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Fabrication and properties of polyvinyl chloride hollow fiber membranes plastified by dioctyl phthalate

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ABSTRACT

Polyvinyl chloride (PVC) hollow fiber membranes were prepared by twin-screw extrusion method. Dioctyl phthalate (DOP) as the plasticizer was used in this study. The influence of stretching and DOP weight fraction on morphology and performance were investigated. The membranes were characterized by scanning electron microscope, pure water flux, mean pore size measurement, and mechanical strength test. The results show that the PVC hollow fiber membrane was a kind of homogeneous membrane. The pure water flux increased with the theoretical draw ratio and the DOP weight fraction increment. The plastic deformation ratio increased with the theoretical draw ratio increment, but decreased with the DOP weight fraction increment. The deformation-recovery ratio was governed by the DOP weight fraction and was slightly controlled by theoretical draw ratio. Both stretching and increment of DOP weight fraction could increase the mean pore size. At the same time, the tensile strength increased and the elongation at break decreased with the increment of theoretical draw ratio. On the contrary, the tensile strength decreased and the elongation at break increased with the increment of DOP weight fraction.

Keywords: Polyvinyl chloride; Hollow fiber membrane; Dioctyl phthalate; Stretching

1. Introduction

Polyvinyl chloride (PVC) as a membrane material possessed many advantages, such as low cost, excellent physical properties, good chemical properties (e.g. acids, alkalis, and solvent resistance) and mechanical properties [1,2]. Many researchers have investigated the structure and performance of PVC membranes that were prepared by phase inversion method. Xu and Xu [3] prepared PVC hollow fiber ultrafiltration membranes from blends of PVC, additives, and solvent. They found that using polyvinyl pyrrolidone (PVP) or polyethylene glycol as additives could improve the membrane porosity and enhance the permeation flux by changing the membrane morphology. PVP immobilized microporous chlorinated polyvinyl chloride membranes was prepared by Kang et al. [4]. They found that the membrane showed an increased hydrophilicity and thermal resistance at a slight expense in water flux rate after immobilized. Khayet et al. [5] studied on the structure

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and performance of PVC hollow fiber membranes prepared at different air gap lengths. Their study showed that the increase of the gap distance increased the outer pore size and the pure water permeation flux of the hollow fibers, but decreased the solute separation factor. PVC hollow fiber membranes for gas separation were prepared by Jones et al. [6]. They found that high polymer content solution spun fibers showed good gas separation properties. At the same time, extensive studies about hydrophilic modification of PVC membranes had been reported in the literature [7–9].

As can be seen from the above-cited references, although the PVC membranes that werepreprared by phase inversion method and its hydrophilic modification had been studied, few reports focused on the preparation of PVC hollow fiber membranes by twin-screw extrusion method. In past studies, some researchers had investigated PVC fibers that were fabricated by melt-spinning method. Kim and Gilbert [10] prepared PVC fibers by a spinning machine and investigated the effect of drawing on the characterization and properties. Park and Lee [11] prepared PVC filament yarns by melt-spinning method and found out the optimum spinning and drawing conditions. Their research showed that the optimum extrusion temperature and die temperature were 175–180˚C and 185–190˚C, and the drawing temperature and drawing ratio were 85–95˚C and 3.4, respectively. As is known that PVC was a thermally unstable polymer, it decomposed and released HCl. Thus, some thermal stabilizer was introduced in the melt-spinning process [10,11]. However, the plasticization could improve the fluidity of PVC in low temperature below melting point and prevented the degradation [12]. Based on what had been mentioned in the literature previously, the preparation of PVC hollow fiber membranes by twin-screw extrusion method had became possible to come true and this research had not been reported yet.

In this study, PVC hollow fiber membranes were prepared by twin-screw extrusion method. Dioctyl phthalate (DOP) as the plasticizer and composite powder as the pore-creating agent were used in this study. The influence of DOP weight fraction and stretching on morphology and performance were investigated.

2. Experimental

2.1. Materials

PVC (fiber grade, DG-1000 k, the average degree of polymerization is 1030) resin was purchased from Tianjin Dagu Chemical Plant (Tianjin, China). DOP (> 99.5%) was obtained from Tianjin Kermel Chemical Reagent Co. Ltd. Calcium/zinc compound thermal stabilizer was supplied by Shenzhenshi AIMSEA Industrial Co. Ltd. The composite powder was provided by Tianjin Motian Membrane Engineering and Technology Co. Ltd.

