멤브레인(Membrane Journal)
Vol. 34 No. 1 February 2024, 20-29

총 설
Print ISSN: 1226-0088
Online ISSN: 2288-7253
DOI: https://doi.org/10.14579/MEMBRANE_JOURNAL.2024.34.1.20

상분리법을 활용한 생분해성 폴리젖산 분리막 제조기술 개발 동향

투미스 아요드 오티토주* · 조 영 훈*,**,†

*한국화학연구원 화학공정연구본부 그린탄소연구센터, **과학기술연합대학원대학교 화학소재 및 공정

(2023년 12월 5일 접수, 2024년 1월 24일 수정, 2024년 1월 25일 채택)

Preparation of Biodegradable Polylactic Acid Membranes via Phase Separation: A Review

Tunmise Ayode Otitoju* and Young Hoon Cho*,,†**

*Green Carbon Research Center, Chemical & Process Technology Research, Korea Research Institute of Chemical Technology, Deajeon 34114, Republic of Korea

**Advanced Materials and Chemical Engineering, University of Science and Technology, Daejeon 34113, Republic of Korea

(Received December 5, 2023, Revised January 24, 2024, Accepted January 25, 2024)

요 약: 분리막 기술은 해수담수화, 기체분리 등 산업용 분리 정제 공정을 비롯하여 우리 주변의 생활용품, 의료 및 헬스케어 제품 등에서 쉽게 찾아볼 수 있다. 최근 지속가능한 친환경 분리막 제조 기술 또한 환경오염을 줄이기 위해 연구되고 있으며, 특히 polylactic acid (PLA), polybutylene adipate terephthalate (PBAT), polybutylene succinate (PBS) 등 생분해성 소재를 활용한 분리막 제조기술이 보고되어 왔다. 기존 분리막 소재와 마찬가지로 생분해성 고분자 소재들 또한 상분리 공정을 통해 다공성 분리막을 제조하는 연구가 이루어지고 있다. 본 총설을 통해 대표적인 생분해성 고분자인 PLA 기반의 상분리 공정을 활용한 분리막 제조 기술 개발 동향을 살펴보고 향후 연구 개발 및 적용 가능성에 대해 고찰해보고자 한다.

Abstract: Membranes are increasingly used in a variety of applications including desalination, gas separation, disposable filters, and healthcare products. Recently, sustainable and green membrane fabrication technology is recognized as one of the decisive initiatives to reach the target of pollution control. Especially, the fabrication of bio-based membranes using such as poly lactic acid (PLA), polybutylene adipate terephthalate (PBAT), and polybutylene succinate (PBS) has attracted considerable attention. The phase inversion method is one of the versatile approaches for preparing PLA membranes. This article reviews the recent advances in PLA membrane preparation via the phase inversion method. Furthermore, it provides a perspective on the potential outlook for future advances. Overall, this review has demonstrated has been conducted in the area of bio-based PLA membranes.

Keywords: *polylactic acid, phase separation, membrane preparation, biodegradable membrane, sustainable membrane*

1. Introduction

The issue of plastic pollution is widespread, endangering animal and human health as well as the natural ecosystem[1]. According to MacLeod *et al.*[2], the annual release of plastic garbage into the world's water reservoirs (oceans rivers, and lakes) is estimated to be between 9 and 23 million metric tons. The usage of conventional, petroleum-based plastics is linked to recyclability, waste management, and overproduction issues, all of which have significantly increased the issue of plastic pollution. Bio-based and biodegradable polymers such as poly (L-lactic acid) or PLA have been offered as potential solutions to these challenges. PLA is an aliphatic that can be produced by fermentation from eco-friendly or natural sources like wheat, corn

---

†Corresponding author(e-mail: yhcho@krict.re.kr; http://orcid.org/0000-0002-8863-1979)

starch, cassava, sugarcane, and other renewable resources[3]. In membrane formation, PLA presents a green alternative to conventional plastics and possesses several outstanding qualities such as minimal toxicity, compatibility, and the ability to degrade organically into compounds over time[4]. Moreover, PLA is highly versatile due to its high transparency and remarkable processability[5]. However, PLA suffers from serious drawbacks that limit its use in various applications. PLA's low melt strength and naturally slow crystallization rate limit its ability to be foamed, formed, and processed[6]. Despite its superior strength and modulus, PLA has a relatively poor toughness and is brittle. Due to its slow crystallization rate and low glass transition temperature (55~60°C), PLA has a low heat deflection temperature (HDT) or low service temperature. This prevents it from being used at too-low service temperatures[3,7]. Owing to its fabrication flexibility, PLA membranes are widely prepared using various techniques such as electrospinning, solvent casting, phase separation, freeze-drying, and particle leaching. These membranes have been extensively applied in membrane applications such as water and wastewater treatment, gas separation, pervaporation, hemodialysis, adsorption, and ion exchange membranes. In this review, we discuss the fabrication of PLA membranes via the phase separation method.

