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Spontaneous formation of microporous poly(lactic acid) coatings

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A B S T R A C T

Microporous poly(lactic acid) (PLA) coatings with fairly homogeneous pore size and distribution were obtained through spin-coating process. Critical effects of the thermal conductivity of the substrate (copper, glass, insulated glass), solvent type (dichloromethane, chloroform and tetrahydrofuran), polymer concentration (3–15% by weight) and relative humidity of the environment (0–85% relative humidity) on the formation and topography of microporous surfaces were investigated. Characterization of the surfaces was achieved via scanning electron microscopy, white light interferometry and static water contact angle measurements. By tuning the production parameters, PLA coatings displaying microporous surfaces with uniform pore sizes and distribution were obtained. Pore sizes varied from 1 to 7 μm depending on the experimental conditions.

1. Introduction

Polymeric coatings with controlled surface porosity are interesting materials that may find uses in various applications including superhydrophobic and self-cleaning surfaces, tissue scaffolds, foul release coatings, photonics, and template for functional materials, catalysts and membranes. A wide range of methods such as thermally induced phase separation [1–3], immersion precipitation [4], non-solvent induced phase separation [5,6], lithography [7], microcontact printing [8,9], salt leaching [10], micromolding [11], freeze-drying [12], gas foaming [13] and utilization of colloidal assemblies as templates [14] have been reported for the preparation of polymeric structures with micro and/or nanoscale pores on the air surface or in bulk/core structures [7,9,15,16]. Another widely utilized approach, termed as the breath figures, which involves the utilization of condensed water droplets from humid air during solvent evaporation of a polymer solution, also reported to produce well-ordered microporous films with honeycomb structures [15–23]. A wide range of polymeric materials, including polystyrene [19], poly(methyl methacrylate) [7], polycarbonate [22], poly(lactic acid) [6,24] and various others [2,10,12] have been used for the production of microporous surfaces by various methods.

Poly(lactic acid) (PLA) is a highly crystalline and biodegradable polyester that can be used as a polymeric carrier for drug release applications and template for cell growth and tissue scaffolding [25]. Three dimensional (3D) scaffolds with controlled porosity play critical roles in tissue engineering applications, where they function as templates that provide temporary structural support to the cells and allow new tissue growth [26]. For this purpose a high degree of porosity with controlled pore size and distribution are necessary to facilitate the cell seeding, adhesion and diffusion through the structure both for the cells and the nutrients. To obtain 3D scaffolds with controlled porosity some of the most widely used techniques include 3D printing and electrospinning or the combination of both.

In this study we investigated the preparation of microporous PLA surfaces via breath figures method which was developed by Francois [17]. In this process, polymer is dissolved in a highly volatile solvent, fast evaporation of which leads to cooling of the solution surface. This cooling results in the condensation of the water vapor onto the solution surface to form water droplets. Through convection and capillary forces, condensed droplets are self-organized throughout the surface. In the later stages of evaporation, solution viscosity increases and polymer molds around water droplets, which leads to surface cavities after complete removal of the solvent and water. In this work we utilized a fairly simple, high speed spin-coating process for casting polymer solutions in various solvents with different polarities, boiling points and evaporation rates. Homogenous microporous PLA thin films with controlled pore sizes were produced by optimization and tuning of the following process parameters; (i) thermal conductivity of the substrate, (ii) polymer concentration, (iii) relative humidity of the environment, and (iv) solvent type.

2. Experimental methods

2.1. Materials

PLA (M_n = 109,000 g/mol, PDI = 1.76, 8% D content) was

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obtained from NatureWorks (PLA polymer 4042D). Molecular weight was determined from GPC measurements using polystyrene standards. Reagent grade tetrahydrofuran (THF), dichloromethane (DCM), and chloroform (CHL) were obtained from Merck and used as received.

2.2. Preparation of microporous PLA films

Microporous films were produced by spin coating of PLA solutions onto 20 × 20 x 1.5 mm glass and copper slides. Glass substrates were cleaned by wiping successively with tetrahydrofuran and isopropyl alcohol. Copper substrates were cleaned by dipping in 1 M HCl solution, followed by repetitive rinsing with distilled water. PLA solutions were prepared in different solvents and at several different concentrations ranging from 3 to 15% (w/v). Spin coating was performed using a Model 7600 Spin Coater by Specialty Coating Systems, Inc., Indianapolis, IN, USA. Relative humidity (RH) was measured by a hygrometer. Spin coating was performed at three different humidity levels. PLA solutions were spin coated at a constant speed of 1000 rpm, under following conditions: (i) in an inert glove box where water content was less than 1 ppm (0% humidity), (ii) under ambient humidity of 33 ± 2% and (iii) under 85 ± 3% humidity. 85% humidity level was achieved and maintained by placing saturated KCl solution into the spin coating chamber [27]. For comparison, PLA films were also coated on a glass substrate using a doctor blade with two different gauge thicknesses of 50 and 200 μm. All films obtained were dried at room temperature overnight and then in a 40 °C oven for 24 h. Samples were kept in a desiccator for further characterization. During the experiments room temperature was 22 ± 1 °C.

