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Surface modification of poly (lactic acid) with an improved alkali-acid hydrolysis method

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ABSTRACT

In this article, an improved alkali-acid hydrolysis method was used to enhance the hydrophilicity of poly (l-lactic acid) (PLLA). Compared with the traditional alkali hydrolysis method, whether the alkali solution was sodium hydroxide or calcium hydroxide, the new surface modification method using citric acid as the wash solution brought a significant decrease of PLLA film's surface water contact angle and a dramatic increase of PLLA's surface roughness in a short time, which indicates that this alkali-acid hydrolysis method can effectively improve the hydrophilicity of PLLA. The evident surface modification effect can be mainly attributed to the catalytic ability of the citric acid's carboxyl group to cleave polyester's ester bond.

1. Introduction

Poly (lactic acid) (PLA) is a common biomaterial because of its good biocompatibility, biodegradability and adjustable property. However, a series of disadvantages such as low mechanical strength, poor hydrophilicity, low surface energy and lack of cell-recognizable signal, limit the use of PLA [1].

In order to improve the surface property of PLA or the copolymer poly (lactic-co-glycolic acid) (PLGA), surface hydrolysis [2–5], surface coating [6–8], plasma treatment [1,9], chemical grafting modification [10,11], and other surface modification methods [12,13] have been developed during the past twenty years. Among all these methods, surface hydrolysis especially surface alkali hydrolysis with sodium hydroxide has been proved as a simple, convenient and effective surface modification method for PLA and PLGA.

In our previous work, we had found a novel surface hydrolysis method for Poly (l-lactic acid) (PLLA) [13]. By adding a wash process of acetic acid into the traditional alkali hydrolysis method, the surface water contact angle of PLLA dramatically decreased while the surface roughness of PLLA increased, which was favorable for the following surface coating process. In this article, citric acid was utilized to obtain a more effective surface modification result, that is, the surface water contact angle of PLLA further decreased while the surface roughness of PLLA further increased compared with the previous method. The modification effect of other acid or alkali 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. Sodium hydroxide, citric acid, acetic acid, and phosphoric acid were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Calcium hydroxide was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd., China. All the acids and alkalis used for surface hydrolysis were of analytical grade.

Surface hydrolysis modification of PLLA film: The PLLA film was prepared by standard solution casting technology and modified by the following surface alkali-acid hydrolysis method. First, the PLLA film underwent a surface alkali hydrolysis by immersing it into a mixture of 10 g/L sodium hydroxide solution and absolute ethanol with the same volume for 1 h at room temperature. Then, the treated film was washed with 0.5% citric acid and deionized water, respectively. Finally, the film was dried under vacuum at room temperature.

Characterization: Surface water contact angle of the PLLA film was gained by a contact angle measurement. Surface roughness of the film was determined by an atomic force microscope.

3. Results and discussions

Fig. 1 gives the surface properties of PLLA films before and after surface hydrolysis. Except the untreated film and the sample

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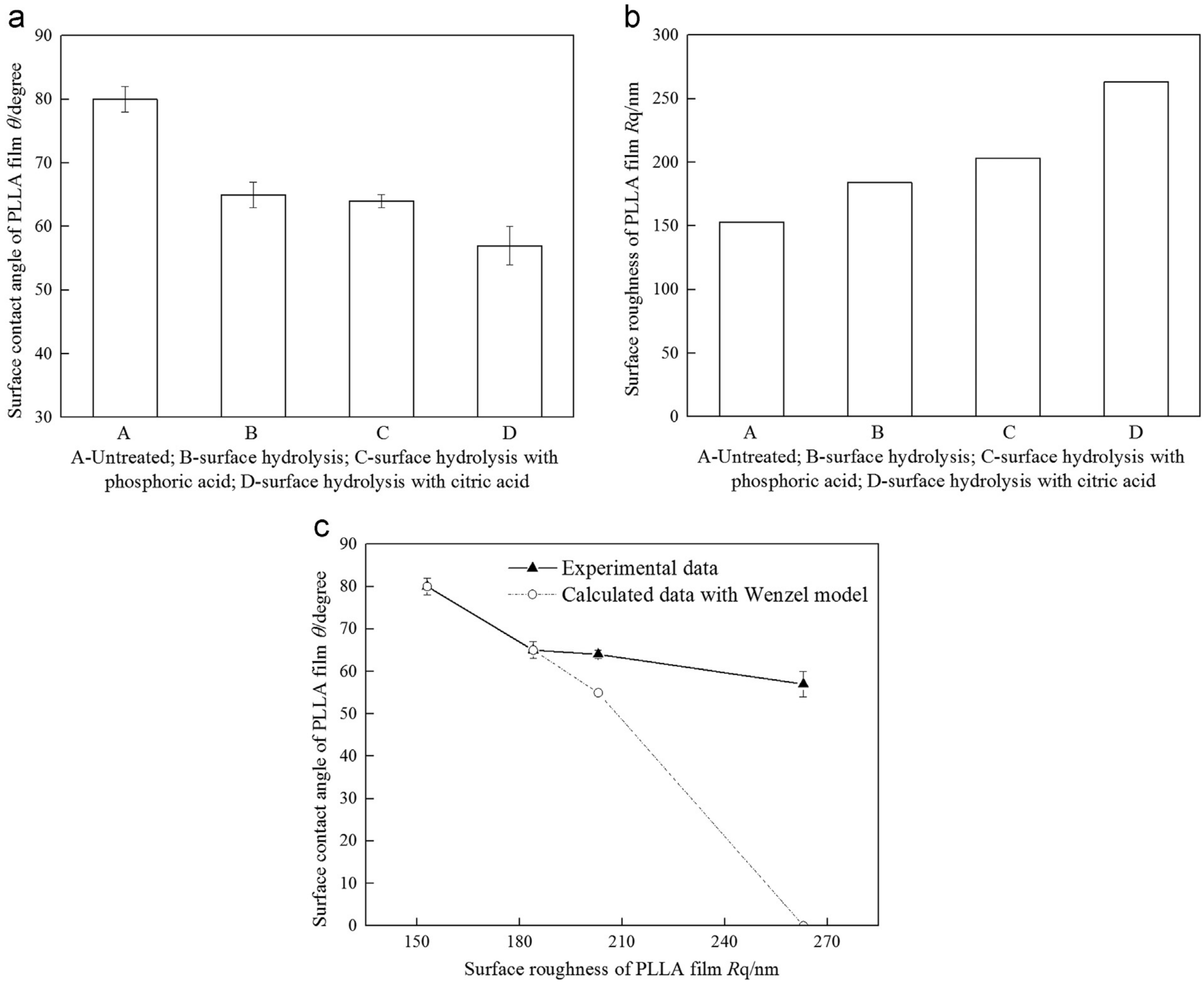