2. PLA Membrane Preparation via Phase Separation

Phase separation is the widely employed method for the preparation of PLA membranes due to its simplicity in forming a porous membrane. It is a controlled demixing process whereby the initially thermodynamically stable polymer solution is transformed from a liquid to a solid state[8]. Controlling the operating conditions is crucial for obtaining membranes with desirable morphology. The velocity of phase separation and solvent removal rate are the primary determinants of the membrane’s morphology and properties. This reaction occurs in a polymer solution and splits the thermodynamically unstable polymer-rich phase from the polymer-poor phase[9]. This transformation can be accomplished via immersion precipitation or nonsolvent induced phase separation (NIPS), precipitation by vapor or evaporation induced phase separation (EIPS), and thermally induced phase separation (TIPS). Among the aforementioned, NIPS, EIPS, and TIPS are frequently employed for the fabrication of PLA membranes.

2.1. Nonsolvent induced phase separation (NIPS)

NIPS is the simplest method and most widely used method for preparing PLA membranes. This process requires a strong solvent and a polymer that is soluble in solvent mixture. After casting the polymer solution onto a glass plate or other appropriate substrate, it is submerged in a coagulation bath containing nonsolvent or solvent-nonsolvent mixture. While the nonsolvent penetrates in the polymer solution, the solvent penetrates into the nonsolvent. This exchange process continues until demixing takes place. Thus, two phases emerge from a homogeneous polymer solution: the liquid-rich phase and the polymer-rich phase, which produces a membrane with an asymmetric structure[10]. The nascent membrane structure is affected by both phase separation and mass transfer. The exchange between the solvent and nonsolvent takes place on the PLA surface, forming a non-uniform porous structure with a wide PSD and poor mechanical properties [11,12]. One drawback of NIPS is the massive amount of wastewater that is contaminated with solvents. The preparation of PLA membranes using NIPs has been the subject of several studies. For instance, Ouda *et al.* prepared a PLA-based membrane using PVP as the pore-forming agent[13]. The PLA membrane showed a uniform surface that was well-dispersed with nano-sized pores. By introducing amino-activated carbon (AC) modified mangrove particles (MAC) into PLA solution, Khamis *et al.* also prepared a green pH-responsive adsorptive membrane (Fig. 1)[14]. With the introduction of 3 wt% of MAC, the porosity slightly increased from 87.5% to 89.6%. The pure and modified PLA membranes demonstrated a porous sublayer with finger-like

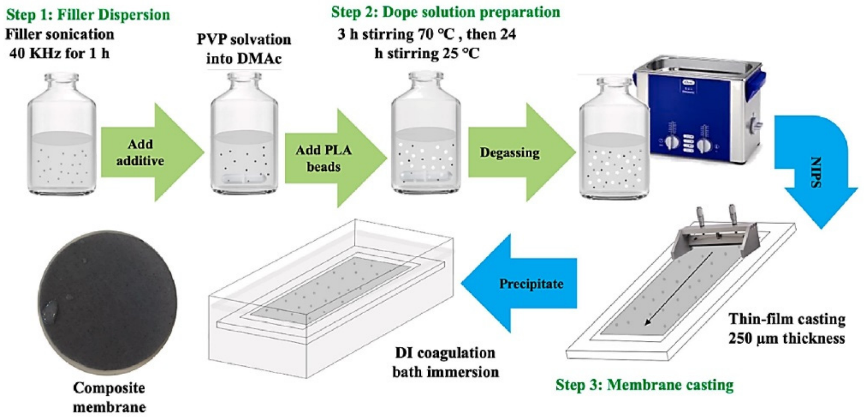


Fig. 1. Phase separation schematic[14].

or macrovoid morphology. The low viscosity of the PLA solution caused the transformation of the finger-like sublayer in PLA to a macrovoid sublayer in 1.5% MAC-PLA.

Gao *et al.* prepared a PLA membrane using PEG and NMP as pore agents and solvents, respectively[15]. PLA membranes show a smooth and compact surface with finger-like morphology. Abuhantash *et al.* reported a PLA/f-MWCNTs membrane at different f-MWCNTs content for oily wastewater treatment[16]. The introduction of f-MWCNTs caused the membrane's finger-like pores, pore size, and pore density to increase. This was due to the interaction between the kinetic and thermodynamic factors during the nonsolvents and solvents exchange. Due to this delay in nonsolvent and solvent exchange rate caused by the increased viscosity of the dope solution, the size of the pores increases. Khalil *et al.* reported a PLA membranes with porosity of around 63%[17,18]. The interconnectivity of membrane pores was impacted by an increase in polymer content, which resulted in the formation of smaller membrane pores. Nasser *et al.* also fabricated PLA ultrafiltration (UF) membrane via NIPS[19]. An increase in PLA content brought on by increase in dope viscosity resulted in the formation of denser surface pores. The diffusion rate of solvent (DMAC) out in the coagulation bath was slowed down by the nonsolvent (water) in the diffusion phase, which inhibits the growth of macrovoids. Xix-rodriguez *et al.* prepared hemocompatible membranes by blending PLA with different amphiphilic block co-polymers; poly(methyl methacrylate)-*b*-poly(2-dimethylamino ethyl methacrylate) (PD), poly(methyl methacrylate)-*b*-poly (2-hydroxyethyl methacrylate) (PH) and poly(methyl methacrylate)-*b*-poly (2-acryloamido-2-methyl-1-propanesulfonic acid) (PA)[20]. All membranes exhibited non-hemolyzing and hemocompatibility properties. The prepared membranes demonstrated a good trade-off between the desirable retention of proteins and the convective transport of middle-sized molecules. The pristine PLA show an asymmetric membrane finger-like structure which had a detrimental effect on its mechanical properties. However, the polymeric blend containing amphiphilic co-polymer present a sponge-like surface morphology. With the addition of amphiphilic co-polymers, the pore size and surface porosity were significantly reduced. Xiong *et al.* reported a PLA stereocomplex UF membrane containing PDLA and PLA with both high rejection and high permeability[21]. Due to the rapid liquid-liquid demixing process, the pure PLA membrane exhibit a smooth top surface, a dense skin layer with a complete finger-like morphology. Upon incorporation of PDLA, the finger-like pores was gradually confined and spherulites while sponge-like pores began to prevail in the cross-section.

