Cross-Linking of Centrifugally Spun Starch/Polyvinyl Alcohol (ST/PVA) Composite Ultrafine Fibers and Antibacterial Activity Loaded with Ag Nanoparticles

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ABSTRACT: In this research, centrifugally spun ultrafine composite starch/polyvinyl alcohol (ST/PVA) fibers with high water stability were prepared by cross-linking with a mixture of glutaraldehyde and formic acid in the form of vapor phase. The effect of cross-linking temperature combined with time on the water stability, crystal structure, and thermal properties of fibers was investigated to obtain the optimum parameters. On this basis, we further prepared Ag-loaded ST/PVA fibers with different contents of nano silver. The structure and properties of Ag-loaded fibers, which cross-linked under the optimum parameters, were analyzed. As a result, the Ag-loaded fibers exhibited excellent water stability and mechanical properties and possessed inhibition zone diameters of 3 and 2 mm to Escherichia coli and Staphylococcus aureus, respectively. The antibacterial property of the Ag-loaded ST/PVA fibers provided a new route for developing less costly antibacterial fiber materials in the future.

1. INTRODUCTION

Biodegradable fibers are useful materials that have been widely used in many applications such as biomedicine, filtration, and food packaging. Nowadays, researchers mainly focus on fabricating fibers from cellulose, protein, polylactic acid (PLA), polyvinyl alcohol (PVA), polycaprolactone (PCL), etc. Among these, micro/nanofibers expressed superior properties such as mechanical properties, cell proliferation efficiency, filtration efficiency, antibacterial efficiency, etc. Centrifugal spinning, as one of the most important methods for preparing micro/nanofibers, has received great attention over the past few decades due to the advantages of no polar requirement for spinning solution/melt, high productivity of fibers, and ease of controlling the fluffy degree of fibrous membranes and engineering. Last century, the method originated from the cotton candy machine and was mainly used for preparing metallic glass fibers, mineral fibers, and functional fibers. However, the development of centrifugal spinning was greatly limited because of chemical fiber spinning, melting spinning, spunbond, and wet/dry spinning showing higher productivity and convenient assembly in preparing microfibers. In the beginning of this century, centrifugal spinning received great attention once again due to the capability for higher productivity of micro/nanofibers. In early 2014, a research group from the USA together with the FibeRio Technology Corporation developed an engineered spinning line with a product of 12,000 g/h and fiber membrane width of 2.2 m. Nowadays, researchers from dozens of countries have concentrated on the centrifugally spun micro/nanofibers from polymers and inorganic metal oxides. These fibers
showed higher mechanical properties, cell proliferation efficiency, filtration efficiency, and antibacterial efficiency and therefore presented great potential applications in tissue engineering, filtration, and antibacterial textiles.13

Our group concentrated on the development of ultrafine fibers using centrifugal spinning at the beginning of 2013. We now have successfully developed the setups of electric-assisted centrifugal spinning, air-assisted centrifugal spinning, and melting centrifugal spinning.14 By using these setups, we not only prepared ultrafine fibers from polyester (PET),15 polyvinylpyrrolidone (PVP),16 polyoxyethylene (PEO),17 and regenerated silk17 but also created highly porous ethyl cellulose fibers,18 alginate-rich nanofibers,19 and grape-tree-like and porous PTFE fibers.20 These fibers expressed high specific surface area, excellent solution absorption, and super-hydrophobic properties and are therefore particularly suitable for application in filtration, wound dressing, and oil/water separation. We also successfully developed centrifugally spun starch-based ultrafine fibers from amylpectin-rich starches with environmentally friendly sodium hydroxide solution as solvent.21 The parameter studies further revealed that the amylpectin ratios of starch suitable for fiber preparation could reach up to 81%,22 which means that centrifugal spinning is particularly suitable for starch-based ultrafine fibers from native starches (amylpectin ratio: 70–80%) and many modified starches. As a comparison, the electrospun starch ultrafine fibers were mainly prepared from modified starches by using dimethyl sulfoxide (DMSO) and formic acid as solvent,23 and the spinning process was not environmentally friendly. Benefiting from the superior biocompatibility of starches, the ultrafine starch fibers presented a great potential application in drug delivery, antibacteria treatment, and tissue engineering.24

However, the large amount of hydrogen bond in starch molecular chains and the amorphous structure resulted in both electrospun and centrifugally spun starch fibers rapid dissolving in water25 and greatly limited the fiber application. Researchers usually attempted to improve the water stability of electrospun starch fiber by using glutaraldehyde as a cross-linker. Wang et al. prepared the starch fiber from starches with amylpectin 30% and cross-linked fiber by glutaraldehyde.26 They demonstrated that the water satiability of fibers greatly improved and the cross-linked fibers expressed excellent antibacterial properties. The obtained centrifugally spun starch fibers also showed rapid dissolution in water, but the water stability of fibers could not be improved by only using glutaraldehyde as solvent. The reason was that both the hydrogen bond and residual sodium hydroxide in fibers induced the rapid dissolving of fiber in water, while the residual sodium hydroxide in fibers did not react with glutaraldehyde. On this basis, we investigated a method for improving the fiber’s water stability by using citric acid/ethanol solution as cross-linker.25b The result showed that citric acid could efficiently improve the water stability of starch fibers, while the cross-linking temperature was required to be high at 165 °C. We also attempted to cross-link obtained fibers by acetic acid/glutaraldehyde at a temperature of 40 °C.25 As a result, the water stability of fibers could be improved, but the water stability of cross-linked fibers was still low.

