Blended Polysulfone/Polyethersulfone (PSF/PES) Membrane with Enhanced Antifouling Property for Separation of Succinate from Organic Acids from Fermentation Broth

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ABSTRACT: Biofouling is a serious challenge in the separation of succinic acid from fermentation broth because of its complex mixture containing substantial amount of dissociated and nondissociated forms of dissolved organics, metabolites, residual mineral salts, and bacteria. A robust blended polysulfone/ polyethersulfone (PSF/PES) membrane was fabricated and presented in this study for alleviating the challenges encountered during biobased succinic acid separation. PSF/PES membranes were fabricated at varying compositions of polymers via the phase inversion technique and coated with poly(vinyl) alcohol (PVA) to enhance its antifouling properties. The synthesized membranes



were characterized for surface morphology, surface functionalities, thermal stability, surface hydrophilicity, and mechanical properties by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis, contact angle measurement, and nanotensile tests, respectively. The performances of PSF/PES membranes for succinic recovery were evaluated from a synthetic fermentation broth, consisting of succinate, formate, and acetate. Influence of different process conditions such as polymer compositions, feed concentrations, and filtration pressures were investigated on the fabricated membranes. From the SEM results, the fabricated membranes showed the formation of pores with a dense outer surface. The membranes also displayed exceptional thermal stability based on the consistent FTIR and contact angle analysis. A notable higher pure water flux of 114.60 $\text{Lm}^{-2} \text{ h}^{-1}$ was observed for 100% PES/PVA and 128.40 $\text{Lm}^{-2} \text{ h}^{-1}$ pure water flux for the 75% PSF/PES-blended membrane coated with PVA. The rejection performance improved with decreasing pressure and low feed concentration. The PSF/PES-blended membrane exhibited a high succinate rejection of 99.9% from synthetic broth. It can be concluded that the PSF/PES/PVA-coated membrane has a great potential in applications for succinic acid separation from synthetic fermentation broth.

KEYWORDS: antifouling properties, blended polymer membranes, fermentation broth, filtration, polyethersulfone, polysulfone, succinic acid

INTRODUCTION

A yearly increase in the market demand for succinic acid (SA) because of its high product value has led to exhaustion of its raw material, *n*-butane.¹ There is a rapid increase in the price of crude oil, causing a high increase in the price of chemically produced SA. Moreover, the process of SA production from nonrenewable sources is less eco-friendly.¹ Thus far, numerous techniques such as reactive extraction,¹ ion-exchange resin,² electrodialysis, precipitation, and pressure filtration^{3,4} have been utilized to separate and purify SA from the fermentation broth.

The advent of innovative technology or upgrading of the existing systems is necessary for effective separation of SA from fermentation broth. Membrane-based separation processes, such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis, are relatively environmentally benign, with process stability and easy scale-up, as compared to traditional processes.⁵ Lately, such processes have received

much consideration in the biochemical industry owing to the modular design, simplicity of operation, less energy consumption, and less usage of chemicals.⁶ UF membranes have been extensively utilized for the separation of solid suspensions or dissolved organic macromolecules,^{7,8} specifically proteins,⁹ in food processing, wastewater treatment, and pharmaceutical manufacturing. This could be due to their unique benefits such as low operating costs, improved separation effectiveness, and ease of operation.¹⁰ Polysulfone (PSF),¹¹ polyethersulfone



Figure 1. Chemical structure of (a) PSF, (b) PES, and (c) PVA.

(PES),¹² cellulose acetate (CA),¹³ polyacrylonitrile (PAN),¹⁴ and polyvinylidene fluoride¹⁵ are frequently utilized as starting materials for commercial fabrication of UF membranes.

Among them, PES and PSF (see Figure 1) have been widely reported for use in the treatment of water, owing to their good membrane-forming performances, remarkable thermal stability, visual transparency, outstanding solubility, and selectivity, as compared to other matching polymers.¹⁶ Furthermore, they are easy to manufacture, affordable, and readily available in commercial markets. Conversely, they are both well-known to be hydrophobic in nature, causing fouling of the membrane and inadequate mechanical strength; hence, their industrial applications as membranes are still limited.¹⁷ Blending of polymers is another common method of improving the hydrophilicity of the membrane. Blending of these PES and PSF polymers can therefore enhance the mechanical, modulus, and thermal stability of the membrane. The optimum composition of these two polymers has been investigated to provide improved separation efficiency of the membrane.^{17,18} Rameetse et al.¹⁷ blended PSF and PES-infused carbon nanotubes for wastewater treatment. Additives such as hydrophilic polymers, amphiphilic copolymers, and inorganic particles are regularly used.¹⁹ Chen et al.²⁰ blended amphiphilic block copolymers, PSF-block-polyethylene glycol, with the PSF base polymer to prepare PSF UF membranes. The blended membranes displayed instantaneous increase in permeability, better fouling resistance, and improved hydrophilicity. Nevertheless, the membrane antifouling ability could not withstand long-term stability due to polyethyleneglycol homopolymer leaching in water during the membrane formation and application.²⁰ Therefore, to improve the performance of blended polymer membranes and overcome the challenge of low resistance to fouling, membrane coatings with a material having hydrophilic properties, such as poly(vinyl) alcohol (PVA), can be employed.

