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Modification of Polyether Sulfone (PES) Hollow Fiber Membranes Characteristics for More Efficient Water Treatment Process

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Abstract

Membrane technology is used to separate water or solvents from salts or pollutants. This technique could be used for water treatment. For using of Polyether sulfone (PES) hollow fiber membranes in water treatment processes, the PES hollow fiber membranes were prepared by dry-wet spinning method and heated in an oven at: 120°C, 150°C and 180°C. The effect of heating on performance of membranes was investigated in a test module with five hollow fibers, each 15 cm long, were potted at both ends with epoxy glue. Then polyethylen glycol (PEG) and polyethylen oxide (PEO) with different molecular weights were passed through hollow fibers. It was found that the membrane shrank by heating, which was evidenced by the reduction in flux and increase in solute separation. The best results were obtained when the hollow fibers were heated at 150°C. A further investigation was made on the effect of heating period, while the temperature was fixed to 150 °C. It was found that heating period affected membrane performance only little.

Keywords: *PES, Hollow fiber membrane, Heating, Membrane performance*

Introduction

Membrane plays a key role our daily life. Richard Bowen says 'If you are tired of membranes, you are tired of life" (1).

The application of membrane technology in water treatment has been well documented (2). In this article, UF membrane was modified by heating. By this method the membrane's pore size reduced. We can use these types of membranes for removal of water pollutants instead of NF membranes that are more expensive. Hollow fiber membranes are a kind of membranes that have high usage in membrane separation technology. They are proper for almost all of membrane separation technologies like reverse osmosis (3), ultra-filtration (4) and gas separation (5).

There are different parameters in the process of hollow fiber preparation that can affect membrane separation, and there are a number of studies recorded in the literature on the subject. Some of the works relevant to the present study are summarized below. During the period of 1988-1990, the pore sizes of the membranes were calculated and the effect of internal coagulants on the membrane performance and the membrane pore size investigated (6).

Spinning conditions such as the flow rate of the internal coagulant, gas pressure and air gap can affect hollow fiber characteristics (7).

In 1992, the development of asymmetric skin type membranes for air separation was investigated. In this research, the hollow fibers were prepared by dry-jet wet spinning technique.

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Hollow fibers also were coated with a silicone elastomer. SEM observation showed that the dense layer was located at outer surface, while the region near the inner surface had an interconnected open-cell structure (8). Thermodynamic conditions during the formation of the PES solution are another parameter that effect on membrane characteristics (9). The objective of this work was to study on the effect of heat treatment on performance of PES ultrafiltration hollow fiber membranes at different temperatures and for different time periods.

Material and Methods

Membrane material and preparation

Polyether sulfone (PES, Victrex 4100 P), supplied by Imperial Chemical Industries, was dried at 80°C without further purification. Polyviny l pyrrolidine (PVP) of molecular weight 10,000, supplied by Sigma Chemical Co., was used as a polymer additive to the casting solution.1-Methyl-2-pyrrolidinone (NMP), supplied by Sigma Chemical Co., was used as the solvent. The composition of casting solution by weight percent (wt %) was PES 21%, PVP 14% and NMP 65%. Hollow fibers were made by the solution spinning technique (7- 13). The casting dope was prepared loaded in to the dope tank. The dope was forced through a spinneret by nitrogen pressure (1.5 psi), and was collected in a coagulant (water) bath that was placed under the spinneret. The distance between the spinneret and the surface of the coagulant is called air gap. The internal coagulant in a 1,000 ml bottle placed at a height of 1 meter above the spinneret went into the central tube of the spinneret under gravitational force at the same time. Hollow fibers were kept in water for at least 24 hours and then in aqueous ethanol solutions with ethanol contents of 30, 60 and 90 vol. %, respectively, for 1 hour. Then, the hollow fibers were kept in 99% ethanol for one day and in 30% glycerol solution for one hour, before being dried at room temperature for 1-2 days. The spinning conditions for the preparation of PES hollow fiber membrane were pressure 1.5(psi), coagulant (Internal and external) water, tem- perature 20˚C, air gap 90(cm). Bore fluid characteristics for PES preparations were: liquid (Water), Volume (1000ml) and height (1m).