In the field of membrane fabrication, the phase separation induced by water droplets has attracted attention as a potential NIPS method for preparing porous membranes. In this process, water droplets are used

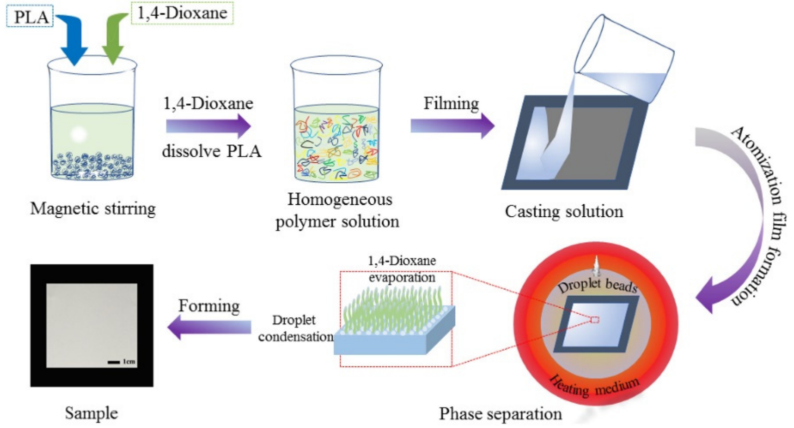


Fig. 2. Schematic illustration for the preparation of PLA membrane by water droplets induced phase separation[22].

during the PLA membrane preparation to induce phase separation in order to reduce the exchange rate between the solvent and nonsolvent while producing membranes with different morphologies[12]. Temperature, polymer-solvent concentration, and the size of the H_2O droplet are important variables that can be altered to tune the structure of PLA membranes. For example, Wang *et al.* prepared PLA porous membranes via H_2O droplets induced phase separation at varying temperature[22]. The schematic illustration of the synthetic route of the porous PLA membrane is shown in Fig. 2. Their result shows that the rate of nonsolvent to solvent exchange was slower than the rate of solvent volatilization. The formation of polymer-poor and polymer-rich phases at higher temperatures was found to be responsible for the improvement in water droplet vitality. On the other hand, an increase in the rate of solvent volatilization resulted in a shorter solidification time. As a result, the volume of the polymer-poor phase decline as the solidification time drops. When the temperature rose from 25 to 75 degrees Celsius, the average pore size also drops. This is similar to study by[23]. In their study, the pore size decreased and became densely packed when the temperature rose from 25 to 100 degrees Celsius. Less water was deposited on the membrane surface at high temperatures because the water droplets move more quickly and evaporate at a faster pace. Consequently, the phase separation speed, porosity and pore size decreases. In another study by Chinyerenwa *et al.*[24], the phase separation process was induced by heating water droplets to a high temperature using an electric heating steam generator. This method was used to shorten the preparation time of PLA membranes produced via water droplet induced phase separation. The schematic illustration of PLA membrane preparation via the hot water droplets induced phase separation is shown in Fig. 3. They found that the hot water droplets induced phase separation was faster than the room-temperature water droplets phase separation. Regular circular pores were formed on the surface of the membrane when water droplets at room-temperature was used as the coagulant. The average pore size rose from 55.12 to 64.76 μm when hot water droplets were substituted for room temperature droplets.

2.2. Thermally induced phase separation (TIPS)

TIPS is a method in which polymers like PLA that cannot be dissolved at room temperature is dissolved in a solvent at high temperatures and the polymer solution is then cast onto a support or glass plate. Then, the temperature is then lowered to allow for demixing. Liquid-liquid phase separation occurs at lower temperatures, resulting in the formation of two new phases: a polymer-poor phase and a polymer-rich[11]. Removing the solvents requires methods such as freeze-drying, extraction, and evaporation. Finally, a porous polymer structure is obtained following the removal of the

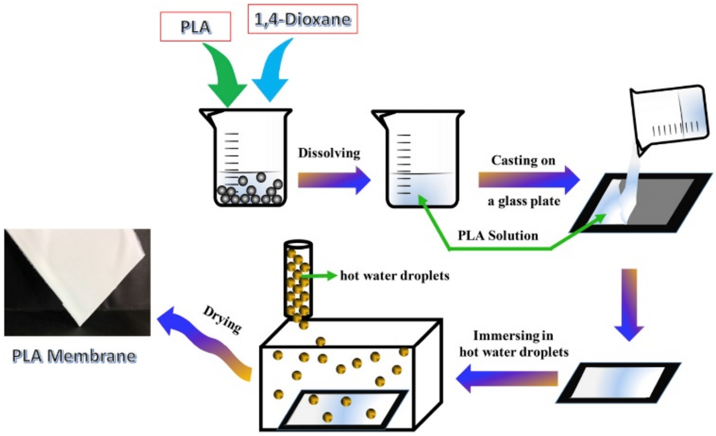


Fig. 3. Schematic illustration for the formation of a PLA membrane by hot water droplets induced phase separation[24].

