Electronic Supplementary Information

Reverse Fabrication Method of Thin-Film Composite Membranes for Hydrogen Separation

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Experimental

Materials

Matrimid®5218 was purchased from Huntsman Corporation. Polysulfone (Mw = 22,000 Da) was purchased from Sigma-Aldrich. DI-water and N-Methyl-2-pyrrolidone (NMP; 99.5% purity) were purchased from Samchun Chemicals (South Korea). THF (99.9%) and n-hexane (95.0%) were purchased from Duksan Pure Chemicals Co., Ltd. (South Korea). PDMS (Sylgard 184) was purchased from Dow Corning. All materials were used without further purification.

Membrane preparation

The TFC membranes were prepared via the reverse method using the following steps with a few variations. First, MI was dissolved in THF at a ratio of 2 wt%/vol% and spin-coated onto a glass substrate at 2000 rpm. The MI-coated glass substrate was dried in a 50 °C oven for 3 h, and then the PSF/NMP solution was cast onto the substrate by doctor-blading with a 300 μm gap between the blade and the substrate, followed by immersion in water for the NIPS process. The time between doctor-blading and the NIPS process was varied to examine its effect on the MI layer. The immersed membrane was pulled out after 20 min and dried at 25 °C for 24 h. Then, the membrane was taped to a glass substrate with a selective layer on the top side to spin-coat the PDMS layer. PDMS/n-hexane solutions of varying concentrations were spin-coated as caulking layers. The membrane was put into an 80 °C oven for 24 h to cure the PDMS layer. The prepared membranes were named PDMS/MI/PSF_X, where X refers to the delay (in seconds) between casting and immersion in water during membrane preparation.

Gas permeation measurements

The gas permeances of pure H_2, CH_4, and N_2 were measured at 30 °C using a constant-pressure/variable-volume apparatus (Airrane Co., Ltd., Korea) equipped with a flat-sheet permeation cell with an effective area of approximately 10.2 cm^2. The feed pressure was varied from 3 bar to 12 bar. The gas permeance was expressed using a gas permeation unit (GPU) [1 GPU = 1×10^{-6} cm^3(STP)/(s·cm^2·cmHg)]. The selectivity of the membranes was defined as the ratio of the permeance for each gas.

Characterization

FT-IR spectroscopy was conducted using an FT-IR spectrometer (Spectrum Two, PerkinElmer, USA) to characterize the interactions between layers. XRD patterns were analyzed with D8 Advance (Bruker, Germany) at a scanning speed of 1° min^{-1} in the 2θ range of 5° to 40°. The atomic percentages of the individual layers of the TFC membranes were determined using XPS (K-Alpha, Thermo Fisher Scientific, USA) at a penetration depth of 10 nm. Imaging of the surface and cross sections was performed using FE-SEM (JSM-7610F-Plus, JEOL, Japan) to examine the structure and thickness of the membranes. All the samples were sputter-coated with platinum for 100 s to enhance their conductivity. The samples used for the cross-sectional images were prepared by immersing them in liquid N_2 and breaking them in half. The mechanical properties of the prepared membranes were tested using a UTM (MultiTest2.5-i, Mecmesin) at a crosshead speed of 20 mm/min to observe the changes in mechanical strength at different delay times. The contact angles of the membrane surfaces were analyzed using a contact angle analyzer (Theta Lite, Biolin Scientific, Sweden) to ensure the successful coating of each layer.

