Ultrathin 12-nm-thick solvent-resistant composite membranes from biosourced dialdehyde starch and priamine building blocks

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ABSTRACT

Biomass-based thin film composite (TFC) membranes are emerging as next-generation organic solvent nanofiltration membranes. However, most of the existing membrane fabrication processes still use toxic chemicals, harsh solvents, and fossil-based supports. We report a plant-based, green TFC membrane fabricated only from sustainable resources. It is the thinnest defect-free nanofilm (only 12-nm-thick) fabricated only from natural resources. Dialdehyde starch was crosslinked with priamine at the interface of a water–eucalyptol solvent system. Interfacial polymerization occurred on a biodegradable cellulose acetate support obtained using phase inversion. The membrane has an ultrathin (12-nm-thick) selective layer, and the molecular weight cut-off and permeance were fine-tuned between 366 and 624 g mol⁻¹ and 7 and 23 L m⁻² h⁻¹ bar⁻¹, respectively. Stable nanofiltration performance under continuous crossflow filtration was achieved for seven days. The sustainability of the membrane fabrication platform was compared with those of other platforms. Our TFC membrane fabrication platform enables the conversion of biomass-based building blocks into high-value-added products.

1. Introduction

Membrane separation consumes less energy than conventional energy-intensive separation techniques. Therefore, it has been adopted by various industrial sectors, including desalination, solvent recycling, petrochemical separation, fine chemical recovery, and natural product extraction. Organic solvent nanofiltration (OSN) is a pressure-driven process that separates molecules in the molecular weight range of 100–2000 g mol⁻¹ in organic media. OSN membranes can be broadly classified in thin film composite (TFC) membranes prepared using interfacial polymerization (IP, Fig. 1) and integrally skinned asymmetric (ISA) membranes fabricated using phase inversion [1]. As TFC membranes comprise composite layers, they provide additional flexible independent layer design [2] than ISA membranes.

Despite efforts to replace solvents [3] with sustainable and biomass-based alternatives [4], most TFC membranes are fabricated from petrochemical-based materials. Toxic solvents in the IP process have been replaced with green alternatives such as p-cymene [5], eucalyptol [6,7], decanoic acid [8], ionic liquids [9] and α-pinene [10]. Plant-based tannic acid was used as the aqueous-phase monomer in the first study of green IP [11]. Since that time, researchers have employed other green monomers such as quercetin [10], morin [12], vanillin [13], and cyclo-dextrins [14]. However, in all of these studies, the counterpart monomer in the other phase was terephthaloyl chloride or trimesoyl chloride (TMC). Both acyl chlorides are toxic and derived from fossil fuels; however, they remain the first choice in TFC development because their high reactivity favors the IP and hastens the reaction time. A truly green membrane fabrication process must abandon acyl chloride-based chemistry.

Recently, our team proposed a Michael addition and Schiff base reaction that uses natural aldehydes and amines as the IP monomers. In the first only green TFC fabrication system, tannic acid was dissolved in aqueous phase and then crosslinked with priamine in the green solvent p-cymene [5]. Then, TFC membranes were developed from chitosan derived from shrimp farming waste and biomass-derived 2,5-furandicarboxaldehyde in eucalyptol [7]. In both systems, the porous support was recycled polyethylene terephthalate and the prepared TFC membranes exhibited excellent solvent resistance. In the latest attempt, the natural crossligner genipin has been coupled with priamine in eucalyptol on an ultra-permeable biodegradable polylactic acid nanofibrous support, thus...
providing a green TFC membrane system for OSN [6]. Tannic acid combined with cyclohexane-1,4-diamine [15], iron [16-18], or TMC [19] resulted in various types of nanofiltration membranes and supports [20].

As one of the most abundant natural biopolymers, starch is renewable, biodegradable, and biocompatible [21]. However, only approx. 3 wt% of potato-based biomass is convertible to pure starch; the biomass residue is discharged [22]. Potato residue waste can be upcycled to obtain the thinnest defect-free nanofilm (only 12-nm-thick) fabricated using CA dissolution and phase inversion of conventional fossil-based solvents (acetone, N,N-dimethyl formamide, or N-methyl-2-pyrrolidinone). Recently, efforts have employed green solvents and renewable bioresources, our methodology supports the fifth and seventh principles of green chemistry and the twelfth sustainable development goal of the United Nations.

