Effect of pore forming agents on the properties and performance of the supported liquid membrane for levulinic acid separation

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ABSTRACT

The porosity of the membrane support plays a crucial role in the performance and efficiency of the supported liquid membrane (SLM) process. The formation of pores and the membrane porosity value can be improved by adding a pore-forming agent in the dope solution during membrane manufacturing. The objective of this study is to investigate the effect of pore-forming additives such as polyethyleneglycol (PEG) 200, PEG 20,000, lithium chloride, Tween-80, and polyvinyl pyrrolidone (PVP 10,000) on the polyethersulfone (PES) membrane properties and their performance in the separation of levulinic acid (LA) using the SLM method. The morphology, contact angle, porosity, and tensile strength of the membrane were evaluated. Among the pore-forming agents tested, PEG 200 emerged as the most effective in inducing a sponge-like structural wall in the PES membrane. It achieved a remarkable porosity level of 87.1%, displaying contact angles of 81.2° and 98° at the top and bottom surfaces, respectively, as well as a high tensile strength of 1032.88 kPa. The membrane achieved the highest extraction of 8.92 g/L LA in the SLM process using a 10 g/L LA aqueous feed solution.

Introduction

Levulinic acid (LA) represents a highly valuable bio-organic acid in increasing demand across various applications [11]. Nevertheless, the primary challenge in LA production lies in the separation or extraction of LA from accompanying by-products. Presently, the supported liquid membrane (SLM) method, known for its exceptional selectivity, offers a feasible and promising solution for LA separation. This method stands out as one of the most suitable processes for recovering desired chemicals from biomass products downstream. Moreover, it is an economically efficient and straightforward approach, boasting significant potential to efficiently isolate and recover the desired product in a single step, utilizing only a minimal volume of liquid membrane [8].

In the SLM process, the polymeric membrane support plays a crucial role. It is recommended to use a highly porous membrane in this process because it can accommodate a larger volume of the organic liquid membrane phase [7]. When there is an increase in the amount of organic liquid membrane within the membrane support, it is anticipated that solute extraction will also increase correspondingly. Enhancing the membrane's porosity can be achieved by augmenting the number of pores in the membrane. Introducing a pore-forming agent into the

polymer solution used for the membrane dope will enhance pore formation, improve pore interconnectivity, and result in a spongy membrane structure, which is highly desirable as support in the SLM [2].

Common pore-forming agents or additives employed in the preparation of polymeric membranes include hydrophilic polymers such as polyethylene glycol (PEG)), inorganic salt like lithium chloride (LiCl), inorganic filler such as titanium oxide, and surfactants like Tween-80) [5]. In a study conducted by Idris et al.[4], different molecular weights of PEG (PEG 200, PEG 400, and PEG 600) were used to fabricate polyethersulfone (PES) ultrafiltration (UF) membranes. Specifically, the PES membrane containing PEG 200 demonstrated a UF membrane with a low molecular weight cut-off (MWCO). As PEG 200 concentration increased in the PES solution, solute separation improved while pure water permeation decreased. Substituting PEG 200 with PEG 400 and PEG 600 led to reduced solute separation but increased pure water permeation [4].

Introducing polyvinyl pyrrolidone (PVP) into the polyamide polymer solution led to notable improvements in membrane porosity and permeability, primarily owing to its hydrophilic properties. Intriguingly, as the concentration of PVP in the dope solution increased, permeability improved without any discernible impact on selectivity [4]. In the

Table 1

Formulations of dope solutions using different types of pore-forming agents at different concentrations.

Membrane code	Dope composition (g)							
	PES	DMAC	Graphene	PEG 200	PEG 20,000	LiCl	Tween- 80	PVP
PEG200-42.5	15	42.5	0.015	42.5				
PEG20K-6	15	79.0	0.015		6			
LICL-4	15	81.0	0.015			4		
MIX-8	15	77.0	0.015		4	1	3	
PVP-7.5	15	77.5	0.015					7.5

context of a polyvinylidene fluoride/polyvinyl chloride casting solution, PVP was found to induce a broader mean pore size distribution in the membrane compared to PEG and LiCl [3]. Furthermore, PVP demonstrated excellent miscibility with PES [10].