Membrane fouling is regarded as one of the prevalent challenges in its application for SA separation and purification as it restricts and affects the membrane performance. Biofouling is a serious issue in the separation and purification of fermentation broth owing to its complex mixture containing a substantial amount of dissociated and nondissociated forms of metabolites, residual mineral salts, dissolved organics, and bacteria.² Separation of a high-purity final product (SA) with improved yield from dissolved organic acids, such as formic, lactic, malic, or acetic acids, has remained a challenge. This is because of the presence of a substantial number of residues such as unreacted glycerol, magnesium(II), and calcium(II) inorganic salts. In addition, a huge amount of lactose or ethanol in the actual postfermentation broth remains after application of the UF process.²² Membrane fouling, resulting in the decrease in membrane permeability, is a major setback in SA recovery and purification. This is due to the accumulated impurities such as proteins, cell debris, salts, and dead-cell deposits, which form a cake layer on the membrane surface after constant operation.^{23,24} Reports have showed that the increase in membrane fouling due to concentration polarization aids the rejection of small inert organic compounds.^{22,25} Therefore, to improve the separation efficiency of SAs from other components in the fermentation broth, a polymer material with excellent properties, robust stability, and improved antifouling properties is required. Researchers have recently focused on the application of polymer membranes for separation of SA from fermentation broth. Wang et al.²⁶ utilized different types of PES UF membranes to clarify microbial cells and proteins from fermentation broth. The membranes showed rapid susceptibility to fouling at high flux during filtration. A succinate rejection of 43.41% was achieved and displayed 17.11 Lm⁻² h⁻¹ permeate flux and 43.31%. However, susceptibility of these membranes to fouling is the major drawback.²⁶ Law and Mohammad²⁷ evaluated the performance of an NF membrane (NF270) for separation of SA from synthetic fermentation broth at different concentrations of the solutes (succinate, acetate, and formate), using a dead-end filtration cell. It was reported that 93.4% succinate rejection was achieved by the membrane. Furthermore, Prochaska et al.²⁸ utilized a three-step separation technique for obtaining SA from an actual fermentation broth. A UF tubular ceramic membrane (TiO₂/ZrO₂), having an effective surface area of 0.0042 m², was used as an intermediate step, with 90% succinate rejection.

To this end, the UF membrane is regarded as one of the developing eco-friendly techniques having the ability to selectively recover SA from fermentation broth by controlling both the membrane type used and the process parameters for optimum separation.²⁵ The performance of the blended PSF/PES membranes has been primarily evaluated for water treatment and proteins with limited studies on recovery of SA from a fermentation broth. This is the first report on the application of this blended PSF/PES membrane for the recovery of SA. It is a study in progress to established proof of concept upon which further studies could be carried out. Thus, results from this study could be instrumental to developing membranes with high performance for SA recovery on a commercial scale, if the membrane synthesis processes are optimized.

Therefore, a robust blended polymeric membrane with exceptional properties which has a limited application for separation of SA with enhanced antifouling properties is investigated for trade-off selectivity and rejection performance in this study. Further modification of blended polymer membranes (PSF/PES) by the cross-linking process using a highly hydrophilic cross-linker PVA (Figure 1) is studied, as the cross-linking process may possibly prepare the membrane for long-term application in concentrated product/byproduct composition.

MATERIALS AND EXPERIMENTAL PROCEDURES

Materials. SA (99%), acetic acid (96%), formic acid (98%), PSF (in bead form with a molecular weight of 22,000 g/mol), pure PES (M_w = 58,000 g/mol with density = 1000 g), and solvent (*N*,*N*-dimethylacetamide, DMA, 97%) were purchased from Merck (Pty) Ltd., South Africa. PVA 87–90% hydrolyzed (average M_w = 30,000–

70,000) was used for membrane coating, and maleic acid was used as a cross-linking agent. All chemicals were used as supplied without any further purification. The nitrogen gas was purchased from AFROX, South Africa. Deionized water and synthetic fermentation broth were prepared in-house.

Fabrication of a Mixed Matrix Membrane. The membranes were fabricated, via the phase inversion technique as described by Daramola et al.²⁹ and Remeetse et al.¹⁷ 20% of PSF/PES pellets measured by weight at varying compositions (100:0, 0:100, 75:25, 50:50, and 25:75) were dissolved in 50 mL of DMA under constant agitation for 12 h, at a temperature of 25 °C. The polymer solution was cast using a doctor blade set at 150 μ m on smooth glass. The glass, together with the solution, was dipped into deionized water for the phase separation step. The fabricated membrane was allowed to dry at room temperature for 24 h.

Membrane Coating. The fabricated membranes were coated by following a procedure reported elsewhere.³⁰ A total of 1 g of PVA was dissolved in 100 mL of deionized water and stirred at 90 °C to form a coating solution. The cross-linking solution was prepared by dissolving 1 g of maleic acid in deionized water to a total volume of 100 mL. The membranes were immersed in the PVA solution for 3 min after which they were cross-linked by immersing into maleic acid solution for an extra 3 min. The membranes were then dried in an oven at 60 °C overnight and characterized.

Characterization of Nanoparticles and Membranes. Scanning electron microscopy (SEM) images of the fabricated membranes were obtained using ZEIS SEM at an accelerating voltage of 20 kV. A portion of the membrane was cut and immersed into liquid nitrogen for the cross section and another part was cut for the surface and both were coated with carbon and gold-palladium and subjected to SEM for observation. Chemical functionalities of the synthesized membranes were checked using a PerkinElmer Fourier transform infrared (FTIR) spectrometer equipped with a high-performance deuterated triglycine sulfate detector and KBr beam splitter. The thermal behavior of the fabricated membrane was determined using a TA instrument SDT Q600 simultaneous DSC/TGA analyzer. The heating rate was 20 °C/ min from room temperature to 800 °C and a nitrogen gas flow of 50 mL/min. The mechanical properties of the membranes were evaluated using a TA.XT plus texture analyzer at a speed of 8.6 mm/s and ambient temperature. The contact angle of the membranes was measured using the sessile drop method (OCA 15 EC GOP, Data physics). Deionized water was used as a probe liquid dispensed at a dosing rate of 1 μ L/s. Equilibrium water content (EWC) can be defined as the moisture level where the membrane neither loses nor gains moisture and it is directly related to porosity.³¹ This is usually done to check how much water a membrane can absorb. EWC is calculated using eq 1

$$EWC = \frac{W_{\rm w} - W_{\rm d}}{W_{\rm w}} \times 100\%$$
⁽¹⁾

where $W_{\rm w}$ is the wet weight of the membrane and $W_{\rm d}$ is the dry weight of the membrane.

The porosity of the membrane measures up the void spaces created by pores within the membrane and was calculated by the mass loss of the wet membrane after drying up using eq 2.^{31,32}

$$porosity = \frac{W_w - W_d}{\rho \cdot V} \times 100\%$$
(2)

where ρ stands for the density of water and V is the membrane total volume.

