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Preparation of poly(L-lactic acid) microfiltration membranes by a nonsolvent-induced phase separation method with the aid of surfactants

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ABSTRACT

Microfiltration membranes of poly(L-lactic acid) (PLLA) have been prepared by a nonsolvent-induced phase separation method with the aid of surfactants. Surfactants with hydrophilic-lipophilic balance (HLB) values of 14.9–15.6 were found to be useful in reducing the shrinkage in thickness of the PLLA membrane. Among the surfactants examined, Tween 80 was the best for preparing microfiltration membranes. The surfactant allowed instantaneous phase separation and seemed to enhance the diffusion of water in the PLLA solution during structure formation. The membrane had asymmetric finger-like structures and showed low membrane resistance and high bacterial cell retention when the membrane was prepared from a 10 wt% PLLA solution in 1,4-dioxane containing 10 wt% Tween 80. Bovine serum albumin molecules passed through the membrane suggesting that the membrane functions as a microfiltration membrane. The membrane was stable at 25 °C but degradable at 60 °C in wet conditions. The membrane can be applied as a compostable microfiltration membrane in food and biochemical industries.

1. Introduction

In bioproduction processes, microfiltration membranes are often used to separate cells and cell residues [1]. Microfiltration membranes made from glassfiber [2] or conventional synthetic polymers such as polysulfone [3] have disposal problems after use. In recent years, poly(L-lactic acid) (PLLA) has attracted attention as a key material for sustainable technology because it is produced from biomass and readily degrades in composting processes and in natural environment [4–6]. Consequently, PLLA microfiltration membranes will reduce waste in food and biochemical industries by degrading via composting after use.

PLLA microfiltration membranes have previously been developed by several methods. The first PLLA microfiltration membranes were prepared by the thermally induced phase separation method from PLLA dissolved in 1,4-dioxane containing water. These membranes retained yeast cells (~5 μm in diameter) but allowed bacterial cells (~1 μm in diameter) to permeate [7]. The retention of bacterial cells was improved by inducing controlled evaporation from the surface of the polymer solution before cooling in the thermally induced phase separation procedure [8]. PLLA microfiltration membranes were also prepared from polymer solutions in dimethyl sulfoxide by nonsolvent and thermally induced phase separation methods. Dimethyl sulfoxide was used to dissolve 10 wt% PLLA at temperatures of 60 °C and higher; however, the polymer solution did not form a membrane but instead formed PLLA particles via the thermally phase separation method. By using a combination of thermally and nonsolvent induced phase separations methods with a polymer solution at 80 °C and a coagulation water bath at 25 °C, PLLA membranes that retained bacterial cells were prepared [9].

Although PLLA microfiltration membranes can be prepared by devising complex phase separation conditions, the practical manufacturing of PLLA membranes will be facilitated if simple nonsolvent induced phase separation methods can be developed. This study considers the development of PLLA microfiltration membranes formed via a nonsolvent induced phase separation method with the aid of surfactants. Surfactants are molecules with both hydrophilic and lipophilic groups and are typically used as solubilizers, detergents, emulsifiers, wetting and spreading agents, and antifoaming agents in accordance with their hydrophilic-lipophilic balance (HLB) values [10].

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Among the surfactant class of compounds, polyoxyethylene(20) sorbitan monooleate (Tween 80) is well known as a reagent to improve the structure of poly(methyl methacrylate), polyethersulfone, and poly (vinylidene fluoride) membranes [11–13]. This study reports mainly on the effect of Tween 80 in polymer solutions on the structure and performance of PLLA membranes. The stability and degradability of the membranes at ordinary and composting temperatures (25 and 60 °C) were also examined.

2. Experimental methods

2.1. Materials

PLLA was a gift from Toyota Motor Corp. The PLLA properties included weight average molecular weight 1.22×10^5 ($M_w/M_n = 3.0$), optical purity 98.5%, melting point 174.0 °C, and glass transition temperature 59.7 °C. Analytical grade 1,4-dioxane was purchased from Wako Pure Chemical Industries. Seven kinds of surfactants, Tween 80 (polyoxyethylene(20) sorbitan monooleate), Tween 20 (polyoxyethylene(20) sorbitan monolaurate), Tween 40 (polyoxyethylene(20) sorbitan monopalmitate), Tween 60 (polyoxyethylene (20) sorbitan monostearate), polyoxyethylene(20) oleyl ether, Span 80 (sorbitan monooleate), and sodium dodecylsulfate (SDS), were purchased from Wako Pure Chemical Industries. Bovine serum albumin was obtained from Sigma-Aldrich. All chemicals were used without further purification.

