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Study on wettability, mechanical property and biocompatibility of electrospun gelatin/zein nanofibers cross-linked by glucose

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ABSTRACT

In this study, the gelatin/zein nanofibers were electrospun and then cross-linked by glucose via Maillard reaction. The morphology observations showed that the average diameter of the cross-linked gelatin/zein nanofibers decreased with the increasing weight ratio of zein. FTIR results indicated that gelatin and zein molecules were homogenously dispersed within the fibers, and the Maillard reaction occurred between the proteins and glucose. The addition of zein affected the mobility of the gelatin chains, leading to the decreased denaturation temperature. The cross-linked fibers with a 1:1 gelatin/zein ratio showed the most hydrophobic surface (water contact angle of 134°), and comparable mechanical properties to the cross-linked gelatin nanofibers, while a higher ratio of zein (more than 50%) resulted in the decreased elastic modulus. The L929 cell cytotoxicity test suggested that the cross-linked gelatin/zein nanofibers exhibited good biocompatibility and non-cytotoxicity.

1. Introduction

Electrospinning is an electrostatic technique to fabricate continuous nanofibers with fascinating features, including high surface area to volume and oriented structures, which make the fibers potential candidates for applications on active packaging, bioactive delivery, and enzyme immobilization (Altan, Aytac, & Uyar, 2018; Ghorani & Tucker, 2015; Wang et al., 2017). During the last few years, electrospinning of biopolymers, such as gelatin, zein, and kafirin protein, has attracted researchers' attention for its potential applications in the food industry (Deng, Kang, Liu, Feng, & Zhang, 2017; Neo, Ray, et al., 2013; Xiao et al., 2016). For use of electrospun nanofibers in food products, edibility and safety are the priority, so more and more studies focused on the electrospun nanofibers solely composed of natural polymers.

Gelatin, as a commonly used FDA approved biopolymer, has long been researched for electrospinning due to its biocompatibility, biodegradability, and easy availability (Kanmani & Rhim, 2014; Mendes, Stephansen, & Chronakis, 2017). Electrospinning of gelatin can be achieved in relatively mild solvents, such as acetic acid/water and ethanol/formic acid/water solutions (Chen, Jao, & Yang, 2009; Deng et al., 2017). The main limitation of gelatin nanofibers is the poor water-resistance. Cross-linking is necessary to prevent the rapid dissolution of gelatin nanofibers and to retain the three dimensional structure. Gelatin nanofibers can be cross-linked by chemical and enzymatic methods (Tavassoli-Kafrani, Goli, & Fathi, 2017; Yao, Lee, Huang, Chen, & Chen, 2017). However, the toxicity of the cross-linkers should be taken into consideration before food contact or oral consumption applications. The majority of the researchers cross-linked gelatin nanofibers via exposure to glutaraldehyde vapor (Laha, Yadav, Majumdar, & Sharma, 2016; Morsy, Hosny, Reicha, & Elnimr, 2017a, 2017b; Serafim et al., 2015). The unreacted glutaraldehyde residue on the cross-linked gelatin nanofibers may be cytotoxic (Siimon et al., 2014; Zhang, Venugopal, Huang, Lim, & Ramakrishna, 2006). Currently, more and more researchers are focusing on non-toxic cross-linking methods. Tavassoli-Kafrani et al. (2017) reported that the incorporation of tannic acid within gelatin nanofibers not only acted as cross-linker in the protein matrix, but also provided antioxidant and antimicrobial functionality for the fibers. It was also reported that the gelatin nanofibers could be cross-linked thermally by Maillard reaction to enhance the mechanical properties (Morsy, Hosny, Reicha, & Elnimr, 2017a, 2017b; Şen & Culha, 2016). The addition of reducing sugar could not only enable the cross-linking by Maillard reaction, but also alter the conformation and interaction of proteins, resulting in nanofibers with tunable properties (Siimon et al., 2014).

Hybrid electrospinning of biopolymers has been a good choice to modify the properties of nanofibers. Zein, as a prolamin protein to be well dissolved in aqueous ethanol or acetic acid solutions (Li et al., 2012; Moomand & Lim, 2015; Torres-Giner, Gimenez, & Lagarón, 2008;

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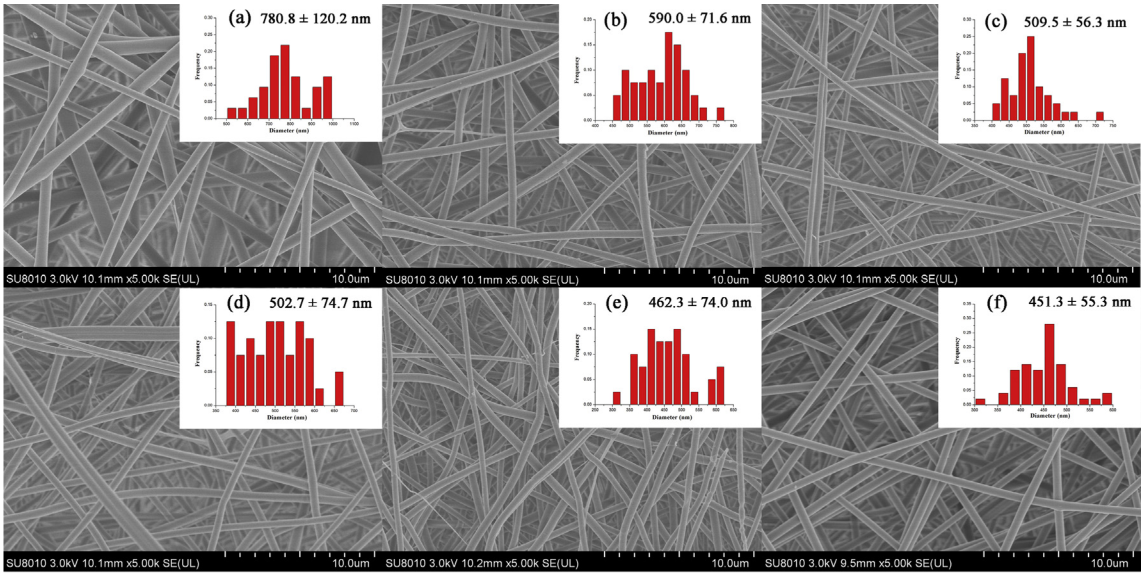

