Duplex surface modification of porous poly (lactic acid) scaffold

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A B S T R A C T
A duplex surface modification method is used to enhance the surface and mechanical properties of porous poly (l-lactic acid) (PLLA) scaffold. The scaffold was first modified by a surface alkali hydrolysis treatment and then it underwent a short-time surface coating process. An acetic acid treatment was introduced to the traditional surface hydrolysis; the result indicates that this novel surface alkali hydrolysis treatment can further improve the hydrophilicity and surface roughness of the PLLA scaffold. Surface hydrolysis also improves the bonding strength of the scaffold with the coating significantly. The existence of the gelatin–hydroxyapatite hybrid coating increases the hydrophilicity, mechanical property and apatite-forming ability of the scaffold considerably.

1. Introduction

Porous poly (lactic acid) (PLA) and poly (lactic-co-glycolic acid) (PLGA) scaffolds have been widely used in tissue engineering because of their good biocompatibility and biodegradability. However, these porous scaffolds have low mechanical strength, poor hydrophilicity, low surface energy and lack of cell-recognizable signal, which limits their use [1].

Numerous surface modification methods, such as plasma treatment [1,2], surface hydrolysis [3–5], surface coating [6–8] and chemical grafting modification [9,10], have been developed to improve the surface property of the porous PLA or PLGA scaffold. Each method has its advantages and disadvantages. For example, surface hydrolysis is a simple and convenient method, but the mechanical property of the scaffold cannot be improved together; surface coating can introduce bioactive materials onto the surface of the porous scaffold to improve its mechanical property as well as its surface property, but the interactions between the matrix and the coating are usually weak. It is believable that combining two or more surface modification methods can obtain more excellent property. Unfortunately, few researchers have investigated the duplex surface modification method of the porous scaffold.

In the present work, a duplex surface modification method that combined a novel surface alkali hydrolysis method with a short-time surface coating process was developed to modify the surface and mechanical property of the porous poly (l-lactic acid) (PLLA) scaffold. The effect of the surface hydrolysis method on the surface coating process was also investigated.

2. Material and methods

Materials: PLLA with an average molecular weight of 100,000 g/mol was purchased from Shandong Institute of Medical Instruments, China. Basic gelatin was purchased from Shanghai Shenhe Chemical Co., Ltd., China. HA particles were synthesized from calcium hydroxide and phosphoric acid using the acid–base neutralization method. Ice particles were prepared by spraying deionized water through a nozzle into liquid nitrogen.

Preparation of porous PLLA scaffold: Porous PLLA scaffold was fabricated using our porogen leaching/freeze-drying method [11]. In brief, sieved ice particles were arranged in the mold to form a porous medium, PLLA dissolved in chloroform was cast into the mold and put into liquid nitrogen, and the porous scaffold was fabricated by removing the mold and freeze-drying at about −55 °C to remove the chloroform solvent and at −5 °C to remove the ice particles.

Duplex surface modification of porous PLLA scaffold: Porous PLLA scaffold with a gelatin coating or a gelatin–hydroxyapatite (gelatin–HA) hybrid coating was prepared by the duplex surface modification method as follows. First, the PLLA scaffold was treated to surface alkali hydrolysis by immersing the scaffold in a mixture of 2 g/L sodium hydroxide solution and absolute ethanol (v/v=1/1) for 1 h at room temperature. Different from the traditional method, the treated scaffold was washed with 0.5% acetic acid and deionized water. Then, the scaffold was dried under vacuum at 40 °C. After surface hydrolysis treatment, the porous scaffold underwent a fast surface coating process similar...
to our surface coating process of porous bioceramics [12]. The gelatin was dissolved in distilled water at 50 °C to form 10% gelatin solution. The porous scaffold was then immersed in the solution and infiltrated for 0.5 h under vacuum at 45 °C. After infiltration, the scaffold was centrifuged in a centrifuge to remove the excess gelatin. The infiltration and centrifugation processes were repeated three times. Finally, PLLA scaffold with a gelatin coating was gained by freeze-drying for 4 h. To obtain porous PLLA scaffold with gelatin–HA hybrid coating, the gelatin solution was replaced by gelatin–HA mixture.