2.2. Measurement of cloud points

The cloud points were measured by titration of water into PLLA–diluent–water system at 25 ± 2 °C. The polymer was dissolved at 1–15 wt% in diluent (1,4-dioxane containing 0–15 wt% of Tween 80) to prepare a 50 g solution in a 100-cm^3 flask with a cork stopper covered with aluminum foil and poly(tetrafluoroethylene) tape and then water was added dropwise. The clouding composition was calculated from the cumulative amount of added water when the polymer solution remained cloudy or a gel formed around water droplet remained after 2 h stirring.

2.3. Membrane preparation

PLLA was dissolved in 1,4-dioxane containing a surfactant in a sealed 100 cm^3 flask. All solutions reported in this study were prepared on a wt% basis. The mixture was first stirred with a PTFE stirring bar and warmed on the stirrer/hot plate at 80 °C for 8 h. The polymer solution was cast on a glass plate with an 80 mm × 80 mm frame made from PTFE plate. The thickness of the frame was 0.5 mm. After removing excess polymer solution with the edge of another glass plate, the polymer solution on the glass plate was immersed in a coagulation bath of water at 25 ± 2 °C and kept there for 2 h. The resulting membrane was removed from the glass plate, washed with water extensively, and kept in water prior to use.

2.4. Filtration experiments

A filtration cell (Amicon model 8010, 4.1 cm^2, Millipore, Bedford, MA) was used without its stirrer for dead-end filtration experiments as reported elsewhere [9]. Water was used to measure the permeation resistance of the membranes. The filtration was mainly performed at a transmembrane pressure of 10 kPa and at 25 ± 2 °C. The membrane resistance, R_m, was calculated using the following equations:

$$J = dv/dt \quad (1)$$

$$R_m = \Delta P/\mu J \quad (2)$$

where J, v, t, ΔP, and μ are permeation flux, permeation volume per unit filtration area, permeation time, transmembrane pressure, and viscosity of permeate, respectively. The viscosity of water at 25 ± 2 °C was 0.89 mPa s [14].

Microbial cell suspensions of *Lactobacillus plantarum* NBRC15891T ($0.7\varphi \times 2.5$ μm) were used to examine the retention of bacterial cells by the membranes as reported elsewhere [9]. The bacterium was cultured statistically in a modified MRS medium [15] where fish extract was substituted for meat extract. The culture broth after 17 h cultivation at 30 °C was diluted 10 times in most cases with 0.85 wt% NaCl solution for filtration experiments. The wet cell concentration was 0.5 kg m^{-3}. The cell leakage was monitored with the absorbance at 660 nm of the initial 30 min permeate (or the initial 10 cm^3 permeate when the filtration finished within 30 min).

Bovine serum albumin (BSA, Sigma) was used to examine the permeation of protein molecules through the membranes. The protein was dissolved at 100 g m^{-3} in 0.1 M sodium-phosphate buffer (pH 6.8). The protein concentration of permeates was determined by BCA Protein Assay Kit (Pierce).

2.5. Scanning electron microscopy

The membrane was immersed in liquid nitrogen and then fractured. It was mounted vertically and horizontally on a sample holder. The surface of the sample was coated with gold-palladium using a sputter coater (MSP-1S, Vacuum Device). A scanning electron microscope (TM-1000, Hitachi) with an accelerating voltage of 15 kV was used to examine the membrane cross-sections and surfaces.

2.6. Degradation experiments

The change of mechanical strength over time for samples incubated in wet conditions of 25 or 60 °C was measured to evaluate non-enzymatic hydrolysis of the PLLA membranes. The PLLA membranes, the thicknesses of which were 0.25–0.35 mm, were cut into rectangular strips of 50 mm × 10 mm to prepare tensile specimens. The membranes were maintained in wet conditions in sealed glass dishes with wet wiping paper. The membranes were incubated at 25 or 60 °C for a maximum of 28 days.

The mechanical strength was evaluated from breaking elongation by tensile testing. The tensile testing was performed at 25 ± 2 °C under wet conditions with a desk-top tensile testing machine (EZ-S-500 N, Shimadzu Corp.). The gauge length and crosshead speed were set at

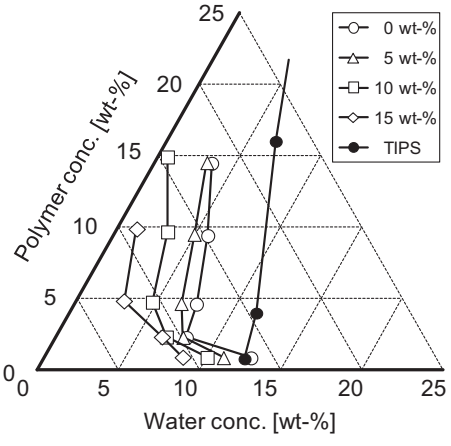

Fig. 1. Experimental cloud points of PLLA–(1,4-dioxane–Tween 80)–water system at different concentrations of Tween 80 (0–15 wt%). The closed circles show the phase separation compositions calculated from the data of thermally induced phase separation of PLLA solutions without Tween 80.