water Technology Development Co., Ltd. (Tianjin, China). PVDF powder (solef 6010, M_W = 30,000 g·mol^{-1}) was purchased from Solvay Specialty Polymers (Changshu, China). N,N-dimethylacetamide (DMAc, Analytical Reagent), poly(ethylene glycol) (PEG, Analytical Reagent, M_W = 2000 g·mol^{-1}) and polyvinylpyrrolidone (PVP, Analytical Reagent, M_W = 10,000) was bought from Kermel Chemical Reagent Co., Ltd. (Tianjin, China). Glycerol Guangfu Technology Development Co., Ltd. (Tianjin, China). Bovine serum albumin (BSA, Analytical Reagent, M_W = 68,000 g·mol^{-1}) was supplied from Beijing Aoboxing Universeen Bio-tech Co., Ltd. (Beijing, China).

2.2. Preparation of recycled PVDF

The procedure for preparation of recycled material was as follows. First, the waste PVDF hollow fiber membrane were cut into about 3 cm and stirred with distilled water for 5 h to remove pollutants, such as deposition of particles, colloids and inorganic crystals. Next, the membranes were dried for 24 h and mixed with DMAc in a special weight ratio. After standing for 48 h, the supernatant of the mixture was filtered at pressure of 0.3–0.6 MPa and the pollutants were intercepted by the filtering device. Finally, the filtrate was placed in distilled water to obtain recycled PVDF. Fig. 1 shows schematic diagram of the filtrating system.

2.3. Preparation of recycled PVDF hollow fiber membranes

The polymer solutions were prepared by the blending of different compositions consisting of recycled PVDF, PVP, PEG and DMAc (as Table 1) under constant mechanical stirring for 4 h at 70°C. The recycled PVDF hollow fiber membranes were prepared using the dry-wet spinning method. And the spinning parameters of dry-wet spinning hollow fiber membranes were shown in Table 2. The obtained membranes were put in glycerol water solutions (three parts glycerol to two parts water) and then dried them in air, so as to retain the porous structure. Before the measurements, we put the resulting membranes in a pure water for 12 h to remove the glycerol. Then, the final membranes were freeze-dried using a freeze dryer (FD-1D-80, Shanghai Hanuo Instruments Co., China). Original PVDF hollow fiber membrane (M1) prepared from PVDF powder is the control group. And the recycled PVDF hollow fiber membranes.

2.4. Characterization

2.4.1. Shear viscosity

Rheological measurement was carried out with a rotational rheometer (Haake MARIII, Thermo Electron GmbH, Fisher, USA). The viscosity of the polymer solution (as Table 1) was investigated as a function of different shear ratesat 70°C. The range of shear rate is 0–1000 s^{-1}.

2.4.2. Melt flow index

The melt flow index (MFI) of recycled PVDF was measured using a HCRZ-400B melt flow indexer (Beijing North

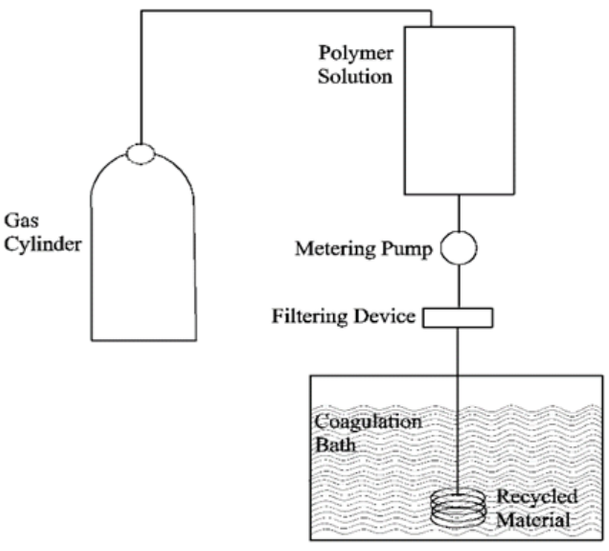

Fig. 1. Schematic diagram of the filtrating system.