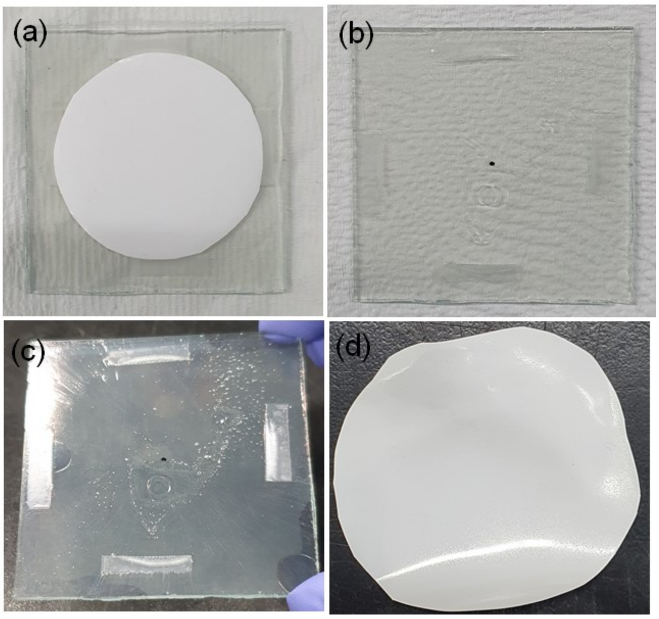


Figure S1. Photos of (a) porous PSF membrane prepared by NIPS, (b, c) MI/PSF membrane prepared by conventional method, and (d) MI/PSF membrane prepared by reverse method.

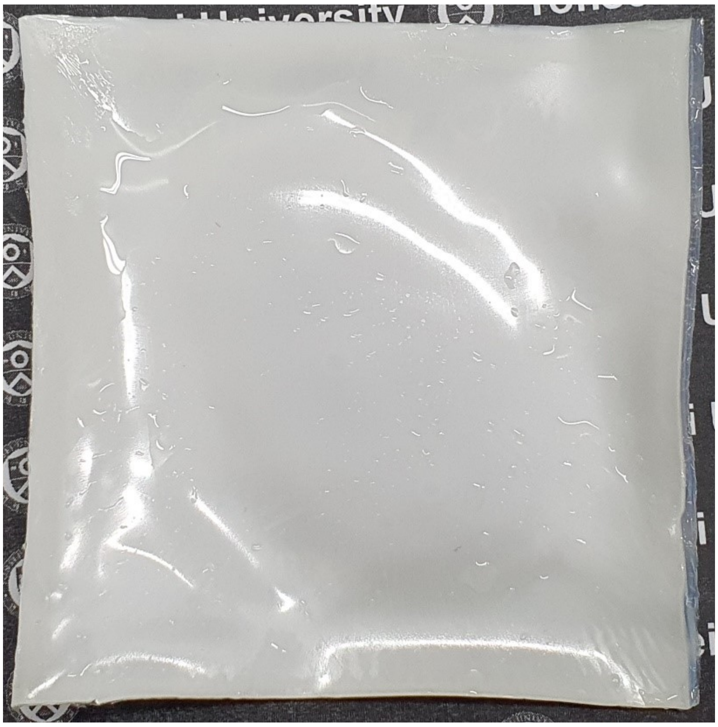


Figure S2. Photo of large area (10 × 10 cm^2) MI/PSF membrane prepared by reverse method.

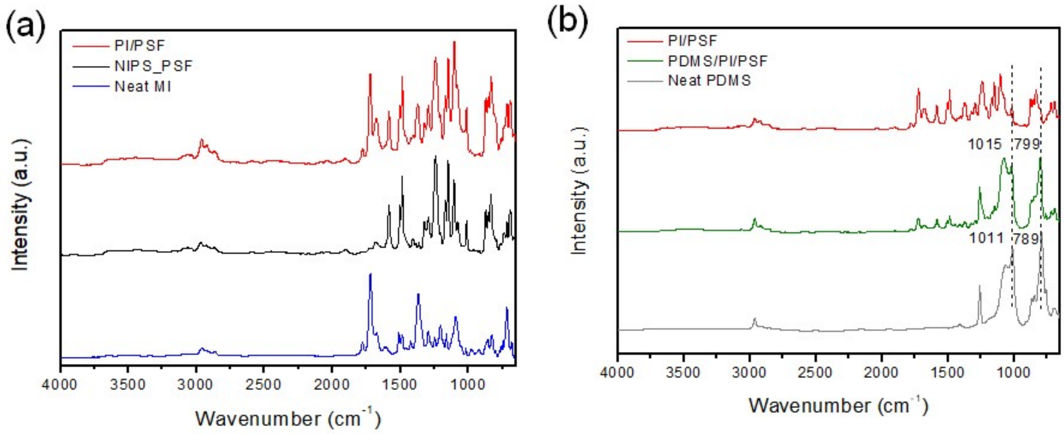


Figure S3. FT-IR spectra of (a) neat MI, PSF membrane deposited by NIPS, PI/PSF membrane deposited by reverse method, and (b) neat PDMS, PI/PSF membrane deposited by reverse method, and PDMS-coated PI/PSF membrane

