

Electronic Supplementary Material

Uncovering the effect of poly(ethylene-co-vinyl alcohol) molecular weight and vinyl alcohol content on morphology, antifouling, and permeation properties of polysulfone ultrafiltration membrane: thermodynamic and formation hydrodynamic behavior

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PSF: polysulfone

EVOH: poly (ethylene-co-vinyl alcohol)

NIPS: non-solvent induced phase separation

BSA: bovine serum albumin

DMAC: N,N-dimethylacetamide

TOC: Total Organic Carbon

DSC: differential scanning calorimeter

SEM: scanning electron microscope

XPS: X-ray photoelectron spectroscopy

FTIR: Fourier Transform Infrared Spectroscopy

CA: contact angle

PWF: pure water flux

UV: ultraviolet- spectrophotometer

PRR: the permeance recovery rate

FP: Fouling potential

Schneier theory analyses of PSF and PSF/EVOH polymer blend compatibility

Successful modification of a hydrophobic polymer through blending with a hydrophilic polymer is generally influenced by the compatibility between the polymers under study. The compatibility can be predicted by the mixing of free energy (ΔG_m). In this study, the Schneier theory was used to explore the compatibility of the proposed blended system. Schneier suggested that compatibility can be estimated by calculating the ΔH_m following the Flory-Huggins theory [1,2]. These parameters are listed in **Table S1**[1,3–5].

Table S1. Membrane compositions of the PSF/EVOH membranes

Membranes	VOH content (mol.%)	PSF (g)	EVOH (g)	DMAc (g)	PEG (20 kDa) (g)
PSF	-	-	-	39	6
PSF/EVOH27	73	8.8	2.2	39	6
PSF/EVOH32	68	8.8	2.2	39	6
PSF/EVOH44	56	8.8	2.2	39	6

The Schneier theory suggests that the critical value of mixing enthalpy (ΔH_m) favors the miscibility of the two polymers due to the ΔG_m decrease. If $\Delta H_m \leq 10 \times 10^{-3} \text{ cal/ mol}^{-1}$, the blend composition is considered compatible. If $\Delta H_m \geq 10 \times 10^{-3} \text{ cal/ mol}^{-1}$, the blend composition is considered incompatible. In the case of two polymeric blend systems, ΔH_m can be calculated using **Eq. S1** [2]:

$$\Delta H_m = \left\{ X_1 M_1 \rho_1 (\delta_1 - \delta_2)^2 \left[\frac{X_2}{(1-X_2)M_2 \rho_2 + (1-X_1)M_1 \rho_1} \right]^2 \right\}^{1/2} \quad (\text{S1})$$

where ΔH_m is the enthalpy of mixing (cal/l), X_1 and X_2 are the mass fraction for polymer 1 (PSF in this study) and polymer 2 (EVOH in this study) and should equal one when added together ($X_1+X_2=1$). M is the molecular weight of the repeating units (g/l), δ is the solubility parameter of the polymer (cal/cm³), and ρ is the polymer density (g/mL).

Compatibility between PSF and EVOH: Schneier theory

The compatibility of PSF and EVOH was initially considered as it would substantially impact the structure and properties of the membrane. The solubility parameter method is often used in research and industry to assess the compatibility of polymer blends. There is a comparison of solubility values presented in **Table S2**. Poor miscibility between PSF and EVOH is illustrated by the great difference of solubility values between PSF (9.63 (cal/cm³)^{1/2} and EVOH27 (10.87 (cal/cm³)^{1/2}), EVOH32 (11.05 (cal/cm³)^{1/2}) and EVOH44 (12.95 (cal/cm³)^{1/2}) shown in **Table S2** [2, 4]. To be miscible, two polymers must have close solubility parameters, which means favorable physical affinity and consequently good miscibility [5].

Table S2. Solubility parameters of casting solution components.

Solvents/polymer	Solubility parameter δ (cal/cm³)^{1/2}	Density (g/ml)	Quantity of molecule group (g/mol)
DMAC	11.1	0.937	/
PEG	11.20	1.125	44
PSF	9.63	1.24	442
EVOH27	10.87	1.21	32
EVOH32	11.05	1.19	39
EVOH44	12.95	1.14	42

In addition, **Fig. S1** shows the enthalpy (ΔH_m) of combining different PSF/EVOH mixed systems with different mass ratios. Evidently, when the mass ratio of PSF/EVOH was less than 5.5/94.5 wt.% (Point a) or greater than 94.5/5.5 wt.% (Point b), ΔH_m of the mixing solution has a value less than $10 \times 10^{-3} \text{ cal mol}^{-1}$. It means the PSF/EVOH blend solutions were compatible in the range of the above mass ratios. In brief, the systems were incompatible in most instances.