2.2. Hollow fiber membrane preparation and treatment

The PVC resin, calcium/zinc compound thermal stabilizer and composite powder were dried for 10 h at 50˚C in an electric blast drying oven to remove moisture before use. Then, PVC, calcium/zinc compound thermal stabilizer and DOP (DOP weight fraction was 22.22, 30.00, 36.36 and 41.67%) in a special weight ratio were mixed in high-speed mixer. After that, the mixture was fed into a twin-screw extruder machine and then through a cutter to obtain the particles. Finally, the particles and composite powder in a special weight ratio were mixed under high-speed agitation and were spun into hollow fibers via twin-screw extrusion method by a twin-screw spinning machine. Nitrogen gas was introduced into the spinneret for hollow formation. The spun fibers were coagulated in a water bath and then rolled up. The spinneret draw ratio was about 3. The prepared membranes were washed and stored in water for 48 h to completely leach out the residual solvents and additives. The initial PVC hollow fiber membrane was prepared.

The initial PVC hollow fiber membranes were stretched by different draw ratios (1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0) at 90˚C in the water bath. Then, it was treated in water bath at 80˚C for 1 h.

2.3. Membrane characterizations

2.3.1. Fourier transform infrared spectroscopy (FTIR)

FTIR spectroscopic measurements were carried out on a BRUKER TEN-SOR37spectrophotometer (German). Scans were 32 signal averaged at a resolution of 4 cm^{-1} from 4,000 to 400 cm^{-1}.

2.3.2. Scanning electron microscopy (SEM)

SEM (Quanta 200, the Netherlands FEI) was used to investigate the morphology of surface and cross-section of membranes. 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.

2.3.3. The pure water flux (PWF) experiments

PWF was measured with hollow fiber modules at 0.1 MPa pressure and constant feed at room temperature. PWF was calculated by the following equation:

$$J = \frac{V}{At} \tag{1}$$

where J is the permeation flux of membrane ($L.m^{-2}.h^{-1}$), V is the quantity of permeation (L), A is the effective area of membrane (m^2), and t is the testing time (h).

2.3.4. Determination of pore size and its distribution

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

2.3.5. Measurement of deformation

Membranes were subjected to stretching at 90°C in water bath, and the process was described as shown in Fig. 1.

Plastic deformation ratio (φ_1) and elastic deformation-recovery ratio (φ_2) were calculated by Eqs. (2) and (3), respectively:

$$\varphi_1(\%) = \frac{L_3 - L_1}{L_1} \times 100\% \tag{2}$$

$$\varphi_2(\%) = \frac{L_2 - L_3}{L_2 - L_1} \times 100\% \tag{3}$$

where L_1 and L_2 represent the length before and after stretching, respectively. L_3 represent the length of membrane, which was measured 48 h later after loosening the tension.

The theoretical draw ratio which can be abbreviated as TDR is calculated by Eq. (4):

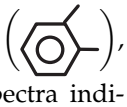
$$\mathrm{TDR} = L_2/L_1 \tag{4}$$

2.3.6. Measurement of mechanical property

At room temperature, membranes mechanical properties of PVC hollow fiber membranes were measured by the Electromechanical Universal Testing Machine (CMT4204, MTS SYSTEMS, China). The gripping range and the tensile rate were 100 mm and 100 mm/min, respectively. Each sample was tested five times to evaluate the average value.

3. Results and discussion

3.1. Chemical composition

The chemical compositions of membranes indicated some properties, such as hydrophilic property, hydrophobic property, acids, alkalis, and solvent resistance and so on. Therefore, the FTIR was used to investigate the chemical compositions of PVC and PVC/DOP. A comparison of the FTIR spectra of PVC and PVC/DOP was shown in Fig. 2. Comparing these two curves, it was noted that the appearance of the bands near to 1,724 and 742 cm^{-1} in PVC/DOP compound was the stretching vibration of carbonyl group (C=O) and 1,2-substituted benzenes group  , respectively. These changes on the FTIR spectra indicated that DOP appeared in the PVC/DOP compound.