Table 1
The composition of the recycled PVDF hollow fiber membranes

Sample	PVDF powder/wt%	F1/wt%	F2/wt%	F3/wt%	PEG/wt%	PVP/wt%	DMAc/wt%
M1	20	–	–	–	10	3	67
M2	–	20	–	–	10	3	67
M3	–	–	20	–	10	3	67
M4	–	–	–	20	10	3	67

Table 2
Spinning parameters of dry-wet spinning hollow fiber membranes

Spinning condition	Value
Outer diameter/mm	1.3
Innerdiameter/mm	0.8
Polymer solution temperature/°C	70
Bore fluid	Pure water
Bore fluid temperature/°C	20
Extra coagulation	Tap water
Extra coagulation temperature/°C	20
Air gap/cm	5
Take up speed/m·min^{-1}	12

Measurement Science and Technology Co., Ltd.). The temperature of the melt was kept at a temperature of 200°C and a 2.16 kg load was applied to extrude the molten sample. A 100 g rod was used as a plunger. The MFI was averaged from five determinations.

2.4.3. Scanning electron microscopy

The surface and cross-section morphologies of PVDF hollow fiber membranes were observed by scanning electron microscopy (SEM, TM3030, Japan). The membranes were immersed in liquid nitrogen for 10–15 s and were frozen. Then the frozen membranes were broken for cross-section observation. Samples were all gold sputtered before testing.

2.4.4. Contact angle measurements

The hydrophobicity of membranes was determined by measuring the static contact angle of the membrane surface with a contact angle goniometer (KrussDSA-100, Germany). In this paper, every sample was tested 5 times.

2.4.5. Porosity and mean pore size

The membrane porosity was defined as the pores volume divided by the total volume of the porous membrane. It can be determined by a gravimetric method. The membrane sample was immersed in the deionized water for at least 24 h. Then the internal core water of the membrane sample was blowout by the rubber pipette bulb. The water attached on the outer membrane surface was wiped by a filter paper. After that, the weight of wet membrane was measured. The weight of dry membrane was measured after drying in electric blast drying oven for 10 h at 30°C. The porosity was calculated according to [25]

$$\varepsilon(\%) = \frac{W_1 - W_2}{\left(\pi/4\right)\left(D^2 - d^2\right)l\rho} \quad (1)$$

where W_1 is the weight of wet membrane (g), W_2 is the weight of dry membrane (g), ρ is the water density (ρ = 1.0 g·cm^{-3}), D is the outer diameter (cm), d is the inner diameter (cm) and l is the length of membrane (cm).

The pore size of each sample were determined by using the capillary flow porometer (Porous Materials Inc., USA), and values were calculated from the pressure of the gas flow.

2.4.6. Tensile strength measurements

The tensile strength of the membranes was obtained at room temperature using an LQ-300LLY-06 electronic yarn tensile tester (Shandong, China). Hollow fiber membranes were fixed vertically between two pairs of tweezers with a length of 20 mm and extended at the tensile rate of 20 mm·min^{-1} until fibers were broken. Each sample was tested five times to evaluate the average value.

2.4.7. X-ray diffraction

The polymeric chain packing efficiency and the crystalline/amorphous nature of the membranes were characterized using Wide Angle X-ray Diffraction Pattern (Panalytical X'PERT PRO MPD X-ray diffractometer).

2.4.8. Ultrafiltration experiments

Pure water flux (PWF) was measured with hollow fiber membranes at 0.1 MPa pressure under the condition outside pressure and was calculated by following equation [26]:

$$J = \frac{V}{S \times t} \quad (2)$$

where J is the PWF (L·m^{-2}·h^{-1}), V is the permeate volume (L), S is the membrane area (m^2), t is the running time (h).

The filtration experiments were then carried out by 1 g·L^{-1} BSA solution. Before the experiments, the deionized water was used to feed in filtration experimental setup for 30 min to stabilize the permeation performance of recycled

PVDF hollow fiber membranes at operating pressure of 0.1 MPa and temperature of 20°C. Then the BSA solution was fed into the cross-flow membranes container. The concentrate flux for the BSA solution was recorded as J_1 based on the water quantity permeating the membranes at the same pressure of 0.1 MPa and was calculated by Eq. (2). The rejection (R) of the protein was defined by following equation [26]:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (3)$$

where C_f and C_p are the concentrations of protein in the feed and the permeate solution, respectively. The concentrations of feed solution and permeate solution were determined by UV spectroscopy at wavelength of 280 nm, using a PERSEE TU-1901 spectrophotometer (Beijing Purkinje General Instrument CO., Ltd.).

