

MORPHOLOGICAL INVESTIGATION OF POLY(LACTIC ACID) ASYMMETRIC MEMBRANE

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Abstract

The use of biodegradable material in membrane technology will be a great solution in reducing unbiodegradable waste in the landfill. The main objective of this preliminary study is to investigate the morphology and mechanical properties of poly(lactic acid) (PLA) flat sheet membrane as the solvent evaporation time was varied and its potential for gas separation process. Dichloromethane was used as a solvent for preparing 15wt% PLA membrane dope solution. The membranes were produced by a simple dry/wet phase inversion technique using a pneumatically controlled casting system with various solvent evaporation times between 10 to 90 s to promote the formation of the desired structure prior to immersion into a water coagulation bath. Prior to the gas permeation test, the prepared membrane were coated with silicone rubber coating to reduce the membrane surface defect and improved the gas separation performance. The membrane surface morphology was examined using scanning electron microscopy (SEM). This preliminary study revealed that the produced membrane possessed an asymmetric structure with a very thin dense layer, a porous substructure and the porosity of the skin surface was reduced as the evaporation time increased. This showed that the membrane had a better molecular rearrangement and this was further supported by the slight improvement of the membrane mechanical strength. Pressure-normalized fluxes of oxygen and nitrogen and the separation factor of O_2/N_2 measured showed that PLA asymmetric membrane has a potential as a membrane material for gas separation. Further improvement is required in term of morphology with defect-free layer to ensure the PLA membrane can perform at its best in a gas separation process.

Keywords: Asymmetric membrane, Biodegradable polymer, Gas separation, Solvent evaporation time.

Nomenclatures

<i>h</i>	Hour
<i>min</i>	Minute
<i>mm/min</i>	Millimeter per minute
<i>s</i>	seconds
<i>wt %</i>	Weight percentage
<i>% (w/w)</i>	Percentage weight/weight

Abbreviations

ASTM	American Society for Testing and Materials
DCM	Dichloromethane
MMSCFD	Million standard cubic feet per day
PDMS	Polydimethylsiloxane
PLA	Poly(lactic acid)
SEM	Scanning electron microscope
UTM	Universal Testing Machine

1. Introduction

The major breakthrough in research and development of membrane technology is the successful commercialization of gas permeation systems. Membrane technology for gas permeation has been identified in varieties of industrial application such as in carbon dioxide removal, oxygen enrichment, helium recovery, sour gas treating and so forth [1]; and recently has been covering many existing and emerging application. According to statistical data, there are more than 10,000 commercial membrane systems in current operation for various gas separation applications and the estimated current total worldwide installed capacity of gas separation system using membrane is about 3500 million standard cubic feet per day (MMSCFD) [2]. Opportunities are immense in future, with significant inroads continually being made in new fields. According to Benny D. Freeman, a professor of chemical engineering at the University of Texas, Austin, gas separation offer a number of benefits; no additional phase change that required a significant energy cost, required a smaller unit than any other types of plants, thus, requiring a small footprint, and lack of mechanical complexity in membrane system [3].

Polymer is the most widely used membrane materials for gas separation due to its process ability into hollow fibres with high surface area and relatively low cost of manufacturing [3]. Petrochemical-based synthetic polymer have brought extensive benefits to mankind in many aspects, but the ecosystem and environment are, therefore, disturbed and polluted as a result of the accumulation of petroleum-based disposal waste [4]. The gradually increasing interest has been paid to the production of biodegradable and biocompatible polymer over the last few years such as cellulose and polyimides for acidic gas separation [5], thermoplastic starch [6], and aliphatic polyesters [7].

Research in biodegradable and bioresorbable polymers has received increase attention in recent years because of their wide application in environmental and clinical medicine and their potential of replacing the non-biodegradable polymer.

Poly(lactic acid) is thermoplastic aliphatic polyester that are generally prepared by ring-opening polymerization of lactide, a cyclic dimer prepared by the controlled depolymerisation of lactic acid, which in turn, is obtained by the microbial fermentation of annual renewable sugar-based materials such as starch or cellulose [8]. Poly(lactic acid) (PLA) is widely used as fibres, films, food packaging, used in medical application, as a textile material and the increasing demand of PLA is not only because of the need to ultimately replace many petroleum-based polymers but also because of their potentially useful physical and mechanical characteristic [7].

In this study, PLA is used as the membrane material for gas separation due to its water-sensitivity, thermal and mechanical properties that are superior to other biodegradable aliphatic polyesters. The main aim for this study is to investigate the effect solvent evaporation time on the molecular alignment, mechanical properties, and membrane gas permeation performance.