2. Experimental

2.1. Materials and methods

Cellulose acetate (Mn approx. 50k based on gel permeation chromatography), eucalyptol (99%), and dimethyl sulfoxide (DMSO EVOL) were received from Sigma Aldrich. Priamine 1071, a diamine derived from plant oil, was provided by Croda. Dialdehyde starch was received from Sungyoung Chemicals. Heptane, toluene, iso-propanol (IPA), ethanol (EtOH), methanol (MeOH), 1,2-dichlorobenzene, methyl tert-butyl ether (MTBE), 2-methyltetrahydrafuran (MeTHF), and butyl acetate (all analytical grade) were obtained from Merck. All chemicals were used as received. Type II deionized (DI) water with a resistivity of 18.2 MΩ cm at 25 °C (Milli-Q) was used throughout all experiments.

2.2. Characterization

The membrane morphology was observed by scanning electron microscopy (SEM) (Quattro SEM and Magellan SEM; FEI). In preparation for SEM analysis, the membrane specimens were sputter-coated with a 4-nm-thick layer of Pt. The surface roughness values of membranes were investigated using an atomic force microscope (AFM) in tapping mode with a cantilever (RTESPA, Bruker). The scan area and scan rate of AFM were (20 × 20) μm² and 0.7 Hz, respectively. The roughness (Ra) values were reported as the arithmetic means and standard deviations of the values at three different positions on each sample surface. Water contact angle (WCA) measurements were performed in triplicate on a drop shape analyzer (Krüss GmbH). The chemical functional groups of the monomers and membranes were examined using attenuated total reflectance Fourier transform infrared spectroscopy (ATR FT-IR, Nicolet iS10, Thermo Fisher Scientific). X-ray photoelectron spectroscopy (XPS) was performed on an Amicus instrument (Kratos Company) using an achromatic Al X-ray source (hv = 1486.6 eV, operating power = 50 W) under ultra-high vacuum conditions (10⁻⁹ mbar). The wide and narrow scan spectra were acquired at a fixed analyzer pass energy of 75 eV. The
narrow scanning spectra were deconvoluted using XPSpeak41. The automatic peak fitting was input with the peak values and optimized until no changes were observed. One-dimensional \(^{13}\text{C}\) CP/MAS solid-state nuclear magnetic resonance (ssNMR) spectra were recorded on a 400-MHz Bruker AVANCE III spectrometer with the following sequence: 90 pulses on the proton (pulse length = 2.4 s), cross-polarization with a typical contact time of 2 ms, and acquisition of the \(^{13}\text{C}\) NMR signal under high-power proton decoupling. The delay between the scans was set to 5 s to allow complete relaxation of the 1H nuclei. The number of scans ranged from 3000 to 10000. An exponential apodization function corresponding to a line broadening of 80 Hz was applied before Fourier transformation. The mechanical properties of the CA support and free-standing thin films were tested by nanoindentation using a NanoTest Vantage instrument. A silicon wafer loaded with the membrane samples was placed in the holder of the nanoindentation instrument, which had been calibrated in advance. The mechanical properties were reported as the averages of three experiments. The pore-size calculation is given in the Supporting Information.

2.3. Preparation of CA support

A 7.5 w/v\% CA polymer dope solution was prepared by dissolving 3.75 g CA in 50 mL of DMSO EVOL green solvent. Homogeneous CA dope solutions were prepared by continuous mixing at room temperature for 20 h. Gas entrapped in the dope solution was then released by degassing in an incubator shaker (200 rpm, 23 °C) for 4 h. The membranes were cast on a clean glass support using an Elcometer 4340 film applicator with a casting knife. All CA supports were cast with a thickness of 250 \(\mu\)m. The film was immediately immersed in a water coagulation bath at 23 °C for 0.5 h. CA supports were then washed three times with DI water and stored in DI water containing 1% methanol to prevent bacterial growth.

2.4. Preparation of dialdehyde starch-priamine TFC

DS was dissolved in DI water using agitation under 80 °C overnight. The membranes were prepared by IP with different reaction times and monomer concentrations. First, DS–priamine free-standing thin films were prepared to examine the chemical properties of the polyimine layer. Because aldehydes react with amines only in acidic media, the pH of the DS solution was adjusted to 6.0 with 1-M aqueous HCl solution. The IP was performed with 5 mL of 0.5 w/v\% aqueous DS solution at pH = 6.0 and 5 mL 2.5 w/v\% priamine in eucalyptol. The effect of reaction time (20, 30, 40, and 50 s) on the free-standing thin film thickness was examined.