3. Results and discussion

3.1. Shear viscosity

As one of the most important factors to compare molecular weight of different polymer materials [27], the shear viscosity of homogeneous polymer solution changes with the polymer molecular weight under the same condition. Fig. 2 shows that the shear viscosity of polymer solution decreased with running time of waste PVDF hollow fiber membranes under the same shear rate. Moreover, the shear viscosity of polymer solution decreased with the increase of shear rate under given shearing condition. If PVDF hollow fiber membrane had been run long time, continuous water rushing and membrane fouling resulted in mechanical and chemical degradation. The degradation of polymer which caused the break of polymer molecular chains led to decreasing shear viscosity of polymer solution. Therefore, viscosity loss can be used to characterize the decrease of PVDF molecular weight.

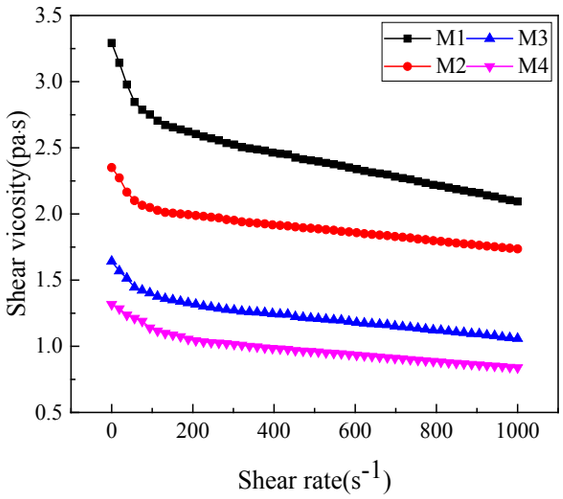

Fig. 2. Viscosity changes with shear rate of polymer solution at 70°C.

3.2. Melt flow index

Melt flow index (MFI) is one of the most common and specified parameters for describing a polymer [28]. It is a simple method for expressing important flow characteristics of polymer, which mainly depended on polymer molecular weight under the same testing condition. The higher molecular weight the polymer has, the longer molecular chain are. When the polymer has longer molecular chain, it has higher MFI.

Fig. 3 shows the MFI of solef6010 and recycled materials. The molecular weight of solef6010 is 30,000 g·mol^{-1}. From Fig. 3 it can be seen that the MFI of waste PVDF hollow fiber membrane was lower than solef6010 and decreased with the running time. Therefore, the performance decay of PVDF hollow fiber membrane is likely due to mechanical or/and chemical degradation and chain scission.

3.3. Morphology of recycled PVDF hollow fiber membranes

Fig. 4 shows the cross-sectional and surface SEM image of the recycled PVDF hollow fiber membranes prepared by waste PVDF hollow fiber membranes. The phase inversion process can result in three parts in membrane morphology: the outer part and inner part with finger-like macrovoids and the middle part with a dense sponge-like structure [29]. In Fig. 4 (A1-D1), it was observed that the outer and inner part thicknesses increased and the middle part thicknesses decreased. According to the results of shear viscosity and MFI, it was known that the decrease of PVDF molecular weight increased the rate of phase inversion. That resulted in more finger-like structure and less sponge-like structure in the recycled PVDF hollow fiber membranes [30]. Although all the spinning parameters had no difference, the decrease of molecular weight gave the possibility of lower thicknesses of membranes [31].

From Fig. 4 (A2-D2) it was found that the surface of recycled PVDF hollow fiber membranes had more pores than original membranes. Although this phenomenon cannot be seen in SEM images clearly, it was in agreement with the result of porosity and mean pore size (as Table 3).