The molecular weight of PVP, ranging from 10,000 to 1,300,000 Da, and its concentration in the polyetherimide dope solution were found to induce a transition in membrane morphology, shifting from a finger-like structure to a spongy configuration [12]. Al Malek et al., [6] also observed that a high concentration of PVP in the PES membrane led to the formation of a denser top layer structure, albeit at the expense of reduced tensile strength and elongation to break value. Thus, this study delves into the influence of various pore-forming additives in the hybrid PES/graphene polymeric membrane on membrane properties and its performance in the SLM process for LA separation. Notably, this research marks the first investigation into the impact of diverse pore-forming agents in PES membranes support for use in the SLM process, to the best of our knowledge.

Methodology

Materials

The base polymer solution was prepared using PES (Radel® A, Solvay, USA), dimethylacetamide (DMAC, Sigma Aldrich), and graphene nanopowder (Low Dimensional Materials Research Centre, University of Malaya). Various pore-forming agents were introduced into the base polymer solution, including PEG 200 (Sigma Aldrich), LiCl (Acros), Tween-80 (Merck), PVP 10,000 (Sigma Aldrich), and PEG 20,000 (Merck). For the formulation of the organic liquid membrane, trioctylamine (TOA, Sigma Aldrich) served as the carrier, and 2-ethyl-1-hexanol (Merck) as the diluent. LA (Sigma Aldrich) and sodium hydroxide (NaOH, Merck) were employed as the feed and stripping agents, respectively. In the measurement of porosity, olive oil from Delima Oil Products Sdn. Bhd was utilized.

Polymeric membrane preparation

Table 1 displays the membrane dope solution's composition, featuring various types of pore-forming agents. All the necessary components were thoroughly mixed under continuous stirring at 400 rpm until a homogeneous solution was achieved. The preparation of flat sheet membranes was carried out using the vapour inducing phase separation (VIPS) method, employing a film applicator machine. These membranes were cast to a thickness of 400 µm at 86% relative humidity, as previously reported in Rajendaren et al. [9].

The selection of the pore-forming composition was guided by values reported in existing literature. To ensure membrane processability and prevent defects, the concentration of pore-forming agents was maintained within a limited range in the membrane dope solution. This approach was adopted because some of these agents can significantly increase dope viscosity, potentially leading to membrane imperfections. Consequently, only small amounts of these agents were incorporated into the dope solution to maintain membrane integrity.

Membrane characterizations

Scanning electron microscopy (SEM) (Brand: Carl Zeiss, Model: EVO 50) was used to observe the morphology of the membrane. The contact angle of both the top and bottom surfaces of the membrane was determined using an optical contact angle measurement system (CAM 101 optical Contact Angle Meter, KSV Instruments). The membrane's porosity was measured using Eq. 1, as detailed in the previous publication [9].

$$\varepsilon = \frac{W_2 - W_1}{\rho V_1} \times 100 \tag{1}$$

Where W_1 and W_2 are the weight of the dry and wet membrane in g, respectively, V_1 is the volume of the membrane (cm^3), and ρ is the density of olive oil (0.8 g/cm^3). The wet weight is measured after the membrane was immersed in olive oil for 24 h. The dry weight is the weight of the membrane after the wet membrane was dried in an oven for 24 h.

The membrane's tensile stress was assessed in accordance with the ISO 527–3 standard. Rectangular membrane samples, measuring 75 mm in length and 25 mm in width, were prepared and subsequently dried overnight in an 80 °C oven. The peak load at a crosshead speed of 5 mm/min was then measured using a CT3 Texture Analyzer by Brookfield Engineering (USA), with a gauge length of 50 mm. The reported tensile stress values were derived from the average measurements of at least two samples.

Flat sheet supported liquid membrane

An organic LM was created using a solution of 0.3 M TOA dissolved in 2-ethyl-1-hexanol. The membrane support, measuring 11 cm × 5 cm, was immersed in the LM for a 24-hour period. Following incubation, any excess LM on the surface of the SLM was removed using filter paper.