Second, TFC membranes were synthesized on CA supports with an effective area of 12.25 cm\(^2\). Each CA support was immersed in 5 mL aqueous DS solution for 2 min at 23 °C. After decanting the excess aqueous solution, the support was immediately immersed in 5 mL priamine in eucalyptol solution for a controlled time to enable the Schiff base reaction between amine and aldehyde moieties. The IP process was terminated by washing three times with pure eucalyptol. The prepared TFC membranes were dried at 23 °C before storing in DI water containing 0.1 v% MeOH. To optimize the reaction conditions, a number of TFC membranes were prepared with different reaction times (20, 30, 40 and 50 s), priamine concentrations (1.0, 1.5, 2.0, and 2.5 w/v\%), and DS monomer concentrations (0.1, 0.3, 0.5, and 0.7 w/v\%) (Table 1).

2.5. Performance tests

The OSN performances of TFC membranes were evaluated using a crossflow membrane separation rig. The retentate stream was recirculated using an ATEX-rated gear pump operated at 1200 mL min\(^{-1}\) (MSE Ltd., United Kingdom). Before filtration, the membranes were rinsed with the filtration solvent and then stored in the solvent for 16 h. The membranes were conditioned to steady-state under the given pressure for

| Table 1 Membrane designations and IP reaction conditions using aqueous-phase DS and priamine in green solvent eucalyptol. The CA support was prepared from 7.5 w/v% polymer dope solution using the green solvent DMSO EVOL. |
|---------------------------------|-----------|----------|-----------|
| Membrane | DS (w/v%) | Priamine (w/v%) | Reaction time (s) |
|----------|-----------|--------------|-------------------|
| M1       | 0.5       | 1.5         | 20                |
| M2       | 0.5       | 1.5         | 30                |
| M3       | 0.5       | 1.5         | 40                |
| M4       | 0.5       | 1.5         | 50                |
| M5       | 0.5       | 2.5         | 30                |
| M6       | 0.5       | 2           | 30                |
| M7       | 0.5       | 1           | 30                |
| M8       | 0.7       | 1.5         | 30                |
| M9       | 0.3       | 1.5         | 30                |
| M10      | 0.1       | 1.5         | 30                |

24 h, then subjected to permeance and rejection measurements. The permeance was calculated from the permeate volume \(V\) measured over a given time period \(t\), the given membrane area \(A\), and the applied pressure \(\Delta P\) as follows:

\[
\text{Permeance} = \frac{V}{\Delta P \times A \times t}
\]

As the filtration solutes, multiple marker dyes and pharmaceuticals, namely styrene dimer (236 g mol\(^{-1}\)), estradil (272 g mol\(^{-1}\)), methyl orange (327 g mol\(^{-1}\)), losartan (423 g mol\(^{-1}\)), valsartan (435 g mol\(^{-1}\)), olouepeir (541 g mol\(^{-1}\)), acid fuchsin (586 g mol\(^{-1}\)), roxithromycin (837 g mol\(^{-1}\)), and rose bengal (1018 g mol\(^{-1}\)) were dissolved in methanol at 0.1 g L\(^{-1}\) concentration. The molecular weight cut-off (MWCO), defined as the molecular weight of a solute having 90% rejection, was estimated by nonlinear interpolation of rejection curves. The solute rejection was determined from the ratio of the permeate and retentate concentrations of solutes (\(c_{\text{permeate}}\) and \(c_{\text{retentate}}\), respectively) as follows:

\[
\text{Rejection} = \left(1 - \frac{c_{\text{permeate}}}{c_{\text{retentate}}}\right) \times 100
\]

the standard deviations of two independent measurements on independently prepared membranes are reported as error bars on the graphs. The long-term stability of M2 was assessed under the above-described conditions using rose bengal markers in methanol at 20 bar in a crossflow nanofiltration rig continuously operated over seven days.

