RESEARCH ON POST-TREATMENT AND APPLICATION OF PVA/SS/AgNPs COMPOSITE NANOFIBERS

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PVA/SS/AgNPs composite nanofibers which prepared by electrospinning were treated by methanol and ethanol vapor respectively. The nanofibers were scanned and analyzed by electron microscope before and after treatment. Sterile cotton gauze was used as the substrate and PVA/SS/AgNPs composite nanomaterials were spun with electrostatic spinning technology was employed as the inner layer to prepare a wound dressing with a double-layer structure. The moisture permeability and air permeability of the wound dressing were tested. The results showed that PVA/SS/AgNPs composite nanofibers were successfully prepared. With the increase of AgNPs content, the average diameter of the fibers increased. After 3 days of treatment with methanol and ethanol vapor respectively, the appearance shape of the nanofibers did not change significantly. The medical dressing, which is made of sterile cotton gauze and PVA/SS/AgNPs nanofibers, not only has excellent air permeability and moisture permeability, but also has antibacterial and skin friendly properties, so it has a good application prospect.

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Keywords: PVA/SS/AgNPs, Electrospinning, Nanofibers, Medical dressing, Performance

1. Introduction

Electrospinning technology was first invented by the American Formhals in 1934, and he continued to study and improve the spinning made by multiple needles or composite spinning, which can significantly increase the spinning efficiency [1-3]. In 1971, the spinning process parameters were researched to find out the multiple influencing factors of electrospinning by Baumgarten in DuPont, which greatly improved the spinning effect [4]. In recent years, the electrostatic spinning technology has been continuously studied and become more and more mature. Electrospinning equipment which is widely used in the preparation of nanofibers is simple and easy to be operated [5-6]. Nanofibers prepared by electrospinning have the characteristics of high porosity, which can improve the performance of medical dressings [7-11].

Polyvinyl alcohol (PVA) is a water-soluble polymer that has good chemical stability, biocompatibility, non-toxicity and good spinnability [12-16]. Silk Sericin (SS) is non-toxic and has anti-oxidation, good biocompatibility and biodegradability [17-20]. AgNPs have highly effective and broad antibacterial properties against bacteria, fungi, etc. The nanofibers spun with AgNPs have the characteristics of high efficiency, safety and continuous resistance to germs [21-22]. When the medical dressing acts on the wound, AgNPs can reduce the infection, accelerate the

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healing, protect damaged skin and avoid human fever [23-26]. The silver-containing nanofibers are compounded with sterile medical cotton gauze. The antibacterial properties of silver ions are used to reduce infections, promote healing and prevent scarring. Silver ion is conducive to pain relief by promoting the release of pain causing substances in the wound [27].

In this paper, PVA/SS (8:3) and AgNPs were used to prepare the spinning solution with deionized water used as the solvent. A double-layer structure composite nano medical dressing was prepared by electrospinning. The outer layer was sterile cotton gauze and the inner layer was PVA/SS/AgNPs composite nano material with different mass ratio. The medical dressing developed by PVA/SS/AgNPs composite nanofibers not only has excellent moisture permeability and air permeability, but also has good antibacterial and skin friendly properties.

2. Experiments

2.1. Experimental materials
PVA (1797, Macklin Inc) is a polymer material that is easily soluble in water and has an alcoholysis degree of 96.0-98.0 % (mol/mol). SS (Favorsun Pharmaceutical Co., Ltd, Shanghai) is a globular protein in the form of yellow powder. The powder sample of AgNPs (Macklin Inc) are black with the diameter of 60-120 nm.

2.2. Experimental instruments
Constant temperature water bath magnetic stirrer: DF-101S; electrostatic high voltage generator: D-ES50PN-10W/DDPM; syringe pump: LSP01-1A; ultrasonic: SYU3-100D; YG601H-11 moisture meter; YG461Z air permeameter.

