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The crystallization behavior of porous poly(lactic acid) prepared by modified solvent casting/particulate leaching technique for potential use of tissue engineering scaffold



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ABSTRACT

The porous poly(lactic acid) (PLA) foams potential for tissue engineering usage are prepared by a modified solvent casting/particulate leaching method with different crystallinity. Since in typical method the porogens are dispersed in the solution and flow with the polymers during the casting and the crystallinity behavior of PLA chains in the limited space cannot be tracked, in this work the processing is modified by diffusing the PLA solution into a steady salt stack. With a thermal treatment before leaching while maintaining the stable structure of the porogens stack, the crystallinity of porous foams is made possible to control. The characterizations indicate that the porous PLA foams have a lower crystallizability than the bulk materials. Pores and caves of around 250 μm size are obtained in samples with different crystallinity. The macro-structures are not much impaired by the crystallization nevertheless the morphological effect of the heating process is still obvious.

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1. Introduction

Porous poly(lactic acid) (PLA) has been developed for tissue engineering scaffolds for decades [1–3]. Including poly(L-lactic acid) (PLLA), poly(D-lactic acid) (PDLA) and PLA-based copolymers like poly(lactic-co-glycolic) acid (PLGA), these bio-based resins have been proved to be a successful candidate of scaffold materials with excellent biocompatibility and biodegradability. The tissue engineering requires sufficient interconnecting inner space in the scaffold for biofactor delivery, tissue growth, and the scaffold should be degradable after tissue's growth meanwhile providing proper mechanical strength to support the tissue engineering system. Therefore the balance of growth space, degradation behavior and mechanical properties is the main concern of constructing a scaffold. With the respect to the particular requirements of certain tissue engineering, nowadays designed preparation and modification techniques of porous PLA scaffold materials become an intensive interests-drawing subject [4–13], which requires more understanding of the basic principles of physical and chemical properties, particularly in the form of scaffold.

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The crystallization of PLA plays an important role in its mechanical properties and degradability. Generally the crystallized polymers have higher strength and mechanical modulus [14]. In the case of PLA, the crystallinity also significantly affects the degradability, with the general behavior that the degradation time is longer with higher crystallinity, as the crystal segments are more stable than amorphous area and prevent water permeation into it. For example, it was reported that PLLA takes more than 5 years for total degradation, whereas only about 1 year for the amorphous PLA or PDLA [15,16]. However unlike the crystallinity control for the inorganic components in the tissue engineering scaffold [17], very rare reports concerned the crystallinity of the polymer scaffold materials. One probable reason is that the preparation of porous scaffolds is a delicately process, where the control of crystallinity is usually difficult or unavailable. Except the solvent casting/particle leaching method, in other widely used preparation methods such as electrospun fiber, phase separation, membrane lamination and gas foaming, the polymers are not able to experience a thermal treating step, i.e. the most common way to control the crystallinity [1]. In some works the crystallinity is controlled by the raw materials itself, i.e. selecting raw materials of different molecular weight associated with different crystallization behaviors, or a particular processing procedure for chain cleavage to control the crystallinity [18]. In some methods, even polymer with high crystallinity cannot be served as the raw materials to prepare the scaffold, for example the gas foaming technique reported by Mooney et al. [19].

Nevertheless, the study of the crystallization of the scaffold should hold considerable practical merits in tissue engineering, for example to fit the scaffold degradation time with the expected tissue growth time by the control of crystallinity (if possible). Also, the scaffold structure may vary with crystallinity and influence the biological behavior of living tissue leaning on it. Park et al. reported a research on the sustained release of human growth hormone from semi-crystalline poly(L-lactic acid) and amorphous poly(D,L-lactico-glycolic acid) microspheres, which reveals that the morphological effect is important on protein release [20].

Crystallinity can be tailored in solvent casting/particulate leaching technique. However in this method the salt as porogens are dispersed in the solution and flow with the polymers during the casting, therefore without the immobilization of porogens the crystallinity behavior in the space-limited gap cannot be tracked [1]. In this work, we modified the solvent casting/particulate leaching technique by diffusing the PLA solution into a steady salt stack instead of solving the porogens. The control of crystallinity was made possible by inserting a thermal treating step before leaching, while maintaining the stable structure of salt stack. We have investigated the morphological effect of limited space on the crystallization of PLA, and the porous structure with different crystallinity under thermal treatments.

2. Experimental

2.1. Materials

The PLA of label 4032D is purchased from Natureworks[®], with L/D ratios from 24:1 to 30:1. The porogen is NaCl of analytical grade. The 1:1 mixture of dichloromethane and chloroform is served as solvent.