Hollow fiber experiments Hollow fiber membranes were heated in an oven with air circulation at 120°C (HF120), 150°C (HF150), 180°C (HF180) for 15 min. Five hollow fibers were selected and cut to a length of 15 cm and potted at both ends with epoxy glue in a test module. The inner diameter of which was 0.44 mm. The effective area of the membrane was 10 cm^2. Also, in order to study the effects of heating on the morphology of the hollow fiber, selected samples of hollow fibers before and after heating were prepared for the Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM) investigation. The feed solution entered the lumen side of the hollow fibers and the permeate was collected from the shell side through an opening made at one of end of the module housing. The feed flow velocity, (0.65-1.0m/s), was so high that the concentration change in the feed could be ignored. The operating pressure and the operating temperature were 345 kPa (50 psi) and 23±1.0 °C, respectively. The polyethylene glycol (PEG) with molecular weight up to 35,000 g/mol and polyethylene oxide (PEO) with molecular weight of 100,000 and 200,000 were used as solutes in the aqueous feed solutions. PEG and PEO concentrations were kept at 200 ppm by weight. The concentrations of feed and permeate solutions were determined by using a Foilio TOC Analyzer Model DC-190 and the solute separation, R, was obtained by the relevant equation (7- 13). The Pure Water Permeation rate (PWP), before passing the feed and the Product Rate(PR), in the presence of solute in the feed were obtained by weighting the permeate sample collected for a predetermined period. All the samples were collected after the hollow fiber membranes

were pressurized under a pure water pressure of 50-psi gauge for 2 h. The heat treatment of the hollow fibers was also carried out at a fixed temperature (150°C) for different time periods; i.e., 1, 5, 15, 30 and 45 min, respectively, which was followed by the ultra-filtration experiments. The pore sizes of hollow fibers were calculated by the relevant equation (7). The pore size distribution was expressed in terms of a log-normal distribution that was obtained by drawing log-normal distribution curve by Sigmaplot program. The mean pore size (μ_p) can be calculated as d_s corresponding to R=50%. Standard deviation (SD) can be determined from the ratio of d_s at R=84.13% and at 50%.

Results

Effect of temperature on PES hollow fibers the results are listed in Table 1. Since the concentration of PEG solutes in the feed solution was very small (200ppm), the osmotic pressure effect was almost negligible. Therefore, only the pure water permeation flux is reported in Table 1. Obviously, the solute separation goes up while PWP goes down as the temperature increases. In particular, the decrease in PWP from HF150 to HF180 was significant.Pore sizes and their distribution also were cal- culated from the transport data given in Table1.

A straight line was obtained with reasonably high correlation coefficient ($r^2 \geq 0.90$), while plotting the percent separation of the PEG/PEO solutes on ordinate versus their diameters on abscissa of a log-normal probability paper as shown in Fig. 1. The values of the mean pore size(μ_p) and the standard deviation (SD) around the mean were determined using Fig. 1, as described in the Materials and Methods section. These values are summarized in Table 2.

Table1: performance data of PES hollow fiber membranes after heat for 15 min (feed solute concentration, 200ppm).

PEG/PEO Solute (g/mol)	HF0		HF120		HF150		HF180	
	PWP ($l/m^2.h$)	R%	PWP ($l/m^2.h$)	R%	PWP ($l/m^2.h$)	R%	PWP ($l/m^2.h$)	R%
PEG3400	594.21	5.3	391.5	5	381.7	10	25.3	37.1
PEG6000	578.58	23.72	342.71	12	357.3	27	22.9	72.2
PEG10000	529.42	37.25	308.34	65	355.7	58	20.4	75.1
PEG20000	514.81	50.93	162.38	76.3	308.1	80	19	89.6
PEG35000	430.40	87.9	157.38	93.5	212.0	97	17.27	96.5
PEO100000	289.77	88.2	135.96	96.3	178.8	98	14.1	98.2
PEO200000	196.21	96.22	102.21	99.6	98.43	99.3	10.34	99.5

Oven temperature: HF0, no heating; HF120, 120°C; HF150, 150°C; HF180, 180°C.