2.3. Preparation of PVA/SS/AgNPs solution
Weigh 0.01, 0.02, 0.03, and 0.04 g AgNPs powder and add 88.99, 88.98, 88.97 and 88.96 g deionized water into the blue-cap bottle, then fully dispersed for 45 min by ultrasonic. Weigh 4 parts 8 g PVA, add them into AgNPs solution, swell for 45 min at room temperature, then heated at 95 °C for 4 h in the constant water bath magnetic stirrer, finally cool to below 60 °C. Weigh 4 parts 3 g SS and pour them into the PVA/AgNPs mixed solution respectively, then placed them in the constant water bath magnetic stirrer at 60 °C for 2 h, at last it was taken out and left them at room temperature for use.

2.4. Electrospun nanofiber membrane
5 ml the spinning solution was sucked with a needle tube which was placed on the electrostatic spinning machine and the point of the needle was connected to the positive pole of the power supply. The aluminum foil which was connected to the negative electrode of the power supply was fixed on the receiving screen and the distance between the needle tip and the foil was 15 cm. The spinning speed was 1.5 mL/h and the kilovoltage was 15 kV. At last the sampe was dried at 60 °C for 6 h in the oven for use.
2.5. PVA/SS/AgNPs nanofibers treated with methanol and ethanol
The PVA/SS/AgNPs nanofibers with different mass ratios were treated with methanol and ethanol vapor for 3 days respectively, then dried at 60 °C in the oven.

2.6. Electron microscope test and analysis
German ZEISS Sigma 500 scanning electron microscope was used. Each nanofiber membrane on the foil was cut into the corresponding size and pasted on the conductive metal sample stage with conductive adhesive. After all samples were pasted, the conductive metal sample stage was placed in the vacuum pump for scanning and photographing. The mean diameter and diameter standard deviation of 100 nanofibers were calculated.

2.7. Preparation of medical dressing samples
A "double-layer" composite nano-medical dressing was prepared by electrostatic spinning technology. The outer layer was sterile cotton gauze and the inner layer was PVA/SS/AgNPs composite nano-material.

2.8. Moisture permeability of medical dressings
The moisture permeability of medical dressings was examined by YG601H-11 moisture meter at 38 °C for 1 h and the relative humidity was 90 %. For different kinds of nanofiber medical dressings, the average value of 3 times was used for comparison experiments.

2.9. Air permeability of medical dressings
YG461Z air permeameter was used at 100 Pa. For different kinds of nanofiber membranes, the mean value of 8 different parts of each nanofiber membrane were selected for comparison experiment.

3. Results discussion and analysis

3.1. Electron microscopy of PVA/SS/AgNPs composite nanofibers
It can be seen from Fig. 1a that when the mass fraction of AgNPs is 0.01 %, there is an obvious bonding phenomenon and a small amount of spindle structure in composite nanofibers. At the same time the fiber evenness irregularity is higher and the diameter is relatively small. Fig. 1c shows that when the mass fraction of AgNPs is 0.03 %, there is no spindle structure in nanofibers, but a small amount of bonding phenomenon between fiber and the unevenness of fiber thickness is obvious. When the mass fraction of AgNPs is 0.02 % and 0.04 % (Fig.1b and Fig.1d) respectively, there is no spindle structure in the nanofibers and the fiber diameter is relatively uniform.

In order to further analyze the filament forming effect of PVA/SS/AgNPs composite nanofibers, the diameters were measured and the average diameter and standard deviation of the diameters were calculated. The results are shown in Table 1.
Fig. 1. Electron micrograph of PVA/SS/AgNPs composite nanofibers with different mass ratios: 
a 8:3:0.01; b 8:3:0.02; c 8:3:0.03; d 8:3:0.04.

Table 1. Mean diameters and standard deviations of PVA/SS/AgNPs composite nanofibers with different mass ratios.

<table>
<thead>
<tr>
<th>PVA:SS:AgNPs</th>
<th>8:3:0.01</th>
<th>8:3:0.02</th>
<th>8:3:0.03</th>
<th>8:3:0.04</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average diameter/nm</td>
<td>370.1</td>
<td>381.8</td>
<td>399.9</td>
<td>455.7</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>107.7</td>
<td>62.8</td>
<td>88.4</td>
<td>119.2</td>
</tr>
</tbody>
</table>

It can be known from Fig. 1 and Table 1 that as the content of AgNPs increases, the conductivity of the composite solution increases, the spinning speed increases, so the diameter of the nanofibers becomes larger and larger. When the mass fraction of AgNPs in the composite nanofibers is 0.02 %, the diameter standard deviation of the SS composite nanofibers is the smallest.