2. Experimental

2.1. Materials

Poly(lactic acid) (PLA) polymer supplied by Shanghai Guanghe Biotech Co. Ltd was used as the membrane material. The organic solvent used was Dichloromethane (DCM) supplied by Merck, Darmstadt, Germany and tap water was used as the coagulant medium during phase inversion process. All chemicals are used as acquired. The silicone coating solution was prepared using polydimethylsiloxane (PDMS), Sylgard 184, procured from Dow Corning and analytical reagent grade n-pentane from Merck, Darmstadt, Germany.

2.2. Preparation of dope solution

Prior to the dope solution preparation of 15 wt.% PLA, the polymer was dried overnight in a vacuum oven at about 60°C. Firstly, DCM was poured into a bottle and stirred using a mechanical stirrer. Poly(lactic acid) polymer was slowly added to avoid agglomeration and the mixing was continued for about 24 h to ensure a homogenous solution was prepared. Then, the solution was degassed using an ultrasonic bath to remove trapped micro-bubbles prior to casting process.

2.3. Preparation of flat sheet asymmetric membrane

Casting process was performed using a pneumatically controlled casting machine. First, the dope solution was cast on a clean glass plate with a casting knife gap setting of 150 µm at an appropriate casting shear. The casting speed was fixed at 8 s and the forced convection residence durations were varied at 10, 30, 60, and 90 s. After an additional of free standing time around 5 s, the nascent membranes were removed from the glass plate by quenching immediately and smoothly into an aqueous bath at room temperature (~28°C) and remained there for about 24 h. Finally, the produced membranes were air dried at room temperature for another 24 h before storing them in sealed plastic bags prior to testing.

2.4. Silicon rubber coating

After the flat sheet membranes were tested, they were dip coated with a 3% (w/w) solution of polydimethylsiloxane (PDMS) dissolved in n-pentane for 5 min. The coated fibers were then allowed to cure at room temperature for 48 h. The purpose of this coating was to seal any surface defects of the membrane surface.

2.5. Scanning electron microscope (SEM)

The morphology and structure of prepared membranes were observed using a scanning electron microscope. These samples were cryogenically prepared prior to positioning on a metal holder for gold coating using sputter coating operated under vacuum. The SEM micrographs of both surface and cross-section of the membranes were taken.

2.6. Tensile test

The mechanical property of membranes can be obtained by measuring its tensile strength. Universal Testing Machine (UTM, Lloyd Instruments, UK) was employed to test the tensile strength of the membrane sample using ASTM D882–12 standard for sample preparation. Samples are measured at a rate of 2 mm/min strain

2.7. Gas permeation test

Gas permeation of pure oxygen (O₂) and nitrogen (N₂) were measured using soap bubble method at 28°C and pressures of 6, 7, 8, 9 and 10 bar. The gas permeation tests were run on 3 sample of the coated membrane with 10 times repetitions.

3. Results and Discussion

3.1. Morphology of poly(lactic acid) (PLA) asymmetric membrane

The formation of dense surface layer occurs during the dry phase when solvent is evaporated out from the membrane surface. Figure 1 illustrates the photomicrographs of dry/wet phase inversion shear cast poly(lactic acid) asymmetric membranes surface at solvent evaporation times of 10s, 30s, 60s and 90s. As shown from Fig. 1(a-d), the increment of solvent evaporation time decreases the porosity of the membrane surface. This may be due to the sufficient time for membrane molecular chains rearrangement that causing the membrane surface to become closely pack thus decreasing the pore size on the membrane surface. Membrane porosity has been considered as one of the important factor that affecting the membrane gas separation performance. Sharpe et al. discussed that the increase in solvent evaporation time had extended the time forth formation and coalescence of the polymer rich phase in becoming more oriented, promoting a more mature and properly formed skin [9]; improving the formation of defect-free surface layer thus enhancing the gas pair selectivity [10].