Fig. 1. Surface properties of PLLA film before or after surface hydrolysis with sodium hydroxide: (a) surface water contact angle of PLLA film, (b) surface roughness of PLLA film, and (c) the relationship between the surface roughness of PLLA film and its surface water contact angle.

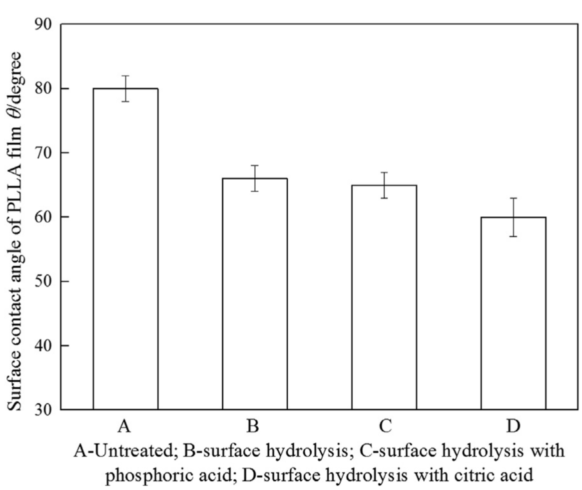

Fig. 2. Surface water contact angles of PLLA film before or after surface hydrolysis with calcium hydroxide.

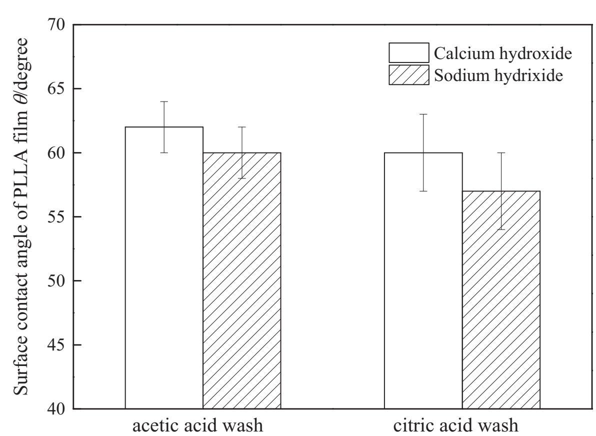

Fig. 3. The comparison of the surface water contact angle between the PLLA film washed with citric acid and the one washed with acetic acid.

washed with citric acid, the result of the PLLA sample hydrolyzed with sodium hydroxide and washed with phosphoric acid or pure deionized water was also shown in Fig. 1. From Fig. 1(a), it is clear that the adding of citric acid (sample D) obviously decreases the surface water contact angle of PLLA film comparing with the traditional method (sample B), while the adding of phosphoric acid (sample C) has no evident effect on the change in the hydrophilicity of PLLA film. It need to be pointed that the sole acid hydrolysis with citric acid or phosphoric acid had no effect on the decrease in the surface water contact angle of PLLA film (for example, even treated with 10% phosphoric acid for 1 h, the surface water contact angle of PLLA film still kept $79 \pm 2^{\circ}$, which was almost the same as the untreated sample), which suggests that the improvement of PLLA film's hydrophilicity is not because