3. Results and discussion

3.1. Membrane design and characterization

To study the reactivity of the DS–priamine monomer system and determine its threshold concentration for film formation, the free-standing thin films were fabricated with multiple reaction times and monomer concentrations. At fixed priamine concentration (2.5 w/v%), the DS concentration was varied from 0.1 to 0.5 w/v%. At fixed DS concentration (0.5 w/v%), the priamine concentration was varied from 0.5 to 2.5 mmol/v%. No films were formed at priamine concentrations below 0.5 w/v%.

During the Schiff base reaction, the aldehyde groups of DS reacted with the primary amine groups of priamine to form a crosslinked –C=N– imine structure (Fig. 2a). In the first step, an unstable tetrahedral carbon intermediate called hemiacetal was formed via the attack of the carbon atom on the carbonyl group by the nitrogen-containing nucleophile (Fig. S3). Subsequent water elimination yielded the final imine structure. The acidity of the reaction media plays a significant role in this reaction: acidic conditions accelerate the imine formation but excess water causes undesired hydrolysis. During the membrane fabrication, the pH was adjusted to 6.0 (the optimal pH determined in preliminary experiments) with 1 M aqueous HCl solution.
Before the IP, a peak at 1660 cm$^{-1}$ assigned to C=O stretching vibrations of the aldehyde groups was found in the spectrum of DS (Fig. 2b). Moreover, the primamine spectrum presented the characteristic peaks of aliphatic C–H stretching between 2700 and 3000 cm$^{-1}$. In the spectrum of the free-standing thin film, a new peak at 1567.8 cm$^{-1}$ was assigned to C–N linkages, confirming successful IP. Successful formation of the imine group between DS and primamine was reported by the maintained C–H stretching bond and the appearance of a new N 1s peak at 400 eV in the wide scanning XPS spectrum of the free-standing thin film (Fig. 2c). In particular, the N atomic content increased to 1.76%, indicating that primamine had successfully reacted with DS. The C 1s high-resolution spectrum of the free-standing thin film was deconvoluted in three peaks (Fig. 2d). The first peak located at 284.4 eV was attributable to C–C and C–H, the second peak at 285.2 eV was related to C–N, and the last peak at 286.3 eV corresponded to C–N. The N 1s high-resolution spectrum of the same sample was deconvoluted into two peaks: one at 399.0 eV because of N=C and another at 401.0 eV because of N–C (Fig. 2e). From these five peaks, we can rationally postulate that the observed imine group resulted from the Schiff base reaction between DS and primamine.

Fig. 2f shows the solid-state $^{13}$C NMR spectra of DS and the DS–primamine free-standing thin film, in addition to the $^1$H NMR spectrum of primamine (Fig. 2f). The peaks below 60 ppm in the thin film spectrum originated from the aliphatic chains of primamine after the IP. The resonance peak of the α carbon atom of DS largely shifted from 87.5 to 77.5 ppm, suggesting the formation of imine groups. The new peak at 163 ppm was attributed to crosslinking at the β-carbon position.

Fig. 3 shows the properties of the DS–primamine TFC membrane and the CA support. The surface SEM image of the CA support demonstrated a defect-free and flat morphology with a WCA of 63° ± 0.1° (Fig. 3a-i),
whereas the cross-sectional image revealed a dense surface layer with a macrovoid-like porous structure at the bottom (Fig. 3a-ii). These results confirm the suitability of the fabricated CA as a support for TFC fabrication: first, the support is hydrophilic and extracts monomers from the aqueous phase; second, the porous inner structure facilitates molecule transport during the IP [32]. After fabricating the selective layer on the support, a gully structure appeared on the surface (Fig. 3b-i) and in the cross-section (Fig. 3b-ii) of the TFC membrane. Interestingly, the coverage of the gully structure on the TFC membrane surface increased with increase in reaction time and monomer concentration (Fig. S1), indicating that the selective layer adhered to the CA support.

The WCA was $63 \pm 0.1^\circ$ on the CA support, increasing to $92 \pm 0.5^\circ$ on the TFC membrane because the long hydrophobic alkyl chains of priamine were incorporated into the selective layer. The increased hydrophobicity facilitated the transport of non-polar solvents to the TFC membrane surface [33]. The selective layer of M2 was approx. 26-nm-thick, as confirmed by AFM analysis (Fig. 3c-i and 3c-ii).

