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Morphology and performance control of PLLA-based porous membranes by phase separation

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ABSTRACT

The structure, porosity and crystallization behavior of poly (L-lactic acid) and poly (L-lactic acid)/polyurethane porous membranes, prepared from ethanol/dioxane and ethanol/water coagulation baths through immersion precipitation, have been systematically investigated. The diffusion rate between solvent and nonsolvent as well as the equilibrium phase diagram of PLLA/solvent/nonsolvent system were also well studied. It has been proved that the ultimate structure and performance of the membranes could be mediated under control by suitable adjustment on phase separation behavior of the ternary system through varying coagulation bath compositions. The results show that the presence of lower ratio of dioxane in ethanol baths endows the resulting membranes with uniform sponge-like structure, higher porosity and crystallinity due to the moderate solidification and crystallization of PLLA, while increasing the water concentration tends to have a modestly opposite effect and obtains membranes with irregular finger-like structure, lower porosity and crystallinity. Under the same coagulation baths, PLLA/PU membranes possess slightly larger pores size and porosity than pure PLLA membranes, but the presence of PU appears to have no effect on the crystallinity of PLLA.

1. Introduction

Porous membranes have been widely applied in many fields, such as filtration process, tissue repairing, organ replacement, and support for cell culture [1–6]. The polymeric scaffold can provide a structural framework or matrix for selected cells to be seeded in vitro, and subsequently the formation of new tissue or a regenerated organ. There are several approaches reported for the preparation of polymer-based porous membranes, such as porogen leaching, gas foaming, emulsion freeze-drying, and phase separation techniques [7–11]. Phase separation approach has been one of the most important controlling procedures to obtain porous structure, including thermally induced phase separation, air-casting of polymer solution, precipitation from vapor phase, and immersion precipitation [12–18], etc. Among all these techniques, immersion precipitation is the first to be commercially explored and one of the most prevalent membrane preparation methods [19]. In a typical procedure, the polymer solution is cast on a glass plate and subsequently immersed into a coagulation bath. There are at least three components involved in this process: polymer, solvent and nonsolvent. The exchange of solvent and nonsolvent leads to phase transition in the ternary system, followed by the precipitation of polymer matrix and formation of porous membrane. The phase transition behavior, depending on the interactions of polymer, solvent and nonsolvent, is responsible for the pore generation and fixation of the porous structure, which can also be modified by the addition of a second polymer, alcohols, or inorganic salts, into the casting solution [20–22].

Poly (L-lactic acid) (PLLA) has been used as porous biodegradable scaffolds for cell transplantation and drug carriers for controlled release due to its superior biocompatibility and biodegradability [23–29]. Some experimental and theoretical researches related to the formation of PLLA membranes by immersion precipitation have been reported [30–33]. Especially, phase separation and morphology modification of PLLA membranes made from systems such as PLLA/chloroform/methanol, PLLA/methylenechloride/methanol, and PLLA/dioxane/water have been extensively emphasized by the determination of cloud points. Liu et al. [2] prepared particulate and porous PLLA membranes by changing PLLA concentration in the casting solution and studying the equilibrium phase diagram of PLLA, methylene chloride, and ethanol. Van de Witte et al. [11] also investigated the correlation between

