Cellulose - Polyethyleneimine Blend Membranes with Anomalous Nanofiltration Performance

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Highlights:

- Low-cost cellulose/polyethyleneimine blend membranes were manufactured.
- The blend membranes showed higher rejections than the corresponding pure membranes.
- The blend membranes showed higher fluxes than the corresponding pure membranes.
- High rejection of negatively charged dyes was obtained combined with an exceptionally high flux.

Abstract

A unique method for the preparation of cellulose-polyethyleneimine (PEI) blend membranes for nanofiltration is presented. Trimethylsilyl cellulose was used as a precursor for the blend membrane fabrication followed by a simple hydrolysis to regenerate the cellulose structure. The resulting homogeneous blend membranes exhibited high neutral solute rejection in water, which was surprisingly better than the performance of the individual membranes due to the strong interactions between the blended polymers. More interestingly, the same membrane demonstrated over five times higher flux of methanol after solvent activation with water as compared to the fluxes of the pure membranes, attributed to formation of nanocracks. High rejection of negatively charged dyes in this solvent with around 450 Da molecular weight cut-off was obtained at an exceptionally high flux of $160 \text{ Lm}^{-2}\text{h}^{-1}$ at a 4.5 bar filtration. The membranes will be beneficial in nanofiltration of polar solvents containing neutral and charged molecules.

1 Introduction

Membrane technology is emerging as a viable process for molecular separation that offers numerous benefits over the conventional processes [1, 2]. It consumes lower energy, generates smaller footprint, and can be operated in a much simpler way. It is projected to consume up to one-tenth of the energy currently used for the conventional distillation [1]. In particular, nanofiltration is developed for molecular separation on the basis of size and charge differences. Beyond drinking

water production and wastewater treatment, nanofiltration has also been applied for the separations carried in organic solvents such as in the pharmaceutical [3, 4], petroleum [5] and food industry [6]. It is essential to produce membranes with sufficiently high flux and rejection, but it is at least as important to identify an environmentally friendly and simple manufacturing process.

Cellulose has emerged as an indispensable membrane material due to its abundant availability, low cost, and environment benignancy. Moreover, cellulose exhibits fascinating physiochemical properties attributed to the repeating β -D-glucopyranose molecules that are covalently bound through acetal linkages (β -1,4-glucan), making it chemically resistant and mechanically robust. However, this unique molecular architecture also leads to cellulose insolubility in the common organic solvents. Only very few usable solvents are known and those are often highly reactive, toxic or impractical for industrial use. Moreover, cellulose membranes typically possess meso- or macropores [7-14], making them suitable only for ultra- or microfiltration. Recently, we proposed the convenient fabrication of cellulose composite membranes using trimethylsilyl cellulose (TMSC) as a precursor [15-18]. The membrane is readily regenerated back into cellulose through an acidic vapor-phase hydrolysis (VPH). Unlike the typical cellulose membranes, cellulose regenerated from TMSC possess micropores suitable for nanofiltration and gas separations. This method has also enabled the fabrication of previously unfeasible cellulose-polydimethylsiloxane blend membranes that are suitable for organic solvent nanofiltration and ethanol-water pervaporation [19].

In this study, we further explored the functionality of our cellulose membrane in combination with polyethyleneimine (PEI) simply by physical blending. Physical blending is a time- and cost-effective method to modulate the membrane performance and often remarkably enhances the properties of the corresponding pure polymers [20, 21]. PEI is an inexpensive and low-toxic commercial polymer that has been used in a wide range of membrane applications. PEI has been employed as a cross-linker to modify membrane surfaces, especially in the fabrication of positively charged nanofiltration membranes [22-29]. Due to its stability in a range of solvents, PEI membranes have also been used for organic solvent nanofiltration with various degrees of success [26, 27, 30]. Combination of PEI and cellulose as an adsorbent has been carried out in the preparation of heterogeneous suspensions [25] or for a two-step cellulose modification [31, 32], as their different solubility characteristics do not allow direct blending. To our knowledge, the fabrication of cellulose-PEI blend membrane for nanofiltration has never been reported.

