

Hydrophilic and organophilic pervaporation of industrially important α , β and α , ω -diols

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1. Preparation of Polysulfone support:

Polysulfone ultrafiltration membrane was made using the non-solvent induced phase inversion process. First, in a beaker, N-Methyl pyrrolidone (85 and 80 g) was heated to 100 °C. Thereafter, polysulfone granule (15 and 20 g) was added, the solution continuously stirred until complete dissolution of PSF granule. The clear PSF solution was later cooled to room temperature and sonicated for 1 h. After removal of all the air bubble, the PSF solution casted was on the glass plate using applicator. The wet membrane thickness was set to 130 µm. After casting, the membrane with glass plate was immediately immersed in the water at room temperature where the phase inversion took place. The membrane was kept for 30 minute and thereafter washed with fresh water and dried at room temperature. The **Fig S1.** shows cross-sectional FE SEM images 15 wt.% and 20 wt.% PSF membranes. It is seen that; 20 wt.% membrane exhibit dense skin separation layer at surface followed by sublayer with initial finger like structure (closed cellular) follow by macrovoid. On other hand, 15 wt.% membrane thin skin layer followed by finger like structure, it seen that finger like structure are inter connected and continuous (open cellular) followed by macrovoid. Furthermore, dense skin layer in 15 wt. % PSF membrane is more thin compared to that of 20 wt. % PSF membrane. Therefore, 15 wt.% PSF was used to fabricate, PDMS-PSF composite membrane. Higher the concentration polymer (PSF) in casting solution create more thick layer in the membrane structure. [1] The **Fig S2** reflects the pore size distribution in the of 15 wt.% PSF membrane and mean pore size for PSF membrane was 29.5 nm observed.

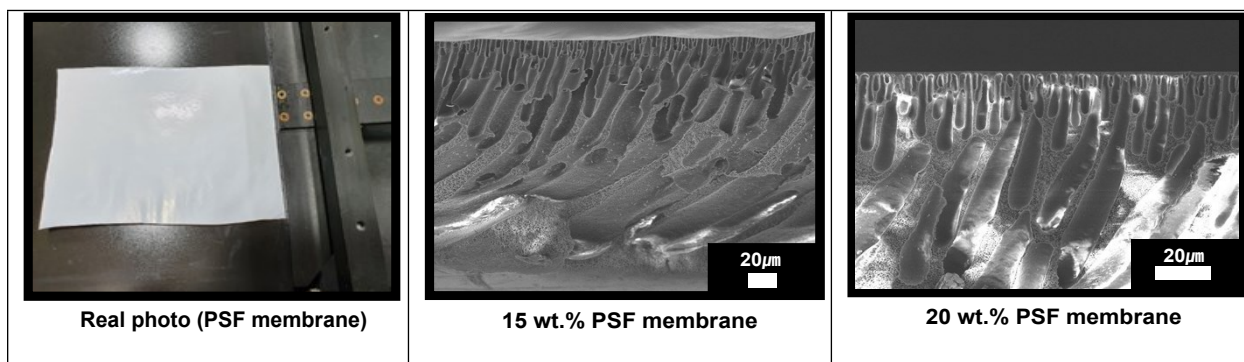


Fig S1 Poly sulfone ultrafiltration asymmetric membrane prepared from the difference concentration of PSF

