Fabrication of PVDF hollow fiber membranes : effects of low-concentration pluronic and spinning conditions

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2014

Loh, C. H., & Wang, R. (2014). Fabrication of PVDF hollow fiber membranes : effects of low-concentration pluronic and spinning conditions. *Journal of membrane science*, 466, 130-141.

<https://hdl.handle.net/10356/79614>

<https://doi.org/10.1016/j.memsci.2014.04.021>

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Table 1

Spinning conditions of PVDF hollow fiber membranes (PVDF: 18 wt%, LiCl: 3 wt%)

Membrane code	Pluronic concentration (wt%)	Bore fluid composition (wt%)	Air gap (cm)	Dope flow rate (g/min)	Bore fluid flow rate (mL/min)	Take-up speed (m/min)	Coagulant temperature (K)
P0-80	0	NMP/water (80/20)	1	6	3.5	8.6	298
P0-00	0	water	25	5	2.5	7.2	298
P0-00H	0	water	25	5	2.5	7.2	323
P2-80	0.2	NMP/water (80/20)	1	6	3.5	8.6	298
P2-00	0.2	water	25	5	2.5	7.2	298
P2-00H	0.2	water	25	5	2.5	7.2	323
P5-80	0.5	NMP/water (80/20)	1	5	3.5	8.6	298
P5-00	0.5	water	25	4	3	7.2	298
P5-00H	0.5	water	25	4	3	7.2	323
P5-00H-A	0.5	water	20	4	3	5.7	323
P5-00H-B	0.5	water	20	4	3	7.2	323

Table 2

Effects of operating modes and take-up speed on PWP and MWCO of PVDF hollow fibers

Membrane code	Outside-in		Inside-out		
	PWP ^a (L/m ² h MPa)	MWCO (kDa)	PWP ^a (L/m ² h MPa)	PWP ^b (L/m ² h MPa)	MWCO (kDa)
P5-00	1430 ± 30	270	1440 ± 20	2090 ± 30	65
P5-00H	1470 ± 20	> 500	1290 ± 110	1900 ± 160	30
P5-00H-A	-	-	1440 ± 120	2060 ± 170	60
P5-00H-B	-	-	1300 ± 10	1900 ± 10	25

^acalculated based on outer surface area^bcalculated based on inner surface area**Table 3**

Crystallinity of PVDF hollow fibers

Membrane code	Melting enthalpy, ΔH_f (J/g)	Crystallinity, X_c (%)
P0-80	58	56
P0-00	54	52
P0-00H	55	53
P2-80	56	54
P2-00	58	56
P2-00H	55	52
P5-80	57	55
P5-00	55	53
P5-00H	55	53

Table 4

Dimensions, contact angle, and collapsing pressure of PVDF hollow fibers

Membrane code	Outer diameter (μm)	Inner diameter (μm)	Thickness (μm)	Contact angle (°)	Collapsing pressure ^a (MPa)
P0-80	900 ± 5	600 ± 9	150 ± 2	71.4 ± 2.4	0.4
P0-00	890 ± 7	640 ± 6	125 ± 1	75.6 ± 2.1	0.45
P0-00H	920 ± 7	650 ± 4	135 ± 4	77.5 ± 1.5	>0.5
P2-80	980 ± 5	620 ± 5	180 ± 3	77.5 ± 0.8	0.3
P2-00	920 ± 2	610 ± 2	155 ± 1	78.9 ± 0.7	0.3
P2-00H	920 ± 3	630 ± 1	145 ± 1	78.4 ± 1.1	0.4
P5-80	990 ± 17	670 ± 11	160 ± 11	75.4 ± 3.4	0.15
P5-00	920 ± 6	630 ± 6	145 ± 2	73.0 ± 0.6	0.15
P5-00H	950 ± 6	640 ± 4	155 ± 2	76.0 ± 1.3	0.25

^aPressure was applied at the shell side of hollow fibers

Table 5

Comparison of various PVDF UF hollow fiber membranes

Additives used (wt%)	PWP ^a (L/m ² ·h MPa)	MWCO ^b (kDa)	BSA rejection ^c (%)	Tensile stress (MPa)	Elongation (%)	Collapsing pressure (MPa)	Reference	Remarks
Pluronic F127 (0.2) + LiCl (3)	1180 (lumen)	5	99	4.0	310	0.4 (shell) 0.55 (lumen)	this work (P2-00H)	
PVDF copolymer (5)	1310	200	84	2.2	230	0.3	[36]	
PVDF copolymer + PEG (8)	2750*	N.A.	95	0.4	150	N.A.	[37]	PWP tested at 0.04 MPa
Fe ³⁺ + Cu ²⁺ + PEG	350	N.A.	92	2.6	100	N.A.	[38]	
PVDF copolymer + TiO ₂ (1)	9740	N.A.	93*	3.3	80	N.A.	[39]	Rejection of dextran 500 kDa
PEG (5)	1370 (lumen)	150	N.A.	7.5	160	N.A.	[40]	
PFSA (3)	270	24*	N.A.	2.6	70	N.A.	[41]	MWCO tested using PEG
water (3)	300	40	N.A.	N.A.	N.A.	N.A.	[17]	
PVP (5)	1900	N.A.	83	N.A.	N.A.	N.A.	[42]	
PFSA (1) + ethanol (1)	120*	8	95*	N.A.	N.A.	N.A.	[43]	PWP tested at 0.2 MPa; Rejection of PEG 10 kDa
PFSA (3)	1370	N.A.	97	N.A.	N.A.	N.A.	[44]	
phosphorus acid (3)	890	290	N.A.	N.A.	N.A.	N.A.	[45]	
1,2-ethanediol	190*	367*	N.A.	N.A.	N.A.	N.A.	[46]	PWP tested at 0.48 MPa; MWCO tested using PEG
LiCl (2) + 1-propanol (7)	870	N.A.	84*	N.A.	N.A.	1.2	[22]	Rejection of dextran 110 kDa
PVP (8)	1100	N.A.	61*	N.A.	N.A.	N.A.	[47]	Rejection of dextran 500 kDa

^aOperating pressure was 0.1 MPa unless otherwise stated^bMWCO was tested using dextran unless otherwise stated^cBSA was used for rejection test unless otherwise stated

*See remarks

Figure 1. Effect of air gap on inner contour of PVDF hollow fibers spun with 0.5 wt% of Pluronic (upper row: 50wt% NMP as bore fluid; lower row: water as bore fluid)

Figure 2. Morphologies of hollow fibers (a) P5-80 and (b) P5-00 (1: cross-section; 2: outer surface; 3: inner surface)

Figure3. Cross-sectional morphology of PVDF hollow fibers

Figure 4. Overall porosity of PVDF hollow fibers (PX-80 includes P0-80, P2-80, and P5-80; similar manner for PX-00 and PX-00H)

Figure 5. Outer surface of PVDF hollow fibers

Figure 6. Outer surface and cross-sectional morphology of PVDF hollow fibers spun at different take-up speed

Figure 7. PWP and MWCO (kDa) of PVDF hollow fibers (PX-80 includes P0-80, P2-80, and P5-80; similar manner for PX-00 and PX-00H)

Figure 8. FTIR spectra for PVDF hollow fibers spun with different amount of Pluronic

Figure 9. Mechanical properties of PVDF hollow fibers: (a) Young's modulus; (b) Tensile stress at break; (c) Elongation at break (PX-80 includes P0-80, P2-80, and P5-80; similar manner for PX-00 and PX-00H)

Figure 10. Sponge-like structure (A, B) and cross-section near lumen (a, b) of hollow fibers P5-80 (A, a) and P5-00 (B, b)