Performance Evaluation of Fabricated Membranes. Synthesis of Single, Binary, and Ternary Solutions of Organic Acids. A synthetic fermentation broth consisting of single-solute, binary-solute, and ternary-solute solutions of SA (118.09 Da), formic acid (46.03 Da), and acetic acid (60.05 Da) was prepared, to evaluate the performance of the fabricated membranes for selective separation of SA in a fermentation broth. The composition of the three-component synthetic solution is comparable to the permeate solution after UF of a real postfermentation broth. The synthetic solutions were prepared by dilution with deionized water of a conductivity not exceeding 3 μ S/cm.

The single (succinate), binary (succinate and formate), and ternary (succinate, formate, and acetate) mixed salt model solution was prepared at varying concentrations of 500, 100, and 100 mg/L, respectively. Sodium hydroxide (NaOH) was used to regulate the pH of the acid solutions to 7 to resemble SA-based fermentation broth.

Performance Evaluation of the Fabricated Membranes. The performance of the membranes was evaluated using a dead-end filtration cell. The dead-end filtration setup consists of a filtration cell where feed is poured, inert nitrogen gas inlet pipe, stirrer bar, and pressure gauge. The setup was fitted with one membrane with an effective membrane surface of 0.0034 m² at a time during the separation. Deionized water was used as pure water. Pure water permeation through the membrane was used to determine the original flux of the membrane for fouling monitoring.^{29,33} The system was equilibrated by soaking the membranes in deionized water overnight before each experiment so as to allow the pores to open and give easy passage of water.²⁷ The nitrogen gas was used to apply pressure into the filtration cell. A stirrer plate together with a magnetic bar in the filtration cell was used to maintain a homogeneous solution. The permeate from the filtration cell was collected in a measuring cylinder, and the permeate volume was recorded. Membrane fluxes for pure water flux, succinate, formate, and acetate (single-, binary-, and ternary-solute solutions) were collected after 1 h at varying pressures (1-5 bars) and calculated using eq 3. The analysis of the permeate was performed using a precalibrated high-performance liquid chromatography model, with an Aminex HPX-87H (300 mm \times 7.8 mm) column equipped with a UV/vis detector. 5 mM sulfuric acid was used as a mobile phase and about 10 μ L of the sample was injected into the column at a flow rate of 0.6 mL/min and 210 nm wavelength. The rejections (selectivity) of succinate by the membranes were obtained using eq 4

$$J_{\rm p} = \frac{V_{\rm p}}{A \cdot t} \tag{3}$$

$$R_{\rm i} = \frac{C_{\rm fi} - C_{\rm pi}}{C_{\rm fi}} \times 100 \tag{4}$$

where J_p is the permeate flux (L/h m²), V_p is the permeate volume (L), A is the effective area of the membrane, t is the time (h), R_i is the succinate rejection in percentage, and $C_{\rm fi}$ and $C_{\rm pi}$ are feed and permeate concentration of succinate, respectively (mg/L).

For each component, retention R(%) (eq 4) can also be defined as

$$R = 1 - \frac{C_p}{C_r} \tag{5}$$

where C_p and C_r are the permeate and retentate (or feed) concentrations, respectively.³⁴

To evaluate the flux recovery of the synthesized membranes, the membranes were cleaned with deionized water for 1 h at 1 bar and flux recovery performance of the membranes was evaluated. The ability of the membrane to recover from fouling was calculated by the flux recovery ratio (FRR) (eq 6). A better antifouling property is indicated by a higher FRR. This indicates that there is a low reduction in flux over time and it is easy to restore the membrane flux with cleaning.³²

$$FRR = \frac{J_{wp}}{J_w} \times 100\%$$
(6)

FRR represents the flux recovery ratio, J_w stands for the initial pure water flux, and J_{wp} represents the water flux of the cleaned membrane. The filtration setup for separation of succinate from organic acids in a simulated fermentation broth is as shown in Figure 2.

RESULTS AND DISCUSSION

Physicochemical Properties of Fabricated Membranes. Table 1 shows the EWC of the fabricated membranes as measured using eq 1. EWC is a vital parameter for characterization indicating the hydrophobicity and hydrophilicity of a membrane. Likewise, it is associated with the



Figure 2. Filtration setup for separation of succinate from organic acids in a simulated fermentation broth.

Table 1. EWC and Porosity of Fabricated Membranes

membrane	EWC (%)	porosity (%)
100% PSF	58.44	41.46 ± 4.7
75% PSF/25% PES	56.26	46.21 ± 6.5
100% PES	62.42	54.80 ± 3.0
75% PES/25% PSF	63.50	57.55 ± 4.4
50% PSF/50% PES	75.10	60.08 ± 2.0
100% PSF/PVA	62.08	53.68 ± 2.5
100% PES/PVA	80.50	64.10 ± 3.8
75% PES/25% PSFPVA	79.60	67.00 ± 1.8
75% PSF/25% PESPVA	70.50	58.50 ± 2.0

membrane porosity. The porosity ε is the ratio of the volume of pores to the total volume of the porous membrane.³⁵ Membrane pores provide room for water molecules to pass through. The results in Table 1 indicate that the pure PES membrane has a higher water content of 62.42%, compared to pure PSF having 58.44% water content. However, blending of PES and PSF increased the membrane water content³⁶ as could be observed

with 25% PSF/75% PES membrane with 63.50% water content. This is also evident with the 50% PSF/50% PES which has the highest EWC of 75.17% and a porosity of 60.08% among the membranes with no PVA coat. Rameetse et al.¹⁷ also reported a similar observation. Similarly, PVA is shown to improve the EWC of the fabricated membranes as could be observed for 100% PSF and 100% PES coated with hydrophilic PVA, having 62.08% and 80.50%, respectively, compared to their pure PSF and pure PES without coating. The increase in the water content could be attributed to the hydroxyl group on the surface of the PVA molecule.³⁷