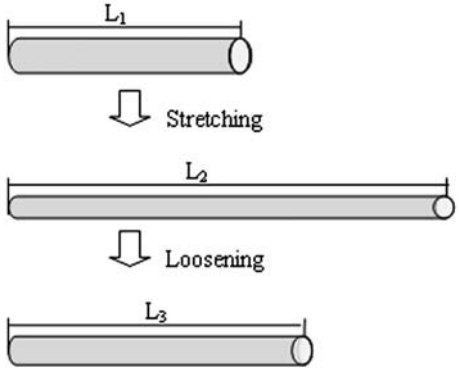


Fig. 1. Schematic diagram of the process of stretching.

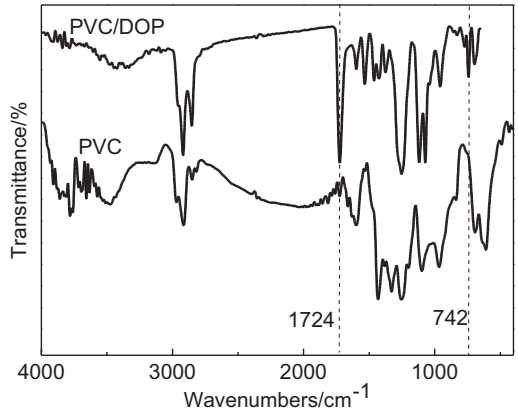


Fig. 2. The FTIR spectra of PVC and PVC/DOP.

3.2. Effects of stretching on membrane

The permeation performances of membranes were strongly related to their structure. Therefore, SEM was used to investigate the PVC hollow fiber membrane morphologies that were fabricated by twin-screw extrusion process. The effects of stretching on cross-section and surface morphologies of PVC hollow fiber membrane were shown in Figs. 3 and 4, respectively. As can be seen from Fig. 3, the PVC hollow fiber membrane was a kind of homogeneous membrane and revealed sponge-like structure. Comparing Fig. 3 (b1) with (b3), it was showed that the pores of cross-section were evenly distributed and porosity improved after stretching in hot water bath. The pores of inner and outer surface could be clearly observed long and narrow after stretching from Fig. 4. These findings were mainly due to the macromolecular motion aggravated at 90℃ in stretching process. Then, the macromolecular chain froze, when the temperature was down to room temperature. The membrane structure changed.

The pore size distribution of PVC hollow fiber membranes that were stretched by different TDR were shown in Fig. 5. As can be seen, the pore size and its distribution range became larger and wider after stretching, respectively. That could be explained that the pores became long and narrow with TDR increment from Fig. 4, the pore size increased. The PWF of PVC hollow fiber membranes that were stretched by different TDR were shown in Fig. 6. From Fig. 6, the PWF was increased with TDR increment. These results could be explained by the fact that the pore size increased with TDR increment as mentioned in Fig. 5.

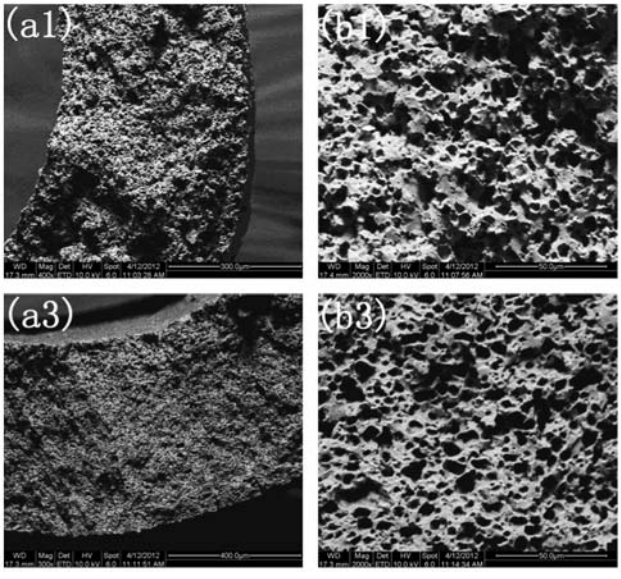


Fig. 3. The cross-section morphology of PVC hollow fiber membranes. ((a)-partial of cross-section, (b)-partial enlargement of cross-section; TDR: (a1) and (b1)-1, (a3) and (b3)-3; DOP weight fraction was 36.36%).

