# Biodegradable Gas Separation Membrane Preparation by Manipulation of Casting Parameters

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Poly(lactic acid) PLA that derived from renewable resources can help our society to reduce the dependence to non-renewable fossil resources. When come to human contact, this polymer and its degradation product are neither toxic nor carcinogenic to human body. The use of poly(lactic acid) (PLA), a biodegradable polymer, as a membrane material would assist the reduction of depending to petroleum-based polymer that will assist in disposal issues on non-biodegradable polymer. This study investigated the effect of evaporation time to the gas separation performance of PLA membrane. Membrane prepared from polymer solution consists of PLA and dichloromethane (DCM) as solvent was fabricated using pneumatically controlled casting system with dry/wet phase inversion method. Permeation test was conducted using pure oxygen and nitrogen gas. The results revealed that as the evaporation time increased, the pore size and surface porosity decreased, while the skin layer thickness increased. Although the morphology of the prepared membranes showed the desirable structure, the gas separation performance of the membrane prepared with polymer concentration of 15 wt% and 60s evaporation time was found to be promising but not yet commercially ready.

## 1. Introduction

Raw natural gas varies substantially in composition from source to source where methane is always the major component, typically 75 % - 90 % of the total, but natural gas also contains significant amounts of ethane, some propane and butane, and 1 – 3 % of other higher hydrocarbons (Baker and Lokhandwala, 2008). Natural gas processing is a complex industrial process designed by separating impurities and various non-methane hydrocarbons and fluids from raw natural gas to produce a pipeline quality dry natural gas. There many ways in which to configure the various unit processes used in the processing of raw natural gas. The most commonly used unit operations in the natural gas processing are cryogenic distillation of air, condensation to remove condensable organic vapors from gas mixture and amine adsorption to remove acids gases. Membrane-based gas separation is currently popular due to its inherent advantages over those more traditional methods. These include low capital and operating costs and ease of operation (Hasbullah *et al.* 2013). Membrane for natural gas processing was first commercialized in the 1980's for $CO_2$ removal and have been the dominant membrane gas separation process since (Scholes et al., 2012). However, most of these membranes are not readily biodegradable and the removal of these membranes will become an additional unbiodegradable waste in the landfill. Thus, PLA has been chosen as the membrane material for this study.
Until the last decade, the main uses of PLA have been limited to medical applications such as implant devices, tissue scaffolds, and internal sutures, because of its high cost, low availability, and limited molecular weight. Recently, new techniques which allow economical production of high molecular weight PLA polymer have broadened its uses (Datta and Henry, 2006). PLA has a comparable mechanical performance as the other

petroleum-based polymer and it degrades slowly against water as compared to other water-soluble polymer (Zhang and Sun, 2005). 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 force convection residence time on the molecular alignment and the membrane gas permeation performance.

## 2. Experimental

### 2.1 Material
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.

### 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. PLA 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 second 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 Differential Scanning Calorimetry (DSC)
The glass transition temperature ($T_g$) measurement was carried out using differential scanning calorimetry under nitrogen condition by (1) heating from room temperature to 200 °C at a rate of 10 °C/min; (2) cooling to 30 °C at 50 °C/min; (3) maintaining for 3 min at 30 °C; and (4) then repeating the above procedure.

### 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 Gas permeation test
Gas permeation of pure oxygen ($O_2$) and nitrogen ($N_2$) were measured using soap bubble method at 28°C and pressures of 6, 7, 8, 9 and 10 bar.