Fig. 1. SEM images and diameter distributions of the cross-linked gelatin/zein nanofibers: (a) MGZ10; (b) MGZ31; (c) MGZ21; (d) MGZ11; (e) MGZ12; (f) MGZ13.

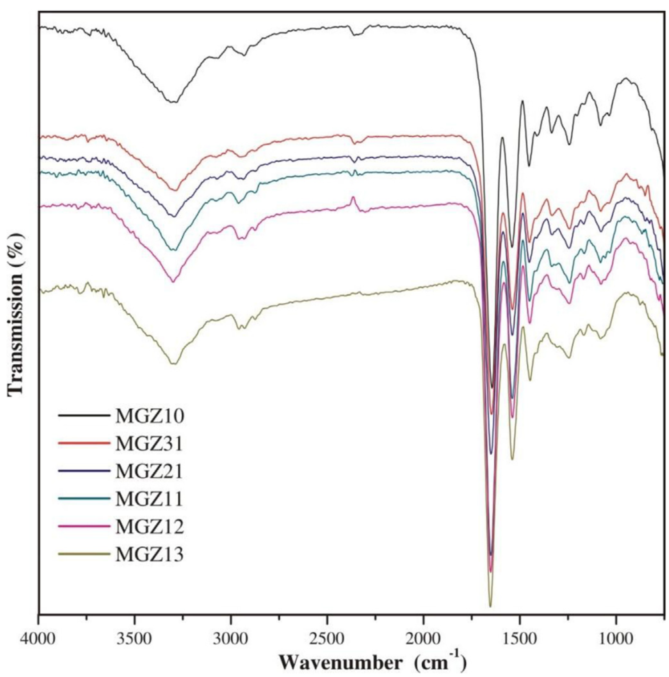

Fig. 2. FTIR spectra of the gelatin/zein nanofibers cross-linked by glucose.

Wang et al., 2017), has been hybrid electrospun with silk fibroin, hordein, cellulose acetate, and chitosan to modify the properties of nanofibers (Ali, Khatri, Oh, Kim, & Kim, 2014; Torres-Giner, Ocio, & Lagaron, 2009; Wang & Chen, 2012; Yao, Li, Song, Li, & Pu, 2009). In our previous research, we found that although the gelatin/zein hybrid nanofibers showed the improved water resistance compared to the corresponding solvent casting films (Deng, Kang, Liu, Feng, & Zhang, 2018), the mechanical strength and long-term solvent resistance were still too weak for further applications (Deng, Zhang, et al., 2018).

In this work, attempts were made to fabricate the glucose cross-linked gelatin/zein nanofibers. Various weight ratios of zein were mixed with gelatin in acetic acid/water solution to prepare hybrid nanofibers and then cross-linked via Maillard reaction. Multiple characterizations of the nanofibers were performed, including scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, swelling ratio, weight loss, water contact angle, differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), and mechanical tests. Furthermore, cytotoxicity test was performed by CCK-8 assay using mouse skin fibroblast cells (L929) to assess the biocompatibility of the nanofibers.

2. Materials and methods

2.1. Chemicals

Gelatin (Type B, Bloom 250, MW ~ 100 kDa) was purchased from Aladdin Reagent Database Inc. Zein from corn (grade Z3625, 22–24 kDa) was purchased from Sigma Aldrich (St. Louis, MO, USA). The other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All the reagents were analytical grade and used as received.

2.2. Production of nanofibers

Electrospinning solutions were prepared by dissolving 30% (w/v) protein with various gelatin/zein weight ratios in acetic acid/water solutions (acetic acid:water = 8:2). Then 5% (w/v) of glucose was

Table 1
The relative absorbance changes (ΔRA) of FTIR of the gelatin/zein nanofibers after cross-linking.

Wavenumber/cm^{-1}	3292	2940	2358	1642	1545	1450	1407	1333	1243	1080	1034
MGZ10	−1.07%	−0.64%	0.65%	2.32%	1.14%	0.45%	−0.34%	0.21%	0.69%	−1.09%	−2.32%
MGZ31	−0.73%	−0.25%	0.27%	1.92%	1.07%	0.40%	−0.12%	0.26%	0.78%	−1.19%	−2.43%
MGZ21	−0.92%	−0.77%	−0.48%	2.30%	1.29%	0.56%	−0.11%	0.38%	0.90%	−0.99%	−2.17%
MGZ11	−0.84%	−0.74%	−0.62%	2.71%	1.09%	0.29%	−0.14%	−0.01%	0.60%	−0.68%	−1.66%
MGZ12	0.12%	0.34%	−0.22%	1.93%	1.13%	0.46%	−0.10%	0.12%	0.45%	−1.33%	−2.89%
MGZ13	1.00%	1.92%	0.02%	1.44%	0.24%	0.50%	0.04%	−0.42%	0.11%	−1.72%	−3.11%