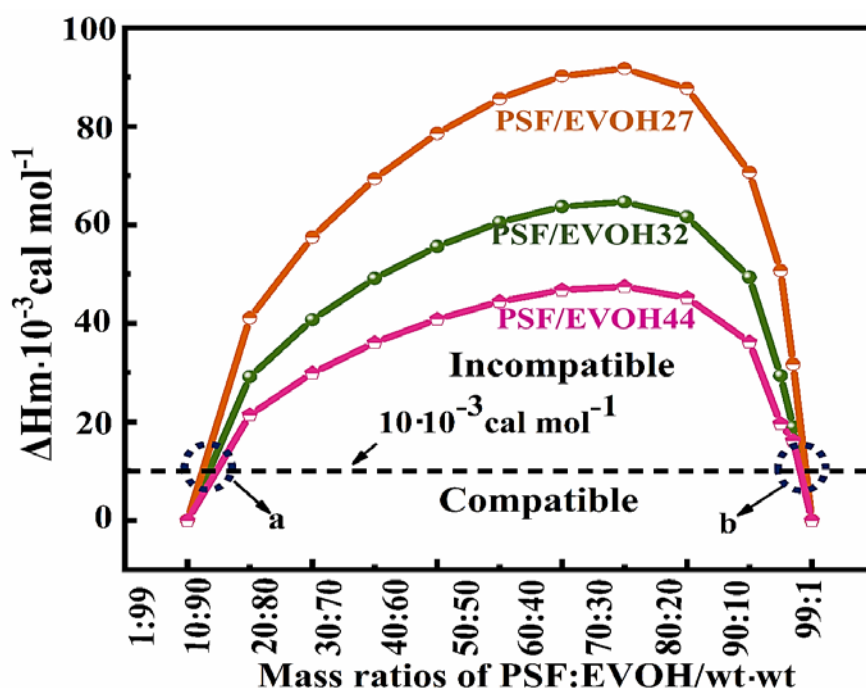


Fig. S1. The mixing enthalpy for different PSF/EVOH systems with different mass ratios.

Essentially, the system is only compatible in two extremely limited contexts. This is to say, the PSF/EVOH blending strategy cannot be used together. On the other hand, hydrogen bonding is made possible by the presence of hydroxyl groups in a mixture. It was therefore expected that the development of miscible blends would result from the presence of additional chemical groups with the ability to participate in hydrogen bonding. PEG as both a compatibilizer and a pore inducer for components was

comparable with the two polymers. The effect of PEG as a compatibilizer was discussed in our previous publication [4].

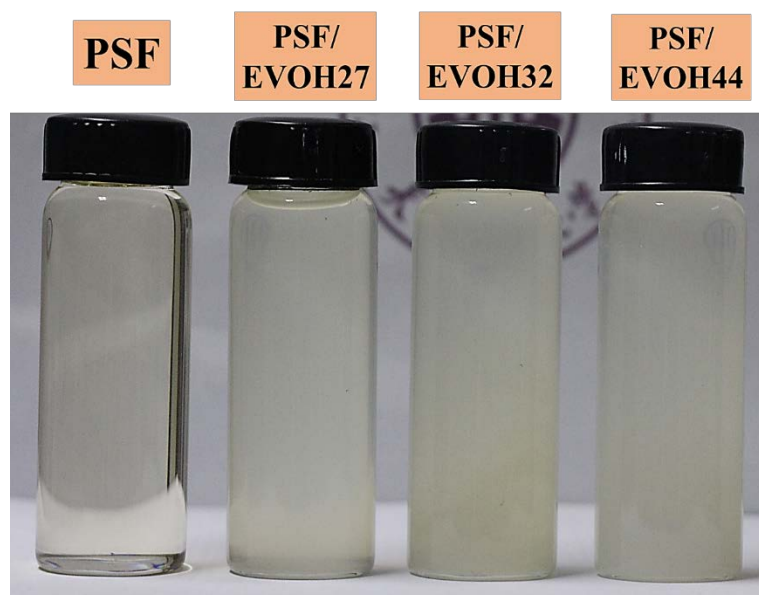


Fig. S2. Digital photos for freshly prepared solutions of polymer blends: PSF, PSF/EVOH27, PSF/EVOH32, PSF/EVOH44 blend systems with PEG20kDa (PSF/EVOH=80/20 wt.%, the polymer concentration of 20 wt.%).

