



Fabrication of rigid poly(lactic acid) foams via thermally induced phase separation



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ABSTRACT

Rigid poly(lactic acid) (PLA) foams were prepared by thermally induced phase separation followed by solvent exchange and vacuum drying. A novel tetrahydrofuran (THF)/water solvent system was used for the induction of liquid–liquid phase separation of PLA solution at three different temperatures; 24 °C, 4 °C and –20 °C. PLA gels obtained were mechanically stabilized by replacing THF/water solvent mixture with ethanol nonsolvent. Characterization of rigid PLA foams was obtained by scanning electron microscopy, mercury intrusion porosimetry, x-ray diffractometry, infrared spectroscopy and differential scanning calorimetry analyses. Effects of fabrication parameters on the morphology and pore structure were systematically examined. The parameters investigated included; (i) polymer concentration, (ii) THF/water ratio and (iii) quench temperature. Results showed that degree of porosity and the morphology of the pores, such as the pore size and shape could be controlled by tuning the fabrication parameters. By controlling the degree of phase separation of PLA solution, foams with dual micro and nano structures were obtained.

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1. Introduction

Poly(lactic acid) (PLA) is an aliphatic thermoplastic polyester derived from renewable resources such as corn, potato and sugar cane [1]. PLA, which is natural and biodegradable, is gaining much interest due to the depletion of the petroleum resources and in consideration of the prevention of the environmental pollution. Conventional polymers that are produced in very large volumes, such as polyolefins, polyesters, polystyrene, acrylics, etc., are mainly derived from petroleum resources for which PLA is a natural alternative. Improvements in mass production allowed PLA to be used in variety of fields, which include; packaging, textile applications, structural foams, automotive and electronics [2]. Owing to its biocompatibility and biodegradability with non-toxic degradation products, PLA is also one of the few synthetic polymers approved by the FDA for biomedical uses, which include applications such as; 3D scaffolds for tissue engineering, sutures, bone fixation, controlled drug delivery, implants and support in human body [3,4].

Similar to PLA films and fibers, PLA foams can substitute widely

used petroleum based rigid polymeric foams, such as polystyrene, polyethylene and rigid polyurethane in variety of applications including packaging, construction, thermal and sound insulation. PLA foams can also be used as scaffolding in tissue engineering or drug delivery [5,6]. Various fabrication methods have been developed for the controlled preparation of polymeric foams, which include fiber bonding, porogen leaching, gas foaming, phase separation and rapid prototyping [7–12]. Thermally induced phase separation is a very simple method compared to others and it has been widely used for production of PLA foams especially for tissue engineering applications [10,13]. In this method, a polymer solution showing upper critical solution temperature (UCST) behavior is prepared at higher temperatures. When temperature is lowered, liquid–liquid phase separation takes place to form two new phases: a polymer rich and a polymer poor phase. After the removal of the solvent, porous polymer structure is obtained. Critical parameters that influence the thermodynamics and kinetics of microphase separation and crystallization are solvent composition, PLA concentration and quench temperature.

Typical polymer–solvent binary phase diagram showing UCST behavior is shown in Fig. 1. In metastable region, phase separation is thermodynamically favorable, however, there exists a kinetic barrier and concentration fluctuations must be large enough to induce liquid–liquid phase separation. In this region, phase separation

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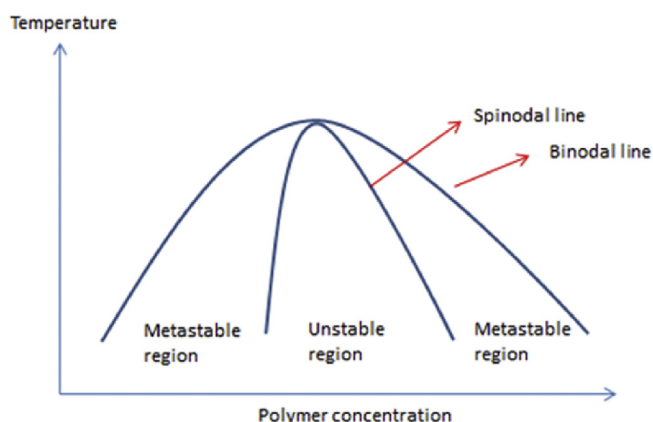


Fig. 1. Polymer solvent binary phase diagram.

takes place via nucleation and growth mechanism. At lower polymer concentrations, phase separation in metastable region produces polymer rich phase beads in polymer poor phase matrix. However, at higher polymer concentrations, phase separation in the metastable region produces polymer poor phase droplets in polymer rich phase matrix [14].