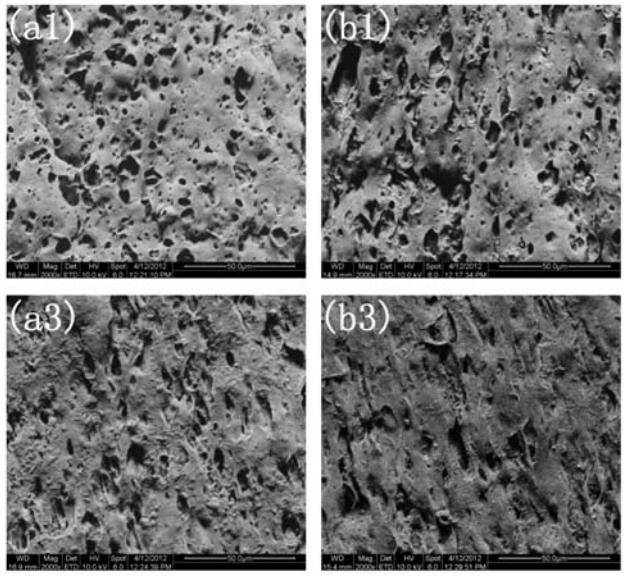


Fig. 4. The surface morphology of PVC hollow fiber membranes. ((a)-inner surface, (b)-outer surface; TDR: (a1) and (b1)-1, (a3) and (b3)-3; DOP weight fraction was 36.36%).

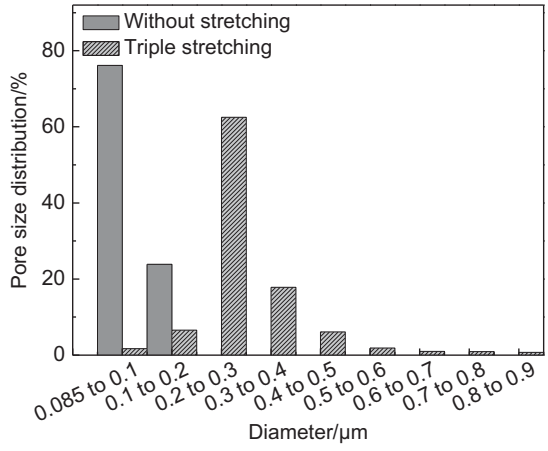


Fig. 5. Pore size distribution of PVC hollow fiber membrane. (DOP weight fraction was 36.36%).

The plasticization of PVC with plasticizers-like dioctyl phthalate gave PVC good softness and plasticity. Thus, the PVC hollow fiber membrane could possess recovery after stretching. The effects of TDR on plastic deformation rate and elastic deformation recovery rate were shown in Fig. 7. It

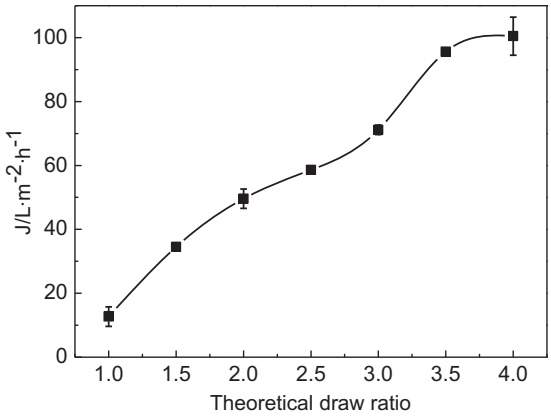


Fig. 6. Effects of TDR on PWF of PVC hollow fiber membrane. (DOP weight fraction was 36.36%).