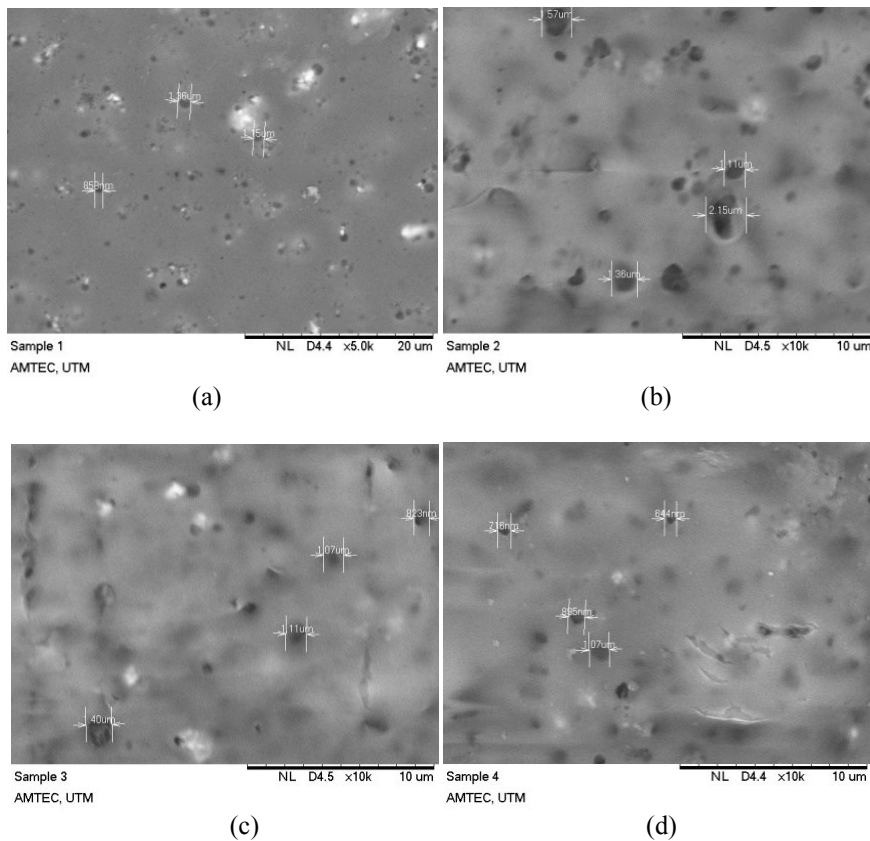


Fig. 1. Scanning Electron Micrograph (SEM) Surface Images of the Flat Sheet Asymmetric Membrane at Evaporation Time. (a) 15 wt.% PLA at 10 s Evaporation Time, (b) 15 wt.% PLA at 30 s Evaporation Time, (c) 15 wt.% PLA at 60 s Evaporation Time (d) 15 wt.% PLA at 90 s Evaporation Time.

3.2. Tensile strength

Mechanical strength of a membrane is important in order to determine the membrane life expectancy and its endurance against harsh condition. The mechanical strength improvement is required in order to maintain the membrane sustainability in industrial application. Figure 2 shows the graph of tensile strength and young modulus of PLA flat sheet membrane at different solvent evaporation time. As the solvent evaporation time increase, the membrane tensile strength and young modulus increase. The increasing in tensile strength is may be due to the greater orientation of the membrane molecular alignment that causes the formation of a compact support structure [11]. Other possibility is the contribution of the interaction within membrane molecule where the increase in solvent evaporation time, which means that more solvent evaporated out from the membrane causing the intermolecular interaction between PLA molecules becomes greater thus increasing the membrane mechanical strength. Figure 2 also shows that the membrane young modulus increases with the increment of solvent evaporation time. The increases in young modulus demonstrate that the

membrane elasticity decreases and increase its brittleness causing the difficulties in handling the membrane for further testing.

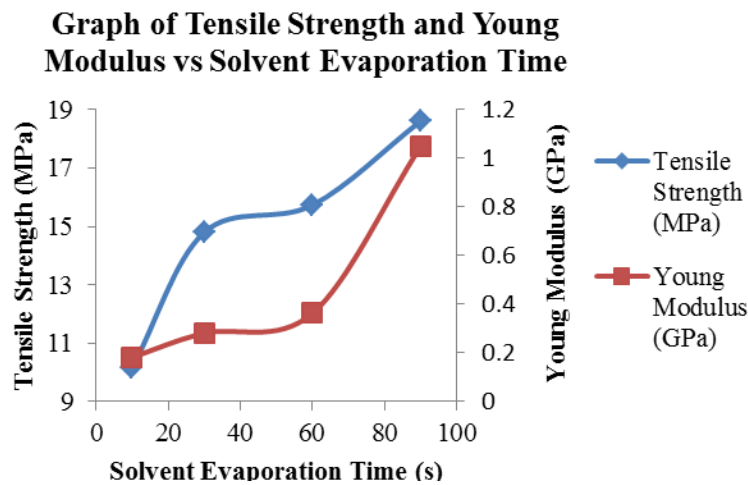


Fig. 2. Graph of Tensile Strength and Young Modulus of PLA Flat Sheet Membranes vs. Solvent Evaporation Time.

3.3. Gas permeation performance

The evaporation step is considered essential for the determination of membrane permeability and selectivity. The permeation tests performed on the asymmetric membranes are predicted to illustrate that the pressure-normalized fluxes of all gases decrease while improving the gas pair selectivity with increasing force convection residence time due to the enhancement of effective skin layer thickness [12]. Figure 3 shows the relationship of solvent evaporation time on gas permeance and selectivity of flat sheet PLA membrane.