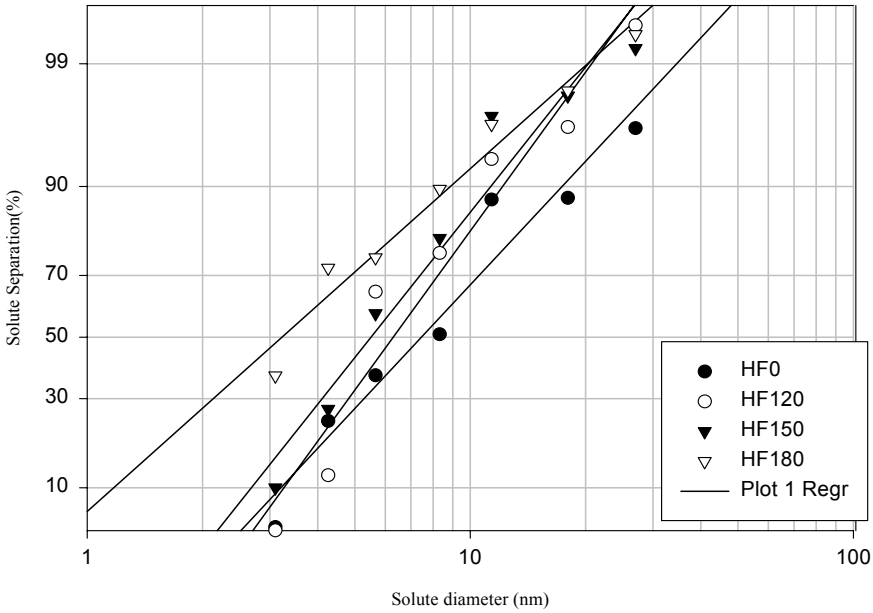

Fig.1: Solute diameter versus separation for PES hollow fiber membranes before and after heating (time of heating 15 min)

Table 2: Mean Pore size (μ_p) and standard deviation (SD) for various membranes after heat for 15 min

Membrane	MWCO kDa	Mean pore size, (nm)	SD
HF0	131	8.32	2.02
HF120	32	5.29	1.79
HF150	29	5.10	1.85
HF180	22	3.56	2.08

Effect of heating in different time periods on hollow fibers Separation versus molecular weight of solute is shown in Fig. 2.

Performance data of PES hollow fiber membranes heated at 150°C for different times (feed solute concentration, 200ppm) are presented in Table 3. The values of the mean pore size (μ_p) and the standard deviation around the mean were determined using Fig. 2 and are summarized in Table 4.

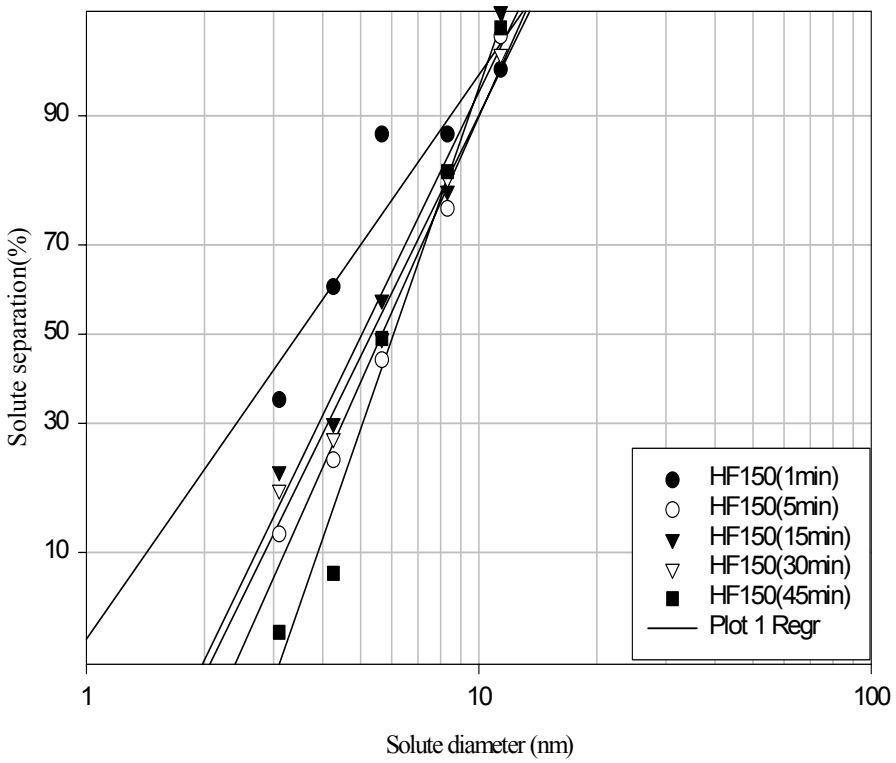

Fig.2: solute diameter versus separation for PES hollow fiber membranes after heating at 150^{0}C and different times

Table 3: Performance data of PES hollow fiber membranes heated at 150°C for different times (feed solute concentration, 200ppm).