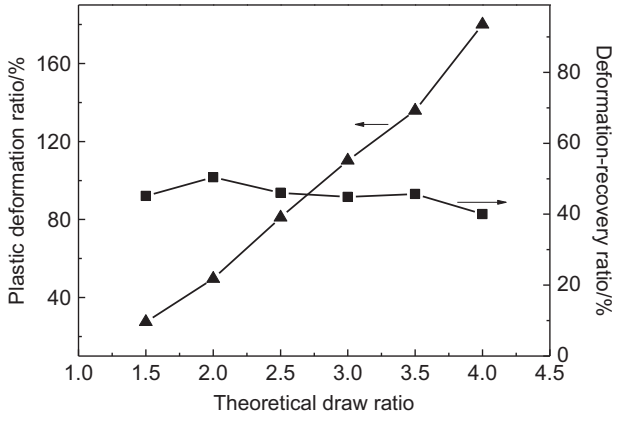


Fig. 7. Effects of TDR on plastic deformation rate and elastic deformation recovery rate of PVC hollow fiber membrane. (DOP weight fraction was 36.36%).

was obviously found that the plastic deformation rate increased with TDR increment and the relationship between plastic deformation rate and TDR was linear. But the deformation-recovery ratio was almost unchanged. This indicated that the deformation-recovery ratio was slightly controlled by TDR. The effect of TDR on the mechanical properties of PVC hollow fiber membranes was shown in Fig. 8. The tensile strength initially increased dramatically and then slowly with TDR increment. Contrary, the elongation at break initially decreased sharply and then slowly. These changes might be due to the increment of orientation degree [10,13]. The macromolecular chains were forced to orientate under tension when stretching. When the tension was big enough, the excess orientation would happen. Then, the macromolecular chains possessed orderliness and the intermolecular forces were large.

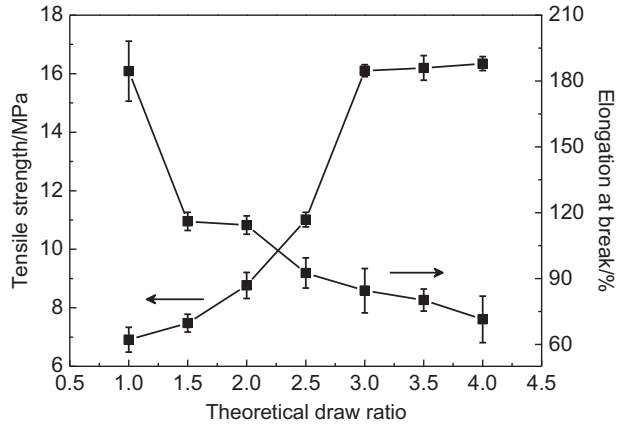


Fig. 8. Effects of TDR on the mechanical properties of PVC hollow fiber membrane. (DOP weight fraction was 36.36%).

3.3. Effects of DOP weight fraction on membrane

As is known, DOP is one of good plasticizers to PVC resin. During the plasticizing process, the plasticizer penetrates into PVC particles and forms a two phase system of liquid–solid called gelation. Then, the gelation was melted when it was fed into the twin-screw in particular temperature and these two phases transformed into a single solid phase [12]. The DOP content in PVC/DOP compound would influence the flexibility of the PVC hollow fiber membranes and also affect its morphology. The effects of DOP weight fraction on partial enlargement of cross-section, inner surface and outer surface morphologies were shown in Fig. 9. It was obviously found that the pore sizes of cross-section were shrunk when the DOP weight fraction reached at 41.67%. The pore sizes on inner surface became big and long with the increment of DOP weight fraction from Fig. 9(b1), (b2), and (b3). The outer surface became smoothly with the increment of DOP weight fraction from Fig. 9(c1), (c2), and (c3). These changes might be due to the increasing of softness of the PVC hollow fiber membranes which increased with the increment of DOP weight fraction from 22.22 to 41.67%.

The pore size distribution of PVC hollow fiber membranes of different DOP weight fraction were shown in Fig. 10. As can be seen, the pore size and its distribution range of high DOP weight fraction became larger and narrower, respectively. That could be explained that the pores of inner surface became big and long with the increment of DOP weight fraction from Fig. 9, the pore size increased. But the pores of high DOP weight fraction hollow fiber membranes were uniformly distributed because the DOP content in PVC/DOP compound would influence the