As the selective layer influences the membrane performance, the thickness, roughness, and WCA of the membrane were examined under different reaction conditions (Fig. 3d). The SEM images, WCs, and AFM images (3D and height measurement profiles) are provided in the Supporting Information (Figs. S1 and S2). Increasing the reaction time from 20 to 50 s increased the selective-layer thickness from 25 to 45 nm. Similarly, increasing the priamine concentration from 1 to 2.5 w/v% and the DS concentration from 0.1 to 0.7 w/v% increased the selective-layer thickness from 12 to 45 nm and from 18 to 58 nm, respectively. Moreover, increasing the priamine concentration increased the WCA from 90 to $101^\circ$ (Fig. 3d-ii) because more hydrophobic aliphatic chains were incorporated at higher priamine concentrations. However, increasing the DS concentration decreased the WCA from $101^\circ$ to $78^\circ$ (Fig. 3d-iii) because DS is rich in polar hydroxyl and unreacted aldehyde groups. All membranes were similarly flat with roughness ($R_a$) values lower than 3 nm. The roughness of the selective layer depends on the convection ability of the monomers. In this study, the DS polymer had low mobility, and so the interface was stable during the IP and the resulting TFC membrane developed a smooth surface. Consequently, an ultrathin, hydrophobic selective layer was formed at low DS and priamine concentrations. Such a layer is expected to enhance the sustainability of the IP system and improve the solvent permeance during OSN.

Nanoindentation measurements demonstrated an approx. 30% higher mechanical strength in the CA support than in the free-standing thin film. The hardness values of the CA support and free film were $1.0 \pm 0.09$ and $0.7 \pm 0.05$ MPa, respectively.

As the DS–priamine selective layer is a crosslinked network, it is insoluble in organic solvents although the CA support layer has limited solubility [34,35] or crosslinked with carboxylic acids [36] or anhydrides [37] prior to IP, the scope of applicable solvents for OSN can be extended.

3.2. Separation performance

The molecular sieving properties of membranes were determined under different conditions. The rejection of various pharmaceutical, natural products, and dye molecules increased with increase in molecular weight (see the MWCO curves in Fig. 4a-i–c-i). The reduction in MWCO values with increase in IP reaction time (Fig. 4a-i) and increase in priamine (Fig. 4b-i) and DS (Fig. 4c-i) concentrations can be attributed to the tightening of membranes.

Prolonging the reaction time from 20 (M1) to 50 s (M4) reduced the MWCO from 484 to 366 g mol$^{-1}$ and reduced the corresponding methanol permeance from 12.3 to 7.1 L m$^{-2}$ h$^{-1}$ bar$^{-1}$ (Fig. 4a-ii). The observed change was attributed to the tighter selective layer formed between the two monomers as the interfacial contact time increased. Similarly, when the priamine concentration increased from 1 w/v% (M7) to 2.5 w/v% (M5), the corresponding MWCO decreased from 624 to 379 g mol$^{-1}$, leading to a methanol permeance drop from 22.8 to 6.9 ±...
0.2 L m⁻² h⁻¹ bar⁻¹ (Fig. 4b-ii). These significant decreases (39% and 69% in MWCO and permeance, respectively) demonstrate that priamine concentration crucially affects the tightness of the selective layer. However, the performance of the TA-priamine selective layer was insensitive to priamine concentration [5]. Therefore, the effect of priamine in TFC membranes largely depends on the counterpart monomer, indicating that additional investigations of IPs using priamine are required.

When the DS concentration increased from 0.1 to 0.7 w/v% (M10 – M8), the MWCO and methanol permeance decreased from 584 to 412 g mol⁻¹ and from 24.3 ± 1.5 to 7.3 ± 0.3 L m⁻² h⁻¹ bar⁻¹, respectively (Fig. 4c-ii). Comparing the effects of the different parameters, the MWCO decreased by 24% over the range of reaction times, and by 39% and 29% over the ranges of priamine and DS concentrations, respectively. That is, the selective layer formation— and hence the separation performance— was less affected by reaction time than by the monomer concentrations. The pore sizes of the prepared TFC membranes ranged from 1.28 (M4) to 1.98 nm (M7) (see Fig. 4a-iii – c-iii). Note that M4 is the tightest membrane (MWCO = 366 g mol⁻¹) and M7 is the loosest membrane (MWCO = 624 g mol⁻¹). As the reaction time increased from 20 to 50 s, the pore size decreased from 1.56 to 1.28 nm (Fig. 4a-iii). Similarly, as the priamine and DS concentrations increased from 1.0 to 2.5 w/v% and from 0.1 to 0.7 w/v%, respectively, the pore sizes of the resultant membranes decreased from 1.98 to 1.28 nm and from 1.88 to 1.48 nm, respectively (Fig. 4b-iii and 4c-iii).