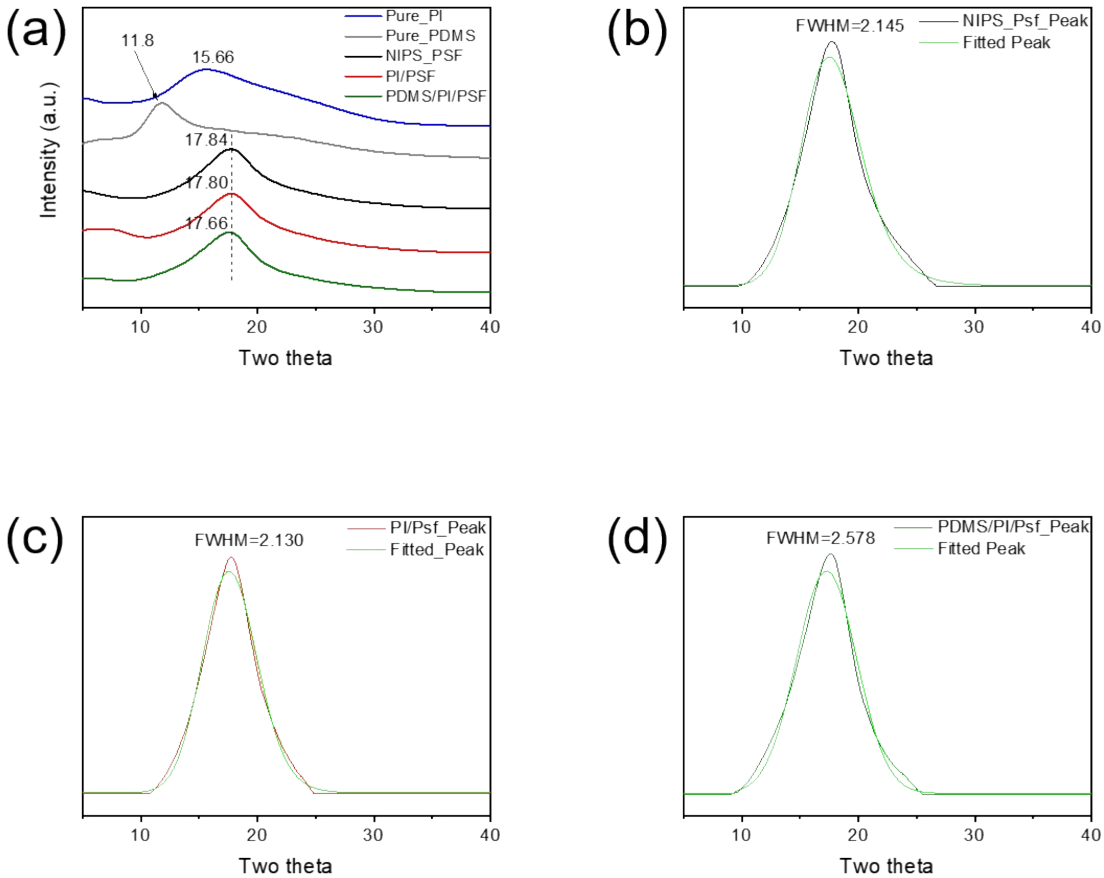