Herein, the idea of blending was pursued by mixing TMSC and branched PEI in chloroform for the membrane fabrication through solution coating, followed by cellulose regeneration and PEI crosslinking. The two polymers are well-miscible without visible phase separation, enabling the creation of homogeneous blend polymers. The abundant hydroxyl and amine groups present in cellulose and PEI respectively are expected to result in strong hydrogen bond interactions useful for the membrane size-sieving properties. Successful fabrication of the blend membranes was proved by infrared spectroscopy and elemental analysis. Membrane performance was evaluated in nanofiltration of neutral and anionic solutes carried out in water and methanol, respectively. The membrane water fluxes were significantly higher than their corresponding methanol fluxes. Therefore, the membranes were subjected to water as an activating solvent prior to methanol filtration. A similar approach has been previously demonstrated with polyamide membranes using dimethylformamide or dimethyl sulfoxide as a swelling agent; the activated membranes exhibited dramatically higher fluxes without compromising the rejection [33-35].

2 Experimental

2.1 Materials

TMSC ($M_w = 122,900 \text{ g mol}^{-1}$, $M_n = 44,700 \text{ g mol}^{-1}$, degree of silylation (D_s) = 2.2, polydispersity index (PDI) = 2.75) was prepared from microcrystalline cellulose (Avicel PH101, Fluka) and was characterized according to our previous work [16, 17]. In brief, cellulose was reacted with hexamethyldisilazane (HMDS) in dimethylacetamide/lithium chloride solvent system at 80°C, followed by product precipitation in methanol and vacuum drying. Branched polyethyleneimine ($M_w = 25,000 \text{ g mol}^{-1}$, $M_n = 10,000 \text{ g mol}^{-1}$) was obtained from Sigma Aldrich. Polyacrylonitrile (PAN) ultrafiltration membrane (20-50 nm pore size) that was supplied by GMT GmbH Germany was used as a support. All other reagents including chloroform, terephthaloyl chloride (TCL), *n*-hexane, hydrochloric acid (HCl), polyethylene glycol (PEG) (200, 400, 600 and 1000 g mol^{-1}) and dyes (listed in Table 1) were purchased from Sigma Aldrich. MilliQ water was used in all water-related experiments.

Figure 1. Fabrication of cellulose-PEI blend membranes on top of PAN support.

2.2 Membrane Preparation

Coating solutions were prepared by dissolving TMSC and PEI (pure polymers or weight ratio of 1:1) in chloroform at room temperature, as detailed in Table 2. The total polymer concentration was set at 2 wt%, except for one variation of the blend membrane (RC-PEI_{1,60}). Schematic of the membrane preparation procedure is presented in Figure 1. Polymer deposition on the PAN support was carried out by spin coating of the polymer solution at a 4,000 rpm speed and 500 rpm^{-1} acceleration. Pure regenerated cellulose (RC) membranes were obtained through a vapor-phase hydrolysis (VPH) of the TMSC coated membranes using 10 wt% HCl solution. Details about the VPH method has been described in our previous work [17]. All membranes, except for the unregenerated TMSC, underwent crosslinking in 0.25 wt% TCL in hexane for 10 min followed by washing of the unreacted crosslinker with hexane and air drying.

Table 1. Dye markers used in the filtration study.

Dye	M_w (gmol ⁻¹)	Charge	Chemical structure
Methyl orange	327.3	-1
Primuline	475.5	-1
Remazol brilliant blue R	626.5	-2
Brilliant blue R	826.0	-1
Reactive black 5	991.8	-4

Table 2. Compositions of the fabricated membranes and their post-treatment.

Membrane	TMSC (wt%)	PEI (wt%)	VPH	Crosslinking
TMSC	2	-	-	-
RC	2	-	15 min	0.25 wt% TCL, 10min
PEI	-	2	-	0.25 wt% TCL, 10min
RC-PEI _{2,15}	1	1	15 min	0.25 wt% TCL, 10min
RC-PEI _{2,60}	1	1	60 min	0.25 wt% TCL, 10min
RC-PEI _{1,60}	0.5	0.5	60 min	0.25 wt% TCL, 10min