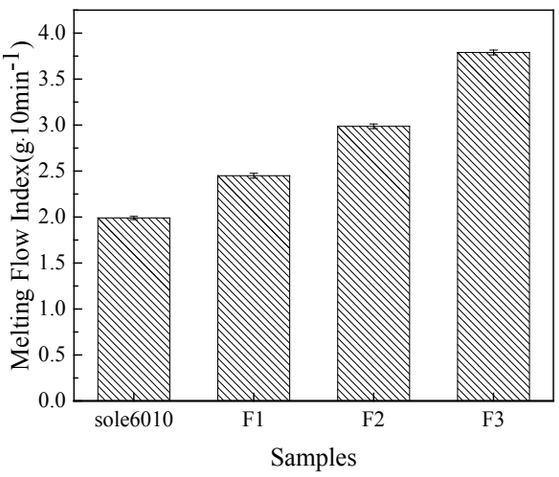

Fig. 3. Melt flow index of solef6010 and recycled materials.

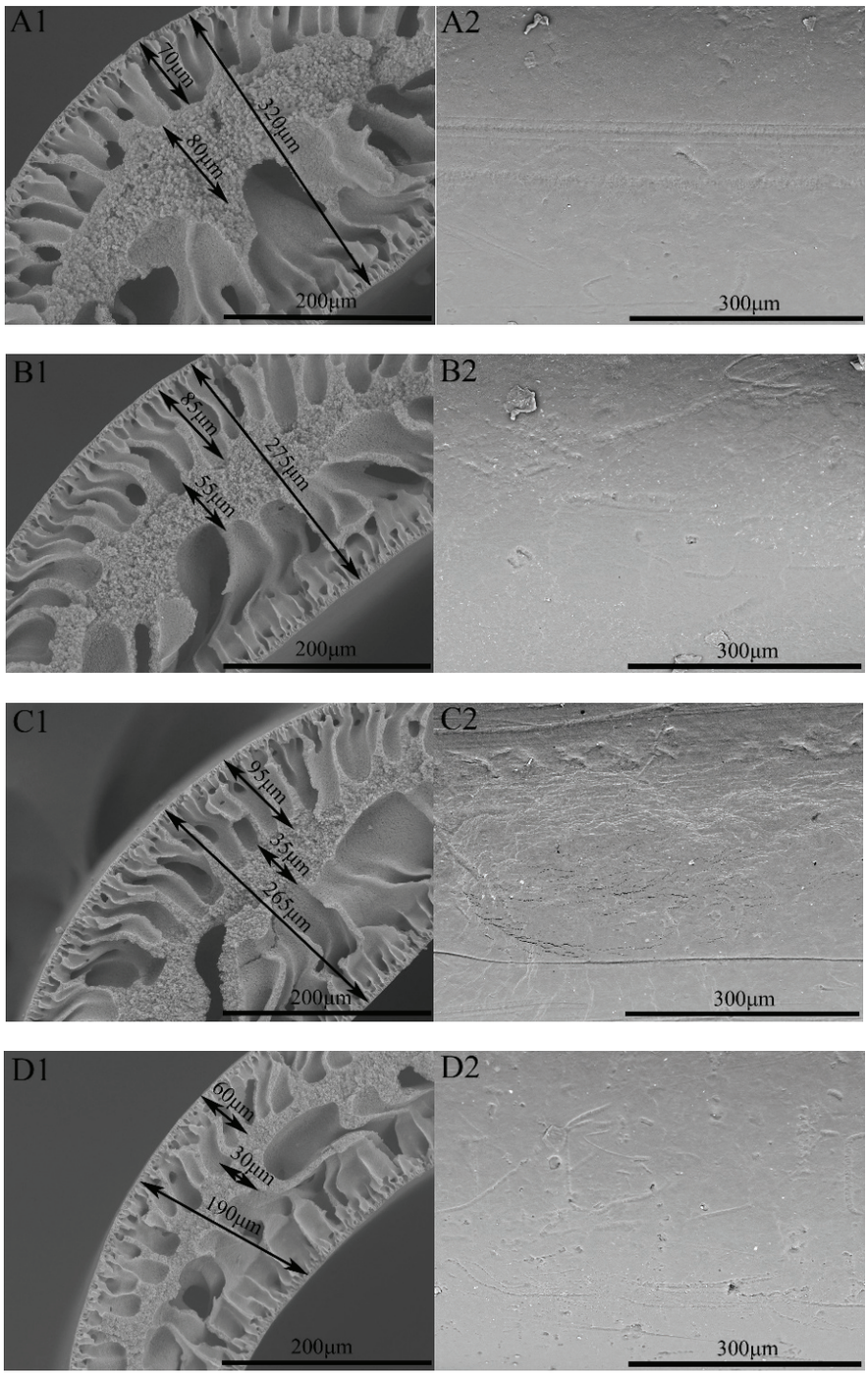

Fig. 4. Morphologies of original and recycled PVDF hollow fiber membranes. A: M1, B: M2, C: M3, D: M4.