2.2. Porous sponge preparation

The PLA pellets are solved into dichloromethane and chloroform (1:1) with the concentration of 50 g/l. The NaCl powder is thoroughly grounded and sieved with 109 μm then 300 μm sieve to screen the particles of sizes in between, and paved onto a petri dish where it forms a ~ 1.5 mm thick disc. The PLA solution is very slowly poured into the dish at the edge. The pouring is as slow as that the solution diffuses inside the salt stack instead of flowing over the surface, also the slow diffusing guarantees that the salt particles are not considerably moved by the liquid flowing to keep the inner structure of the salt stack stable. After pouring, the salt-PLA solution composite is then placed in vacuum for 12 h for drying out the solvent. The product is a solid dry PLA-glued salt composite ready for thermal treatment. The composite is placed in water for 48 h to leach out the salts after the thermal treatment for recrystallization. The leached samples are freeze-dried for 2 h and stored in vacuum ready for characterizations.

2.3. Recrystallization

The recrystallization of composite is processed by the heating and cooling process. Four samples were made to have different crystallinity. One sample was kept as the original composite without thermal treatment for reference (sample R). The other three composites are heated in oven at 165 $^{\circ}\text{C}$ for 0.5 h, then one composite (sample A) was immediately quenched in liquid nitrogen; sample B was linearly cooled down at the rate 10 $^{\circ}\text{C}/30$ min.; sample C was linearly cooled at 10 $^{\circ}\text{C}/30$ min till 105 $^{\circ}\text{C}$, kept at 105 $^{\circ}\text{C}$ for 24 h, then cooled down with the same rate to room temperature. For comparison we also made two bulk PLA samples

with the same crystallization process of sample B and C and they were labeled as sample B' and C'.

2.4. Characterization

The crystallinity of samples were characterized by X-ray Diffraction (XRD) (D/max-2200/PC, Rigaku Corporation). The porous structure of samples were revealed by Scanning Electron Microscope (SEM) (Nova NanoSEM 450, FEI).

3. Results and discussion

3.1. The crystallization behavior

The XRD results firstly dispel the doubt about the possibility of crystallization in confined geometry. Fig. 1a shows the XRD of three thermal treated samples A, B and C (Note that the sample R is not included because its XRD curve almost overlap with the sample A, i.e. amorphous), and the bulk samples of B' and C' are shown in Fig. 1b. With the comparison of the bulk behavior, clear crystal peaks at $2\theta = 16.6^{\circ}$ and other minor peaks ($2\theta = 12.4^{\circ}, 14.8^{\circ}, 19.0^{\circ}, 22.4^{\circ}, 24.0^{\circ}, 25.3^{\circ}, 29.1^{\circ}$) indicate that the heat treatment makes the crystallization possible but we can see significant impact of confined geometry,

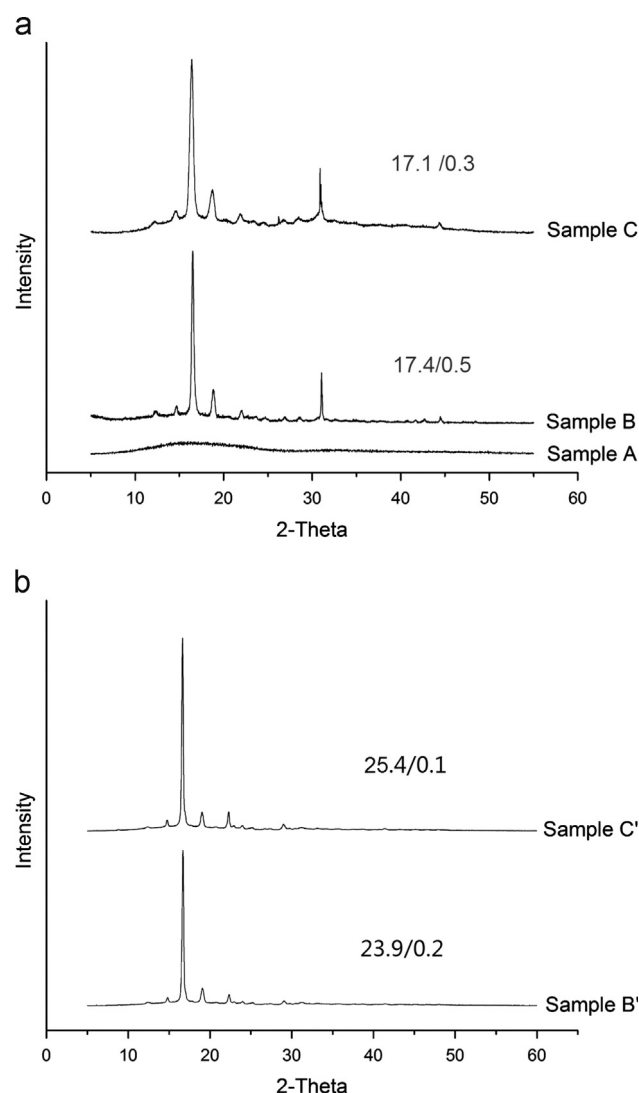


Fig. 1. The XRD characterizations of (a) heat-treated porous samples A, B and C and (b) bulk samples B' and C' with the same heat treatment.

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