2.3 Characterizations

Typically, about 2-3 membranes of each variation were characterized. The attenuated total reflection – infrared (ATR-IR) spectra of the membranes were collected using a Fischer Scientific Nicolet iS10 spectrometer and were recorded in the range between 500 and 4,000 cm^{-1} over 16 scans. The bare PAN support was measured as a background. Energy-dispersive X-ray spectroscopy (EDX) analysis was performed using an OXFORD EDX equipped with an X-MaxN detector, an 80 mm^2 SDD sensor and AZtecEnergy analysis software. The accelerating voltage was 5 keV with a probe current of 2 nA. The membrane surface zeta potential was tested using a SurPASS electrokinetic analyzer (Anton Paar, Austria) with a background of 10 mM NaCl solution. Titration was carried out from basic to acidic pH with the addition of a 0.1M HCl solution. The membrane hydrophilicity was determined by a dynamic water contact angle (WCA) measurement using a Kruss drop shape analyzer—DSA100 with monochrome interline CCD camera over 60 s. The drop volume was 2 μL . Surface and cross-section SEM imaging were performed on the 3 nm iridium-coated membranes using a Zeiss Merlin microscope (Carl Zeiss NTS GmbH, Oberkochen, Germany) at about 4 mm working distance. Prior to mounting, the samples for cross-section imaging were fractured in liquid nitrogen. The surface topographies were analyzed by an atomic force microscopy (AFM) on an ICON Veeco microscope operating in the tapping mode using commercial silicon TM AFM tips (MPP 12100). Spectroscopic ellipsometer J. A. Woollam M-2000 DI equipped with focusing optics (short axis 300 micron) was used to determine the membrane thicknesses. Three angles of incidence (i.e. 65, 70 and 75 degrees) were used in a wavelength range of 193 – 1,690 nm, and 3 different locations were measured on each sample. The thicknesses were determined using the well-known Cauchy formula, following the method described in literature [36].

2.4 Nanofiltration Study

All nanofiltration experiments were carried out using a commercial HP4750 dead-end filtration cell (Sterlitech Corporation, USA) with an effective area of 13.85 cm² and pressurized by nitrogen. The membrane flux, J_w (Lm⁻²h⁻¹), which is the pressure-normalized flux, was calculated using eq. (1),

$$J_w = \frac{V}{A \times \Delta t} \quad (1)$$

where V is the volume of the permeate (L), A is the active membrane area (m²), and Δt is the time for permeate collection (h). Rejection experiments were carried out either using PEG (1 gL⁻¹) or dye solution (20 mgL⁻¹, Table 1) as markers. Rejection values were determined as a ratio of permeate concentration over the averaged concentration of the initial and final feed solution following eq. (2). The concentration of dyes and PEG was monitored using a NanoDrop 2000/2000c spectrophotometer (Thermo Fisher Scientific) and a gel permeation chromatography (GPC), respectively.

$$\text{Rejection (\%)} = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2)$$

3 Results and Discussion

3.1 Membrane Chemical and Physical Properties

3.1.1 ATR - IR

The IR spectra of the membranes are presented in Figure 2. Silylation of cellulose into TMSC was confirmed by the appearance of Si-C stretching vibrations at 747, 838 and 1,248 cm⁻¹, explaining its solubility in various nonpolar and polar aprotic solvents. Upon 15 min of hydrolysis (VPH), the Si-C peaks disappeared in the RC spectrum, indicating a complete regeneration of cellulose. Furthermore, the completion of cellulose regeneration was also validated by the appearance of strong peaks at 3,340 cm⁻¹ and 1,050 cm⁻¹, which corresponded to the reorganized O-H and C-O bonds in the cellulose chains, respectively. The presence of N-H stretching vibration of amine groups at 3,425 cm⁻¹, which is the characteristic bond of PEI, was observed both in the pure PEI and RC-PEI blends, as expected. Owing to the presence of a large amount of base (proton acceptor) in the PEI chains, the Si-C peaks were still observed in the RC-PEI_{2,15} spectrum after 15 min VPH. Hence, a longer reaction of 60 min was performed on the RC-PEI_{2,60} membrane to allow a complete

regeneration. In the case of blend membranes, crosslinking by TCL mainly occurred on the primary and secondary amine of PEI and was confirmed by the appearance of the C=O stretching of amide groups evidenced at around $1,610\text{ cm}^{-1}$. The cellulose hydroxyl was crosslinked to a lesser extent, which is seen in the RC spectrum as a small ester peak near $1,750\text{ cm}^{-1}$. Due to the lower reactivity of the cellulose hydroxyl, it can be assumed that frequently only one of the TCL carboxylic acid chloride group reacts, leaving the second group free to be hydrolyzed to carboxylic acid. Moreover, cellulose has a typical densely packed structure due to the intensive hydrogen bonds present in the inter- and intra-molecules. TMSC is a disordered form of cellulose, suggesting that upon mixing, the PEI chains will be well-entrapped in the blend network. After complete TMSC hydrolysis one glucose unit consists of 5 oxygen atoms with free electron pairs (see Figure S1); along with the large amount of -NH- groups in the PEI chains, a strong hydrogen bond interaction between the two polymers can be expected.

