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Characterization of gelatin/zein nanofibers by hybrid electrospinning

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ABSTRACT

In this work, the gelatin/zein nanofibers by hybrid electrospinning were fabricated. The morphology observations by field emission scanning electron microscopy showed that the diameter of gelatin/zein nanofibers was significantly increased with the increasing gelatin ratio. The results of Fourier transform infrared spectroscopy and differential scanning calorimetry indicated that gelatin and zein strongly interacted via hydrogen bonding. The homogeneous mixing resulted in the crystalline structure for the gelatin/zein nanofiber at a 1:1 wt ratio, which showed a hydrophobic surface (water contact angle of 118°). The mechanical tests showed that the gelatin/zein nanofibers with weight ratios of 1:3 and 1:2 gave rise to much higher elongation at break of 87.9% and 69.0%, indicating good deformability and flexibility. In contrast to the pure gelatin or zein nanofibers, the gelatin/zein fibers preserved the 3D porous structures after immersed in water or ethanol for 24 h.

1. Introduction

Electrospinning has been one of the simple, versatile, and promising processes to produce continuous nanofibers from polymers because of structural integrity and specific fiber arrangements. Due to unique characteristics of electrospun fibers, e.g., high surface area to volume, these fibers are excellent candidates for various applications, including filtration, scaffolds in tissue engineering, drug delivery, enzyme immobilization, and biosensors (Fabra, López-Rubio, & Lagaron, 2016; Sóti et al., 2016; Wang et al., 2017). Nanofiber applications in the agriculture and food industries are relatively recent, and new means are needed to produce nanofibers that are solely composed of food biopolymers, which are generally renewable, biodegradable and biocompatible (Mendes, Stephansen, & Chronakis, 2017). However, most studies to date focused on the electrospinning of synthetic polymers since the electrospinning of biopolymers is associated with considerable difficulties due to the fact that biopolymers (e.g. polysaccharides and proteins) often have distributed molecular weights and complex chemical structures (Kriegel, Arrechi, Kit, McClements, & Weiss, 2008). During the past few decades, biopolymers such as collagen, gelatin, zein, chitin, alginate, have been successfully electrospun solely or mixed with synthetic polymers (Fernandez, Torres-Giner, & Lagaron, 2009; Mendes, Gorzelanny, Halter, Schneider, & Chronakis, 2016; Okutan, Terzi, & Altay, 2014).

As a biopolymer easily obtained from partial hydrolysis of collagen, gelatin is one of the most commonly used FDA approved biopolymer because of its biocompatibility, biodegradability, and easy availability (Feng, Fu, & Yang, 2017; Feng, Ng, Mikš-Krajnik, & Yang, 2017; Steyaert, Rahier, Van Vlierberghe, Olijve, & De Clerck, 2016). It has been electrospun from different solvents such as acetic acid, formic acid, and ethyl acetate (Ki et al., 2005; Okutan et al., 2014) for applications in bioactive encapsulation, active packaging, and tissue engineering. Due to the poor water-resistance of gelatin nanofibers that leads to rapid degradation upon contact with water, cross-linking agents such as glutaraldehyde and genipin have been added to improve the stability (Panzavolta et al., 2011), but the toxicity of these crosslinking agents has long been concerned in the food industry (Farris, Song, & Huang, 2009).

Zein is a class of alcohol-soluble prolamin proteins that can be

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electrospun from different solvents, such as ethanol, acetic acid, and aqueous methanol (Moomand & Lim, 2015; Torres-Giner, Gimenez, & Lagarón, 2008; Wang et al., 2017). Although pure zein nanofibers were successfully fabricated in previous studies, the nanofibers were found to have poor mechanical properties and solvent resistance (Zhang et al., 2015). Hybrid electrospinning of zein and other biopolymers has been considered as a feasible approach to solve the problems. It was reported that hybrid electrospinning of zein and silk fibroin improved the mechanical strength of zein nanofibers as the content of silk fibroin increased (Yao, Li, Song, Li, & Pu, 2009). Wang and Chen (2012) reported that the hydrophobic zein dispersed in a hordein matrix significantly improved the wet stability of hordein nanofibers in both water and ethanol, and strengthened the mechanical properties of the electrospun pure zein or hordein nanofibers.

Therefore, we hypothesize that zein might be uniformly dispersed in gelatin network to improve the water resistance of gelatin nanofibers by hybrid electrospinning. The effects of gelatin/zein ratio on the morphology, diameter distribution, and porosity of the nanofibers were investigated. The fabricated nanofibers were characterized using Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), X-ray diffraction (XRD), mechanical test, and water contact angle measurements. The solvent resistances of the gelatin/zein nanofibers were tested against water and ethanol as well.