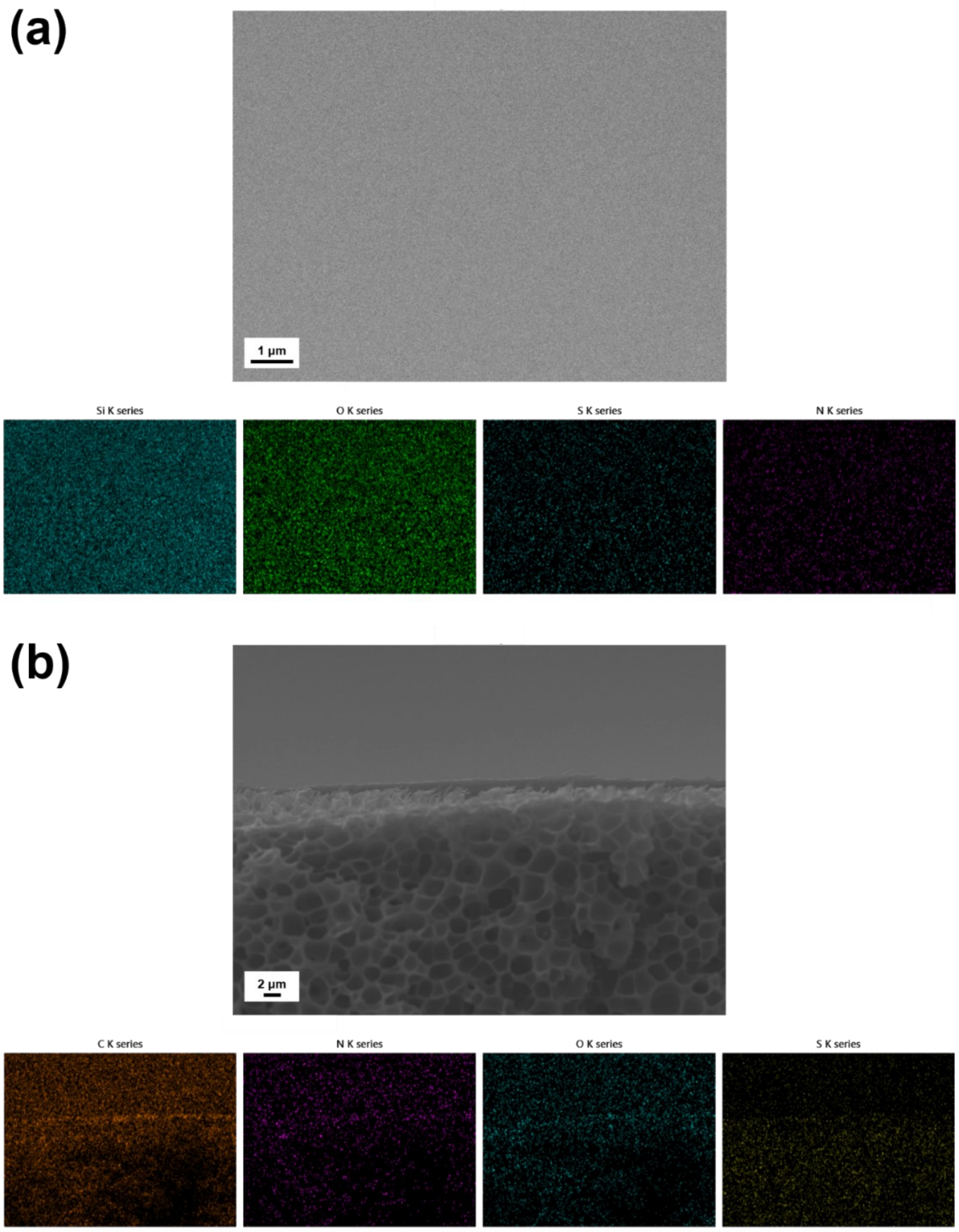