## 3. Result and discussion

### 3.1 Glass transition temperature
Figure 1 shows the graph of differential scanning calorimetry for pure PLA polymer and PLA flat sheet asymmetric membranes. As seen in Figure 1, the glass transition temperature ($T_g$) of PLA membrane has nearly the same as pure PLA polymer which is within 60 °C to 65 °C and the melting point ($T_m$) is between 150 °C to 170 °C. This is in accordance as Nishiyama et al. (2007) finding that the $T_g$ of PLA with different molecular weight and L:D ratio is remained around 60 °C. This shows that the changes in molecular weight; L:D ratio; and concentration may not significantly affect the glass transition temperature and the melting point of the PLA polymer. Table 1 summarized the value of $T_g$ and $T_m$ of PLA obtained from this work and previous research.
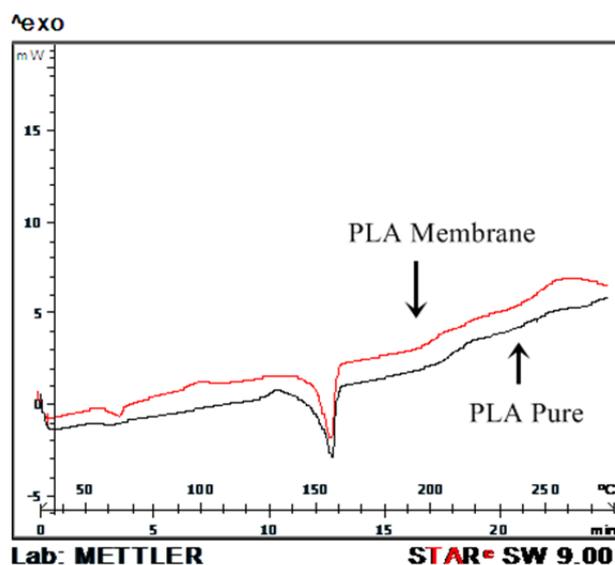
*Figure 1: Graph of differential scanning calorimetry of pure PLA polymer and 20 wt % PLA flat sheet asymmetric membrane*

*Table 1: Glass transition temperature and melting temperature PLA*

| Melting Temperature ($T_m$) | Glass Transition Temperature ($T_g$) | References |
|---|---|---|
| 150 °C to 170 °C | 60 °C to 65 °C | This work |
| 150 °C to 170 °C | 60 °C | (Nishiyama *et al.* 2010) |

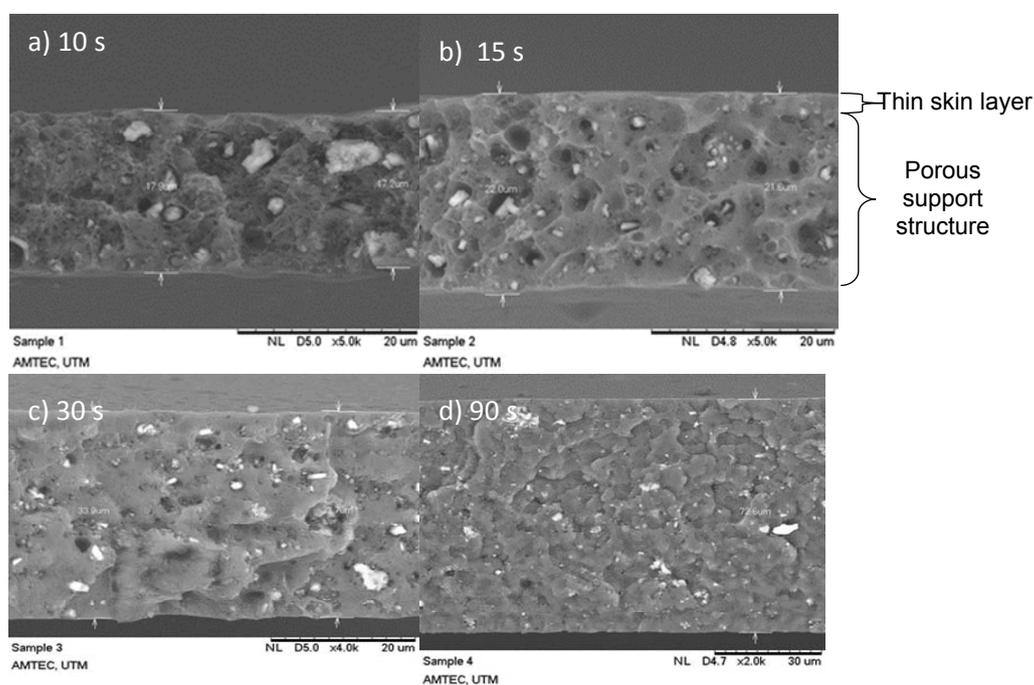## 3.2 Morphology of poly(lactic acid) (PLA) asymmetric membrane



*Figure 2: Scanning Electron Micrograph (SEM) cross-section images of the flat sheet asymmetric membrane at constant concentration and different evaporation time.*