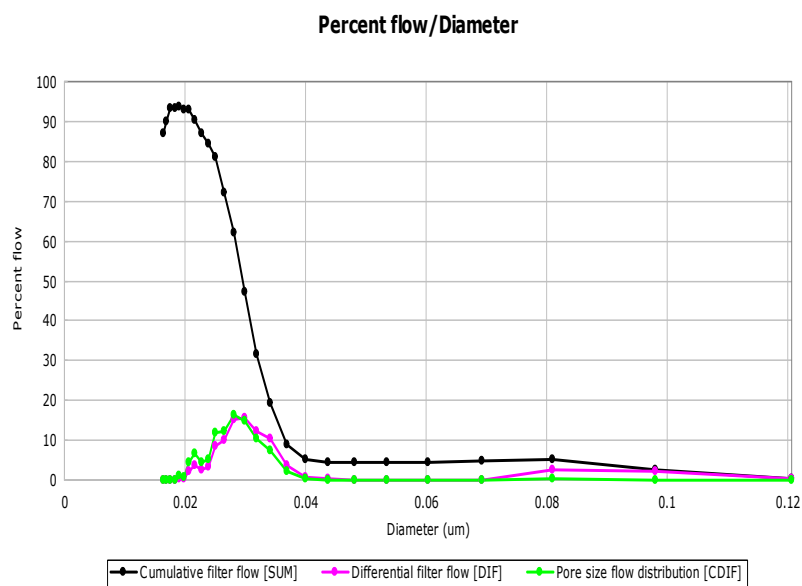


Fig S2 Poly sulfone ultrafiltration (15 wt.%) asymmetric membranes pore size distribution graphs.

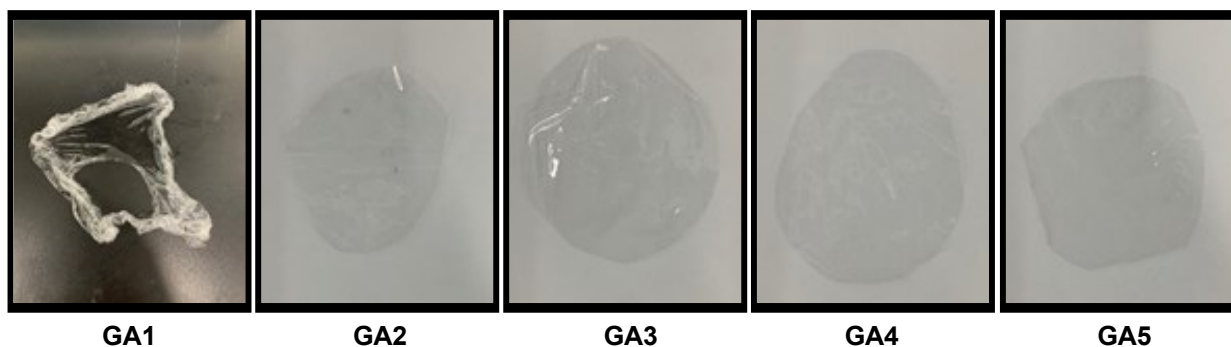


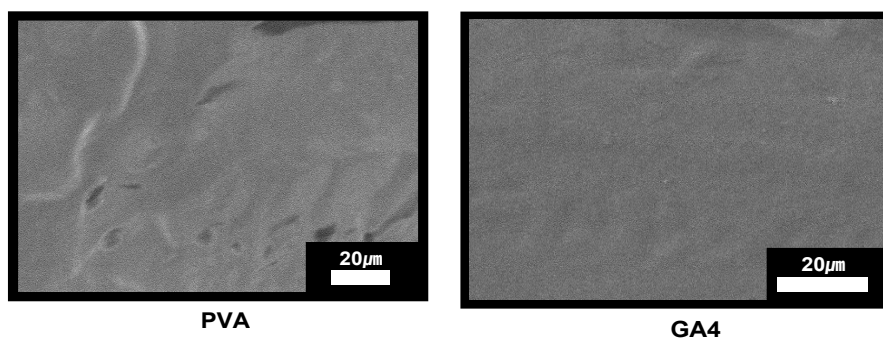
Figure S3. The Real photographs of different degree of glutaraldehyde crosslinked PVA membrane