The porosity of the membranes is relative to the EWC. The higher the porosity, the higher the water content of the membrane. Membrane porosity in this study was determined and calculated from eq 2 from the weight of the membranes in wet and dry states. The results are presented in Table 1. As observed, the porosity of PES (54.80%) is higher than that of PSF (41.46%), which could be responsible for the higher water content observed. This is an indication that there is availability of pores for easy passage of water. In addition, blending PSF and PES (with higher or equal percentage of PES) has shown to enhance the membrane porosity with a porosity of the 75% PES/25% of PSF membrane (57.55%) higher than that of the corresponding 100% PES (54.80%).³⁸ The results obtained in this study are consistent with the literature.^{39,40}

Surface Morphology of Fabricated Membranes. Figure 3a–d depicts the surface morphologies of (a) 100% PSF, (b) 100% PES, (c) 75% PSF/25% PES, and (d) 25% PSF/75% PES membranes. The surface morphologies of the fabricated membranes show the formation of pores with a dense outer surface.⁴¹ The SEM image of pure PSF in Figure 3a shows clear and uniform morphological features. The layers of 100% PSF, 100% PES, 75% PSF/25% PES, and 25% PSF/75% PES membranes are highly porous with visible pores. It can be seen that the pore sizes of the membranes increased upon blending (Figure 3c,d), which may result in enhanced flux and permeability of the membranes during filtration.⁴⁰



Figure 3. Surface morphologies of (a) 100% PSF, (b) 100% PES, (c) 75% PSF/25% PES, and (d) 25% PSF/75% PES.



Figure 4. Cross-sectional views of (a) 100% PSF, (b) 100% PES, (c) 25% PSF/75% PES, (d) 50% PSF/50% PES, and (e) 75% PSF/25% PES.

Figure 4 depicts the cross-sectional view of (a) 100% PSF, (b) 100% PES, (c) 25% PSF/75% PES, (d) 50% PSF/50% PES, and (e) 75% PSF/25% PES. Figure 4a,b shows cross-sectional views of the fabricated membranes with the characteristic asymmetric structure with a dense skin top layer and porous sublayer with a large pore wall thickness. A similar observation was reported by Ngobeni et al.⁴² for pure PSF. Machodi and Daramola⁴³ reported the same observation for PES membranes. The SEM images of the cross-sectional view of the membrane in Figure 4c,d are illustrated by a layer of finger-like pores that further merge into macrovoids at the bottom, comparable to other reported studies on blended membranes.¹⁷ Furthermore, it can be seen that the macrovoids are vertical to the surface of the membrane. This alignment could provide enhanced water flux through the membrane.⁴⁴

Figure 5a,b depicts the surface morphology of the PVA-coated fabricated membranes, 75% PFF/25% PES (PVA) and 25%



Figure 5. Surface morphology of (a) 75% PFF/25% PES (PVA) and (b) 25% PSF/75% PES (PVA).

PSF/75% PES (PVA), respectively. A PVA layer can be observed on top of the porous layers of the fabricated membranes indicating no evidently visible pores on the SEM images. The results obtained in this study are consistent with the work of Maphutha et al.⁴⁵ and Rameetse et al.¹⁷

Thermal Stability of Fabricated Membranes. Figure 6 illustrates the (a) TGA profile of 100% PSF, 100% PES, and 75% PSF/25% PES and (b) thermograms of 100% PSF, 100% PES, and blended membranes (coated and noncoated). According to

Ayyaru and Ahn,46 the TGA profile revealed that PES membranes decomposed between the temperatures of 400 and 500 °C. This agrees with the current study. PES weight loss is significant at a temperature below 400 °C, as compared to the PSF membrane at about 500 °C. As it can be seen from the thermogram in Figure 6b, the PES membrane exhibited the minimum thermal stability. Figure 6a,b also shows that blended membranes (PES/PSF) are more thermally stable compared to nonblended membranes. Good thermal stability of all blended membranes is indicative of little weight loss observed below 500 °C, with a 25% PSF/75% PES membrane having the highest thermal stability among all. Figure 6b shows the derivative weight loss curve of the fabricated membrane. Occurrence of a single peak of all is a confirmation that the polymers are uniformly blended. This is indicating that no separation of phase occurred during polymer blending.

Surface Functionalities of Fabricated Membranes. FTIR has been extensively used to describe surface functionalities of polymers and blended polymer membranes.⁴³ FTIR spectra of the fabricated pure PSF, pure PES, blended PSF/PES, and PVA-coated membrane samples are depicted in Figure 7. All the fabricated membranes showed similar characteristics. The observed peak at 629 cm⁻¹ is ascribed to the C-O stretching and 837-873 cm⁻¹ is attributed to the C=C stretching on the aromatic ring structure. The peaks at 1153, 1244, and 1325 cm⁻¹ could be ascribed to the sulfonyl (O=S=O) group, whereas the aromatic ether (C-O-C) group is signified by the peak at 1296 cm^{-1} .⁴⁴ The sharp peak observed at 706 cm⁻¹ indicates the C-S stretching. The peak observed at $2890-2940 \text{ cm}^{-1}$ could be attributed to C-H stretching of an alkane. The broad band at 3365 cm⁻¹ identified in the spectra of 25% PSF/75% PES/PVA [see Figure 7, spectrum (b)] corresponds to the stretching vibration of O-H, which could be attributed to the characteristic hydroxyl group of the cross-linking network, signifying the successful coating of the fabricated membranes with a PVA layer. Observations reported in this study are consistent with the literature.43,44,48

Atomic Force Microscopy (Surface Roughness) of Fabricated Membranes. Figure 8a-d represents the 3-D atomic force microscopy (AFM) images, indicating the surface roughness of pure PSF (100% PSF), pure PES (100% PES),



Figure 6. (a) TGA profile and (b) thermograms of 100% PSF, 100% PES, and blended membranes (coated and noncoated).