PLA membranes were cast at different evaporation time of 10, 30, 60, and 90 s in order to investigate the influence of solvent evaporation time on the membrane morphology and its gas separation performance. Figure 2 illustrates the scanning electron microscope (SEM) images of the cross section and dense layer morphology of dry/wet phase inversion PLA membranes. As shown in Figure 2, all membrane samples have an asymmetric structure consist of a very thin dense layer at the top and porous sublayer at the bottom. The top dense surface function as the site for gas permeation and the bottom porous sublayer function as a mechanical support. From Figure 2 (a) to (d), the porosity of the membrane decreases as the solvent evaporation time increases from 10 s to 90 s. According to Ismail et al. (2003), when the force convection residence time increase, lesser free volume or a tighter dense and oriented structure is precipitated instantaneously at the outer surface of the membrane during dry phase inversion process (Ismail et al., 2003). The increase in the solvent evaporation may have cause the intermolecular attraction between the PLA molecules to become greater and subsequently aligning themselves to be more oriented thus, the pack support layer become tighter structure. The tighter dense structures prevent the non-solvent from penetrating into the membrane during the wet phase inversion process, thus, decreasing the membrane porosity. The presence of the crystallites in membrane structure that appear as white area might be due to the crystallinity properties of the PLA polymer. The linear oriented cast films have less than 4 % crystalline which is lower crystallinity than the biaxially oriented film which have approximately 16 % crystalline (Lehermeier et al., 2001).
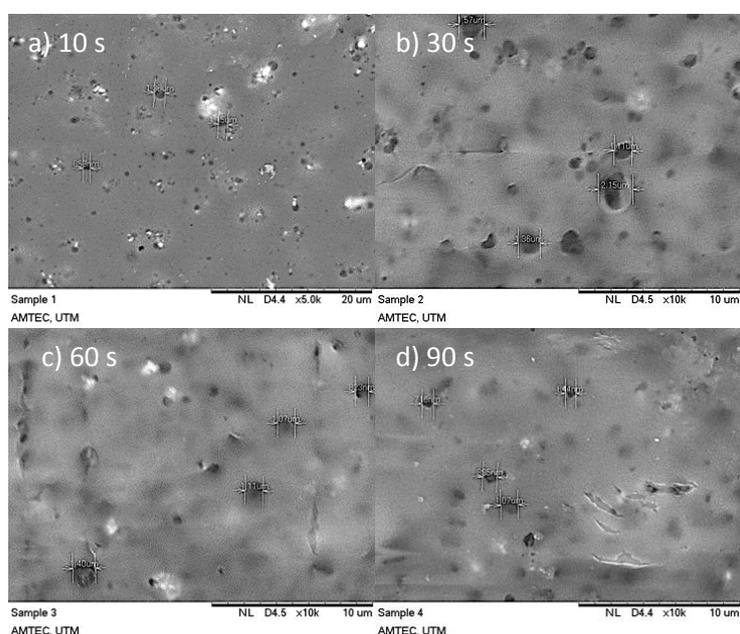


*Figure 3. Scanning Electron Micrograph (SEM) surface images of the flat sheet asymmetric membrane at constant concentration and different solvent evaporation time.*

The visible appearance of white area on the membrane surface in Figure 3 may suggest that the membrane has higher crystallinity and percentage of crystalline. The dense surface layer formed when solvent evaporated out from the membrane surface and this layer will influence the gas permeation of the prepared membrane. In order to increase the efficiency of the membrane for gas separation, the dense surface layer should be defect-free (Khulbe et al., 2008). As shown in Figure 3, the porosity of the membrane surface decrease as the solvent evaporation time increase may be because of the enhancement of the membrane molecular orientation causing the membrane surface to become closely pack thus decreasing the pore size on the membrane surface and reducing defects.

### 3.3 Gas permeation performance

One of the crucial factors in determining the performance of membrane in gas separation is the formation of skin layer. In order to investigate the gas separation performance of PLA membranes, they were tested with pure $O_2$ and $N_2$ gases at various pressures. Figure 4 shows the $O_2$ and $N_2$ permeability and selectivity of $O_2/N_2$ of the asymmetric membranes. At pressure of 6 bar, the permeability of $O_2$ gas is higher than $N_2$ may be because the $O_2$ gas molecule has smaller kinetic diameter than $N_2$ gas. According to Graham's Law, $O_2$