In the previous report, we found that the PVA could effectively improve the mechanical property of starch fibers and the obtained ST/PVA fibrous membranes show great potential application in disposable nonwoven fabrics.14c In this work, we aimed to further broaden the application of ST/PVA fibers by improving the water stability. For this purpose, the cross-linker composed of glutaraldehyde/formic acid was used for cross-linking fibers in the form of vapor phase by controlling the temperature and time. Additionally, we also prepared Ag-loaded ST/PVA fibers and the antibacterial properties were studied.

2. RESULTS AND DISCUSSION

2.1. Cross-Linking of ST/PVA Fibers. As we have widely demonstrated, centrifugal spinning is especially suitable for the ultrafine fiber preparation from native starches.21,27 However, the low tensile strength and water stability of pure starch fibers, due to of the highly branched amylpectin and large amount of hydroxyl, greatly limited the applications. In our previous paper, we provided a route for improving the tensile strength of pure starch fibers by adding PVA and the tensile strength was improved over 3 times than pure starch fibers, although the problem of low water stability of fibers was still not improved.14c On this basis, we prepared the ST/PVA fiber from a solution with a starch/PVA mass ratio of 60/40 by using the centrifugal spinning setup designed by our group (Figure 1), and the spinning solution was obtained by blending a starch solution of 12% (w/w) and a PVA solution of 8% (w/w) with a mass ratio of 50/50 according to our previous report.24c Then, we cross-linked fibers in the form of vapor phase with glutaraldehyde/formic acid as cross-linker to improve the water stability of fibers by controlling the temperature and time. The cross-linking mechanism was based on two reactions of acid–base neutralization between NaOH and formic acid and etherification between PVA and glutaraldehyde.28

The morphology combined with the fiber diameter distribution of the cross-linked fibers is shown in Figure 2. From Figure 2a–e,1, we could observe that the color of fibrous membranes gradually tended to change from white to yellow...
with the cross-linking temperature increasing from 60 to 140 °C combined with time decreasing from 10 to 2 h (Table 1). The reason was probably due to the oxidation of starch during the cross-linking process.\textsuperscript{29} As could be obtained from Figure 2\textsubscript{a2-4}\textemdash\textsubscript{e2-4}, all of the cross-linked fibrous membranes expressed a well morphology and fiber diameter distributions showed no obvious change with cross-linking conditions. When the cross-linked fibers were immersed in water for 12 h, the fibers showed a swell in diameters but the degree of swelling decreased with the increase in cross-linking temperature, which indicated that the water stability was greatly improved (Figure 2\textsubscript{a3-4}\textemdash\textsubscript{e3-4}). Specifically, the fibers cross-linked at 60 °C for 10 h
were almost dissolved after immersing in water for 12 h, which suggested that the fibers did not form the cross-linked structures at the condition. The results also suggested that the temperature was the main parameter affecting the degree of cross-linking of fibers. Additionally, it should be noted that although the fibers cross-linked at 140 °C for 2 h expressed high water stability, the more serious oxidation of fibers made the fibrous membrane show slight brittleness. Therefore, although the water stability of cross-linked fibers could be further improved by increasing the cross-linking temperature, the brittleness of the obtained fibrous membranes would depict a limit to their applications. As a result, the optimum parameter for cross-linking ST/PVA fibers was concluded to be 120 °C for 4 h. As a comparison, we also treated the as-spun ST/PVA fibers at 140 °C for 2 h without a cross-linker. As could be observed from Figure 2f1, the treated fibers kept well fiber morphology same with as-spun fibers but would dissolve in water. Thus, the improvements in the water stability of ST/PVA fibers were completely attributed to the cross-linker.

2.2. Structure Analysis. Figure 3 shows the chemical structures of cross-linked fibers measured by FTIR and XRD. As we demonstrated in a previous paper, the starch and PVA powders were not reacted during the fiber preparation process and a new peak appeared at 1583 cm⁻¹ for ST/PVA belonging to water molecules absorbed in the amorphous structure of starch. In this work, the peak appeared at 1585 cm⁻¹ and was more obvious for the fibers cross-linked at temperatures of 120 and 140 °C. The cross-linking included two different reactions of neutralization reaction between sodium hydroxide and formic acid and aldolization between PVA and glutaraldehyde. Both of the reactions generated the water molecules continuously and increased with the improvement of cross-linking degree. Therefore, the fibers cross-linked at temperatures of 120 and 140 °C generated more water molecules. In this process, most of the generated water molecules were removed continuously due to the high cross-linking temperature. However, the remaining water molecules and reabsorbed water molecules due to the high hydrophilicity of cross-linked fibers still presented a peak at 1585 cm⁻¹ (Figure 3a). For the thermally treated fibers, the water molecules were greatly removed, and therefore, no peak appeared at 1585 cm⁻¹.