2.3. Characterization of porous films

Nikon Eclipse ME 600 optical microscope (OM) equipped with a digital camera was used to capture the images. Microporous PLA surfaces obtained were investigated by a field-emission scanning electron microscope (FESEM) (Zeiss Ultra Plus Scanning Electron Microscope) operating at 2–5 kV. Samples were coated with a 5 nm layer of gold to minimize charging, prior to FESEM analysis. Average pore size analysis was performed by measuring and averaging 50 pores from three different regions of 20 × 20 x 1.5 mm glass or copper substrates with a diagonal length of 28.2 mm. Topography and depth profiles of the surfaces were determined by White Light Interferometry (WLI) using a Bruker Contour GT Motion 3D Microscope and Non-Contact Surface Profiler at the vertical scanning interferometry (VSI) mode. For a precise determination, at least 10 surface maps with dimensions of 47 × 63 μm^2 were obtained from different parts of the sample. Static water contact angle measurements were performed at ambient temperature (22 ± 1 °C) on a Dataphysics OCA 35 goniometer equipped with SCA 20 software. For each sample, an average of 10 different contact angle readings were taken using 5 μL droplets of deionized triple distilled water.

3. Results and discussion

Dew point is the temperature at which water vapor becomes saturated at a given relative humidity. In breath figures method, solution temperature is dropped below dew point by evaporative cooling. In order to provide rapid and sufficient cooling, highly volatile solvents such as such carbon disulfide [28] and dichloromethane [29] are generally used. Rate of solvent evaporation can also be enhanced by applying air flow [30] or using high speed processes such as spin coating [31] or electrospinning [32]. Spin coating is a widely utilized method, especially in the microelectronics industry for the production of uniform thin films on planar substrates [33]. This study deals with the production of thin, porous PLA films by spin coating under controlled humidity. Homogenously distributed, microporous PLA surfaces with controlled properties are obtained by; (i) minimizing the heat transfer in the substrate, (ii) tuning the polymer concentration, (iii) controlling the relative humidity, and (iv) using different solvents.

Table 1
Thermal conductivities of the substrates used.

	Thermal conductivity (W/mK)
Copper [39]	400
Glass [40]	1.1
Cardboard [41]	0.23

3.1. Optimization of substrate properties

In the spin coating process, the material to be coated is placed onto the center of the spin-coater. As the rotation starts, polymer solution is spread throughout the substrate via centrifugal forces. In order to prevent displacement of the substrate, substrate is placed on a chuck through which vacuum is applied. During high speed spinning, due to rapid solvent evaporation solution cools down. However, the vacuum chuck can act as a local heat reservoir to re-supply heat to the substrate. In other words, substrate regions directly contacting the vacuum chuck experience less cooling [34–36]. Therefore, the degree of thermal conduction is crucial for controlling the condensation of vapor during spin coating.

In the first part of this study thin, microporous PLA films were obtained by the spin coating of 10% by polymer weight/solvent volume (w/v) solutions in DCM onto three different substrates of quite different thermal conductivities (Table 1), which were thin copper foils, glass slides and cardboard insulated glass slides. Upon formation of the pores, due to light scattering the films turn opaque [37,38]. As shown in the optical microscope image provided in Fig. 1-a, when a thin copper foil is used as the substrate a smooth and transparent PLA film was obtained without any pore formation. Copper has high thermal conductivity and heat transfer from the chuck can take place very rapidly preventing the cooling of the solution below the dew point during the spin coating process. When a poorer heat conductor, glass is used as the substrate, pore formation was observed (Fig. 1-b). However pores only formed at positions equally distant from the center, leaving a transparent disc in the middle of the film. Center of the substrate is in direct contact with the chuck, this is probably the reason why no pore formation is observed in the middle part. Since heat transfer decreases with increasing radial position and glass is a poor conductor of heat, pore formation is observed only at the edges where evaporative cooling becomes sufficient. In order to obtain an even distribution of pores throughout the substrate, thermal conductivity of the glass slide was reduced by adhering a 2 mm thick insulating cardboard layer under it using a double layered scotch tape. Cardboard is a readily available material, which has very low heat conductivity. When the glass/cardboard composite substrate is used, a microporous and translucent film was formed (Fig. 1-c). As can be seen in the SEM image provided in Fig. 2, the PLA film obtained displayed fairly homogeneous pore sizes that are evenly distributed on the surface. SEM micrographs of the other two films produced using copper and glass substrates are provided as supplementary information. As a result of these observations in this study all coating experiments were performed by using cardboard insulated glass substrates.

3.2. Effect of polymer concentration on pore formation

In order to investigate the influence of polymer concentration on the pore formation, DCM solutions with PLA concentrations varying between 3 and 15% (w/v) were spin coated at 33 ± 2% relative humidity. When PLA concentration was less than 3%, disordered morphologies were obtained. We believe this is due to very low solution