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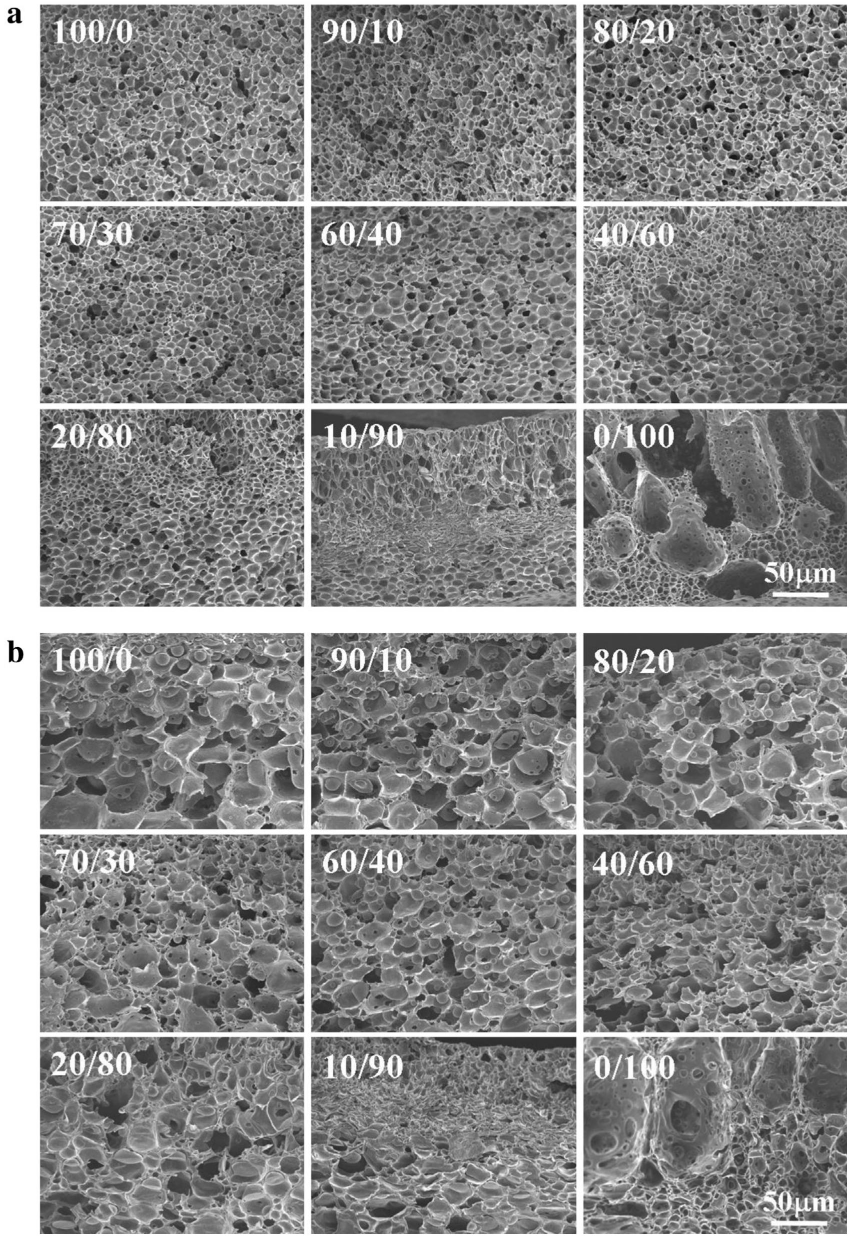

Fig. 1. SEM micrographs (cross sections) of membranes prepared from PLLA/dioxane (a) and PLLA/PU/dioxane (b) solutions by immersing in ethanol/water baths. The corresponding ratio of ethanol/water and the scale bar are shown in the images.

the ultimate porous structure and the phase diagram of polymer/solvent/nonslovent, and found that the demixing process, including liquid–liquid demixing and solid–liquid demixing, is the key factor affecting the morphology evolution. Zoppi et al. [34] systematically studied the phase separation mechanism during immersion precipitation, which indicates that the nucleation and growth predominate in concentrated polymer solutions and spinodal decomposition in diluted solutions.

As a matter of fact, the inherent brittleness and low bioactivity of PLLA limit its large-scale application [35,36], and there have been a variety of methods to tailor the properties of PLLA, such as addition of organic molecules, inorganic particles, and other polymers [37–42]. Polyurethane (PU), as an excellent elastomer, shows good impact toughness, and has unique combination of high biocompatibility, biostability, and bioactivity. Therefore, blending PU with PLLA has been adopted to mediate the impact resistance and other physical properties of PLLA-based materials [43–45]. On the other hand, coagulation bath composition has great influence on the phase separation of polymer/solvent/nonsolvent system, which is critical to the ultimate morphology and performance of PLLA membranes. In the present work, PLLA and PLLA/PU porous membranes were fabricated through immersion precipitation. Two coagulation bath systems, including ethanol/water and ethanol/dioxane, have been adopted to regulate the phase separation of the ternary solution. The main goal is to illustrate the influence of phase separation rate and stage on the structure, porosity and crystallization behavior of the ultimate PLLA membranes. Based on the experimental observations, a possible formation mechanism for the porous PLLA and PLLA/PU membranes has been proposed.