blended PSF/PES (25% PSF/75% PES), and blended PSF/PES coated with PVA (25% PSF/75% PES/PVA) membranes, respectively. $R_{\rm a}$ and $R_{\rm ms}$ represent the mean and root mean square roughness of the membranes, respectively. It could be observed that Figure 8a has the highest surface average roughness of 130.58 nm and a root square mean of 163.36 nm. This could be due to the hydrophobic nature of pure PSF. The same observations were reported in studies investigated by Ntshangase et al.⁴⁰ and Ngobeni et al.⁴² Increased surface roughness could result in higher rejection by membranes as reported by Zaman et al.⁴⁹ High roughness of membranes could also result in membrane fouling because of easy deposit of foulants on the valleys on the membrane surface.⁴⁶ In Figure 8c, blended PSF/PES showed a decrease in the surface roughness of the membrane with $R_{\rm a}$ and $R_{\rm ms}$ values of 26.48 and 20.87 nm, respectively, which could result in enhanced hydrophilicity of the membranes. Figure 8d shows a further decrease in surface roughness of the blended membrane after coating with PVA,

compared to the roughness of the surface of pure PSF and pure PES and the nonblended membrane in figure (a-c), respectively.⁴⁴ These AFM results confirm the relationship between surface roughness and the membrane porosity, indicating the decrease in surface roughness, pore size, and porosity of the blended membrane after the formation of a PVA layer on the surface of the membrane. However, hydrophilicity of the membrane was significantly enhanced.^{44,50} The PVA-coated membrane (25% PSF/75% PES) may be less susceptible to fouling as lower roughness values induce low adhesive forces on the membrane, hence less adhesion of particles on the membrane surface.⁵¹ The results obtained in this study are consistent with the literature.

Contact Angle Measurement of Fabricated Membranes. Figure 9 shows the contact angle measurements to investigate the surface hydrophilicity of the membranes (wettability by water). This could be used in predicting the performance of the membranes or their susceptibility to



Figure 7. FTIR spectra of fabricated membranes.



Figure 8. AFM images of fabricated (a) pure PSF, (b) pure PES membranes, (c) 25% PSF/75% PES, and (d) 25% PSF/75% PES/PVA.



Figure 9. Contact angle measurement of fabricated membranes.



Figure 10. Mechanical properties of fabricated membranes: (a) ultimate tensile strength and (b) Young's modulus.

Table 2. Pure Water Flux Through Fabricated Membranes

	pure water flux (L/m ² h)							
P (bar)	100% PSF	75% PSF	25% PSF	100% PES	100% PSF/PVA	75% PSF/PVA	25% PSF/PVA	100% PES/PVA
1	0.73	1.46	5.41	5.96	1.17	2.78	26.00	36.00
2	1.29	3.07	8.42	9.80	1.99	4.50	39.00	45.00
3	3.74	6.61	10.64	12.11	4.50	7.19	45.80	50.80
4	5.85	11.26	19.94	21.58	7.46	11.70	90.40	78.50
5	11.11	16.18	29.24	32.16	12.51	16.76	128.40	114.60

fouling.⁵² The hydrophobic membrane tends to have a higher contact angle, and the hydrophilic membrane has a lower contact angle.⁵³ The pure PSF (100% PSF) showed the highest contact angle (70.55°) of all the membranes. This is attributed to the hydrophobic nature of the membrane.⁵⁴ However, coating the membrane surface with PVA reduced the contact angle of the pure PSF membrane from 70.55 to 57.58°. The improvement in wettability of the membrane can be attributed to the hydroxyl group on the surface of the PVA layer of the membrane,³⁷ hence enhancing the hydrophilicity of the membrane. It can also be observed that blending of the PSF/ PES polymer enhanced the hydrophilicity of the membranes, in the case of 25% PSF/75% PES with 54.39° contact angle and 75% PSF 25% PES having a contact angle of 60.60° with reference to pure PES without coating. This corroborates with the results obtained for EWC of the blended membranes in

Table 1 and the explanation that blending of polymers increases the porosity of membranes. 38

Mechanical Properties of Fabricated Membranes. Figure 10a,b depicts the mechanical properties of the membranes measured based on their tensile strength and Young's modulus indicating how much force a membrane can withstand before breaking. The pure PSF membrane showed a higher tensile strength of 15.77 MPa compared to the tensile strength (10.13 MPa) of the pure PES membrane. All membranes coated with PVA showed higher tensile strength and Young's modulus compared to the noncoated membranes. The 75% PSF/25% PES/PVA membrane displayed the highest tensile strength and Young's modulus of 18.49 and 15.51 MPa, respectively. Generally, the increase in porosity decreases the mechanical strength of polymeric membranes. ⁵⁵ However, this was not the case in this present study. The observed increase in tensile strength upon coating with PVA was also reported by



Figure 11. Permeate flux of (a) single (succinate 500 mg/L) and (b) binary (succinate and formic 100 mg/L) solutes through fabricated membranes. Experimental conditions: pH: 7; time: 1 h; temperature: 25 $^{\circ}$ C; and stirring speed: 250 rpm.



Figure 12. Variation of (a) pure water permeability, (b) single-solute permeability, and (c) ternary-solute permeability, as a function of TMP. Experimental conditions: [single solute: succinate (500 mg/L); binary solute: succinate (500 mg/L) and formate (100 mg/L); ternary solute: succinate (500 mg/L), formate (100 mg/L), and acetate (100 mg/L); pH: 7; time: 1 h; and stirring speed: 250 rpm].



Figure 13. Rejection of succinate in fermentation broth consisting of (a) single solute (succinate: 500 mg/L), (b) binary solute (succinate and formate 100 mg/L), and (c) ternary (succinate, formate, and acetate 100 mg/L) solute. Experimental conditions: TMP: 1 bar; time: 1 h; temperature: 25 °C; stirring speed: 250 rpm; and pH: 7.