Figure S4. (a) XRD patterns of raw materials and membranes fabricated by reverse method and (b, c, d) FWHM verified with fitted peaks

Table S1. XPS elemental analysis of membranes prepared via the reverse method

	C	O	N	Si	S
NIPS_PSF	84.26	12.83	-	-	2.92
MI/PSF	84.46	12.09	3.45	-	-
PDMS/MI/PSF	45.77	27.62	-	26.61	-



(a)
1 µm
Si K series
O K series
S K series
N K series
(b)
2 µm
C K series
N K series
O K series
S K series

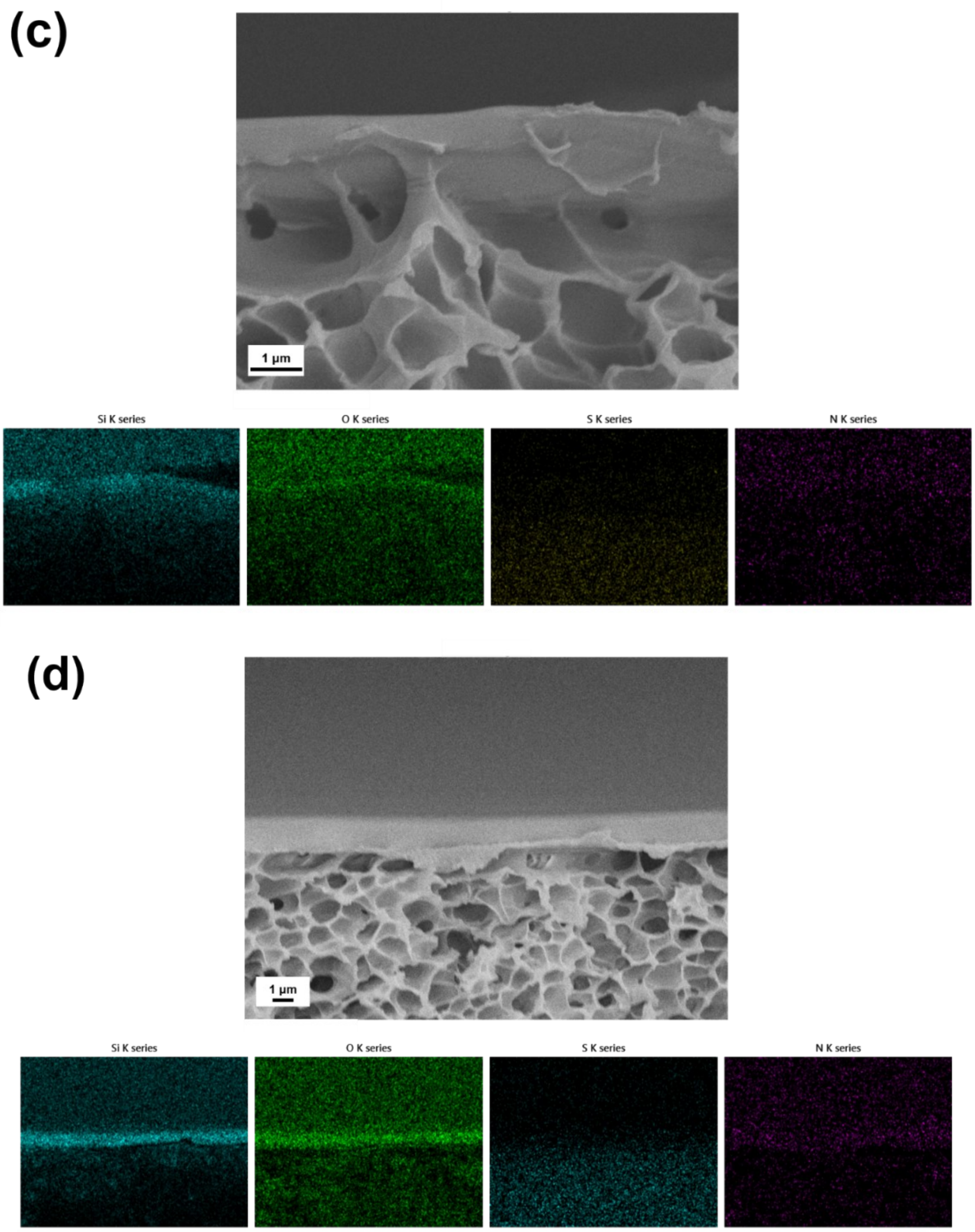


Figure S5. SEM-EDS images of (a) surface images of 5% PDMS/MI/PSF and cross-sectional images of (b) MI/PSF, (c) 5% PDMS/MI/PSF, (d) 10% PDMS/MI/PSF membranes prepared by reverse method

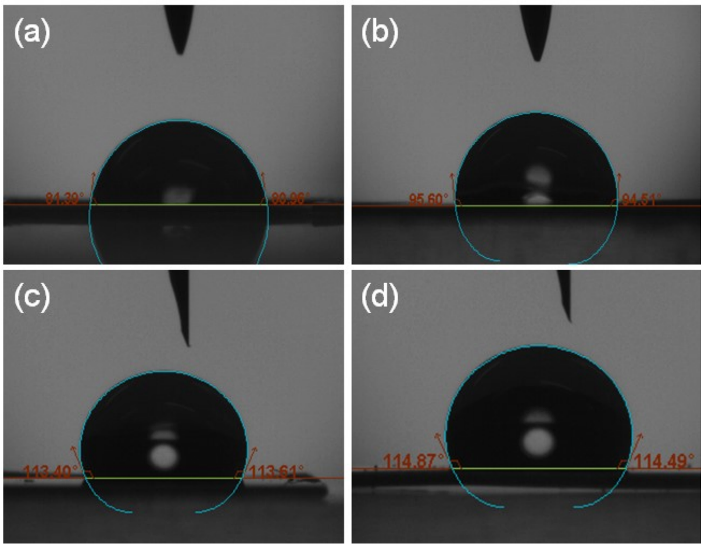


Figure S6. Contact angle of DI water on the membranes with different coatings: (a) NIPS_PSF, (b) MI/PSF, and PDMS/MI/PSF membranes coated with (c) 5% PDMS and (d) 10% PDMS solution