Characterization: SEM images and EDX spectra were obtained on a field-emission scanning electron microscope and an attached energy-dispersive spectrometer operated at 20 kV. XPS spectra were obtained on an X-ray photoelectron spectrometer. Water contact angle of the PLLA film was gained by contact angle measurement. Surface roughness of the film was determined by an atomic force microscope. Water absorption rate of the PLLA scaffold was determined by weighing the scaffold before and after immersing in deionized water for 24 h. Porosity of the porous scaffold was determined by the Archimedes method with absolute ethanol as the immersion medium. Compressive strength of the scaffold was gained by an electronic universal testing machine.

3. Results and discussions

As shown in Fig. 1, the surface alkali hydrolysis treatment, especially the additional acetic acid treatment decreases the water contact angle of PLLA film and increases the water absorption rate of PLLA scaffold, which indicates that the hydrophilicity of PLLA has been enhanced significantly. Moreover, the surface roughness result shows that traditional surface hydrolysis increases the roughness of PLLA surface slightly while the additional acetic acid treatment increases the roughness of PLLA surface significantly, which suggests that the increase of the water contact angle is partly attributed to the rougher surface after surface hydrolysis according to the Wenzel model [13].

Table 1 lists the relative compositions of C1s and O1s region of PLLA surfaces with and without additional acetic acid treatment according to the XPS analysis. The result shows that the fraction of C–O or COOH increased while the fractions of C–O and C–H or C–C decreased with additional acetic acid treatment. It is known to all that acetic acid can react with sodium hydroxide. During the reaction, acetic acid and sodium hydroxide ionized to generate hydrogen and hydroxyl ions, which can catalyze the hydrolysis reaction of PLLA. Therefore, more hydrophobic ester bonds were cleaved to hydrophilic hydroxyl groups and carboxylic acid groups, resulting in the increase of surface roughness and hydrophilicity of PLLA.

Fig. 2 illustrates the SEM images of the gelatin-coated PLLA scaffolds with and without surface hydrolysis. Because of the weak interaction between the PLLA matrix and gelatin coating, the coating is partially separated from the matrix of untreated PLLA scaffold (Fig. 2(a)). In contrast, the gelatin coating is in close contact with the PLLA matrix after surface hydrolysis, indicating that the surface hydrolysis treatment significantly enhanced the bonding strength between the modified PLLA scaffold and gelatin coating (Fig. 2(b)). It is evident that the increase in hydrophilicity and surface roughness of the PLLA scaffold after surface hydrolysis benefit the deposition of gelatin onto the surface of the scaffold. Moreover, the mechanical chimeric between the gelatin coating and porous scaffold increases with the increase in surface roughness, which makes the bonding strength between the scaffold and the gelatin coating increase further. In addition, the acetic acid treatment resulted in more fractions of COOH on the surface of PLLA scaffold, which may contribute to the bonding between the scaffold and basic gelatin coating.

As given in Fig. 3, water absorption rate and compressive strength of the scaffold increase while the porosity decreases after the duplex surface modification. It can be seen that the increase in the water absorption rate mainly contributes to the addition of gelatin while the increase in compressive strength belongs to the addition of HA. The porosities of two modified scaffolds are also higher than 85%, which indicates that the duplex surface modification is suitable to fabricate the porous scaffold used in tissue engineering.

Fig. 4 shows SEM images and EDX spectra of the pure PLLA scaffolds and the porous scaffold with gelatin–HA hybrid coating.
after incubation in simulated body fluid (SBF) for 1 d. The appearance of white particles in the SEM image of the modified scaffold and Ca and P elements found in the corresponding EDX spectrum suggest the existence of apatite on the surface of the scaffold, which indicates that the gelatin–HA hybrid coating increases the apatite-forming ability of the PLLA scaffold significantly.

4. Conclusions

Porous PLLA scaffold was modified by a novel duplex surface modification method that combined a surface hydrolysis method with a surface coating process. Compared with the traditional surface alkali hydrolysis, additional acetic acid treatment further improves the hydrophilicity of the scaffold. Surface hydrolysis treatment also enhances the bonding strength of the scaffold with the coating. The hydrophilicity, mechanical property and apatite-forming ability of the scaffold have been increased significantly after being coated with a gelatin–HA hybrid coating.

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References