solvent. The critical parameters that influence the kinetics and thermodynamics of microphase separation and crystallization are the solvent composition, quench temperature and polymer concentration. The advantages of TIPS include high porosity, process simplicity, the ability to create micro-structures with narrow PSD, minimal tendency to produce defeats, and high reproducibility[10]. For example, Tanaka *et al.* prepared microfiltration PLA membranes via TIPS[25]. The surface has pores of ∼ 10 μm, which was smaller than the internal and bottom pores of ~20 μm. Furthermore, uneven macroscopic structures were formed when the membrane was dried for 5 min or longer. In another study, asymmetric porous membranes were prepared by combining nonsolvent-induced and thermally induced phase separation (N-TIPS)[26]. This led to the formation of an asymmetric membrane structure with smooth and rough sides. It was assumed that the membrane structure at the smooth side was formed via nonsolvent phase separation. This is because the polymer solution came in contact with water, inducing the phase separation at 60 to 80 degrees Celsius. However, the structure of rough side was thought to have been formed via TIPS. This is because the side of the glass plate shielded the polymer solution from of H_2O influx while the polymer solution was cooled by the H_2O bath (25°C) through the plate. When the membrane was utilized as a depth filter, a rapid filtration rate was achieved.

2.3. Evaporation induced phase separation (EIPS)

EIPS, a polymer is dissolved in a mixture of solvent and nonsolvent to prepare a homogeneous solution, where the nonsolvent is less volatile than the solvent. Phase separation and the demixing of the polymer-solvent-nonsolvent system occurs as a result of the solvent evaporation, producing a porous film. Altering the polymer-solvent-nonsolvent solutions' composition allows for the control over the pore structures. For instance, Iulianelli *et al.* prepared dense PLA membranes with thicknesses between 23 and 30 μm by EIP for the treatment of gaseous streams rich in CH_4 and CO_2[27]. They used PLA at a different thickness to fabricate symmetric dense flat sheet membranes for the treatment of gaseous streams rich in CH_4 and CO_2[28]. They also used a modified PLA-based polymer (PLA Easy FilTM– White) to synthesize dense membranes for CO_2 separation[29]. Wu *et al.* combined PIM-1 and PLA to prepare a PLA/PIM-1 membranes with gas good selectivity and permeability for fruit storage application[30]. The preparation process of PLA/PIM-1 membranes is shown in Fig. 4. A high-temperature method was first used to prepare the PIM-1 polymer. At higher PIM-1 content (> 0.25%), the mechanical properties of PLA/PIM-1 membrane were slightly lower than that of the neat PLA membrane. They also combined chitosan (CA) and alizarin (AL) into PLA solution to produce a pH responsive PLA membrane (PLA/CA) for food packaging[31]. Fig. 5 shows the

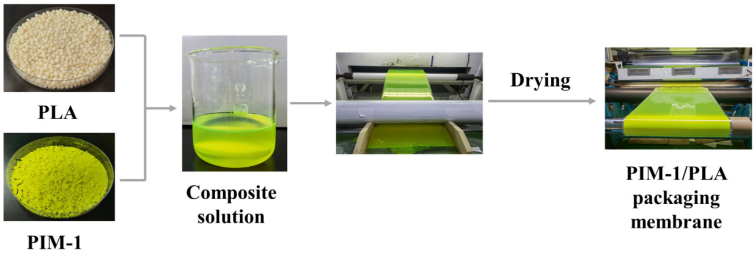
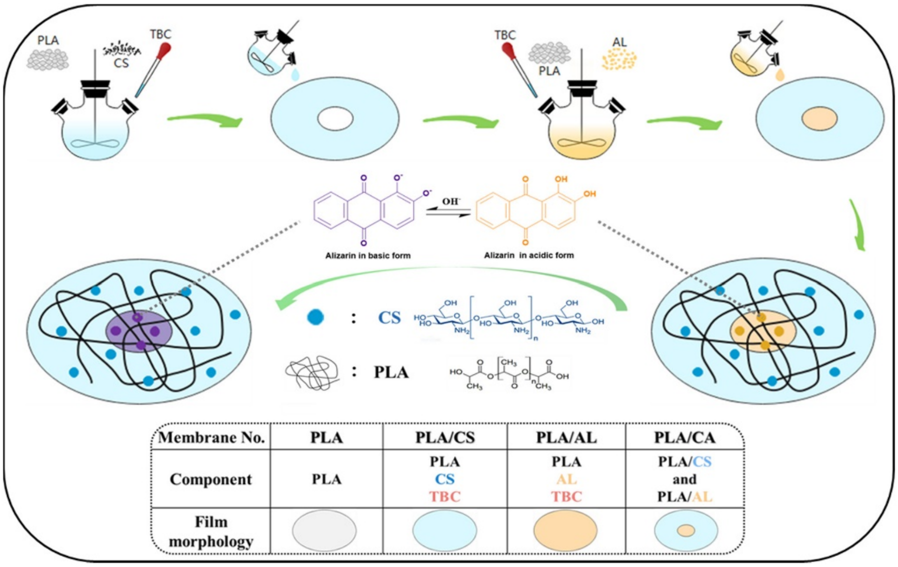


Fig. 4. The preparation process of PLA/PIM-1 membranes[30].