The membrane support, with an active surface area of 42 cm^2, was then positioned and secured between the compartments of a membrane cell, both of which were made of Teflon. This inserted membrane served as the partition that separated the feed and stripping sides within the SLM system. For the circulation of the feed and strip phases, each containing 150 mL, a Masterflex L/S peristaltic pump was employed at a flow rate of 75 mL/min. The SLM was run for 8 h.

Sample analysis

The concentration of the LA in the samples was determined using the Synergy Hydro C18 HPLC column (Phenomenex, 250 mm × 4.6 mm, 4 µm particle size). The mobile phase consisted of 0.02 M potassium dihydrogen phosphate adjusted to a pH of 2.9. Detection of LA was achieved using an ultraviolet (UV) detector set at a wavelength of 221 nm. The column was maintained at 30 °C and operated for 22 min with a flow rate of 0.8 mL/min [9]. The LA extraction yield was subsequently computed using Eq. 2.

$$Extraction \quad yield \quad (\%) = \frac{[LA]_{0h,f} - [LA]_{8h,f}}{[LA]_{0h,f}} \times 100 \tag{2}$$

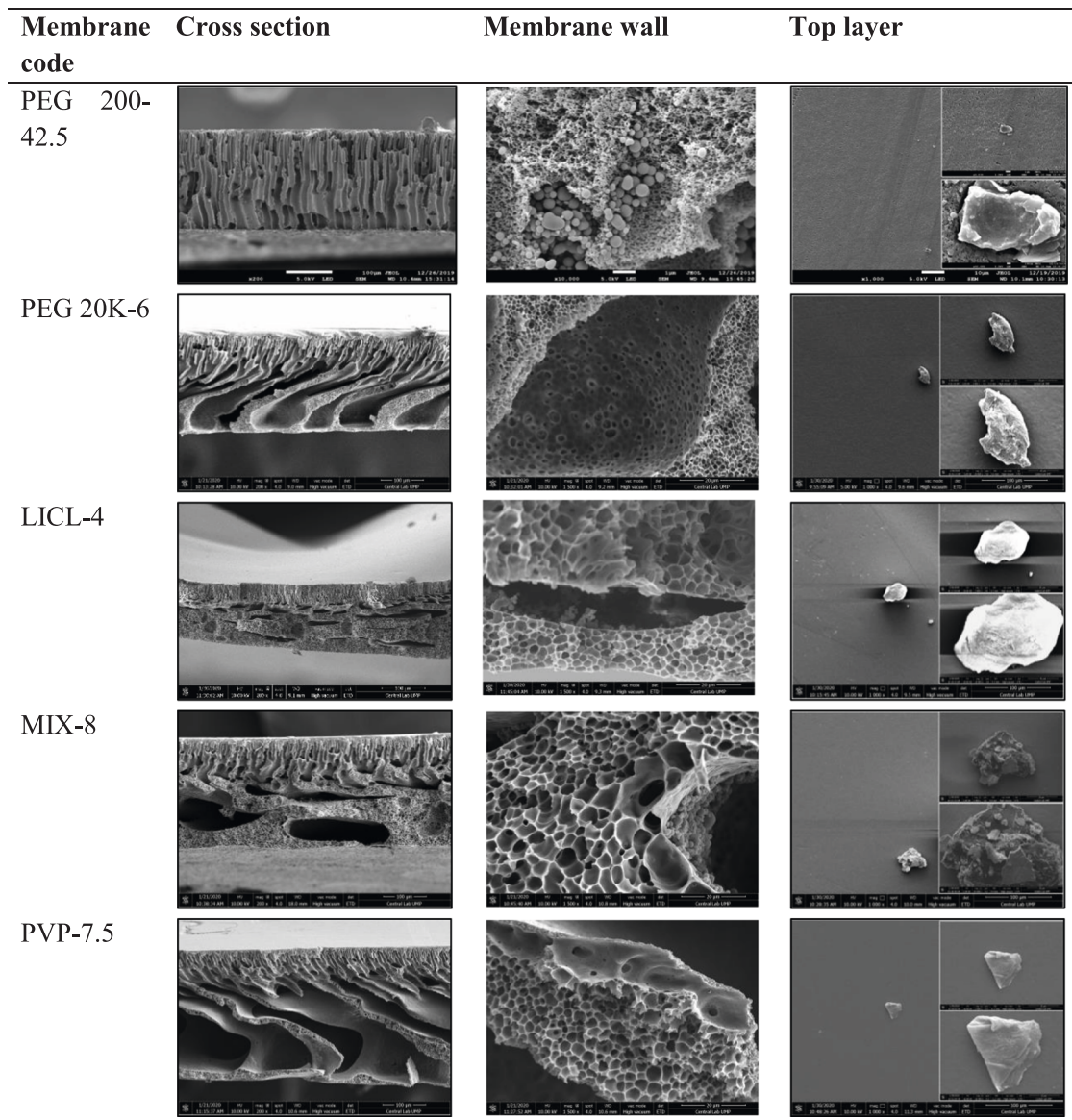| Membrane code	Cross section	Membrane wall	Top layer
PEG 200-42.5			
PEG 20K-6			
LICL-4			
MIX-8			
PVP-7.5			