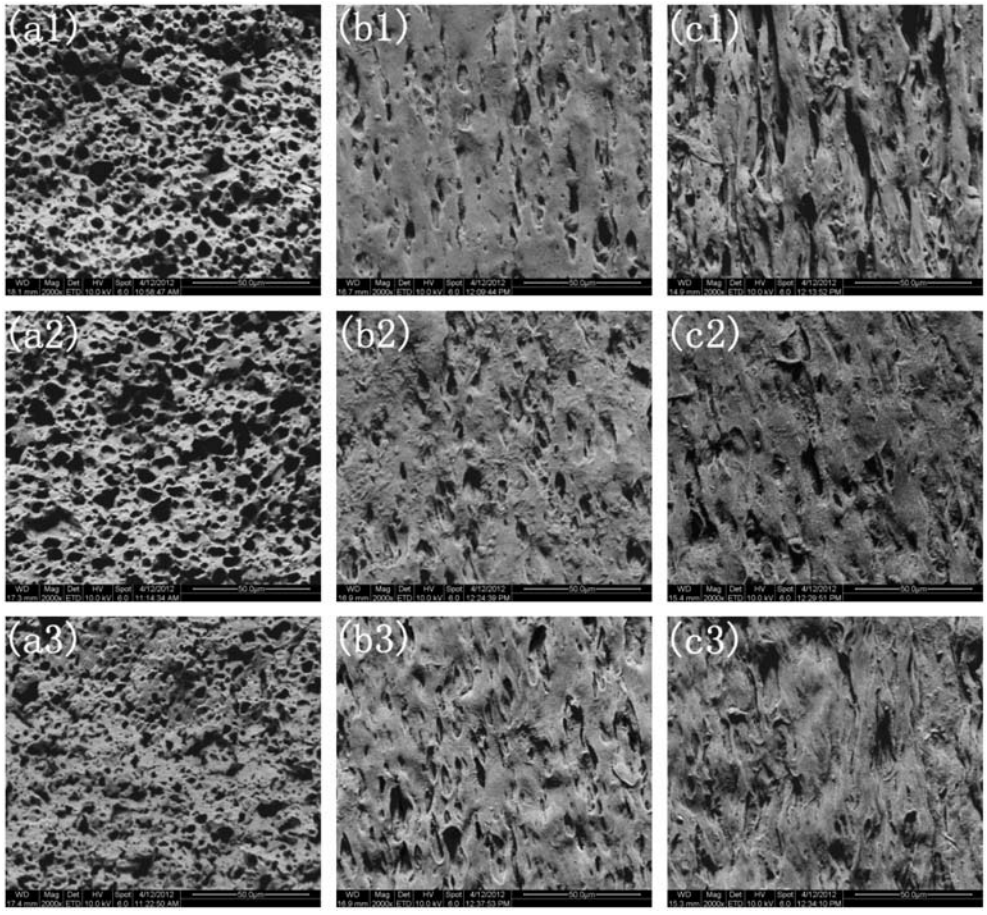


Fig. 9. The morphology of PVC hollow fiber membranes. ((a1–a3) cross-section, (b1–b3) inner surface, (c1–c3) outer surface; TDR: 3; DOP weight fraction: 1–22.22%, 2–30.00%, 3–41.67%).

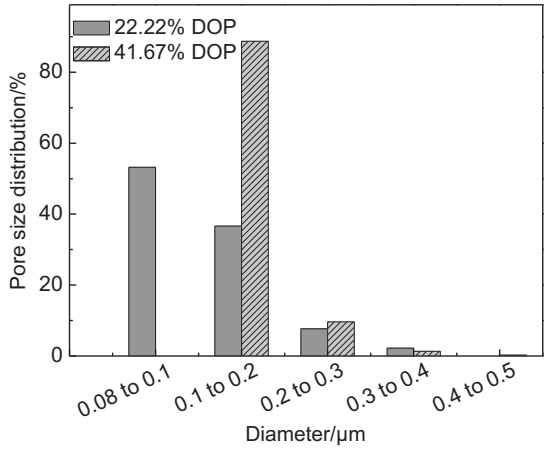


Fig. 10. Pore size distribution of PVC hollow fiber membrane. (TDR = 3).

flexibility of the PVC hollow fiber membranes as mentioned previously when stretching. The PWF of PVC hollow fiber membranes of different DOP weight fraction were shown in Fig. 11. From Fig. 11, the PWF of double stretching and triple stretching were increased with DOP weight fraction increment. These results could be explained by the fact that the pore