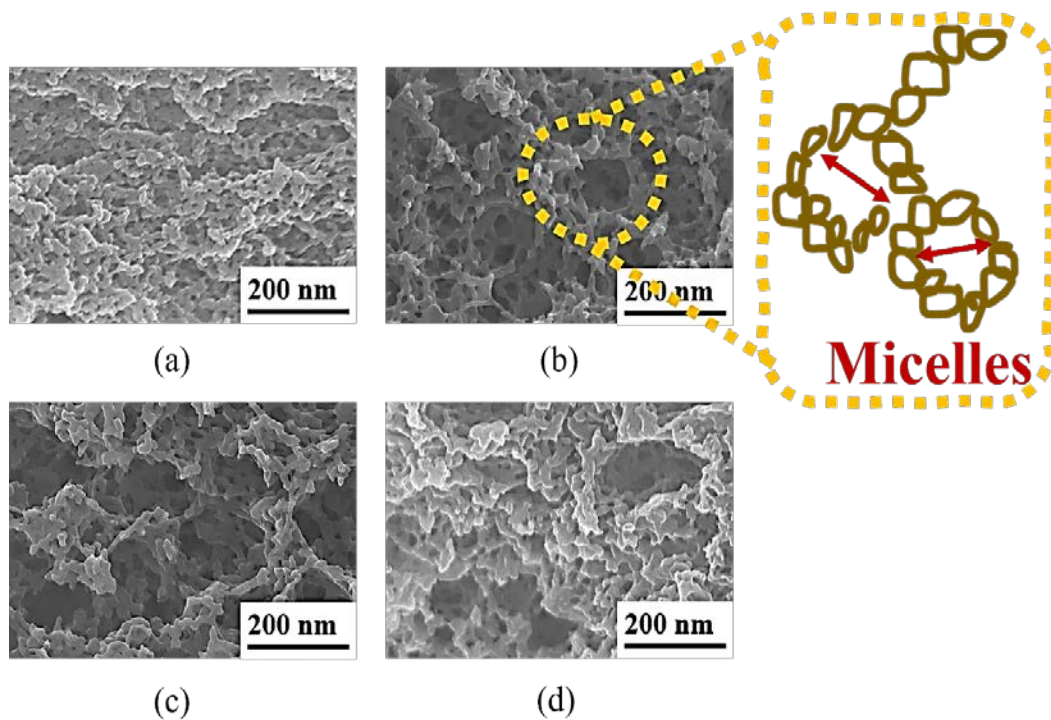


Fig. S3. SEM images of pristine PSF (a) and PSF/EVOH blend membranes obtained from PSF/EVOH27 (80/20 wt.%) PEG(b), PSF/EVOH32 (80/20 wt.%) /PEG(c), PSF/EVOH44 (80/20 wt.%) /PEG(d) blend systems.

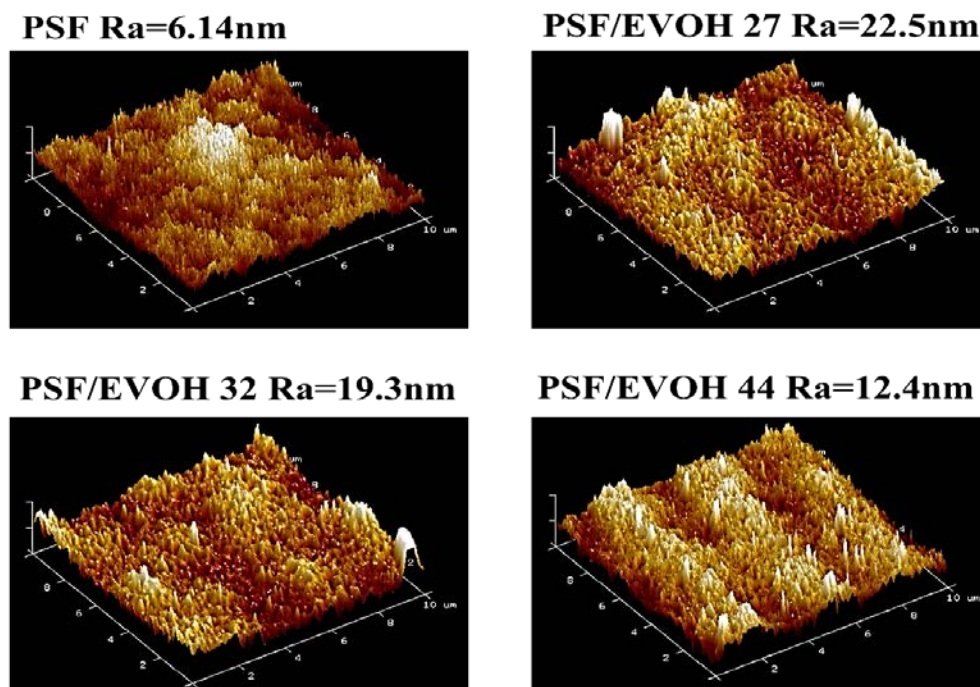


Fig. S4. Topographic anatomy and top surface roughness of pristine PSF and PSF/EVOH blends.