To correlate the membrane performance with the applied pressure, the temperature was varied from 5 to 40 bar in 5-bar increments. This test was performed on M2 in MeOH (Fig. 5a-i). The flux through M2 increased from 123.3 ± 10.9 at 10 bar to 353.8 ± 15.9 L m⁻² h⁻¹ at 40 bar. The flux-pressure correlation was nonlinear, indicating that pressure influenced the compaction or the diffusion coefficient of the membrane [38]. The positive relationship between flux and pressure confirmed that the solvent permeance was pressure-driven [39]. The compaction was then studied by reducing the pressure from 40 bar to 5 bar in the same 5-bar increments (Fig. 5a-ii). Under pressurization, the permeance of the membrane decreased from 12.3 to 8.8 L m⁻² h⁻¹ bar⁻¹ with a relatively high standard deviation (up to 1.09 L m⁻² h⁻¹ bar⁻¹); however, during depressurization, the permeance remained constant (8.9 ± 0.19 L m⁻² h⁻¹ bar⁻¹) with a relatively low standard deviation (up to 0.45 L m⁻² h⁻¹ bar⁻¹). These results indicate that compression was irreversible and enhanced the reproducibility of the results and reliability of the membrane.

Rejection of oleuropein remained high over the pressure range, increasing by approx. 3% as the pressure increased from 5 to 40 bar. In parallel, rejection of the styrene dimer significantly increased (by 1.7 times) culminating at 55% at 40 bar. This result can be explained by the different solvent-solute-membrane interactions. According to Spiegler–Kedem theory, solute permeation is governed by diffusion and convection [40]. When the solute molecule (MW = 236.4 g mol⁻¹ for the styrene dimer) is smaller than the pore size of the membrane (MWCO = 441 g mol⁻¹ for M2), the permeation process is dominated by diffusion and the rejection is a rapidly increasing function of applied pressure [39].

The durability of M2 was examined in a continuous crossflow filtration system for seven days under a pressure of 20 bar (Fig. 5b). The methanol permeance started at 12.9 L m⁻² h⁻¹ bar⁻¹, slightly declined to 10.6 L m⁻² h⁻¹ bar⁻¹ after 1 day of filtration, and remained at that level afterwards. Furthermore, the rejection of rose bengal (1017 g mol⁻¹ exceeded 99% throughout the seven days of continuous operation. These results confirmed the outstanding OSN performance of our TFC membrane and suggested its industrial feasibility.

The permeance was a monotonic nonlinear function of the solvent parameter (R² = 0.8888; Fig. 5c). The solvent parameter depends on the molar diameter dₘₐₓ, viscosity η, and the solubility parameter due to dipole forces δᵥ MeOH (η = 0.49 × 10⁻³ Pa s, δᵥ = 0.51 nm; see Table S2) yielded the highest permeance (11.22 L m⁻² h⁻¹ bar⁻¹) among the solvents. However, the nonpolar solvents heptane (dₘₐₓ = 0.78) and toluene (dₘₐₓ = 0.7) yielded the lowest permeances.

To place the separation performance in context, panels d-i and d-ii of Fig. 5 compare the permeances of the organic solvents for mixed matrix, TFC and ISA membranes in various solvents reported in the literature. The permeances obtained in all studies are plotted as functions of time (Fig. 5d-i). The permeance and rejection of styrene-dimer rejection. Our DS-priamine membranes fabricated under different IP conditions manifested the typical rejection–permeance trade-off. Our DS-priamine membranes achieved the highest MeOH permeances among the compared membranes, comparable to the acetone permeances reported in other studies; moreover, the styrene-dimer rejection was modest (Fig. 5d-ii). Both the DS and priamine...
concentrations influenced the tightness of the fabricated membrane (M5–M10 and M2). The methanol permeance and styrene-dimer rejection were 6.91 L m⁻² h⁻¹ bar⁻¹ and 44.5%, respectively, for the tightest membrane (M5, among M5–M10 and M2), and 24.3 L m⁻² h⁻¹ bar⁻¹ and 32.3%, respectively, for the loosest membrane (M10).