Membrane No.	PLA	PLA/CS	PLA/AL	PLA/CA
Component	PLA	PLA CS TBC	PLA AL TBC	PLA/CS and PLA/AL
Film morphology				

Fig. 5. Preparation process and phase morphology of PLA/CA membrane[31].

preparation process and phase morphology of PLA/CA films. The pure PLA and PLA composite films present flat and smooth surfaces. Moreover, the thickness of PLA/AL and PLA/CS composite films increases upon adding CS and AL. Zereshki *et al.* prepared PLA/PVP membranes containing different contents of PVP for ethanol/ethyl tert-butyl ether azeotropic separation[32]. The membrane showed a porous structure at higher PVP concentrations in its cross-sectional micrographs. They also prepared microfiltration PLA membranes with varying PVP content[33]. While pure PLA membrane shows a completely dense surface, PLA membranes containing PVP show a closed cellular structure. Galiano *et al.* reported PLA green membranes using ethyl lactate as solvent via combining EIPS with NIPS (E-NIPS)[34]. The membrane prepared at the shortest evaporation time (ET) of 0.5 min presents a macrovoid structure due to the instantaneous demixing rate, which occurred in water. As ET increases, the macrovoid structure gradually disappears. At higher ET, a fully or rigid dense skill layer structure was formed due to the complete solvent evaporation. Msahel *et al.* also prepared PLA membranes via E-NIPS[35]. The pristine membrane presents a dense and compact surface morphology. The introduction of the Fe-MOF was accompanied by the formation of small agglomerated particles on the membrane surface. Karakoca *et al.* investigate the potential of the Halloysite-PLA nanocomposite membrane for desalination[36]. The membrane cross-section image shows a dense skin layer with a complete honeycomb morphology at the bottom layer.

Table 1. Summaries of the Application of PLA Membranes Prepared via the Phase Separation Methods

Applications	Polymer	Solvent	Additive	Preparation method	Representative separation performance	Ref.
Water purification	PLA	1, 4-dioxane	-	TIPS	Cell retention: 99.4%; BSA retention: 8%	[25]
	PLA stereocomplex	NMP	PDLA	NIPS	PWF: ~3325 kg/m^{2}h; BSA rejection: 88%	[21]
	PLA	DMAc	PVP	NIPS	NH_4^+-$N_{synthetic}$ rejection: 96%; NH_4^+-N_{raw} rejection: 87%; PO_4^{3-}-$P_{synthetic}$ rejection: 22%; PO_4^{3-}-P_{raw} rejection: 52%.	[19]
	PLA-PVP	NMP	-	NIPS	Porosity: 55%; Perrmeability: 359 kg/m^{2}hbar; HM flux: 350 LMH; NOM flux: 208 kg/m^{2}h; NOM rejection: 81.5%	[13]
	3MAC-PLA	DMAc	MAC	NIPS	Flux: 2306.6 kg/m^{2}hbar; Cu^{2+} removal: 88%; Ni^{2+} removal: 39.1%; Pb^{2+} removal: 82%	[14]
	PVP/PLA-M	DMAc	f-GO/MWCNTs-COOH nanohybrid	NIPS	Flux: 32.68~46.85 kg/m^{2}hbar; FRR: 69%; COD removal: 79.6~85.58%	[37]
	PLA-PVP	DMAc	f-MWCNTs	NIPS	PWF: 485 kg/m^{2}hbar; PF: 281 kg/m^{2}hbar; Oil rejection: 100%; FRR: 60%	[16]
	PLA	DMAc	PVP	NIPS	PWF: 27 kg/m^{2}h; BSA removal: 91%; COD removal: 82.138%; FRR: 89%	[18]
	PLA	DMAc	PVP	NIPS	$BSA_{synthetic}$ rejection: 92%; BSA_{raw} rejection: 89%	[17]
Gas separation	PLA	Chloroform	-	EIPS	$P(H_2)$: ~25 Barrer; $P(CH_4)$: ~8.25 Barrer; $P(O_2)$: ~3.6 Barrer; $P(N_2)$: ~3.4 Barrer; $P(CO_2)$: ~1 Barrer; Ideal selectivity (H_2/CO_2): 26.5; Ideal selectivity (H_2/CH_4): 10; Ideal selectivity (H_2/N_2): 5.7; Ideal selectivity (H_2/O_2): 5.5	[28]
	PLA	Chloroform	-	EIPS	$P(CO_2)$: ~11 Barrer; Ideal selectivity (CO_2/CH_4): 220~230	[29]
Pervaporation	PLA	Ethyl lactate	-	E-NIPS	Permeation flux: 0.21 kg/m^{2}h	[34]
	PLA	Chloroform	PVP	EIPS	Flux: 0.05 kg/m^{2}h	[33]
	PLA	Chloroform	PVP	EIPS	Flux: 1.35 kg/m^{2}h; Separator factor: 3.7; Flux: 3.6 kg/m^{2}h	[32]
	PLA	Chloroform	Fe-MOF	E-NIPS	Flux: 0.28 kg/m^{2}h; Selectivity: 17.5	[35]
Desalination (Pervaporation)	PLA-MIL 140 A	Chloroform, DMF	MIL 140 A	NIPS	Flux: 12.2 kg/m^{2}h; Rejection: 99.92%	[38]
	PLA-PEG	Chloroform, DMF	Hal	E-NIPS	Flux: 13.14 kg/m^{2}h; Rejection: 99.95%.	[36]
Hemodialysis	PLA	DMAc	PA, PD, PH	NIPS	PWF: 120~500 kg/m^{2}h; Urea clearance: 70~80%; Lysozyme clearance: 15~40.5%; BSA retention: 65~93%; FRR: 62~69%	[20]
	PLA-PEG	NMP	-	NIPS	Flux: 120 kg/m^{2}h; Lysozyme clearance: 13.7%; BSA rejection: 93.7%	[15]
Food packaging	PIM-1/PLA EMAP	DCM	PIM-1	EIPS	O_2 permeance: 3027.82 cm^3/m^2·24 h · 0.1 MPa; CO_2 permeance: 5648.99 cm^3/m^2·24 h · 0.1 MPa; CO_2/O_2 separation coefficient (α): 1.87	[30]
	PLA	DMF	CS and AL	EIPS	Antioxidant activities: 43.3%; Inhibitory rates against Escherichia coli: 87.91%; Inhibitory rates against Staphylococcus aureus: 75.17%	[31]