gas has a smaller diameter than $N_2$ gas despite its larger molecular weight and permeates approximately 3-4 times faster than $N_2$. 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 $N_2$ gas to permeate faster. The gas permeation of $O_2$ and $N_2$ gas increase as the pressure increase because of the increasing driving force for the gas to permeate through the membrane thus the permeability of both gases are higher. The selectivity of the membrane for $O_2/N_2$ selectivity decrease as the pressure increase might be because of the trade-off between membrane permeability and permselectivity (Adewole et al., 2013). Robeson (1991) claim that the selectivity for the gas pair is inversely proportional to the permeability of the specific pair (Robeson, 1991). Due to the membrane surface defect, the permeability of both gases is higher thus lowering the gas pair selectivity. In order to improve the gas separation performance, the membrane need to be further coated to reduce the membrane surface defect. As the pressure drop increase, the gas permeability decreases but the permselectivity are enhanced. The gas permeation test was performed only on 15 wt% PLA at 60 s evaporation time due to the other prepared membranes are currently not readily be tested.
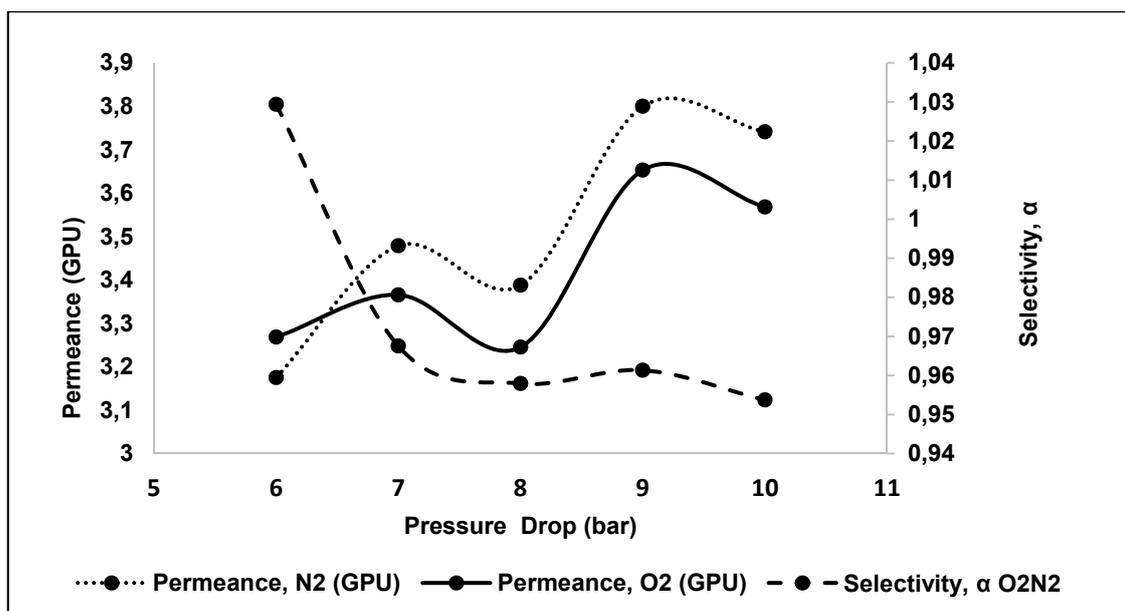


Figure 4. Graph of Gas Permeance and Selectivity of $O_2/N_2$ of 15 wt % PLA at 60 s evaporation time

## 4. Conclusion

Poly(lactic acid) polymer is a highly versatile, rigid thermoplastic, biodegradable aliphatic polyester offers a great promise in a wide range of commodity application. PLA has been chosen over a wide range of biodegradable polymer because of its good barrier property as a packaging material and performs better than the synthetic material. In order to introduce the biodegradable PLA polymer as a membrane material for natural gas processing application, the fundamental parameter such as solvent evaporation time is necessary to be studied in order to produces a membrane with high separation factor. The PLA membrane has been prepared by casting the dope solution at different solvent evaporation time. The glass transition temperature ($T_g$) and melting point ($T_m$) of both pure polymer resin and PLA membrane have no significant different where the $T_g$ was found to be between 60 °C to 65 °C and the Tm is between 150 °C to 170 °C. The prepared membranes that formed via dry/wet phase inversion process possessed an asymmetric structure with thin skin layer at the top and porous structure at the bottom. The porosity of the membrane surface decrease with increasing evaporation time. As the evaporation time increase, the formation of bottom layer support structure become more compact, thus decrease the membrane porosity. The gas permeation tests determined that the increment in gas pressure drop would increase the permeability of the PLA asymmetric membrane thus decrease the selectivity of $O_2/N_2$ gases. The membrane is recommended for further testing by coating the membrane using silicon rubber coated material (PDMS).

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