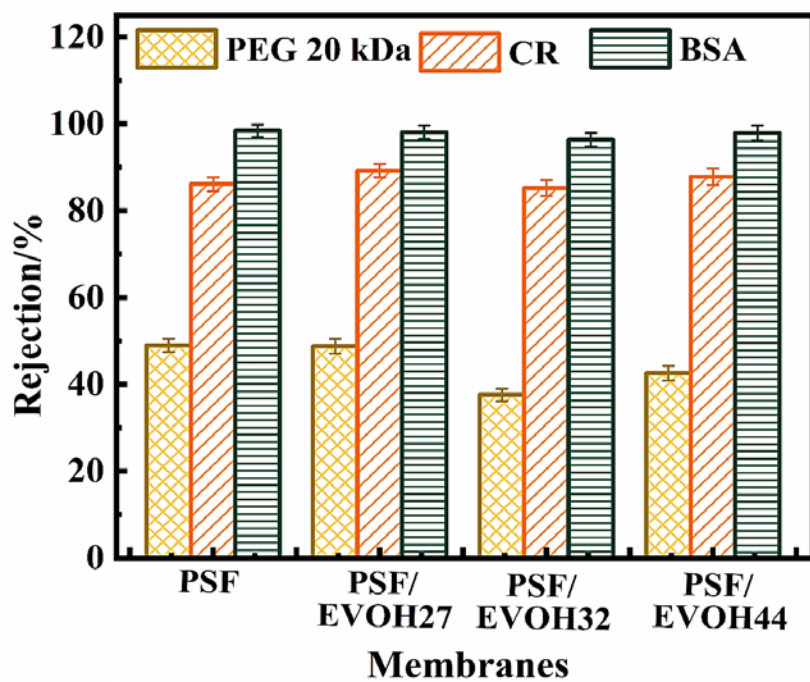


Fig. S5. BSA and CR rejection behavior of pristine PSF and PSF/EVOH blends.

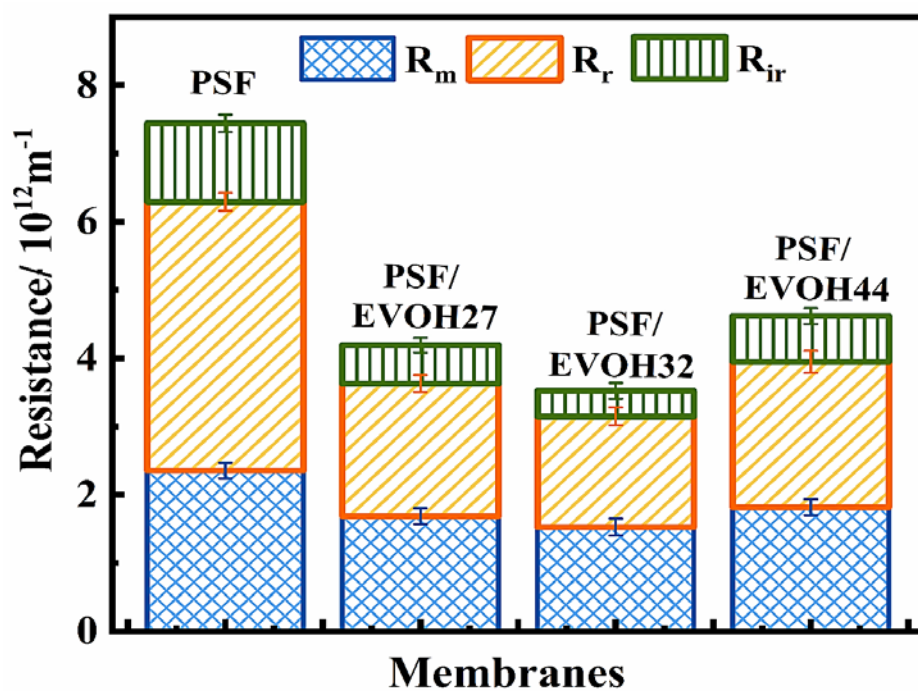


Fig. S6. Series of filtration resistances collected at the operating point (III) for pure water using PSF and PSF/EVOH blends.

References

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