Fig. 1. Morphology of the membrane.

Where $[LA]_{0\,h,f}$ and $[LA]_{8\,h,f}$ are initial and final concentrations of LA in the feed phase, respectively.

Results and discussion

Morphology of support membrane

Fig. 1 displays images depicting both the cross-sectional membrane wall and the upper surface of the prepared membranes. In the cross-section of PEG 200–42.5, there was a discernible porous thin skin layer at the top, accompanied by a sub-layer resembling finger-like macrovoids. Throughout the cross-section of PEG 200–42.5, a sponge-like structure was observed. The inclusion of another pore-forming agent in the dope solution resulted in the formation of a porous structure extending throughout the membrane. In the case of PEG 200–42.5, PEG 20 K-6, and PVP-7.5, finger-like macrovoids were evident from top to bottom. Conversely, LICL-4 and MIX-8 exhibited short finger-like macrovoids at the top, succeeded by a densely porous layer containing numerous closed macrovoids.

The introduction of LiCl into the casting solution led to an increase in dynamic viscosity and disrupted the thermodynamic properties of the

Table 2
Properties of the membranes.

Membrane code	Average porosity (%)	Empty space (cm^3)	Average contact angle of surface (°)		Tensile stress (kPa)
			Top	Bottom	
PEG 200-42.5	87.1 ± 3.20	0.9631	81.2 ± 1.77	98.0 ± 1.38	1091.55 ± 42.26
PEG 20 K-6	68.7 ± 4.75	1.0099	48.4 ± 0.49	74.9 ± 0.86	807.16 ± 29.97
LICL-4	45.5 ± 2.27	0.8218	71.5 ± 0.97	87.2 ± 0.91	1136.09 ± 105.94
MIX-8	62.0 ± 1.69	1.0152	61.3 ± 0.59	76.1 ± 1.28	655.56 ± 98.49
PVP-7.5	58.4 ± 1.58	1.1695	0	0	803.27 ± 51.94

solution. Consequently, this accelerated the phase separation process, resulting in the formation of closed macrovoids at the lower section of the membrane [5]. In the case of PEG 20 K-6 and PVP-7.5, the diameter of the finger-like macrovoids exhibited a significant enlargement from the upper to the lower regions due to the fusion of two or more regions of

Table 3
Performance of the membranes after 8 h of the SLM process.

Membrane code	LA at feed phase (g/L) after SLM	Extraction yield (%)
PEG 200-42.5	1.08	89.2
PEG 20 K-6	8.91	10.9
LICL-4	9.46	5.4
MIX-8	9.44	5.6
PVP-7.5	9.52	4.8

poorly mixed polymer before solidification of the wall took place. There is some agglomerated graphene embedded in the top surface of the membranes, as shown in Fig. 1.