2. Characterizations of PVA and PDMS membranes

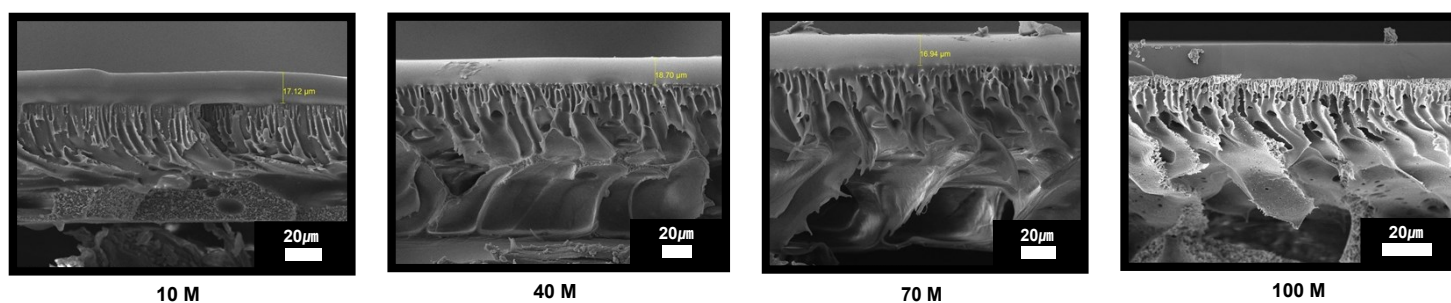
2.1 Field emission scanning electron microscope (FE-SEM) analysis

The pristine PVA and GA4 membrane were analyzed for the examination of cross-sectional morphology by FE-SEM analysis. The FE-SEM cross-sectional micrographs for PVA and GA4 is shown in **Fig S4a**. It can be seen that, there is no obvious different between the both of membranes. Since, polymer matrixes of both of membranes is homogeneous and dense with no visible defect can see from the **Fig. S4a**.

The membranes were designated with respect to different molar ratio of alcoxy in TEOS to hydroxyl in PDMS of the membrane that is 10 M, 40 M, 70 M, 100 M. The thickness of the PDMS active layer of membrane is range from 16 to 20 μm is shown in **Fig. S4b**. Additionally it can be seen from the figure that support and active layer have good adhesion and membrane divided in to three regions and that is active layer followed by finger like porous channel and in bottom macro void is present.



(a)



(b)

Figure S4 a) Cross-sectional micrographs of PVA membranes and b) different PDMS coated PSF membranes

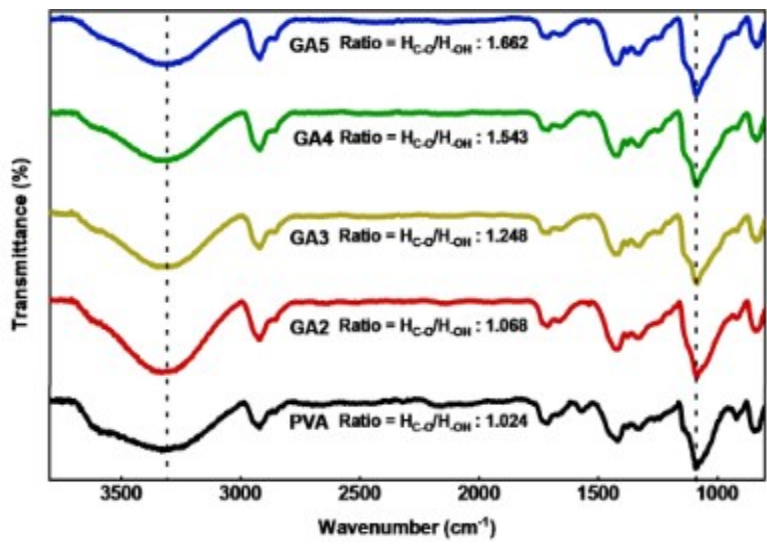
2.2 FTIR analysis

Fig. S5a describes the FTIR spectra of PVA and different GA crosslinked PVA membranes. Characteristic O-H stretching vibration bands at $3320\text{--}3300\text{ cm}^{-1}$ of the PVA hydroxyl groups is observed in all spectra. The stretching peaks in the range of $1080\text{--}1135\text{ cm}^{-1}$ corresponds to formation of acetal linkages between PVA and GA molecules (-C-O-C-) and existence of (-C-O-) functional moieties in PVA backbone can be observed in all the spectra. [2] For crosslinking density calculation of PVA-GA reaction, peak intensity ratio of -C-O-C- group (1090 cm^{-1}) and that of OH group ($3320\text{--}3300\text{ cm}^{-1}$) were calculated [3] and shown in **Fig. S5a**. By increasing in GA content in crosslinking solution, the intensity ratio of peaks corresponds to -C-O-C to -OH was increased and which demonstrate the possible crosslinking reaction between GA