2. Materials and methods

2.1. Chemicals

Zein from corn (grade Z3625, 22–24 kDa) was obtained commercially from Sigma Aldrich (St. Louis, MO, USA). Gelatin (Type B, Bloom 250) was purchased from Aladdin, Inc. (Shanghai, China). The other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All reagents were used without further purification and the water used was double-distilled.

2.2. Nanofiber fabrication

Blend solutions at a final protein concentration of 30% (w/v) with gelatin/zein weight ratios of 0/1, 1/3, 1/2, 1/1, 2/1, 3/1, and 1/0, denoted as GZ01, GZ13, GZ12, GZ11, GZ21, GZ31, and GZ10, were prepared by dissolving certain amounts of gelatin and zein in 80% (v/v) acetic acid with sufficient stirring at room temperature. Prior to electrospinning, the solutions were characterized for their shear viscosity at 100 s^{-1} by a stress-controlled rheometer (MCR 302, Anton Paar, Austria) using cone-plate geometry with 50 mm diameter and 1° angle at a temperature of 25 °C.

The syringe loaded with the polymer solution was fitted with a 20 G steel needle and was pumped at a flow rate of 1.0 mL/h using a syringe pump (LSP02-1B, Baoding Longer Precision Pump Co., Ltd., China). A voltage of 15 kV (Gamma High Voltage, USA) was applied and the tip-collector distance was kept at 10 cm. The fabricated nanofibers were collected on a grounded rotating drum. The electrospinning conditions were kept at 25 °C with a humidity of approximately 50% throughout the experiments.

2.3. Morphology of nanofibers

Morphologies of the nanofibers were observed using a field emission scanning electron microscopy (SU8010, Hitachi, Japan). The average fiber diameters and their diameter distributions were determined by measuring 40 fibers for each image from 5 randomly selected SEM images using Nano Measure software.

2.4. Porosity of nanofibers

The nanofibers were cut into equal pieces (1 × 1 cm^2) and weighted using a high accuracy balance (AB104-S, Mettler Toledo, Italy). The thickness was measured using a digital micrometer at minimum three different places. The apparent density (ρ_S) was determined using the weight and average thickness of the fibers. The material density (ρ_M) was determined on the basis of gelatin (1.41 g/cm^3) and zein (1.22 g/cm^3) density, and their mass percentage compositions adapted from Laha, Yadav, Majumdar, and Sharma (2016).

The porosity was determined from the mass and the volume by the following equation:

$$\%\text{porosity} = \left[1 - \left(\frac{\rho_S}{\rho_M}\right)\right] \times 100 \quad (1)$$

where ρ_S and ρ_M are the apparent densities of the nanofibers and material, respectively.

2.5. X-ray diffraction

The crystal structures of the gelatin/zein nanofibers were investigated by X-ray diffraction (XRD) using the X'Pert Pro diffractometer (PA Analytical B.V., The Netherlands) with a CuKα radiation source operated at a tube voltage of 40 kV and a tube current of 35 mA. A diffraction range of 10°–60° (2θ) was selected. The experiments were carried out in triplicate.

2.6. Thermal analysis

Differential scanning calorimetry (Mettler-Toledo, Switzerland) was performed under a nitrogen atmosphere at a flow rate of 50 mL/min. Samples were sealed in 40 μL aluminum pans and heated from 30 to 250 °C with a heating rate of 10 °C/min.

Thermogravimetric analysis (TA Instruments Q500, USA) was conducted under a nitrogen atmosphere (50 mL/min) and the temperature was increased from 50 to 600 °C with a heating rate of 10 °C/min.

2.7. FTIR analysis

Fourier transform infrared spectroscopy (FTIR) of the nanofibers were recorded using a Nicolet 170-SX instrument (Thermo Nicolet Ltd., USA) at a resolution of 2 cm^{-1} with 32 scans over the wavenumber range of 400–4000 cm^{-1}. All FTIR experiments were performed in triplicate.

2.8. Mechanical strength

The mechanical strength was tested according to the previously reported method (Xu, Shi, Yang, Zhang, & Zhu, 2015). Fiber samples were cut into 40 × 10 mm strips. A universal tester (AJS-J, Shimadzu, Japan) equipped with a 5 N capacity load cell was utilized to measure the mechanical properties. All the tests were controlled by a model at a speed of 1 mm/min. The data for elastic modulus, tensile strength and elongation at break were reported from the stress-strain curves as means ± SD (n = 5).

2.9. Water contact angle

The water contact angle was measured with a sessile drop method by a DCA 20 contact angle meter (Data Physics Co., Ltd., Germany). The nanofibers were fixed to glass slides, and a droplet of Milli-Q water (3 μL) was added to the surface. The equilibration