Ntshangase et al.⁴⁰ Although morphology is not only related to porosity, the mechanical property of polymer blends considers the strength and toughness of the materials, which are described as inherently past of the morphology. Therefore, the increase in the tensile strength of this membrane could be attributed to enhanced toughness and strength of the membranes due to polymer blending and the PVA coating.^{56,57}

Performance Evaluation of Membranes. *Pure Water Flux of Fabricated Membranes.* Table 2 presents the pure water flux through the fabricated membranes at varying pressures of 1-5 bar. The results showed that the pure water flux for all fabricated membranes increased with increasing operating pressure. This is due to the permeation driving force, which increased the capillary pressure of the membranes, resulting in high permeation flux.⁵⁸ The pure water flux for the



Figure 14. Effect of solute concentration on selective rejection of succinate acid from synthetic fermentation broth of ternary-solute solution. Experimental conditions: TMP: 1 bar; time: 1 h; temperature: 25 °C; stirring speed: 250 rpm; and pH: 7.

pure PES membrane $(5.96 \text{ Lm}^{-2} \text{ h}^{-1})$ was observed to be higher than the pure water flux for the pure PSF membrane $(0.73 \text{ Lm}^{-2} \text{ h}^{-1})$ at 1 bar and the same trend was observed as the pressure increased from 1 to 5 bar. Blending of membranes seemed to improve flux as observed for 25% PSF and 75% PSF, compared to nonblended membranes. This could be associated with the larger pores as shown by SEM images for these membranes that allowed easy passage of water through them. However, a notable higher flux was observed with the pure PES coated with PVA (100% PES/PVA) with a permeate flux of 114.60 Lm^{-2} h⁻¹ and the PSF/PES-blended membrane with a higher percentage of PES (75%) coated with PVA (25% PSF/75% PES/PVA), having

a permeate flux of 128.40 $\text{Lm}^{-2} \text{h}^{-1}$. This is an indication that coating of the membrane surface with PVA enhanced permeability, porosity, and hydrophilicity of the membrane. This is due to of the hydrophilic nature of the PVA, resulting in improved flux. The results obtained in this study are consistent with the investigations of Ngobeni et al.,⁴² Ntshangase et al.,⁴⁰ Jamshidi et al.,⁵⁹ and Daramola et al.²⁹

Figure 11a,b depicts the permeate flux of synthetic singlesolute (succinate) and binary-solute solutions, respectively. Results showed an increase in permeate flux as the operating pressure increased in both cases. This observation could be attributed to the water droplets that rapidly permeate through the membrane pores and denser surface of the PVA under the higher pressure as suggested by Jin et al.⁶⁰ and Daramola et al.²⁹ In addition, it could be seen that permeate flux for pure PSF $(11.11 \text{ Lm}^{-2} \text{ h}^{-1})$ is lower than the permeate flux for pure PSF coated with PVA $(12.51 \text{ Lm}^{-2} \text{ h}^{-1})$ at an operating pressure of 5 bar. Likewise, the pure PES membrane displayed a membrane flux of 34.15 Lm⁻² h⁻¹, 67.5% higher than the flux for the pure PSF membrane for single-solute solutions. This higher flux could be associated with larger pores on the surface of the pure PES, as observed through SEM images and the higher EWC and porosity presented in Table 1. However, the permeate flux of single solutes is higher than the permeate flux of binary-solute solution containing a mixture of succinate and formate as observed for all fabricated membranes at a pressure of 5 bar. This could be due to membrane fouling and evident competitive sorption between the organic acid components and water.²⁵

It could be observed in Figure 11b that increasing the feed pressure from 4 to 5 bar did not show any significant change in the permeate flux, except for 100% PES/PVA that showed reduction in the permeate flux from 4.15 to 4.09 $Lm^{-2}h^{-1}$. This deviation in fluxes could also be a result of the PVA layer becoming denser at the higher pressure.⁶⁰ In addition, there could be a higher rate of convective transport of the solute to the membrane surface at increased pressure, causing an increase in the concentration of the solute at the membrane interphase. Therefore, this increased the possibility of generation of concentration polarization on the membrane surface. Furthermore, blending of PSF and PES polymers seems to improve the permeate flux of the membranes as could be observed for 25% PSF/75% PES (25 PSF) and 75% PSF/25% PES (75 PSF), having permeate fluxes of 16.08 and 29.24 Lm⁻² h⁻¹ respectively, compared to pure PSF having a permeate flux of 11.11 Lm^{-2} h⁻¹. These results are consistent with the observations reported by Dogan,⁶¹ Pabby et al.,⁶² and Zaman et al.⁶³

Permeability of Pure Water and Organic Solutes (Succinate, Formate, and Acetate) in a Synthetic Fermentation Broth. Figure 12a-d depicts the permeability of pure water, single solute, binary solutes, and ternary solutes, respectively, with reference to a transmembrane pressure (TMP) of 1, 1.5, and 2 bar. The results show that the permeability increased with increasing TMP for pure water and single solute (succinate). This could be a result of change in the structure of the membranes upon blending. This is consistent with the results of Daramola et al.²⁹ However, a decline in permeability with an increase in TMP was observed for both binary and ternary solutes when compared with its performance during pure water permeation. This could be attributed to fouling of the membrane surface due to the presence of more than one solute in the fermentation broth and its deposition on the surface of the membrane.²⁹

Rejection of Succinate in the Single-, Binary-, and Ternary-Solute Mixtures by the Fabricated Membranes. The performance of the membrane was also investigated for the rejection of succinate from single-solute solution (only succinate), binary-solute solution (succinate and formate), and ternary-solute solution (succinate, formate, and acetate), as shown in Figure 13a-c, respectively, at different polymer compositions (0, 25, and 75%). Results showed that either pure polymer membranes coated with PVA or noncoated displayed higher succinate rejections compared to the blended membranes. However, in Figure 13a, succinate rejection for the pure PES membrane coated with PVA dropped from 99.8% rejection in single-solute solution to 60% rejection in binary-solute solution (Figure 13b) and to 12% with ternary-solute solution in Figure 13c. It could be observed that in all the three cases (single, binary, and ternary solutions), the rejections of succinate were fairly good. This could be associated with the increase in permeate flux, observed as a result of larger porosities and higher EWCs, as presented in Table 1. This observation also agrees with the membrane morphology obtained in Figure 3d for the blended membranes, where the membrane skin layer is highly porous with the visible pores compared to pure PSF and pure PES membranes (Figure 3a,b, respectively), thus resulting in the increase in fluxes and decrease in succinate rejection. It can be explained that the solutes easily or freely passed through the pores of the membranes. Blended membranes have also been studied to increase the permeate flux of the membrane, thereby reducing selectivity. Further investigations are therefore required for the development of membranes with high flux and higher selectivity. Similar results were reported in previous studies using PI for rejection of isopropanol²⁶ and toluene.⁴ These results could also indicate that the PVA coating layer may be dissolved or destroyed when contacting with binary solutes and ternary solutes.