In the unstable region, there is no kinetic barrier to phase separation. Even very small concentration fluctuations can give rise to liquid-liquid phase separation via spinodal decomposition. In the initial stage of spinodal decomposition pathway, a bicontinuous polymeric network is formed. Initial polymeric network is highly exposed to polymer poor phase, which has higher energy and thus thermodynamically unfavorable. In order to minimize the interfacial free energy, coarsening of polymeric network takes place. Main coarsening processes are coalescence, hydrodynamic flow and Ostwald ripening [15,16]. Initially formed bicontinuous structure coarsens over time and eventually forms solvent droplets. These solvent droplets can further coarsen in the polymeric matrix and get larger in size by different mechanisms [17].

In principle, phase separation process is terminated when the thermodynamic driving force, which is the minimization of interfacial energy is fulfilled. However, gelation or vitrification of polymer rich phase may cease the separation of phases, before the system reaches eventual minimum energy state, or in other words kinetically arrest the phase separated system. For a given polymer type, foam morphology is mainly controlled by the parameters which affect the thermodynamics and kinetics of the liquid-liquid phase separation. These parameters include; polymer molecular weight and concentration, solvent type, quench temperature, quench rate, aging time, isomer content and crystallizability [14]. After the completion or arrest of the phase separation, solvent can be removed by three different ways; supercritical drying, freeze drying or exchange with a nonsolvent followed by vacuum drying.

Freeze drying is time and energy consuming and creates surface skin problems. Aging time can be controlled and phase separation can be terminated anytime with supercritical and freeze drying methods. Solvent exchange is quite simple and does not require advanced equipment. However, to obtain a homogenous foam, nonsolvent exchange should be performed after the phase separation is completed. Otherwise nonsolvent presence may alter the outcome in an uncontrolled manner. Very surprisingly, for solvent exchange method no example has been found in the literature where aging time is controlled [18–25].

In this study effects of the following parameters on the structure and morphology of PLA foams obtained by thermally induced phase separation, followed by solvent exchange, were investigated; (i) polymer concentration, (ii) solvent composition or THF/water ratio and (iii) quench temperature.

2. Experimental

2.1. Materials

PLA ($M_n = 109,000$ g/mol, PDI = 1.76 and 8% D content) was obtained from Natureworks (PLA polymer 4042D). Molecular weight was determined by GPC measurements using polystyrene standards. Reagent grade tetrahydrofuran (THF) and ethanol were obtained from Merck and were used as received. Deionized and double distilled water was used in all experiments.

2.2. Fabrication of PLA foams

PLA, THF and water were introduced into a Pyrex test tube with a diameter of 1.0 cm and height of 10 cm. Test tube was covered with a rubber stopper and solutions were prepared in a 60 °C bath by mixing with a magnetic stirrer. Homogenous solutions with PLA concentrations ranging from 6 to 10 wt% were quenched at three different temperatures –20, 4 and 24 °C for 12 h for the induction of thermally induced phase separation. Solvent compositions (THF/water ratio) and PLA concentrations were determined after some preliminary studies, where it was observed that solutions containing less than 6 wt% PLA did not produce foams. On the other hand it was not possible to obtain homogeneous solutions in THF/water ratios employed, when PLA concentration was higher than 10 wt%. Quench temperatures were selected for their practicality such that; (24 °C) is the ambient or room temperature, (4 °C) is typical temperature in a refrigerator, and (–20 °C) is the temperature of the freezer in a typical refrigerator. Following quenching, test tubes containing PLA gels were filled and replaced with ethanol twice in 12 h durations. Resulting gels were taken out of the test tubes and were dried in a vacuum oven at room temperature until constant weight. Foams were kept in a desiccator for further characterization. Fig. 2 provides pictures taken at various stages of

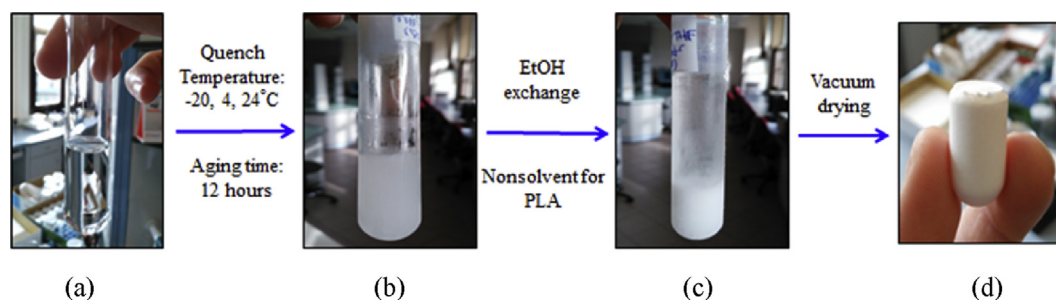


Fig. 2. Pictures showing various stages of PLA foam fabrication process. (a) Polymer solution, (b) gel formed after quenching, (c) wet foam after nonsolvent addition, and (d) rigid foam obtained after vacuum drying.

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