



# Poly (L-Lactic acid)/silk fibroin composite membranes with improved crystallinity and thermal stability from non-solvent induced phase separation processes involving hexafluoroisopropanol



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## ABSTRACT

The crystallinity of semi-crystallized Poly (L-Lactic acid) (PLLA) is low, especially as a porous membrane prepared from non-solvent induced phase separation (NIPS) process. To improve the crystallinity and thermal stability of PLLA porous membranes, hexafluoroisopropanol (HFIP) was added into the PLLA casting solution together with a small amount of Silk Fibroin (SF). It is found that by optimizing the additive amounts of HFIP and SF, PLLA composite membranes with improved crystallinity (up to 47.1%) and endurance to temperature (above 90 °C) could be prepared with comparable mechanical property to the virgin PLLA membranes. The effects of HFIP in NMP solution on PLLA during the NIPS process was further investigated using dynamic rheological methods relating to the crystallinity of the formed PLLA porous membranes.

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## 1. Introduction

As a semi-crystalline polymer, PLLA has a relatively longer crystallization half time around 180 s [1–3]. Its low crystallinity has gravely affected its thermo-stability and restrained its potential applicability in many fields. Great efforts have been taken to improve its crystallinity [4–11], including the addition of nucleates to increase its nucleation density and plasticizers to increase chain mobility. The nucleation agents used include minerals (talc, clay), organic compounds (sodium stearate, calcium lactate, 1, 3, 5-benzene tri-carboxamide) [5], bio-based materials (starch, cellulose nano-crystal) [6], carbon nano-tubes [8] and PDLA [9] according to their source and mode of actions. The nucleating agents will shorten the nucleation induction period and increase the number of primary nucleation sites. The plasticizers used include high molecular weight ones, such as polyethylene glycol (PEG) and

polypropylene glycol (PPG), and low molecular weight ones, such as citrate esters, adipates, and carbon dioxides [2]. The intense interaction between plasticizers and PLLA will increase the chain mobility of PLLA and thus facilitate the movement of chains from amorphous phase into organized states.

As a novel type bio-based and biocompatible material, PLLA could be fabricated into various products by blow molding and injection molding. Recently, PLLA based porous separation membranes with higher biocompatibility and after-use decomposability were prepared using non-solvent induced phase separation (NIPS) processes for BSA filtration [12–17] and hemodialysis [18]. During the NIPS procedure, the solidification of PLLA from the solution in coagulating bath tends to be completed in a very short period of time at low temperature, not sufficient for PLLA chains to fold and self-assemble into crystalline phases, resulting in PLLA membranes with low crystallinity and poor thermal stability [19].

Although having higher crystallinity, better thermal stability and mechanical property are critical for realizing potential applications for the formed PLLA membranes related reports about the crystalline behavior of PLLA during non-solvent induced phase separation are still scarce. Conventional nucleating agents or plasticizers to improve the crystallinity of PLLA products from thermal process may not work during the non-solvent induced phase

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separation process. To improve the crystallinity of PLLA based porous membrane, in this paper, a novel NIPS process is investigated using HFIP as a co-solvent while silk fibroin was added to reduce brittleness associated with higher crystallinity. The mechanism of crystallinity enhancement from HFIP for PLLA membrane during NIPS was also investigated in the efforts.

## 2. Experiments

### 2.1. Materials

Poly lactide (model 4032D, Mw: 170kD, melt index 6g/10min (210 °C, 2.16 kg), specific gravity 1.24 g/L, Natural works, US) was used to fabricate membrane after 24 h vacuum drying at 70 °C. Hexafluoroisopropanol (HFIP) and 1-Methyl-2-pyrrolidinone (NMP, AR) were all purchased from Aladdin and directly used without further purification. Silk fibroin (SF) was self-prepared from the virgin silkworm cocoons following procedures as previously reported [20–22]. In brief, selected silkworm cocoons were cut into fragments and boiled in a 0.02 M Na<sub>2</sub>CO<sub>3</sub>/water solution for about 30 min to extract the glue-like sericin proteins. The resulting fibroin filaments were extensively rinsed in distilled water for three times and dissolved in 9.3 M LiBr (Aladdin, Lithium bromide, 99%) water solution for 4 h at 70 °C. The salt was removed by dialyzing with a cellulose film (Sinopharm Chemical Reagent Co., Ltd, MWCO: 800–14000) against distilled water for 72 h at room temperature. The silk fibroin solution was frozen below –20 °C for 24 h and then frozen dried using a vacuum freeze-drying equipment to form the silk fibroin powder could be obtained.