Membrane Properties

Table 2 provides an overview of the membrane support's properties. The empty space within the membrane is a crucial characteristic that determines the capacity for accommodating liquid membrane within the support. Typically, membranes with larger pore sizes or a high degree of interconnected micropores tend to exhibit a greater empty space. Among the membranes, PVP-7.5 displayed the most substantial empty space, measuring at 1.1695 cm^3. This observation aligns with the formation of larger macrovoids in the PVP-7.5 membrane, as evidenced in Fig. 1. In contrast, the LICL-4 membrane exhibited the lowest empty space value, which was 0.8218 cm^3. Upon examination using SEM imagery, it became apparent that LICL-4 featured a dense structure with small microporous pores distributed throughout its cross-sectional membrane structure. Additionally, the presence of numerous highly interconnected, small-sized cylindrical micropores in the PEG 20 K-6 membrane contributed to an improved empty space for oil impregnation, measured at 1.0099 cm^3.

The porous membranes, characterized by large finger-like macrovoids in PEG 20 K-6, exhibited the lowest average contact angle values and were classified as hydrophilic membranes. Notably, PVP-7.5 displayed a contact angle value of zero, attributable to the extensive macrovoids present throughout the membrane, particularly in proximity to its top and bottom surfaces. Childress and Brant [1] proposed that these macrovoids could induce the capillary penetration of liquid during contact angle measurements, resulting in a reading of 0°. In contrast, the PEG 200–42.5 membrane, featuring a sponge-like structure at both its top and bottom layers, demonstrated the most hydrophobic surfaces, with contact angle measurements of $81.2 \pm 1.77°$ and $98 \pm 1.38°$, respectively.

The mechanical strength of PEG 200–42.5, characterized by its sponge-like structure, and LICL-4, which exhibits a compact-like structure, displayed robust tensile strengths of 1091.55 ± 42.26 kPa and 1136.09 ± 105.94 kPa, respectively. Consequently, these membranes are anticipated to possess exceptional resistance to the pressures generated during the SLM process. As a result, the stability of the SLM system utilizing these membranes is expected to be significantly enhanced. On the other hand, the unsymmetrical structures of PEG 20 K-6 and MIX-8, featuring a compact top layer and a more porous or loose bottom layer, resulted in lower tensile stress. Consequently, these membranes may be susceptible to rupture when subjected to high pressures during the SLM process. In Table 2, significant fluctuations in tensile stress for the LICL-4 and MIX-8 membranes are apparent due to their notably inconsistent structures. Fig. 1 highlights distinct differences in membrane thickness among various sections of the LICL-4 membrane. Furthermore, the MIX-8 membrane exhibits considerable variations in macrovoid size across its structure, contributing to the considerable deviation in tensile stress measurements.

Extraction of LA

The hydrophilic nature of PEG 20 K-6, LICL-4, MIX-8, and PVP-7.5,

along with their large macrovoids featuring porous wall structures, led to a weak capillary force between the macrovoids and the liquid membrane (LM). Consequently, the LM readily leaked from the membrane support, resulting in a notably low LA extraction yield, as detailed in Table 3. During the SLM (system, distinct LM droplets were clearly observed at the stripping phase. In contrast, PEG 200–42.5, characterized by its sponge-like structure, high contact angles, and average porosity value, demonstrated the highest LA extraction capability (89.2%) in the SLM process. No LM leakage was detected during the utilization of this support.

Conclusion

Pore-forming agents have exerted a significant influence on the characteristics of the membrane support and its performance within the SLM process. A membrane support featuring a sponge-like structural wall proves to be more suitable for SLM applications when compared to a membrane with a porous wall structure. The hydrophilic attributes of the membrane can lead to the loss of liquid membrane during the SLM process, ultimately compromising the separation of LA. Similarly, a membrane with low porosity values can result in diminished LA extraction and make it easier for the liquid membrane to be washed out. In summary, among the various pore-forming agents examined in this study, PEG 200 stands out as the most effective. PEG 200 has successfully modified the PES membrane, yielding an efficient membrane support for LA separation in the SLM process.

CRediT authorship contribution statement

Vikneswary Rajendaren: Investigation, Writing – original draft; **Syed M. Saufi:** Supervision, Conceptualization, Writing – review & editing; **M. A. K. M. Zahari:** Supervision, Conceptualization.

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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