Figure 2. ATR-IR spectra of the TMSC, regenerated cellulose (RC), PEI and the corresponding RC-PEI blend membranes.

3.1.2 EDX

Energy-dispersive X-ray (EDX) map presented in Figure 3 displays the blending quality of the two polymers in the blend membranes. The presence of nitrogen and oxygen represent the characteristic atom of PEI and cellulose, respectively. Even though cellulose was mixed with PEI while in the form of hydrophobic TMSC, the results suggested a homogenous distribution of all characteristic elements without observable microphase separation, which was indicative of the well polymer mixing. This remark is concomitant with the hypothesis about the hydrogen bond interaction within the blend network. The good compatibility between cellulose and PEI has also been recognized in the paper manufacturing industry, where PEI was used as a surface modifier for cellulose fibers [37]. In addition to the polymer miscibility, the absence of silicon on the EDX map highlighted the complete cleavage of the silyl groups in TMSC upon the 60 min acidic hydrolysis.

Figure 3. EDX elemental map of the RC-PEI_{2,60} and RC-PEI_{1,60} membrane.

3.1.3 Water contact angle

Surface properties of the membranes were examined by measuring the dynamic water contact angles (WCA). First, we characterized the WCA of the RC-PEI_{2,60} membrane right after coating (unregenerated and uncrosslinked) to support our conclusion on the completion of the hydrolysis. Figure 4A shows the dynamic water contact angle of the membrane before and after 60 min VPH. A high WCA of around 112° was observed for the membrane before VPH due to the hydrophobic silyl groups in TMSC, which was also reported in our previous work [16, 17]. After hydrolysis, the membrane contact angle decreased significantly to around 40°, confirming the complete evolution of TMSC into cellulose as also earlier deduced from the FTIR results (Figure 2).

Figure 4. Dynamic water contact angle of **A.** the uncrosslinked RC-PEI_{2,60} before and after VPH, and **B.** all the crosslinked membranes.

Water contact angles of the crosslinked membranes were measured to investigate the crosslinker effects on the membrane hydrophilicity (Figure 4B). As branched PEI is a water-soluble polymer, high surface hydrophilicity is expected. However, one molecule of the crosslinker (TCL) contains one aromatic ring that is hydrophobic in nature. As a result, the crosslinking of PEI with TCL increases the water contact angle due to the increase in hydrophobicity. Cellulose on the other hand is a hydrophilic polymer; a WCA of around 30° was observed for the crosslinked RC membrane. This value is a typical WCA for cellulose films as reported in the literature [38-41], but is slightly higher than the WCA of our previously reported uncrosslinked cellulose membrane [17], indicating the low degree of the crosslinking. In the case of blend RC-PEI membranes, the contribution of the strong hydrophilicity of the cellulose on the membrane surface explains their lower WCA than that

of the PEI membrane. Furthermore, the WCA of RC-PEI_{2,60} was higher than that of the RC-PEI_{1,60} most probably due to the higher presence of TCL on the RC-PEI_{2,60} surface. We also speculated that the presence of defects, which will be discussed in the next section, also contributed to the lower WCA of the RC-PEI_{1,60} membrane.

3.1.4 SEM and AFM

Morphological characterization of the membranes fabricated from RC, PEI, and their blends showed a thin and dense selective layer on the top of porous PAN supports as presented in Figure 5. The good adherence between the active layer and support was observed in all of the cross-sectional SEM images. The membrane thicknesses determined by ellipsometry are presented in Table 3. The RC membrane displayed to be the thickest, with the thickness around 500 nm, which was similar to it of the RC-PEI_{2,60}. On the other hand, the PEI membrane was found to be around 200 nm thick, which was close to the thickness of the RC-PEI_{1,60}.