NMP: N-methyl-2-pyrrolidone; AC: activated carbon; MAC: amino-functionalized activated carbon-modified mangrove; PIM: Polymers of intrinsic microporosity; EMAP: equilibrium modified atmosphere packaging; DCM: dichloromethane; PD: poly(methyl methacrylate)-*b*-poly(2-dimethylamino ethyl methacrylate), PH: poly (methyl methacrylate)-*b*-poly(2-hydroxyethyl methacrylate) and PA: poly(methyl methacrylate)-*b*-poly(2-acryloamido-2-methyl-1-propanesulfonic acid); CS: chitosan and AL: alizarin; PSI: Pervaporation separation index; Hal: Halloysite nanotube; f-MWCNTs: Amino-SiO_2 functionalized multi-walled carbon nanotubes; COD: chemical oxygen demand; PWF: pure water flux; FRR: flux recovery ratio; PF: permeate flux; BSA: Bovine serum albumin.

3. Applications

Due to its biodegradability and biocompatibility, PLA membrane prepared via the phase separation method has been widely applied in numerous membrane-based applications such as water purification, wastewater treatment, gas separation, food and fruit packaging, hemodialysis pervaporation, and desalination. For instance, PLA membranes can offer excellent selectivity and permeability for gas application and filtration performance for liquid separation. The applications of PLA membranes prepared via the phase separation method are shown in Table 1.

4. Conclusion

PLA is one of the commonly used bio-based polymers for the preparation of polymeric membranes. It has received significant attention due to its numerous properties, including biodegradability, biocompatibility, easy processability, low cost, and safe waste disposal. Numerous works have been conducted on the preparation of PLA membranes via the phase separation method and its applicability for diverse applications. However, there is a major challenge in its dissolution in various organic solvents. The solubility of PLA in nonpolar organic solvents holds great potential for the preparation of membranes via phase separation such as NIPS. However, these limitations can be overcome by blending with various fillers or polymers. On the other hand, the common solvents used to fabricate PLA membranes are mostly toxic polar aprotic solvents such as chloroform, dichloromethane, 1, 4-dioxane, N-methylpyrrolidone, dimethylformamide, and dimethylacetamide. Hence, future works should replace these toxic materials with environmentally friendly alternatives such as Polarclean, Tamisolve, Cyrene, and γ-butyrolactone in order to maintain the sustainable development of membrane technology.

Acknowledgement

This work is supported by the project “Development of separation and purification technology for manufacturing eco-friendly chemicals based on green carbon” of KRICT (KK2411-40) funded by Ministry of Science and ICT Korea.

