ELSEVIER

Desalination 193 (2006) 367–374

DESALINATION

www.elsevier.com/locate/desal

Microfiltration membrane of polymer blend of poly(L-lactic acid) and poly(ε-caprolactone)

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Received 15 March; accepted 27 June 2005

Abstract

Biodegradable filtration membranes can be applied in food and biochemical processes to clarify products or to yield particles from suspensions, and then degrade in composting processes. In this study we developed microfiltration membranes from a polymer blend of poly(ε-caprolactone) (PCL) and poly(L-lactic acid) (PLLA). The membranes were formed via the thermally induced phase separation process and were used to separate yeast cells from their suspension. The blend ratio (PCL:PLLA) of 4:1 was important to prepare the biodegradable polymer-blend membrane with the ability of the retention of yeast cells and without exfoliation of the membrane. The permeation resistance of PCL–PLLA blend (4:1) membranes was as high as that of PCL membranes and was three-order lower than that of a PLLA membrane. In the filtration of yeast cell suspensions the increase of the permeation resistance during the filtration was much lower with a PCL–PLLA (4:1) membrane than with a PLLA membrane. The PCL–PLLA (4:1) membrane captured the cells as a depth filter while the PLLA membrane did as a screen filter.

Keywords: Biodegradable polymer; Microfiltration membrane; Thermally-induced phase separation; Poly(ε-caprolactone); Poly(L-lactic acid); Depth filter

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Presented at the International Congress on Membranes and Membrane Processes (ICOM), Seoul, Korea, 21–26 August 2005.

0011-9164/06/$– See front matter
doi:10.1016/j.desal.2005.06.068

1. Introduction

Biodegradable polymers have received much attention because they degrade in natural environments and composting processes, while other recalcitrant plastics are often harmful to wild animals when they remain in the environment [1]. Recently, we have been developing microfiltration membranes of poly(L-lactic acid) (PLLA) [2] via thermally induced phase separation method [3]. The membranes can be applied in food and biochemical processes to clarify products or to remove particles from suspensions. After their use, the biodegradable membranes can be degraded in composting processes. The monomer of PLLA is produced from agricultural products (corn, sugarcane, sweet potato, sago palm, etc.) and by-products (rice and wheat bran, molasses, lactose in whey, etc.). Its production cost is independent of oil price. Unfortunately, the cost of PLLA is significantly higher than conventional plastics at this time. Despite the current cost of synthetic biodegradable polymers such as poly(ε-caprolactone) (PCL) and poly(butylene succinate), it is worth considering them as alternative membrane materials for environmental reasons, and because the cost of these polymers will decrease as production levels increase.

In this paper we report on the development of microfiltration membranes of PCL. First we tried to develop a membrane of this polymer, but its pore size was very large and the membrane leaked bakers' yeast cells. Then we developed microfiltration membranes of a polymer blend of PCL and PLLA. The filtration characteristics of the PCL–PLLA membranes were examined with water and yeast cell suspensions.

2. Experimental

2.1. Materials

PCL was purchased from Wako Pure Chemical Industries (Osaka, Japan). The weight average molecular weight was $7–10\times10^4$. PLLA was gifted from Toyota Motor Corp. (Toyota, Japan). The weight average molecular weight, optical purity, melting point, and glass transition temperature were 1.22×10^5 (M_w/M_n = 3.0), 98.5%, 174.0°C, and 59.7°C, respectively. Analytical grade 1,4-dioxane (b.p. = 101.4°C, m.p. = 11.8°C) was used without further purification.

2.2. Phase diagrams

1,4-dioxane (solubility parameter = 20.3 $MPa^{0.5}$) [4] was used to dissolve PCL (solubility parameter = 19.1–21.2 $MPa^{0.5}$) [5,6] and poly(lactic acid) (solubility parameter = 20.5–21.1 $MPa^{0.5}$) [7] for the preparation of membranes. Water (solubility parameter = 47.9 $MPa^{0.5}$) [4], which is miscible with 1,4-dioxane, but is a non-solvent for PCL and PLLA, was added to the polymer–1,4-dioxane solution so that the liquid–liquid phase separation occurs in cooling [2,8].

PCL or PLLA was dissolved in a 1,4-dioxane–water mixture in a 100-cm^3 flask, sealed with a cork stopper which had been covered with aluminum foil and polytetrafluoroethylene tape. The polymer concentration and the water content in the diluent were 1–20 wt-% and 4–20 wt-%, respectively. Polymer was first dissolved in 1,4-dioxane at 80–90°C on a stirrer/hot plate (Model PC-420, Corning, New York, NY) and then water was added. After dissolution, the solution was kept at 80°C (or 90°C) for more than 30 min by placing the sealed flask in an oven. The solution was then placed in a water bath at 12–90°C and held at that temperature for a period of ten minutes. The cloud point temperature was defined in this study as the temperature at which the solution turned cloudy during the 10 min period, having been clear during the 10 min hold time at a temperature 1°C above the cloud point temperature.

2.3. Membrane formation

Membranes were prepared in an apparatus (Fig. 1) composed of three stainless steel pie pans (22.8 cm in diameter, G&S Metal products Co.,