The SEM and AFM images of the membrane surfaces also suggested that the PAN supports were uniformly covered by the active layer without any observable voids. The blend membranes showed a rougher surface profile than the pure membranes with a root-mean-square (R_{RMS}) of 18.6 and 26.06 for RC-PEI_{2,60} and RC-PEI_{1,60}, respectively. Formation of the crater-like structure on the blend membranes was probably associated with water condensation upon polymer coating, which is similar to the breath figure phenomena [42-44]. The solvent (chloroform) is hydrophobic, it evaporates fast and cools down upon evaporation; this can induce the formation of water microdroplets on the surface due to the condensation of the water vapor in the atmosphere (around 50% relative humidity). However, the blend surface also contained some hydrophilic PEI segment that will keep the water droplets sitting on the surface upon the fast solvent evaporation, imprinting the crater-like feature. This phenomenon was not observed in the spin coating of TMSC solution alone probably due to the slippery effect raised from the high surface hydrophobicity. Water repellency of the strongly hydrophobic surfaces has been long recognized in nature as in the case of lotus leaves [45] and in the synthetic superhydrophobic surfaces [46, 47]. In our case, the strongly hydrophobic polymer solution in combination with the high spinning speed repelled the microdroplets, preventing it from sitting on the surface. In the case of PEI alone, owing to its high hydrophilicity the water molecules quickly penetrated into the membrane instead of forming droplets, resulting in smoother surface profile.

Figure 5. SEM and AFM images of RC, PEI and the blend membranes.

Table 3. Membranes thicknesses determined using ellipsometry.

Membrane	Thickness (nm)
RC	548.3 ± 27.5

PEI	185.7 ± 13.3
RC-PEI _{2,60}	518.0 ± 27.4
RC-PEI _{1,60}	242.3 ± 8.5

3.1.5 Zeta Potential

Figure 6 shows that the RC membrane was negatively charged at $\text{pH} > 5$ mainly due to the deprotonation of the large amount of hydroxyl groups as well as the oxidation of the aldehyde on the cellulose end-groups into carboxylic acids upon acidic hydrolysis (VPH), as previously reported in the literature [48-51]. The zeta potential was very similar to that of the uncrosslinked RC membranes [15], again signifying the minor effects of the crosslinking. As a cationic polymer, PEI should possess a positive zeta potential at neutral pH [23, 25, 26, 28]. However, upon crosslinking, the free acyl groups of the crosslinking agent (TCL) will be easily deprotonated into carboxylic acids and thus contribute to the overall surface charges. The negative zeta potential of the crosslinked PEI membrane (isoelectric point around pH 4) indicated the significant presence of the deprotonated TCL. A similar finding of a negative surface charge of PEI membranes in neutral pH was also reported in the literature and was attributed to the TCL crosslinking [52]. The isoelectric point of the RC-PEI_{2,60} membrane was similar to that of the RC membrane, with less surface charges especially in basic pH. This was probably caused by the presence of hydrogen bonds between the PEI and cellulose chains that impeded further reaction with TCL.

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5 Figure 6. Electrokinetic properties of the membranes.

5.2 Nanofiltration Performance Evaluation

The nanofiltration performance of the RC-PEI blend membranes was evaluated and compared with that of the RC and PEI membrane. PEG aqueous solutions with a concentration of 1 gL^{-1} were used as feed. Typically, the performance of the blend polymeric membranes falls between that of the pure membranes. In this experiment, the pure RC membrane exhibited a water flux of $6 \text{ Lm}^{-2}\text{h}^{-1}$ (feed pressure 4.5 bar) with a rejection to PEG 400 Da of around 80%, whilst the PEI membrane had a higher flux of around $8 \text{ Lm}^{-2}\text{h}^{-1}$ with a lower PEG rejection, as expected from the permeability-selectivity trade-off. To our surprise, the blend RC-PEI_{2,60} membrane showed a better rejection of this PEG up to 90% with the estimated molecular weight cut-off of about 400 Da, while demonstrating a similar flux to that of the pure PEI membrane. We speculated that this anomalous behavior can be attributed to the created hydrogen bonds between the blending polymer matrices that led to hindered passage of the solute molecules. Having a thinner blend membrane (RC-PEI_{1,60}) (see Table 3) however sacrificed the rejection possibly due to the presence of defects, which allow the PEG molecules to pass easily. In addition, the performance of the blend membranes was found to be stable over 2 weeks of filtration and immersion in water (see Figure S2), indicating no issue of polymer leaching. In addition to the great manifestation of crosslinkages, this could again be a beneficial effect of the strong interaction within the blend network.

