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# Gelatin nanofibers prepared by spiral-electrospinning and cross-linked by vapor and liquid-phase glutaraldehyde



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## ABSTRACT

The aim of this study was to mass-produce gelatin nanofibers by spiral-electrospinning and investigate the performance of different cross-linking methods such as glutaraldehyde vapor and liquid phase cross-linking. Compared with conventional single-needle electrospinning, nanofibers produced by spiral-electrospinning were finer and an enhancement of more than 1000 times over the traditionally obtained nanofibers productivity was obtained. The mechanical testing showed the tensile strength of nanofiber membranes increased from 1.33 to 2.60 MPa after glutaraldehyde vapor cross-linking and from 1.33 to 5.08 MPa after liquid phase cross-linking. Moreover, SEM and FTIR analysis indicated the nanofiber membrane obtained by liquid phase cross-linking had better properties and was an ideal material for wound dressing applications.

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## 1. Introduction

Electrospinning was a versatile technique to fabricate continuous nanofibers with many outstanding characteristics such as high porosity, high ratio of surface area to mass and superior mechanical properties [1]. So, electrospun nanofibrous had many important applications in various fields, such as wound dressing and tissue engineering [2]. Conventional single-needle electrospinning was widely used to produce nanofibers, but the system was inefficient for industrial production of nanofibers due to low production rate. Although multi-needle nozzle configuration may improve the productivity, a complicated interaction between nozzles weakened the electric field at the nozzle tip and led to non-uniform nanofibers [3]. Needleless electrospinning setups had attracted much attention over the past decades as an effective approach to enhance the productivity of electrospinning. However, those needleless electrospinning systems still needed to improve the fiber uniformity, while increased the production rate.

Gelatin was commercially made from skins and skeletons of bovine and porcine. Due to its biodegradability, biocompatibility and non-toxicity, it has been used extensively in the medical, food and other industries [4]. As a principal structural element of the native extracellular matrix (ECM) in many native tissues, gelatin had emerged as an important polymer to electrospin for diverse bioclinical applications [5]. However, the gelatin nanofibers had as

a drawback a poor structural consistency in wet conditions [6]. So cross-linking of gelatin nanofibers was necessary to increase their stability in aqueous environments. The process could be achieved by either physical methods, such as heat and radiation, or chemical methods by vapor or liquid phase cross-linking which exploited many chemical agents to modify gelatin functional side groups [7].

In this study, the spiral-electrospinning technique was used for massive production of gelatin nanofibers, and water was chosen as the solvent to examine the electrospinnability of gelatin aqueous solution. The productivity was about 100 g/h, which was thousands of times higher than that of conventional single needle electrospinning. Moreover, a comparative study between glutaraldehyde vapor phase cross-linking and liquid cross-linking was carried out. The SEM, FT-IR and texture analyzer were used to analyze the changes of the morphology, functional groups and mechanical properties of GE nanofibers.

## 2. Experimental

### 2.1. Material

Gelatin powder (GE) was obtained from Baotou Dongbao Bio-Tech Co., Ltd., China. Glutaraldehyde (GA, AR) was purchased from sinopharm chemical Reagent Beijing Co., Ltd.

Electrospinning setup: the scheme of the novel needleless electrospinning system was shown in Fig. 1, which contained five major components: a teflon solution reservoir, a helix-slice spinneret, a

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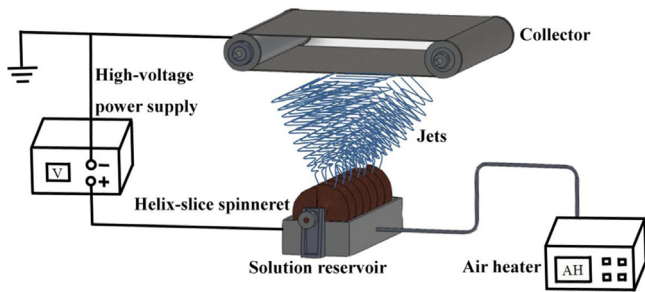


Fig. 1. The diagram of spiral electrospinning.

grounded collector, a high-voltage direct-current power supply and an air heater. As the helix slice was rotated, every edge of the spinneret was coated by polymer solution. Once the electric field exceeded the critical value needed to overcome the surface tension, multi-fluid jets ejected from the edge of helix slice.

## 2.2. Electrospinning process and cross-linking reaction

**Method A:** Ten percent GE solution was prepared by dissolving GE in deionized water with vigorous stirring for 6 h at 40 °C. Then, the solution was poured in the teflon reservoir and electrospun for 1 h, an air heater was used to control the solution temperature (40 °C). The distance between the helix slice and the collector was 170 mm, voltage was 80 kV and the rotating speed of spinneret was 10 rpm. Five different concentrations (0.1, 0.5, 1.0, 3.0, 5.0 M) of GA solution were prepared and the GE nanofibers were exposed to the GA vapor for 1 h at each concentration. The total cross-linking procedure was carried out in a sealed vessel.