3.4. Porosity and mean pore size

The characterization of the recycled PVDF hollow fiber membranes is tabulated in Table 3. This measurement was repeated at least three times for each sample. It was seen obviously that all the parameters increased as the running time rising. The reason was that the molecular weight decreased with the running time which can be obtained from the results of Figs. 2 and 3. The molecular weight of waste PVDF hollow fiber membranes had a significant effect on the rate of phase separation. The decrease of the molecular weight decreased the viscosity of the polymer solution which facilitated

Table 3
Characterization of recycled PVDF hollow fiber membranes

Sample	Mean pore size (μm)	Porosity (%)	PWF ($L \cdot m^{-2} \cdot h^{-1}$)	Concentrate flux ($L \cdot m^{-2} \cdot h^{-}$)
M1	0.104±0.03	37.64±1.51	106.44±2.79	67.47±5.71
M2	0.189±0.01	42.83±1.27	122.84±3.19	81.53±1.59
M3	0.199±0.01	47.68±1.22	146.36±1.92	95.48±2.13
M4	0.233±0.02	51.39±1.46	155.44±3.87	104.72±1.83

diluent movement and droplet growth [32]. Therefore, lower molecular weight polymer induced the structure of recycled PVDF hollow fiber membrane to grow better. In other words, lower molecular weight polymer would resulted in a porous membrane with relatively higher porosity and mean pore size [33].

3.5. Contact angle measurements

In order to investigate the influence of running time on wettability of recycled PVDF hollow fiber membranes, the contact angle formed between the liquid-gas tangent and membrane-droplet was measured [34]. In addition, the pollutants might increase the contact angle of membrane surface [35]. From Fig. 5 it is clearly seen that all recycled PVDF hollow fiber membranes have almost the same value of 83°. The feasible reason was that most of pollutants had be removed which had no impact on wettability of recycled PVDF hollow fiber membranes.

3.6. Mechanical properties

The tensile strength of original and recycled PVDF hollow fiber membranes was measured in order to study the effect of running time on the mechanical properties. The obtained results are presented in Fig. 6. In general, the mechanical properties of membranes depended on the polymer properties such as crystallization degree, the crystal thickness, the amorphous thickness as well as the membrane pore structures which were mainly affected by polymer molecular weight [36]. From result of shear viscosity and MFI, it was found that PVDF molecular weight decreased with the running time. Therefore, as Fig. 6 presents the mechanical properties of M1 were highest and that of recycled PVDF hollow fiber membranes decreased with the running time of waste membranes.

3.7. X-ray diffraction

PVDF crystals have five different polymorphs, α, β, γ, δ and ε and they had different effects on properties and performance of membranes [37]. The XRD patterns of recycled PVDF hollow fiber membranes are shown in Fig. 7. It was revealed that all samples had same and evident peaks at 18.6°, 26.8° and 36.3° corresponding to α-crystalline phase [38] and at 20.8° indicating β-crystalline phase of PVDF [39]. From Fig. 7 it can been clearly seen that peaks at 18.6°, 26.8° and 36.3°of M1 were stronger than other samples. In other words, α-crystal phase of M1 was more than other samples.

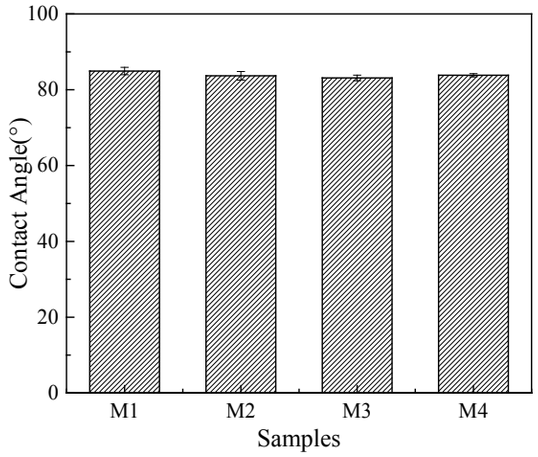

Fig. 5. The water contact angle of original and recycled PVDF hollow fiber membranes.