Figure 7. Nanofiltration performance using water as a solvent. **A.** water flux, **B.** PEG rejection. Feed pressure: 4.5 bar.

Intrigued by the interesting results obtained in the filtration of aqueous solutions, we then continued to investigate the membrane performance using another polar solvent. Among the typical industrial solvents, methanol was chosen as it is heavily used particularly in the chemical, agricultural and pharmaceutical industries. Herein, the negatively charged dyes were used as markers as they are easily detected by UV/Vis spectroscopy and are present in a wide range of molecular weights. In this study, our results showed that all the membranes, except the RC-PEI_{1,60}, demonstrated a similar flux of around 2 Lm⁻²h⁻¹, which was lower than their corresponding water fluxes.

Both PEI and cellulose are strongly hydrophilic, favoring the permeation of highly polar solvents across their swollen matrices. Compared to water, methanol has a lower polarity index (methanol = 5.1; water = 10.2) that could lead to less membrane swelling in the membrane and result in lower fluxes. Inspired by these flux differences, the membranes were soaked in water for minimum 6 hours, prior to the experiment with methanol. We speculated that this activation step could keep the membrane matrix in a highly swollen state during filtration of the less polar solvent. According to the results presented in Figure 8A, the solvent activation led to no significant flux enhancements in the case of the pure membranes, while surprisingly improved the flux of the RC-PEI_{2,60} membrane by more than four times as compared to its value before activation. This interesting finding could probably be explained by the presence of nanocracks at the polymer-polymer interfaces that were formed during soaking in water, considering that cellulose and PEI have different swelling behavior. These gaps then served as additional channels for the solvent passage, resulting in higher

flux. This hypothesis is drawn according to the fact that similar activation effect was not observed in the pure membranes. This phenomenon is probably analogue to the role of nanocracks in the hydrophobic-coated hydrophilic membrane as water channels and self-regulating valves to control the membrane humidity [53]. The RC-PEI_{1,60} membrane displayed approximately similar flux before and after activation since the contribution of the pin-holes were more dominant.

Using dyes as markers, all the membranes showed good rejections in methanol regardless the solvent activation (Figure 8B-C). Given that the membranes (see Figure 6) and the dyes are negatively charged, the higher dye rejections were strongly attributed to the charge repulsion effects, which would still be noticeable in the polar solvents like methanol. The implication of this electrostatic interaction was more obvious in the case of the RC-PEI_{1,60} membrane. Even though this membrane displayed poor rejection to the neutral PEG, much higher dye rejections with around 450 Da molecular weight cut-off were obtained at a remarkably high flux of 160 Lm⁻²h⁻¹, indicating that the pin-hole sizes were not large enough to hinder the strong repulsion interaction between the membrane wall and the solutes. These charge effects can be beneficial in the organic solvent nanofiltration of charged pharmaceutical compounds such as insulin, phenylephrine, N-acetylprocainamide, procaine, and naphazoline.

Proven that cellulose regenerated from TMSC exhibits very low to zero rejection to monovalent salts [15, 16] combined with the typical capability of PEI membranes in removing heavy metals [32, 54-57], our blend membranes could also find applications in the di- and monovalent salt separations currently required in many industrial processes. Our work also provides a simple route to combine cellulose with any other polymers that are soluble in the same solvents as TMSC, with a good compatibility.

Figure 8. Nanofiltration performance using methanol as a solvent. **A.** methanol flux before and after solvent activation with water, and dye rejection of the membranes **B.** before and **C.** after activation with water. Feed pressure: 4.5 bar.

Conclusions

Nanofiltration membranes with an unusual separation performance were prepared by blending trimethylsilyl cellulose (TMSC), a cellulose precursor, and branched polyethyleneimine (PEI) followed by a simple cellulose regeneration method. Both polymers mixed very well in the fabricated membranes and interacted through hydrogen bonds, improving the membrane sieving properties. This was reflected in the higher rejection of the blend membranes as compared to the performance of the pure membranes. The blend membranes also exhibited a higher flux of methanol after solvent activation with water, most probably due to the presence of nanocracks. High rejection of the negatively charged dyes with around 450 Da molecular weight cut-off in this solvent was accompanied by an extraordinary high flux of $160 \text{ Lm}^{-2}\text{h}^{-1}$ flux at a 4.5 bar filtration, attributed to

the charge effects. The membranes could be useful for the nanomolecules separations found in chemical and pharmaceutical industries.

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