**Method B:** As GE nanofibers can be dissolved instantly in water, so cross-linking by liquid phase must be performed in the electrospinning process.

GE solutions were prepared by dissolving a measured amount of GE in deionized water and stirred for 6 h at 40 °C. Then, GA was added to prepare five different concentrations (0.0, 0.1, 0.5, 1.0, 3.0, 5.0 M) of GA solution, and the final GE concentration was 10 wt%. The mixed solution was evenly stirred, poured in the teflon reservoir, and electrospun for 1 h. An air heater controlled the solution temperature; the processing parameters were the same as those in the method A. The product with a large surface area-to-volume ratio and a small pore size was stored in a desiccator under vacuum for several days to remove any residual solvent.

## 2.3. Characterization

Morphological investigations of the precipitated samples were carried out with an S-4800 scanning electron microscope (SEM, Hitachi, Japan). The functional groups in the GE membrane were characterized by FT-IR. The mechanical properties were measured by a texture analyzer, the GE nanofiber membranes were cut into rectangular mats of approximate length 50 mm, width 10 mm, and thickness 1 mm with load speed of 0.5 mm/s.

## 3. Results and discussion

**Cross-linking reaction of GA:** Fig. 2a showed an SEM image of gelatin nanofibers electrospun from GE aqueous solution, the randomly collected nanofibers with average fiber diameter of 292 nm were free of bead defects. However, the non-cross-linked nanofiber membrane was found instantly dissolving in water as it swelled considerably and nanofibers started to fuse with each other and destroy porous openings of the membrane (Fig. 2a').

Maintaining the peculiar biomimetic nanofibrous morphology and interfiber pores of nanofiber membrane was important for medical applications where high surface areas and high porosity were considered advantageous [8]. To investigate the effect of GA cross-linking, vapor phase and liquid cross-linking was applied. As a result of the cross-linking process, electrospun nanofibers became strongly interconnected, forming an apparently robust and stiffer network.

**Method A:** the vapor phase cross-linking was made by employing a sealed vessel with different concentrations of GA (0.1, 0.3, 0.5, 1.0, 3.0 M) and the vessel was tightly closed with the GE nanofiber membrane attached onto the inside of the lid exposed to the GA vapor for 1 h at ambient temperature. As the GA concentration increased, not more than 1.0 M, the nanofibers, which were originally straight, became merged among each other and formed interfiber bonding/fused mostly at the intersection point of nanofibers (Fig. 2b–f). When the GA concentration was above 1.0 M, the nanofiber membrane (Fig. 2f) became visibly shrank; the nanofibers became strongly entangled and interconnected. Fig. 2b'–f' showed the SEM images of nanofibers after rinsing in water. The junction zones appeared fused together and the nanofibers became swell. However, as the GA concentration increased, the changes of nanofiber morphology decreased in aqueous environments.

**Method B:** the liquid phase cross-linking was performed by adding GA to GE solution. Fig. 2g–k showed SEM images of GE nanofiber membranes cross-linked by different concentrations (0.1, 0.3, 0.5, 1.0, 3.0 M) of GA. As the GA concentration increased, the formed interfiber bonding/fusing at the intersection points of nanofibers rose. When the GA concentration was above 1.0 M, the GE nanofibers fused and formed a plane because of excessive cross-linking. In the images recorded after nanofibers immersion in water (Fig. 2g'–k'), the fibers showed a morphology change and many junction zones merged together. However, the liquid cross-linked nanofibers with GA concentrations of 1.0 M were found to be stable and their morphology remained intact as it was electrospun. The nanofibers after excessive cross-linking also did not change too much in wet conditions, as the membrane have become a plane.

Compared the vapor phase and liquid cross-linking, the nanofiber membranes by liquid phase were evenly cross-linked and tightly packed, but the cross-linking degree of membranes by vapor phase had the feature of hierarchy, the middle layers of membrane were poorly cross-linked, so excessive cross-linking by vapor phase led to the membranes shrinking. Immersing the cross-linked GE nanofibers in water, the membranes morphology by liquid phase had fewer changes.

## 3.1. Mechanical properties

Fig. 3 showed typical tensile stress–strain curves before (neat GE) and after (GA vapor or liquid phase) cross-linking. The ultimate tensile strength of the GE nanofiber membrane was measured to be 1.33 MPa and its ultimate strain was 41.78%, whereas after GA vapor cross-linking, the ultimate tensile strength of the GE nanofiber membrane increased about 1.95 fold to be 2.60 MPa and its ultimate strain decreased to 28.23%. Moreover, after GA liquid cross-linking, the ultimate tensile strength of the GE nanofiber membrane increased about 3.82 fold to be 5.08 MPa and its ultimate strain decreased to 22.9%. The enhanced ultimate tensile strength indicated that GA cross-linking made GE nanofiber membrane became mechanically more strong and stable. In addition, liquid phase cross-linking ensured that nanofibers had a rigid web of interfiber bonding and membrane was tightly packed, so the liquid phase cross-linking was a better choice.

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