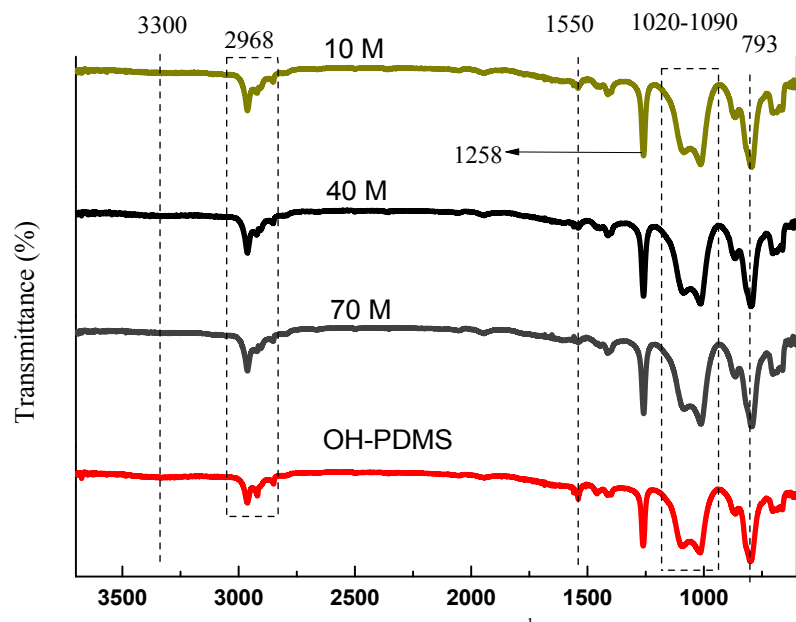
and PVA. Additionally, peaks attributed to the C-H stretching of the aldehyde at 2840 and 2750 cm^{-1} were observed and that reflects the presence of unreacted glutaraldehyde.

Fig. S5b reflects the FTIR spectra of OH-PDMS and all the TEOS crosslinked PDMS membranes. The FTIR peaks at frequency 2968, 1550, 1258, 1020-1090, and 793 cm^{-1} corresponds to $-\text{CH}_3$ (Asymmetric stretching), (Si)-O-H...O (Si) hydrogen bonded with oxygen of siloxane, $-\text{CH}_3$ (symmetric Stretching deformation), Si-O-Si Stretching and Si- CH_3 (stretching) respectively [4-6] can be seen in the **Fig. S5b**. Additionally, in the OH-PDMS spectrum, small broad peak at 3300 cm^{-1} corresponds to OH stretching vibration was observed. However, on reaction of hydroxyl in PDMS and alkoxy in TEOS it was observed that, the peak corresponds to OH stretching vibration (3300 cm^{-1}) diminished as well decreased of intensity of hydrogen bonded peaks at 1550 cm^{-1} can be seen from the OH-PDMS to 70 M membrane. Additionally, Peak corresponding to Si-O-Si is also slightly increased with increase of TEOS content, therefore, it is confirming the crosslinking of OH-Terminated PDMS with TEOS. There is report in the literature, which dictates the condensation reaction of OH in PDMS and alcoxide in TEOS and as well as OH in PVA and CHO in glutaraldehyde is spontaneous and in their work they postulated reaction mechanism of PVA-GA and PDMS reaction.

Therefore, based on the FTIR analysis carried out in this study and that of in literature survey [7-11] a postulated reaction scheme for both of PDMS-TEOS and PVA-Glutaraldehyde is shown in **Fig. S6**.