### 2.2. Preparation of PLLA porous composite membranes

PLLA membranes were fabricated by following the non-solvent induced phase separation method. A fixed amount of PLLA (18 wt%) and HFIP (0 wt%, 4 wt%, 6 wt%, 8 wt%) and solvents (NMP) were added into a 250 mL flask. After stirred at 80 °C for 12 h, the homogenous solutions were obtained. Then the casting solution was casted onto a clean glass plate with a blade (200 μm in thickness), and coagulated in non-solvent bath at room temperature. The solidified PLLA membranes were subsequently transferred and kept into pure deionized water for 1 day before dried in air for further testing. In addition, when HFIP was fixed to 8 wt%, 0.02 wt% and 0.04 wt% of silk fibroin were respectively pre-dissolved in HFIP, and then added into the homogenous PLLA/NMP solution to form PLLA/NMP/HFIP/SF complex solutions. Casting the complex solutions to prepare modified PLLA following the above depicted procedure to form PLLA/SF composite porous membranes. The detailed codes of all resulted PLLA membranes are listed in Table 1.

### 2.3. Characterization

#### 2.3.1. Crystallization behavior of PLLA membranes

Wide-angle X-ray scattering (WAXS) (Bruker AXS, Germany) was used to detect the resulted membranes' crystalline form. For

the scattering experiments, Cu K $\alpha$  radiation was chosen and the detecting range was from 5° to 45° with a scanning rate of 4°/min. Differential Scanning Calorimetry (DSC) (Perkin-Elmer, USA) was used to definitely measure their crystallinity, enthalpy change value and melting behavior. During the experiments, first heating, cooling and second heating were performed. To detail, membrane samples were firstly heated from 25 °C to 200 °C at a heating rate of 10 °C/min, kept constant temperature at 200 °C for 3 min, then cooled from 200 °C to 25 °C at a heating rate of –10 °C/min and finally heated to 180 °C at a heating rate of 10 °C/min. The DSC scans were carried out in a flowing-nitrogen atmosphere. The degree of crystallinity ( $X_c$ ) was determined according to Eq. (1):

$$X_c(\%) = \frac{(\Delta H_m + \Delta H_c)}{93\text{J/g}} \times 100 \quad (1)$$

#### 2.3.2. Enhanced crystallization mechanism

In order to understand the effect of HFIP on the crystalline behavior of PLLA, dynamic rheology of various complex PLLA/NMP/HFIP solutions as well as the simplex PLLA/NMP solution was determined using a rotational rheometer (Anton Paar, Austria), where dynamical temperature and frequency ( $\omega$ ) sweep were separately performed. During the temperature sweep process, all the casting solutions with various HFIP concentrations were kept at 80 °C and subsequently slowly cooled at a 3 °C/min temperature falling rate, meanwhile the strain was set to 0.1% and frequency to 10 rad/s. For the frequency sweep, measurements were performed at a constant temperature of 80 °C and  $\omega$  changed from 0.1 rad/s to 600 rad/s, while the strain was kept at 0.1%.

#### 2.3.3. Mechanical properties

The tensile stress and tensile strain of PLLA membranes fabricated with 8 wt% of HFIP and different SF adding amounts as well as the simplex membrane samples were measured using a tensile apparatus (Instron 5567, USA). A membrane sample sized 10 cm × 1 cm was fixed vertically between two tweezers with an original of 50 mm. Then the membrane samples were extended at a constant elongation rate of 5 mm/min until it was broken.

#### 2.3.4. Membrane characterization

Cross section morphology of the membranes named M0, M-8HFIP, M-8H-2SF and M-8H-4SF was observed by scanning electron microscopy (SEM, Hitachi, S4800, Japan). The porosity of membranes was measured by comparing the weight of wet membrane and dried one. Membrane maintained in distilled water was weighed after whipping off excess surface water with filter paper. Then the wet membrane was placed in an air-circulating oven at 50 °C until no longer change in weight. The porosity was determined according to Eq. (2):

$$\text{Porosity} = \frac{(M_{\text{wet}} - M_{\text{dry}})}{M_{\text{wet}}} \times 100\% \quad (2)$$

Besides, the through-pore sizes of membranes were determined by a liquid-liquid porometer (LLP-1200A, Porous Materials Inc. US). All the samples were wetted by the silwick solution (Porous Materials Inc. US). By increasing the pressure, the silwick was pushed out by isopropanol from the occupied through-pores. The flow rate was measured until all through-pores were empty and the sample was considered dry. The pore diameter is calculated.

#### 2.3.5. Residual HFIP and SF measurement

In order to detect HFIP, the final PLLA membranes were immersed in deionized water for various days. The F and S contents

**Table 1**  
Casting solution composition and sample numbers.

Code	PLLA (wt%)	NMP (wt%)	HFIP (wt%)	SF (wt%)
M0	18	82	–	–
M-4HFIP	18	78	4	–
M-6HFIP	18	76	6	–
M-8HFIP	18	74	8	–
M-8H-2SF	18	73.98	8	0.02
M-8H-4SF	18	73.96	8	0.04

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