PEG Solute (g/mol)	HF150(1min)		HF150(5min)		HF150(15min)		HF150(30min)		HF150(45min)	
	PWP l/m^2.h	R%	PWP l/m^2.h	R%	PWP l/m^2.h	R%	PWP l/m^2.h	R%	PWP l/m^2.h	R%
6000	415.19	61.1	403.67	23.2	381.7	27	357.3	27.3	133.12	8.2
10000	390.36	88.4	269.08	44.2	357.3	58	213.76	49.1	61.25	49.25
20000	307.73	88.7	269.08	77.3	355.7	80	199.16	82.5	54.49	83.32
35000	199.19	94.6	204.54	96.5	308.1	97	180.09	95.3	46.02	96.45

Table 4: Mean Pore size (μ_p) and standard deviation (σ_p) for various membranes for different time

Membrane	MWCO kDa	μ_p (nm)	SD
HF150 (1min)	25	3.8	2.0
HF150 (5min)	30	6.1	1.56
HF150 (15min)	29	5.1	1.79
HF150 (30min)	29	5.74	1.525
HF150 (45min)	28	5.725	1.49

Discussions

In spite of previous studies, there are no reports about the effect of the heat treatment at high temperature in air on the performance of PES ultra-filtration membranes, when they are either in flat sheet or in hollow fiber configurations. In previous studies, the effect of polyether sulfone (PES) concentration on the performance of flat sheet and hollow fiber membranes was evaluated. They showed that the performance of both flat sheet and hollow fiber membranes was strongly dependent on whether the PES concentration was above or below a critical value(6). The effect of dope solution characteristics on the PES membrane morphology by using light scattering Atomic Force Microscopy (AFM) and SEM was studied in the other researches (10, 11). Detailed analysis of surface images of PES indicated that low fluidity of the dope solution developed resulted in the membrane morphology of a spong-like structure with a smooth surface layer. In an interesting report, the influence of water as non-solvent additive on the properties of the polymer solution, gas separation properties and structures of PES hollow fiber membranes was studied when they were prepared by the spinning technique. In this report, the effects of various spinning conditions including polymer concentration, length of air gap, and non-solvent strength of the internal coagulant on the flux and structure of hollow fiber were studied (12, 13). In the present study, the effect of heat treatment on performance of PES ultra-filtration hollow fiber membranes at different temperatures and for different time periods was studied. From Fig.1 and Table1 can be concluded that mean pore size of samples decreased with an increase in temperature, while standard deviation increased. It should be noted that the mean pore size was higher for the membranes having a higher MWCO. Considering both the solute separation and PWP given in Table 1, it was concluded that the membrane heated at 150°C was the best. Therefore, a further study was carried out on the effect of heating time when the temperature was fixed to 150°C. According to the results that have been listed in Table 3 and shown along with in Table 1, MWCO decreased remarkably from no heating to 1min heating at 150°C (from 131kDa to 25kDa) and then increased at 5 min heating (30kDa). Further increased in heating period did not affect the MWCO. On the other hand, a steady decrease in PWP was observed with an increase in heating period, with one exception at 15 min. From these results, it is concluded that 1 min heating period at 150°C is the best combination of heating time and temperature. From Table 4, it is concluded that pore size decreased from 8.16 nm without heating to 3.8 nm with one min heating and then increased about 6 nm for 5 min heating. It is clear from the results of this investigation that heat treatment has a significant contributing factor on membrane characteristic and performance. The temperature can affect the shape of membrane and shrink it. Furthermore, the effect of heating time when the temperature was fixed to 150°C, were studied. From those results, it is concluded that 1 min heating period at 150°C is the best combination of heating time and temperature. Also pore size decreased from without heating with one min heating and then increased about for 5 min heating.

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