(a)



(b)

Fig. S5 FTIR (ATR mode) spectra for a) PVA, PVA-GA crosslinked membrane and (b) OH PDMS and different PDMS free standing membrane

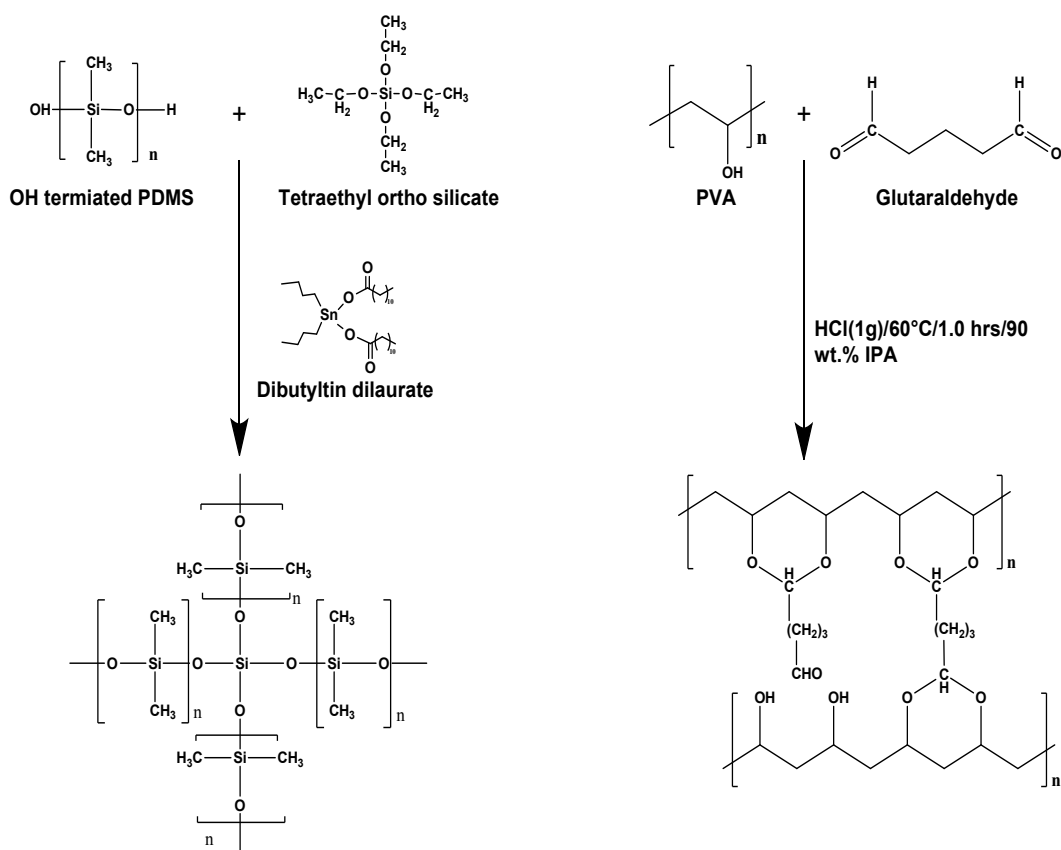


Fig. S6 Postulated crosslinking reaction schemes for PVA-glutaraldehyde and OH-PDMS-TEOS membranes.

2.3 Thermogravimetric analysis

Fig. S7 shows the TGA curves for PVA and GA crosslinked PVA membranes. It is shown that, the thermal stability of PVA membrane have increased due to the crosslinking. Since degradation temperature of PVA membrane was shifted from 250 °C to 340 °C this due to the presence cross-linked acetal linkage due to crosslinking reaction GA and PVA [12]