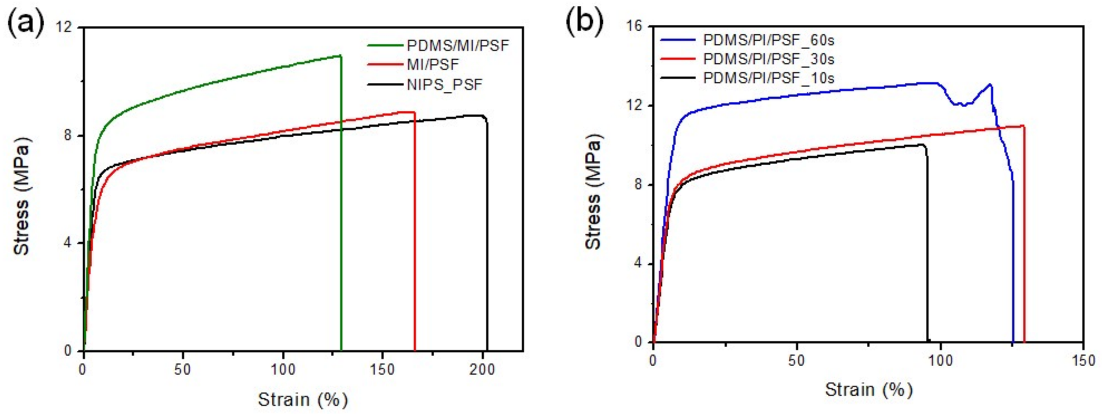


Figure S7. UTM results of (a) membranes with different layers and (b) PDMS/MI/PSF membranes prepared by reverse method with different delay times

Table S2. Gas separation performances of various TFC membranes based on all-polymeric selective layer

Selective Materials	Support Material	P_{feed}(bar)	T(°C)	P_{H2}(GPU)	Selectivity (H_2/CH_4)	Ref
PDMS/PEI	PEI	1	25	4.3	96	[1]
P(DVB-co-ZnTPC)-80	PTMSP	5.07	25	45.0	550	[2]
P(DVB-co-ZnTPC)-40	PTMSP	5.07	25	68.3	210	[2]
P(ZnTPC)-20	PTMSP	5.07	25	272	133	[2]
P(ZnTPC)-40	PTMSP	5.07	25	139	143	[2]
P(ZnTPC)-80	PTMSP	5.07	25	76.9	402	[2]
PBDI	α-Al_2O_3	1	100	71.7	47.5	[3]
Poly(PFMMD)	PAN	3.45	22	1140	57	[4]
Poly(PFMMD-co-PFMD) 1	PAN	3.45	22	1490	80	[4]
Poly(PFMMD-co-PFMD) 2	PAN	3.45	22	1100	157	[4]
Poly(PFMMD-co-PFMD) 3	PAN	3.45	22	1200	162	[4]
Poly(PFMMD-co-CTFE) 1	PAN	3.45	22	633	144	[4]
Poly(PFMMD-co-CTFE) 2	PAN	3.45	22	457	194	[4]
Poly(PFMMD-co-CTFE) 3	PAN	3.45	22	254	284	[4]
Matrimid	PAN/PPS	1.3	20	41.48	44.23	[5]
PDMS/Matrimid	PAN/PPS	1.3	20	40.37	58.82	[5]
X-linked Matrimid	PAN/PPS	1.3	20	47.03	47.96	[5]
Matrimid	PBI/PPS	1	30	16.93	76.17	[6]
Matrimid/PBI	Hollow Fiber	3.5/10	35	43.2	29.6	[7]
PDMS/Matrimid/PBI	Hollow Fiber	3.5/10	35	31.6	141.5	[7]
PDMS/MI_10	PSF	3, 12	30	27.9	69.3	This work
PDMS/MI_30	PSF	3, 12	30	41.4	55.0	This work

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