Reference

1. L. Roman, Q. Schuyler, C. Wilcox, and B. D. Hardesty, “Plastic pollution is killing marine megafauna, but how do we prioritize policies to reduce mortality?”, *Conserv. Lett.*, **14**, e12781 (2021).
2. M. MacLeod, H. P. H. Arp, M. B. Tekman, and A. Jahnke, “The global threat from plastic pollution”, *Science*, **373**, 61-65 (2021).
3. F. Iñiguez-Franco, R. Auras, M. Rubino, K. Dolan, H. Soto-Valdez, and S. Selke, “Effect of nanoparticles on the hydrolytic degradation of PLA-nanocomposites by water-ethanol solutions”, *Polym. Degrad. Stab.*, **146**, 287-297 (2017).
4. J. Bustillos, D. Montero, P. Nautiyal, A. Loganathan, B. Boesl, and A. Agarwal, “Integration of graphene in poly(lactic) acid by 3D printing to develop creep and wear-resistant hierarchical nanocomposites”, *Polym. Compos.*, **39**, 3877-3888 (2018).
5. M. Nofar, D. Sacligil, P. J. Carreau, M. R. Kamal, and M.-C. Heuzey, “Poly (lactic acid) blends: Processing, properties and applications”, *Int. J. Biol. Macromol.*, **125**, 307-360 (2019).
6. M. Nofar and C. B. Park, “Poly (lactic acid) foaming”, *Prog. Polym. Sci.*, **39**, 1721-1741 (2014).
7. Z. N. Diyana, R. Jumaidin, M. Z. Selamat, I. Ghazali, N. Julmohammad, N. Huda, and R. A. Ilyas, “Physical properties of thermoplastic starch derived from natural resources and its blends: A review”, *Polymers*, **13**, 1396 (2021).
8. T. A. Otitoju, A. L. Ahmad, and B. S. Ooi, “Superhydrophilic (superwetting) surfaces: A review on fabrication and application”, *J. Ind. Eng. Chem.*, **47**, 19-40 (2017).

9. A. Figoli, T. Marino, and F. Galiano, “2 - Polymeric membranes in biorefinery, In: A. Figoli”, A. Cassano, A. Basile (Eds.), *Membrane Technologies for Biorefining*, pp. 29-59, Woodhead Publishing (2016).
10. S. Zare and A. Kargari, “4 - Membrane properties in membrane distillation”, pp. 107-156, In: V. G. Gude (Ed.), *Emerging Technologies for Sustainable Desalination Handbook*, Butterworth-Heinemann (2018).
11. H. Wang, W. Qiao, S. Ma, L. Wang, C. Liu, Y. Zhou, S. Gu, W. Xu, J. Shi, and H. Yang, “Effect of temperature on the thermal property and crystallization behavior of poly (lactic acid) porous membrane prepared via phase separation induced by water microdroplets”, *Int. J. Biol. Macromol.*, **147**, 1185-1192 (2020).
12. H. Yang, Q. Ye, Y. Zhou, Y. Xiang, Q. Xing, X. Dong, D. Wang, and W. Xu, “Formation, morphology and control of high-performance biomedical polyurethane porous membranes by water micro-droplet induced phase inversion”, *Polymer*, **55**, 5500-5508 (2014).
13. M. Ouda, Y. Ibrahim, P. Kallem, B. Govindan, F. Banat, and S. W. Hasan, “Highly permeable, environmentally-friendly, antifouling polylactic acid-hydroxyapatite/polydopamine (PLA-HAp/PDA) ultrafiltration membranes”, *J. Clean. Prod.*, **330**, 129871 (2022).
14. F. Khamis, H. M. Hegab, F. Banat, H. A. Arafat, and S. W. Hasan, “Development of sustainable pH-responsive adsorptive modified mangrove-based polylactic acid ultrafiltration membrane for the removal of heavy metals from aqueous solution”, *Chem. Eng. J.*, **474**, 145471 (2023).
15. A. Gao, F. Liu, L. Xue, “Preparation and evaluation of heparin-immobilized poly (lactic acid) (PLA) membrane for hemodialysis”, *J. Membr. Sci.*, **452**, 390-399 (2014).
16. F. Abuhantash, H. M. Hegab, I. H. Aljundi, and S. W. Hasan, “Synergistic design of polylactic acid/functionalized multi-walled carbon nanotubes composite membrane for enhanced oil-water separation”, *J. Environ. Chem. Eng.*, **11**, 111566 (2023).
17. H. Khalil, H. M. Hegab, L. Nassar, V. S. Wadi, V. Naddeo, A. F. Yousef, F. Banat, and S. W. Hasan, “Asymmetrical ultrafiltration membranes based on polylactic acid for the removal of organic substances from wastewater”, *J. Water Process. Eng.*, **45**, 102510 (2022).
18. H. Khalil, V. S. Wadi, H. M. Hegab, L. Nassar, V. Naddeo, A. F. Yousef, F. Banat, and S. W. Hasan, “High-performance f-GO/MWCNTs-COOH nanohybrid-based polylactic acid mixed matrix membrane for wastewater treatment”, *J. Water Process. Eng.*, **53**, 103784 (2023).
19. L. Nassar, H. M. Hegab, H. Khalil, V. S. Wadi, V. Naddeo, F. Banat, and S. W. Hasan, “Development of green polylactic acid asymmetric ultrafiltration membranes for nutrient removal”, *Sci. Total Environ.*, **824**, 153869 (2022).
20. C. Xix-Rodriguez, P. Varguez-Catzim, A. Alonzo-García, N. Rodriguez-Fuentes, H. Vázquez-Torres, A. González-Diaz, M. Aguilar-Vega, and M. O. González-Díaz, “Amphiphilic poly(lactic acid) membranes with low fouling and enhanced hemodiafiltration”, *Sep. Purif. Technol.*, **259**, 118124 (2021).
21. Z. Xiong, Y. Zhong, H. Lin, F. Liu, T. Li, and J. Li, “PDLA/PLLA ultrafiltration membrane with excellent permeability, rejection and fouling resistance via stereocomplexation”, *J. Membr. Sci.*, **533**, 103-111 (2017).
22. H. Wang, L. Wang, C. Liu, Y. Xu, Y. Zhuang, Y. Zhou, S. Gu, W. Xu, and H. Yang, “Effect of temperature on the morphology of poly (lactic acid) porous membrane prepared via phase inversion induced by water droplets”, *Int. J. Biol. Macromol.*, **133**, 902-910 (2019).
23. C. Liu, W. Qiao, C. Wang, H. Wang, Y. Zhou, S. Gu, W. Xu, Y. Zhuang, J. Shi, and H. Yang, “Effect of poly (lactic acid) porous membrane prepared via phase inversion induced by water droplets on 3T3 cell behavior”, *Int. J. Biol. Macromol.*, **183**, 2205-2214 (2021).
24. A. C. Chinyerenwa, H. Wang, Q. Zhang, Y.