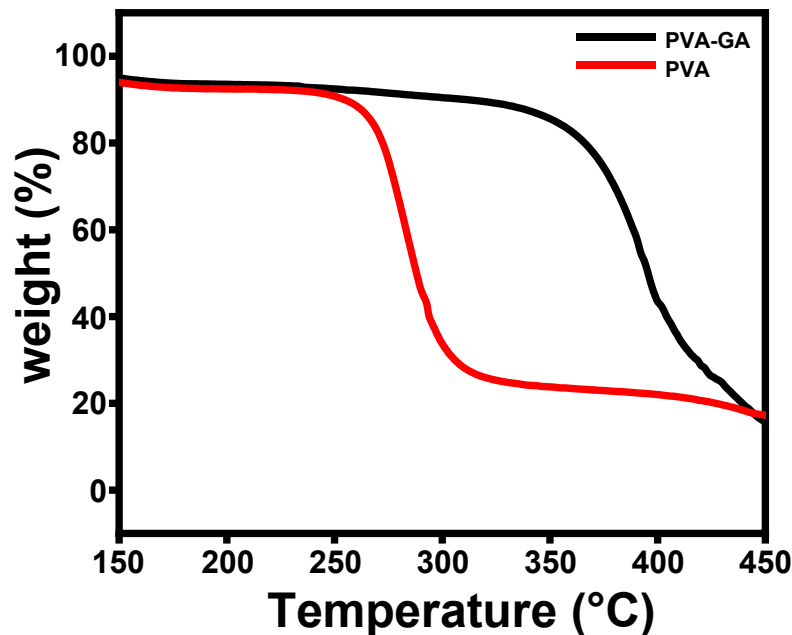


Fig S7. TGA curve of PVA and GA-PVA crosslinked membrane

2.4 Swelling study

The extent of membrane swelling in specific liquids depends on the crosslinking density, the morphology of the membrane, and the free volume available in the membrane matrix, which strongly affects the sorption mechanism. Therefore, it is important to measure the degree of swelling because, in the PV process, this controls the transport of the permeating molecules under a chemical potential gradient. **Fig. S8** shows effect crosslinking density on swelling degree of membrane swelling with feed containing 25/75 1,2 HDO/water at 30 °C performed for 24 h. It seen that, the degree of membrane swelling decreased with crosslinking density as GA increased from the 2 to 5 wt.%, the degree of membrane swelling decreased from 345 to 139%.

Further **Fig. S8** also shows the effect of GA content on the tensile strength of membrane. Commentary to swelling degree, as GA acts as crosslinking agent when increased which reduces the free volume as well

as PVA chain mobility in the membrane structure and therefore increases the tensile strength of membrane [13].

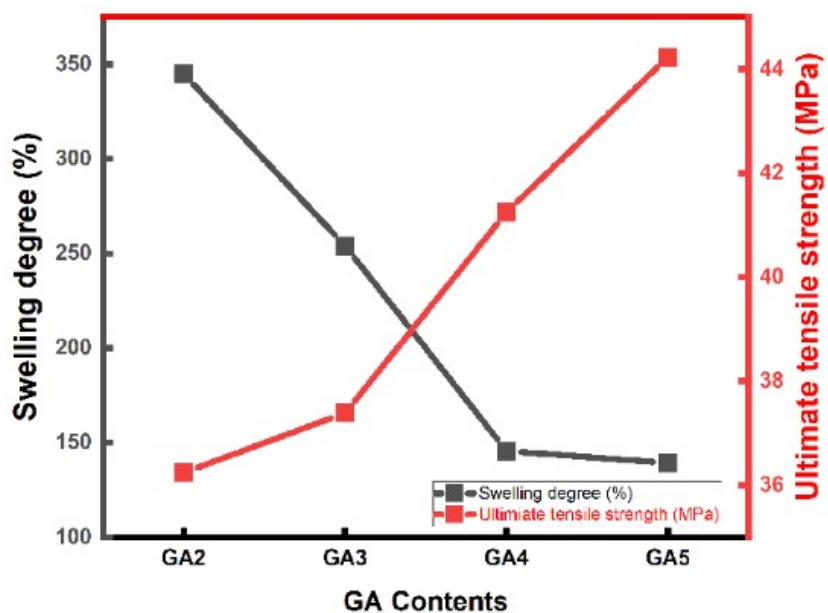


Figure S8 Effect of GA concentration in crosslinking solution on membrane swelling, feed 25/75 (1,2 HDO/water, w/w %) at 30 °C and Tensile strength.

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