### 3.3. Sustainability evaluation

The proposed IP incorporates DS and priamine monomers into an all-natural, biomass-based, solvent-resistant TFC membrane, thus developing a green selective layer on a biodegradable CA support. The IP solvents (water and eucalyptol), monomers (DS and priamine), and support (CA) are fully sustainable. To evaluate the sustainability of the system, the total numbers of moles of monomers and additives per 100 mL of solution during the IP were compared with those reported in the literature (Fig. 6). Because DS is categorized as non-hazardous in the Globally Harmonized System (GHS) of Classification and Labeling of Chemicals, it is not represented by a GHS pictogram. The total number of moles of monomers per 100 mL in the IP varied from 1.3 to 2.7 mmol, including 0.8–2.0 mmol of priamine. The optimized membrane M2 required 1.9 mmol of monomers per 100 mL of solution. Although HCl is required for pH adjustment to 6.0 during the solution preparation, the minimal HCl consumption (only 5 × 10⁻⁵ mmol) exerts negligible adverse impact. However, IPs using acetic acid, citric acid, or another green acid should be explored in future.

Conventional IPs require large quantities of the fossil-based chemicals TMC and MPD (40.8 mmol without additives, increasing to 87 mmol in TMC-based IP involving polyethyleneimine) [41] (Fig. 6a). The incorporation of all natural biomass-derived monomers is a paradigm shift in IP. Until recently, TFC systems were not truly green because they employed acyl chlorides for crosslinking [5–7]. Nine membranes fabricated via petroleum-based IP consumed more chemicals than our membranes, whereas three membranes required comparable resources to ours (Fig. 6a). Moreover, our DS–priamine system was among the top five green IP systems (Fig. 6b).

The hazards and toxicities of the involved chemicals were represented by GHS classification pictograms (Fig. 6c), which were proposed first for reactions [42] and later for membranes [5]. The pictogram of each chemical was obtained from the Material Safety Data Sheet and was enlarged by the ratio of the calculated total mole number per 100 mL to 1.0 mmol 100 mL⁻¹ (the calculation details are given in Table S4, while the chemical hazards and their corresponding pictograms are summarized in Table S5). Comparing the sizes and categories of the resized pictograms, the hazardous categories were less severe and the pictograms were smaller for our designed TFC system than for the existing publications, in both the petroleum and green TFC fields. Therefore, the sustainability of our green DS–priamine TFC system was largely enhanced by the decreased toxicity and mitigated environmental burden. Moreover, the organic phase of our system replaces the conventional petroleum-based solvents such as toluene and hexane with a green solvent (eucalyptol), further minimizing the hazards of our TFC fabrication system.

### 4. Conclusion

In this study, the IP process of a green TFC membrane preparation was governed by a simple one-step Schiff base reaction. Natural biomass-derived dialdehyde starch in the aqueous phase and priamine in a green organic phase were employed during the selective layer preparation. Moreover, a cellulose acetate phase-inversed membrane was adopted as a green and biodegradable support. The membrane resulting from the solely green TFC-membrane fabrication system was only 12 nm thick and exhibited outstanding OSN performance, with a methanol permeance as high as 11.3 L m⁻² h⁻¹ bar⁻¹. Moreover, the tested MWCOs ranged from 366 to 624 g mol⁻¹, indicating a nanofiltration profile of the membrane. During a long-term stability test in methanol for seven days, the rose bengal rejection remained stable at virtually 100% while the methanol permeance remained steady at 11.3 L m⁻² h⁻¹ bar⁻¹. Compared with previously reported membranes, our green TFC membrane was confirmed as ultra-permeable with modest styrene rejection (43%) owing to the ultrathin hydrophobic selective layer. The reported TFC membrane design is a “kill two birds with one stone” technique that converts biomass residue to a sustainable and biodegradable OSN membrane. This new method paves the approach for next-generation OSN membrane fabrication from abundant and sustainable bioresources.
Author's contribution

Cong Yang: Conceptualization, Data curation, Formal analysis, Investigation, Visualization, Writing – original draft. Gyorgy Szekely: Conceptualization, Resources, Methodology, Investigation, Writing – review & editing, Supervision, Funding acquisition, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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