3.2. Electron microscopy of PVA/SS/AgNPs composite nanofibers treated with methanol vapor

As can be seen from Fig. 1, Fig. 2, Table 1 and Table 2, the average diameter and diameter standard deviation of the PVA/SS/AgNPs composite nanofibers treated with methanol vapor have no significant change. In Fig. 2 and Table 2, when AgNPs are 0.01 g, 0.03 g and 0.04 g, the average fiber diameter of PVA/SS/AgNPs composite nanofibers treated with methanol vapor
become thinner, but AgNPs is 0.02 g, and the average fiber diameter become thicker; when AgNPs is 0.01 g, the diameter standard deviation of nanofibers is smallest, but AgNPs are 0.02 g, 0.03 g, and 0.04 g, the standard deviation of nanofiber diameter increase. The bonding between the composite nanofibers is more obvious and the nanofibers have a bending phenomenon simultaneously.

![Electron micrograph of PVA/SS/AgNPs composite nanofibers treated with methanol vapor](image)

**Fig. 2.** Electron micrograph of PVA/SS/AgNPs composite nanofibers treated with methanol vapor  
*a* 8:3:0.01; *b* 8:3:0.02; *c* 8:3:0.03; *d* 8:3:0.04.

<table>
<thead>
<tr>
<th>PVA:SS:AgNPs</th>
<th>8:3:0.01</th>
<th>8:3:0.02</th>
<th>8:3:0.03</th>
<th>8:3:0.04</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average diameter/nm</td>
<td>367.9</td>
<td>394.7</td>
<td>397.7</td>
<td>420.0</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>99.7</td>
<td>83.0</td>
<td>108.1</td>
<td>120.8</td>
</tr>
</tbody>
</table>

**3.3. Electron microscopy of PVA/SS/AgNPs composite nanofibers treated with ethanol vapor**

As can be seen from Fig. 1, Fig. 3, Table 1 and Table 3, the average diameter and diameter standard deviation of the PVA/SS/AgNPs composite nanofibers treated with ethanol vapor have no significant change. In Fig. 3 and Table 3, when AgNPs are 0.01 g, 0.03 g and 0.04 g, the average fiber diameter become thinner, but AgNPs is 0.02 g, the average fiber diameter becomes thicker.
When AgNPs are 0.01 g and 0.04 g, the standard deviation of fiber diameter becomes smaller. While AgNPs are 0.02 g and 0.03 g, the standard deviation of the diameter becomes thicker. At the same time, the morphology of the composite nanofibers treated with ethanol vapor changes. When AgNPs is 0.02 g, it can be seen that the nanofibers are bent after treatment and the surface of the fibers was not as smooth and even as before (Fig. 1b and Fig. 3b). When AgNPs is 0.04 g, the nanofibers have a slight bending phenomenon and the bonding phenomenon is also more obvious than before ethanol treatment (Fig. 1d and Fig. 3d).

![Electron micrograph of PVA/SS/AgNPs composite nanofibers treated with ethanol vapor](image)

**Fig. 3.** Electron micrograph of PVA/SS/AgNPs composite nanofibers treated with ethanol vapor. 

![Electron micrograph of PVA/SS/AgNPs composite nanofibers treated with ethanol vapor](image)

**Table 3.** Mean diameter and standard deviation of PVA/SS/AgNPs composite nanofibers with different mass ratios after ethanol vapor treatment.

<table>
<thead>
<tr>
<th>PVA:SS:AgNPs</th>
<th>8:3:0.01</th>
<th>8:3:0.02</th>
<th>8:3:0.03</th>
<th>8:3:0.04</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average diameter/nm</td>
<td>349.7</td>
<td>384.7</td>
<td>389.1</td>
<td>427.1</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>96.7</td>
<td>79.5</td>
<td>95.4</td>
<td>95.3</td>
</tr>
</tbody>
</table>

**3.4. Moisture permeability**

In this experiment, PVA/SS/AgNPs composite nanofiber medical dressings with different mass ratios (8:0:0, 8:3:0, 8:3:0.01, 8:3:0.02, 8:3:0.03 and 8:3:0.04) were examined, the results are shown in Table 4.
It can be seen from Table 4 that PVA/SS composite nanofiber medical dressing has better moisture permeability than the PVA nanofiber medical dressing. In this experiment, no more than 0.03 g AgNPs of PVA/SS/AgNPs composite nanofiber medical dressing has better moisture permeability than PVA nanofiber medical dressing, but it is worse than PVA/SS composite nanofiber medical dressing. With the content of AgNPs increasing, the moisture permeability of PVA/SS/AgNPs composite nanofiber medical dressings increases.