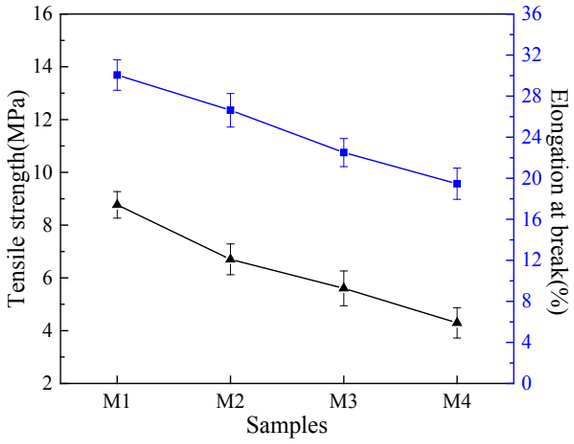

Fig. 6. Tensile strength and elongation of original and recycled PVDF hollow fiber membranes.

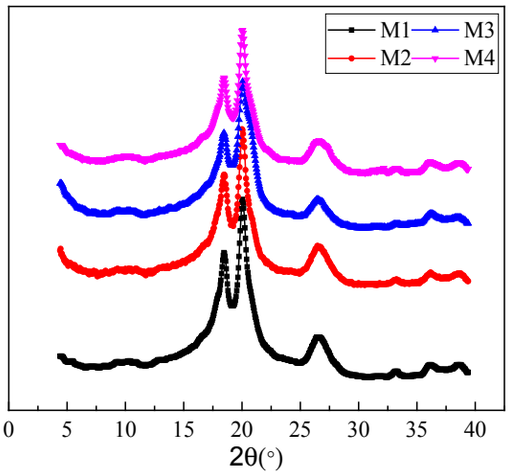

Fig. 7. XRD results for original and recycled PVDF hollow fiber membranes.

Calculated by fitting the diffraction peak, the crystallization degree of samples was 41.51%, 37.57%, 36.24% and 33.98%. According to the result of shear viscosity and melt flow index, it can be seen that the decrease of PVDF molecular weight had a significant impact on phase separation and crystallization [40].

3.8. Ultrafiltration performance

Fig. 8 shows the recycled PVDF hollow fiber membranes' time-dependent pure water flux (Fig. 8a), concentrate flux (Fig. 8b) and rejection ratio (Fig. 8c) to BSA solution, respectively. The permeation flux (pure water flux and concentrate flux) of membrane is mainly attributed to hydrophobicity and structure. According to the results of Section 3.5, the hydrophobicity of membranes had no significant difference. Therefore, in our work, the permeability depended on the structure of membrane. From Fig. 8a it can be clearly seen that the stable PWF and concentrate flux of M1 were up to 106.44 $L{\cdot}m^{-2}{\cdot}h^{-1}$ and 67.47 $L{\cdot}m^{-2}{\cdot}h^{-1}$ which were much lower than the recycled PVDF hollow fiber membranes. In addition, the stable PWF and concentrate flux of the recycled PVDF hollow fiber membranes decreased because of the decrease of molecular weight. The main reason was that lower molecular weight polymer would resulted in a porous membrane with relatively larger macrovoids and larger overall porosity [41]. Water can permeate through the recycled PVDF hollow fiber membrane with smaller thickness. In addition, the smaller and less pores (as shown in Table 3) on recycled PVDF hollow fiber membranes surface resulted in higher rejection ratio. Therefore, the rejection ratio (Fig. 8c) decreased with the running time and the result was opposite to pure water flux (Fig. 8a) and the concentrate flux (Fig. 8b). Compared with the previous reports about PVDF hollow fiber membranes [42–44], the ultrafiltration performance of recycled PVDF hollow fiber membranes had no significant difference.

Furthermore, Figs. 8a and 8b also show that the PWF and concentrate flux can reached stable in a period of time and decayed are very small. It was illustrated that the structure of recycled PVDF hollow fiber membranes had good pressure resistance.