Effect of Solute Concentration on Permeate Flux and Selective Rejection of Succinate from the Ternary Mixture. Influence of feed concentration on the selective rejection of succinate, formate, and acetate from a ternary-solute solution was studied and the results are depicted in Figure 14ac. The concentrations of the solutes (succinate, formate, and acetates) are varied (500 mg/L, 1000 mg/L, and 1500 mg/L) in the ratio 1:1:1. In Figure 14a, as anticipated, the rejection of succinate continuously decreased as the feed concentration increased for all studied membranes. This is because of the charged solute transfer, which is dependent on the combination of electrostatic interactions between the charged solute and the fixed charge on the surface of the membrane and the steric hindrance effects. The studied membranes displayed high succinate rejection at lower concentrations, due to the dormancy of the electrostatics. Therefore, increasing the concentration of succinate reduced succinate rejection, owing to the screening effect that weakens the electrostatic repulsion. Kang et al.⁶⁴ and Khunnonkwao et al.³⁴ also reported similar observations. Therefore, the results obtained in this study are comparable with the literature.

However, formate and acetate showed lower membrane rejections for all the studied membranes compared to the membrane rejection of succinate. It could be concluded that succinate, having a higher charge (divalent), was more rejected by the membranes compared to the ionic solutes (formate and acetate) with a lower charge (monovalent) and these rejection behaviors were true for all the concentrations studied. The observed difference in the rejection of ionic solutes with the



Figure 15. Recovery flux ration for fabricated membranes. Experimental conditions: operating pressure: 3 bar, TMP: 1 bar, time: 1 h; and stirring speed: 250 rpm.

Table 3. Comparison of Results Obtai	ned in This Study with the Literature ^a
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membranes	feed concentration (mg/L) $S_{uc}/Ace/F_m$	operating conditions	organic acid	flux (Lm ⁻² h ⁻¹)	rejection (%)	refs
UF (PES 100)		$P = 2$ bar, $A = 0.0045$ m ² , $T = 1$ h, $T_p = 25$ °C	fermentation media	17.11	43.31	26
NF 270	$S_{uc} = 22.4$ Ace = 3.6 $F_m = 3.4$	$P = 30$ bar, $T_p = 25$ °C, pH = 6.9	$S_{\rm uc}$, Ace, $F_{\rm m}$	45.00	93.40	27
$UF_{TiO_2/ZrO_2}^{\ \ b}$	$S_{uc} = 23.3$ Ace = 8.4 $F_m = 9.9$	TMP = 4 bar, $T = 3$ h, $T_p = 25$ °C, $A = 0.0042$ m ²	$S_{\rm uc}$, Ace, $F_{\rm m}$	542.90	90.00	28
NF45	$S_{\rm uc} = 0.7 \text{ M Ace} = 0.1 \text{ M}$	$T = 25 \ ^{\circ}\text{C}, \ \text{pH} = 7$	$S_{\rm uc}$, Ace		<60.00	34
UF (100% PSF)	$S_{\rm uc} = 0.5$	P = 3 bar, $T = 1$ h, $A = 0.0034$ m ² , $T = 25$ °C, pH = 7	$S_{\rm uc},$ Ace, $F_{\rm m}$	3.24	99.90	this study
	$Ace = 0.1$ $F_{\rm m} = 0.1$					
UF (100% PES)	$S_{\rm uc} = 0.5$	$P = 3$ bar, $T = 1$ h, $A = 0.0034$ m ² , $T_p = 25$ °C, pH = 7	$S_{\rm uc}$, Ace, $F_{\rm m}$	4.33	99.9	this study
	Ace = 0.1					
	$F_{m} = 0.1$					
blended UF (75PSF/PES/PVA)	$S_{\rm uc} = 0.5$	$P = 3$ bar, $T = 1$ h, $A = 0.0034$ m ² , $T_p = 25$ °C, pH = 7	$S_{\rm uc}$, Ace, $F_{\rm m}$	4.53	99.8	this study
	Ace = 0.1					
	$F_{\rm m} = 0.1$					

^{*a*}UF—ultrafiltration, NF—nanofiltration; S_{uc} = succinate, Ace = acetate, F_m = formate, T_p = temperature, T = time, P = pressure, and A = area. ^{*b*}UF_{TiO2/ZrO2} = UF tubular ceramic membrane.

monovalent and divalent anions could be because of the pumping effect of the monovalent anions by the divalent anions, which is best described by the Donnan exclusion and electroneutrality of the counterion.⁶³ Due to the higher valency possessed by the divalent anions, they tend to stay at a distance away from the surface of the membrane owing to the strong repulsion, while driving the monovalent anions in the direction of the membrane surface to attain an electroneutrality in the membrane phase. As a result, this increases the concentration of the monovalent anions in the divalent anions in the direction of the divalent anions. Therefore, a lower rejection of acetate and formate was observed compared to succinate. Kang and Chang⁶⁵ and Zaman et al.⁶³ reported a similar observation.