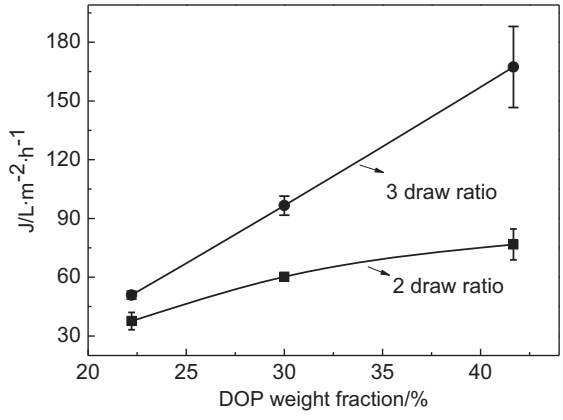


Fig. 11. Effects of DOP weight fraction on PWF of PVC hollow fiber membrane.

size increased with DOP weight fraction increment as mentioned in Fig. 10.

The effects of DOP weight fraction on plastic deformation rate and elastic deformation recovery rate were shown in Fig. 12. It was obviously found that the plastic deformation rate decreased with increment of DOP weight fraction. On the contrary, the deformation-recovery ratio increased. Associating with the Fig. 7, the deformation-recovery ratio was governed by the DOP weight fraction and was slightly controlled by TDR. The effect of DOP weight fraction on the mechanical properties of PVC hollow fiber membranes was shown in Fig. 13. The tensile strength initially decreased slowly and then dramatically with increment of DOP weight fraction. However, the elongation at break increased systematically with increment of DOP weight fraction. That indicated that the increment of DOP weight fraction improved the flexibility of the PVC hollow fiber membranes as mentioned previously.

4. Conclusions

PVC hollow fiber membranes were fabricated by twin-screw extrusion method and it was a kind of homogeneous membrane. The PWF increased with the TDR and the DOP weight fraction increment. The plastic deformation ratio increased with the TDR increment, but decreased with the DOP weight fraction increment. The deformation-recovery ratio was governed by the DOP weight fraction and was slightly controlled by TDR. Both stretching and increment of DOP weight fraction could increase the pore size. At the same time, the tensile strength increased and the elongation at break decreased with the increment of TDR. On the contrary, the tensile strength decreased and the elongation at break increased with the increment of DOP weight fraction.

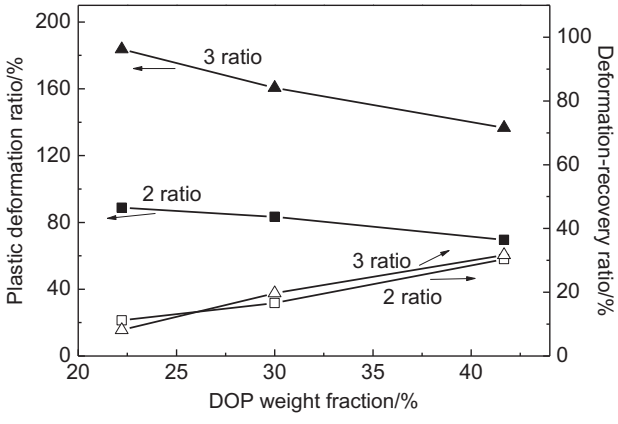


Fig. 12. Effects of DOP weight fraction on plastic deformation rate and elastic deformation recovery rate of PVC hollow fiber membrane.

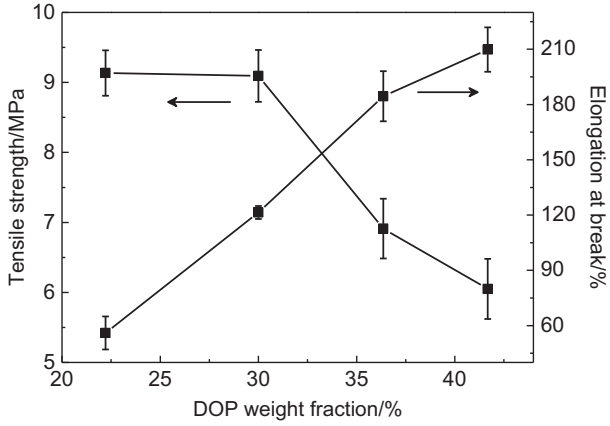


Fig. 13. Effects of DOP weight fraction on the mechanical properties of PVC hollow fiber membrane. (TDR = 1).

Acknowledgments

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