Zhuang, K. H. Munna, C. Ying, H. Yang, and W. Xu, “Structure and thermal properties of porous polylactic acid membranes prepared via phase inversion induced by hot water droplets”, *Polymer*, **141**, 62-69 (2018).

25. T. Tanaka, M. Ueno, Y. Watanabe, T. Kouya, M. Taniguchi, and D. R. Lloyd, “Poly(L-lactic acid) microfiltration membrane formation via thermally induced phase separation with drying”, *J. Chem. Eng. Japan*, **44**, 467-475 (2011).
26. T. Tanaka, T. Nishimoto, K. Tsukamoto, M. Yoshida, T. Kouya, M. Taniguchi, and D. R. Lloyd, “Formation of depth filter microfiltration membranes of poly(l-lactic acid) via phase separation”, *J. Membr. Sci.*, **396**, 101-109 (2012).
27. A. Iulianelli, F. Russo, F. Galiano, G. Desiderio, A. Basile, and A. Figoli, “PLA easy fil − white-based membranes for CO_2 separation”, *GREENH GASES*, **9**, 360-369 (2019).
28. A. Iulianelli, C. Algieri, L. Donato, A. Garofalo, F. Galiano, G. Bagnato, A. Basile, and A. Figoli, “New PEEK-WC and PLA membranes for H_2 separation”, *Int. J. Hydrog. Energy*, **42**, 22138-22148 (2017).
29. A. Iulianelli, F. Russo, F. Galiano, M. Manisco, and A. Figoli, “Novel bio-polymer based membranes for CO_2/CH_4 separation”, *Int. J. Greenh. Gas Control*, **117**, 103657 (2022).
30. Y. Wu, K. Xiao, L. zhu, and Q. Luo, “Preparation and application of equilibrium modified atmosphere packaging membranes with polylactic acid and polymers of intrinsic microporosity”, *Food Packag. Shelf Life*, **37**, 101063 (2023).
31. Y. Wu, Y. Ma, Y. Gao, Y. Liu, and C. Gao, “Poly (lactic acid)-based pH responsive membrane combined with chitosan and alizarin for food packaging”, *Int. J. Biol. Macromol.*, **214**, 348-359 (2022).
32. S. Zereshki, A. Figoli, S. S. Madaeni, F. Galiano, and E. Drioli, “Pervaporation separation of ethanol/ETBE mixture using poly(lactic acid)/poly(vinyl pyrrolidone) blend membranes”, *J. Membr. Sci.*, **373**, 29-35 (2011).
33. S. Zereshki, A. Figoli, S. S. Madaeni, S. Simone, J. C. Jansen, M. Esmailinezhad, and E. Drioli, “Poly(lactic acid)/poly(vinyl pyrrolidone) blend membranes: Effect of membrane composition on pervaporation separation of ethanol/cyclohexane mixture”, *J. Membr. Sci.*, **362**, 105-112 (2010).
34. F. Galiano, A. H. Ghanim, K. T. Rashid, T. Marino, S. Simone, Q. F. Alsalhy, and A. Figoli, “Preparation and characterization of green polylactic acid (PLA) membranes for organic/organic separation by pervaporation”, *Clean Technol. Environ. Policy*, **21**, 109-120 (2019).
35. A. Msahel, F. Galiano, M. Pilloni, F. Russo, A. Hafiane, R. Castro-Muñoz, V. B. Kumar, A. Gedanken, G. Ennas, Z. Porat, A. Scano, S. B. Hamouda, and A. Figoli, “Exploring the effect of iron metal-organic framework particles in polylactic acid membranes for the azeotropic separation of organic/organic mixtures by pervaporation”, *Membranes*, **11**, 65 (2021).
36. F. U. Nigiz and B. Karakoca, “Halloysite nanotube doped poly lactic acid membrane preparation and seawater desalination”, *Appl Clay Sci*, **231**, 106721 (2023).
37. S. Cairone, H. M. Hegab, H. Khalil, L. Nassar, V. S. Wadi, V. Naddeo, S. W. Hasan, “Novel eco-friendly polylactic acid nanocomposite integrated membrane system for sustainable wastewater treatment: Performance evaluation and antifouling analysis”, *Sci. Total Environ.*, **912**, 168715 (2024).
38. F. U. Nigiz and B. Karakoca, “Pervaporative desalination using MIL 140 A loaded polylactic acid nanocomposite membrane”, *Process Saf. Environ. Prot.*, **169**, 447-457 (2023).