4. Conclusions

In this study, three types of waste PVDF hollow fiber membrane were investigated. From the results of shear viscosity and melt flow index, it was observed that the PVDF molecular weight decreased with the running timeat the MBR facility (1-3-5 years). In addition, three types of recycled PVDF hollow fiber membrane and one type of original PVDF hollow fiber membrane as control group had been successfully prepared via dry-wet spinning method. The recycled PVDF hollow fiber membranes were subjected to characterization and performance testing. The results indicated that the permeability, porosity and crystallinity of recycled PVDF hollow fiber membranes increased with the increase of waste PVDF hollow fiber membranes' running time. But the mechanical

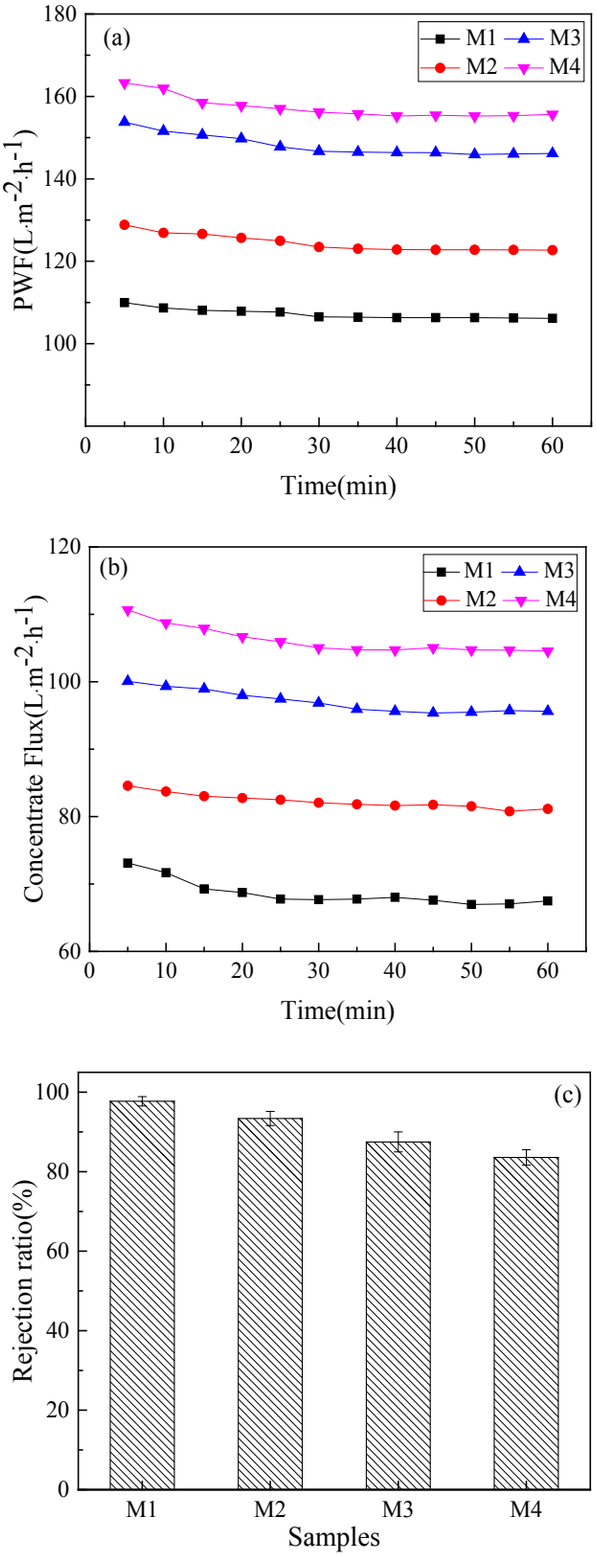

Fig. 8. Ultrafiltration performance of original and recycled PVDF hollow fiber membranes to BSA protein solution (operation pressure 0.1 MPa): (a) pure water flux, (b) concentrate flux, (c) rejection ratio.

properties and BSA rejection ratio of recycled PVDF hollow fiber membranes were worse than the original PVDF hollow fiber membrane. Moreover, the wettability of recycled PVDF hollow fiber membranes was similar to original PVDF hollow fiber membrane.

Acknowledgments

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