### 3.5 Air permeability

In this experiment, PVA/SS/AgNPs composite nanofiber medical dressings with different mass ratios (8:3:0, 8:3:0.01, 8:3:0.02, 8:3:0.03 and 8:3:0.04) were adopted for air permeability. The results were average by 8 different parts of each PVA/SS/AgNPs composite nanofiber medical dressings, as shown in Table 5.
Table 5. Air permeability of PVA/SS/AgNPs composite nanofiber medical dressings with different mass ratios.

<table>
<thead>
<tr>
<th>PVA:SS:AgNPs Serial number</th>
<th>8:3:0</th>
<th>8:3:0.01</th>
<th>8:3:0.02</th>
<th>8:3:0.03</th>
<th>8:3:0.04</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>56.7</td>
<td>48.4</td>
<td>39.2</td>
<td>29.8</td>
<td>15.9</td>
</tr>
<tr>
<td>2</td>
<td>51.4</td>
<td>40.5</td>
<td>36.3</td>
<td>28</td>
<td>15.9</td>
</tr>
<tr>
<td>3</td>
<td>50.9</td>
<td>43.2</td>
<td>39.8</td>
<td>22.4</td>
<td>14.8</td>
</tr>
<tr>
<td>4</td>
<td>54.8</td>
<td>49.6</td>
<td>35.5</td>
<td>25.8</td>
<td>15.3</td>
</tr>
<tr>
<td>5</td>
<td>51.5</td>
<td>49.6</td>
<td>35.3</td>
<td>26.4</td>
<td>14.2</td>
</tr>
<tr>
<td>6</td>
<td>53.3</td>
<td>46.5</td>
<td>32.9</td>
<td>29.3</td>
<td>15.1</td>
</tr>
<tr>
<td>7</td>
<td>54.6</td>
<td>43.1</td>
<td>32.3</td>
<td>21.5</td>
<td>14.9</td>
</tr>
<tr>
<td>8</td>
<td>51</td>
<td>43.8</td>
<td>32.9</td>
<td>21.6</td>
<td>15.6</td>
</tr>
<tr>
<td>Average value</td>
<td>53.03</td>
<td>41.84</td>
<td>35.53</td>
<td>21.85</td>
<td>15.21</td>
</tr>
</tbody>
</table>

It can be seen from Table 5 that the breathability of the PVA/SS/AgNPs composite nanofiber medical dressing decreases with the content of AgNPs increasing. This is mainly because silver ions have conductivity. The number of silver ions in the solution increases as the content of AgNPs increases, which increases the conductivity of the solution and spinning speed of nanofibers, so the thickness of medical dressings increases and breathability reduces.

4. Conclusions

PVA/SS/AgNPs composite nanofibers with different mass ratios were successfully prepared by electrostatic spinning technology. When the AgNPs content was 0.02g, the composite nanofibers have relatively small diameter, minimum standard deviation and smooth surface. After 3 days of steam treatment with methanol and ethanol respectively, PVA/SS/AgNPs composite nanofibers did not change significantly. In this experiment, no more than 0.03 g AgNPs, PVA/SS/AgNPs composite nanofiber medical dressing has better moisture permeability than PVA nanofiber medical dressing, but it is worse than PVA/SS composite nanofiber medical dressing. With the increase of AgNPs content, the moisture permeability of PVA/SS/AgNPs composite nanofiber medical dressings increased and the air permeability of medical dressings gradually decreased. PVA/SS/AgNPs composite nanofiber medical dressing not only has excellent moisture permeability and breathability, but also is skin-friendly and antibacterial, so it has a good application prospect.

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References