Furthermore, in Figure 14a, pure PSF, pure PES, and pure PSF coated with PVA showed higher selectivity at all feed concentrations compared to other solutes. However, Figure 14b,c shows that the rejection of acetate and formate by the pure PES membrane is lower compared to that of pure PSF and blended PSF/PES. In Figure 14c, it could also be observed that the rejection of formate decreased more compared to that of acetate (Figure 14b) at an increasing feed concentration from 500 to 1500 mg/L. This can be described by the smaller degree of dissociation of formic acid (pK_a 3.6) compared to that of acetic acid (pK_a 4.7); thus, formic acid was more completely dissociated than acetic acid at the studied pH.^{63,66}

FRR for Studied Fabricated Membranes. Fouling can be categorized into organic, inorganic, or biofouling which can be

reversible or irreversible subject to the type of foulants present.⁶⁷ According to Arnal et al.,67 the extent of fouling in membranes can be minimized by feed pretreatment, operation conditions, and membrane cleaning. Nevertheless, the feed pretreatment and optimization of the operating conditions do not eliminate the problem of membrane fouling; hence, to increase the life of the membrane, cleaning methods have to be applied to reverse the fouling in cases where it is reversible. Figure 15 depicts the FRR of the fabricated membranes after being washed for 30 min with deionized water. The results showed that the blended membrane with a higher percentage of PSF showed the highest recovery ratio of 96%. This is more than the recovery ratio for pure PES, even though PSF is more hydrophobic. This could be a result of increase in the membrane permeate flux, resulting from higher flux associated with the hydrophilic PES membrane which decreased its selectivity.^{17,29,42} Comparing the 100% PES membrane and 100% PES/PVA membrane, it could be seen that the latter was able to recover 91% of its initial flux compared to 86% initial flux recovery for the 100% PES membrane without polymer coating. This is an indication that the PVA coating of the membrane improved the flux recovery ability of the membrane that may result in enhanced performance. The results obtained in this study showed that cleaning of the membrane surface could alleviate fouling issue and prolong the life of the membranes. In a study conducted by Prochaska et al.,²⁸ the flux obtained after the three-step cleaning procedure finally reached approximately the same value. However, it is noteworthy that the application of hydraulic (water) and chemical (sodium hydroxide) bath was used for cleaning the membranes after UF of broth, resulting in possible restoration of the initial flux of the UF membrane, whereas only deionized water was used in this current study.

Comparison of Membrane Performance's Results to the Literature for Separation of SA from Fermentation Broth. Table 3 presents the comparison of performance of membranes fabricated for selective separation of SA from synthetic fermentation broth in this current study with the relevant literature. It can be seen that all the membranes presented in Table 3 for this current study outperformed all other membranes studied by other authors. Law and Mohammad²⁵ evaluated the performance of the NF membrane (NF270) for separation of SA from synthetic fermentation broth at different concentrations of the solutes (succinate, acetate, and formate), using a dead-end filtration cell. It was reported that 93.4% SA rejection was achieved for the membrane, which is about 6.5% lower than the result obtained in this current study. Although, lower fluxes of 3.24, 4.33, and 4.53 Lm^{-2} h⁻¹ for 100% PSF, 100% PES, and 75% PSF/25% PES/PVA, respectively, were obtained in this study compared to 45 Lm^{-2} h⁻¹ for the NF270 studied by Law and Mohammad.²⁷ The higher flux reported by Law and Mohammad²⁷ could be a result of the more hydrophilic nature of the NF270 membrane used, compared to what was used in this study.

Prochaska et al.²⁸ utilized a three-step separation technique for obtaining SA from an actual fermentation broth. The UF tubular ceramic membrane (TiO_2/ZrO_2), with an effective surface area of 0.0042 m², was used as an intermediate step. The membrane achieved about 90% succinate rejection. This membrane displayed a higher initial water flux of 542.9 Lm⁻² h⁻¹ compared to an extreme low flux obtained in this study. The higher initial water flux obtained in Prochaska et al.²⁸ could be a result of a larger effective surface area (0.0042 m²) of the membrane used compared to the 0.0034 m² effective membrane surface area used in this study. However, the rejection of succinate for all the studied membranes for this study in Table 1 outperformed the UF tubular ceramic membrane used by Prochaska et al.²⁸

Wang et al.²⁶ employed a PES UF membrane with an effective surface area of 0.0045 m² for the separation of SA from a synthetic fermentation broth. The membrane displayed 17.11 Lm^{-2} h⁻¹ permeate flux and 43.31% succinate rejection. A higher succinate rejection of 99.9% was obtained for the pure PES membrane used in this study, compared to the succinate rejection of 43.41% achieved by the PES UF membrane used by Wang et al.²⁶ Furthermore, the higher permeate flux of 17.11 Lm^{-2} h⁻¹ obtained by Wang et al.²⁴ compared to 4.33 Lm^{-2} h⁻¹ achieved by the PES membrane used in this study could be a result of the membrane with a larger effective surface area used. The results obtained in this study have therefore shown to be comparable with the literature.

CONCLUSIONS

In this study, PSF and PES polymers were blended at varying compositions and coated with PVA to improve its antifouling property. Results showed that robust blended polymer membranes with a unique antifouling property were successfully fabricated. SEM results showed a dissimilarity in terms of pore sizes on the surface of the fabricated membrane surfaces and the pores existing within the membrane. The results have shown that blending of PSF and PES enhanced permeability and revealed enhanced hydrophilicity of the membranes as shown by contact angle measurement. This was further confirmed by the decrease in membrane roughness as shown by the AFM results. Membrane selectivity for succinate reduced for pure PSF coated with PVA and pure PES coated with PVA. However, blended PSF/PES coated with PVA had improved selectivity for succinate with a rejection of 98.9%. Coating the membranes with PVA had a direct influence on the characteristic flux exhibited by the membranes. The increase in water permeation was noticed across the membranes after coating with PVA. The enhanced membrane filtration performance also confirmed that coating the membrane with PVA improved permeate flux and reduced fouling. The 75% PSF/25% PES membrane showed the highest initial flux recovery of 96%. Most importantly, this study has established a proof of concept that the blended PSF/PES membrane coated with PVA with high mechanical strength, with desired surface and antifouling properties, has been successfully fabricated for the separation of SA from other dissolved organic acids (acetate and formate) in a synthetic fermentation broth.

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Notes

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ABBREVIATIONS

AFM, atomic force microscopy; EWC, equilibrium water content; FTIR, Fourier transform infrared; NF, nanofiltration; PES, polyethersulfone; PSF, polysulfone; PVA, poly(vinyl) alcohol; SA, succinic acid; SEM, scanning electron microscopy; TGA, thermogravimetric analysis; UF, ultrafiltration

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