The result shows based on 15 wt.% PLA at 60s evaporation time while other samples were currently not readily being tested. Based on the figure, at pressure 6 bar, the permeability of O_2 gas is higher than N_2 may be because of the kinetic diameter of O_2 gas is smaller than N_2 gas and make it easy to past through the membrane as accordance to Graham's Law where, O_2 gas can permeates approximately 3-4 times faster than N_2 despite its larger molecular weight due to O_2 has a smaller diameter than N_2 gas. At higher pressure, the permeability of N_2 gas is higher than the O_2 gas might be due to the prominent membrane surface defect that causing the lighter gas, N_2 to permeate faster. As the pressure increased, the gas permeation of O_2 and N_2 gas increased because of the increasing driving force for the gas to permeate through the membrane thus the permeability of both gases were increasing.

The selectivity of O_2/N_2 gas decreased as the pressure increased may possibly because of the trade-off between membrane permeability and selectivity [13]. Due to the membrane prominent surface defect, the permeability of both gases was higher thus lowering the gas pair selectivity.

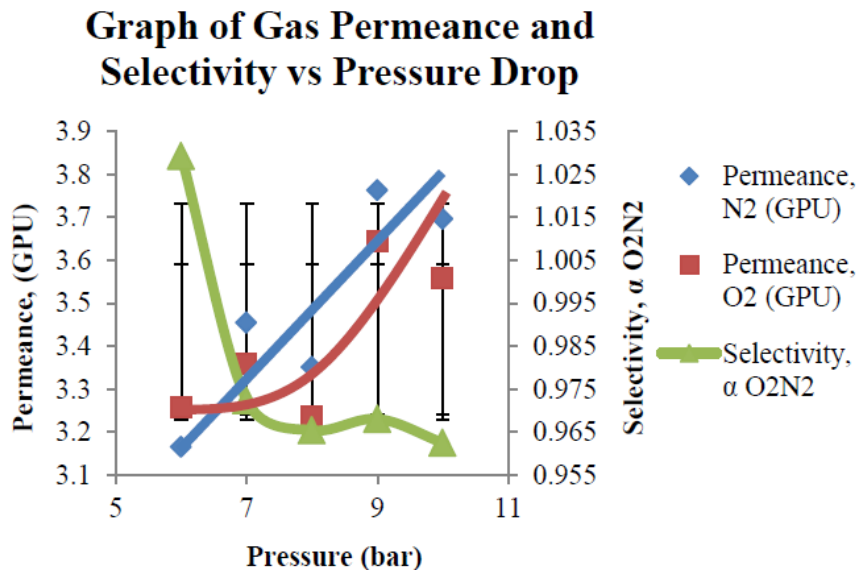


Fig. 3. Graph of Gas Permeance and Selectivity of O₂/N₂ of 15 wt.% PLA (Coated) at 60 s Evaporation Time.

4. Conclusions

Poly(lactic acid) polymer is biodegradable aliphatic polyester that possesses comparable chemical and mechanical properties than other biodegradable polymer and becoming one of the promising replacements for the non-biodegradable petroleum-based synthetic polymer. The PLA flat sheet asymmetric membrane was prepared by casting the dope solution at different solvent evaporation time via dry/wet phase inversion process and one of the crucial fabricating parameter of flat sheet asymmetric membrane is solvent evaporation time.

The changes applied on solvent evaporation time affecting the molecular orientation of the flat sheet asymmetric membrane morphology thus changing its thermal and mechanical properties. The porosity of the membrane surface decreases with increasing evaporation time. As the evaporation time increase, the membrane molecular alignment becomes more oriented and compact thus reducing the porosity and surface defect. Tensile strength of the PLA membrane was improved by increasing the solvent evaporation time.

As the solvent evaporation time increased, the tensile strength of the membranes was increased due to the improvement on the compactness of membrane molecular structure, however, the elasticity of the membrane decrease causing the membrane to become too brittle and currently difficult to handle for further testing. The gas permeation tests determined that the increment in gas pressure drop would increase the permeability of all gases through the PLA asymmetric membrane but decreased the selectivity of O₂/N₂ gases. This preliminary result shows that PLA asymmetric membrane has a potential as gas separation membrane and applicable in O₂/N₂ separation system. The membrane is recommended for further testing by using a different formulation of dope solution concentration.

Acknowledgment

We gratefully acknowledge the financial support from the Universiti Teknologi Malaysia and Ministry of Education (Grant No: 04H70 and 4L116).

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