As we have reported, the ST/PVA fibers presented an amorphous structure due to the semicrystalline structure of starch and PVA being destroyed during the dissolving process. Similar results were obtained in this work for the fibers cross-linked below 100 °C that also showed amorphous structures (Figure 3b). The peak at 2θ of 19.7° tended to be sharper with further increasing the cross-linking temperature up to 120 and 140 °C. This peak belonged to the amorphous phase of PVA and was stronger than the crystalline peaks at 2θ of 19.4 and 20.2°. As has been widely demonstrated, starch retrogradation induced the molecular chain to rearrange into order and increased with the increasing of temperature. Thus, the increasing of peaks was probably due to more molecular chains rearranged into order during the cross-linking process at high-temperature conditions. More importantly, the thermal treatment of as-spun fibers without a cross-linker presented a new peak at 2θ of 11.2°, which further demonstrated the increasing of peaks attributed to the starch retrogradation.

2.3. Effects of PVA Ratios on the Structure of Obtained Fibers. Figure 4 presents the thermogravimetry (TG) and differential thermogravimetry (DTG) curves for the fibers cross-linked at different conditions and thermally treated without a cross-linker. All cross-linked samples expressed two main stages of thermal degradation (Figure 4a–e). The parameters that characterize the thermal decomposition are as follows: T_peak is the temperature at which the degradation rate is maximum, and W is the weight loss. The first T_peak was attributed to water molecular evaporation in fibers, and results in Table 2 demonstrated that the water in fibers range between 13.72 and 16.46% (w/w). The second T_peak was attributed to the thermal decomposition of starch and the dehydration of hydroxyl groups at a low temperature of PVA. For the thermally treated fibers without a cross-linker (Figure 4f), the most obvious difference was that weight loss at the first T_peak was lower than that of all cross-linked fibers (Table 2). The reason was due to the fact that thermal treatment greatly removed water molecules in fibers. It was also indicated that part of the water molecules in cross-linked fibers was attributed to the cross-linking process, which further verified the results of FTIR. In addition, the third inconspicuous stage of thermal degradation for all samples that appeared at above 350 °C probably belonged to the chain-scission at the high temperature of remaining PVA.

As could be observed from Table 2, the temperature tended to slightly increase with the increase in cross-linking temper-
therefore improve the thermal stability of molecular chains of starch to rearrange into order, and cross-linking at higher temperatures would induce more order. The results were consistent with the XRD results that showed no obvious variation, which reflected that the effect of cross-linking on fibers' thermal properties was fairly limited.

2.4. Ag-Loaded Fiber Preparation. Nano silver was added directly into the ST/PVA composite solution with a mass ratio of 15, 20, and 25% and then used for fiber preparation by using the centrifugal spinning setup made by our group. The obtained fibers were further cross-linked at a temperature 120 °C for 4 h. The morphology, diameter distributions, and EDS of the cross-linked Ag-loaded fibers are presented in Figure 5. We could observe from Figure 4a1–c1 that fibers showed a relatively smooth surface. The beaded free fibers were obtained from composite solutions with different nano silver contents, which suggested the excellent spinnability of the solution in the centrifugal spinning system (Figure 5a2–c2). The obtained fibers also depicted a relatively narrow diameter distribution with different nano silver contents and kept almost constant with pure ST/PVA fibers (Figure 5a3–c3). Additionally, the atom content of nano silver on the surface of fibers showed an increasing trend from 0.27 to 0.94 at. %, a trend attributed to the dispersion of nano silver in the spinning solution (Figure 5a4–c4).

2.5. Structure and Properties of Ag-Loaded Fibers. Figure 6 shows the crystalline structures and thermal properties of Ag-loaded fibers with different nano silver contents. Comparing with the XRD patterns of pure ST/PVA fibers in Figure 3b, a new sharp peak appeared at 2θ of 38° for all of the Ag-loaded fibers (Figure 6a). As has been widely proven, the peak was the Ag planes (111) and confirmed the existence of nano silver in obtained fibers. As shown in Figure 6b,c and Table 3, both T_{peak}’s for water evaporation and thermal decomposition were improved with the addition of nano silver in ST/PVAFibers, reflecting that the thermal stability was improved in the presence of nano silver in fibers. The weight loss for water evaporation decreased compared with pure ST/PVA fibers and indicated the decrease of water in fibers. However, the weight loss for thermal decomposition increased with the addition of nano silver, which was probably due to the fact that the nano silver in the fibers could catalyze CO₂ elimination from polymer chains and accelerate the degradation process.

The mechanical properties of as-spun, cross-linked, cross-linked (immersed), and Ag-loaded fibrous membranes are shown in Figure 7 and Table 4. As could be observed, the tensile strength of the as-spun, cross-linked, and cross-linked (immersed) fibrous membranes was 1.56 ± 0.09, 1.72 ± 0.54, and 1.75 ± 0.25 MPa, respectively. However, the strain at breaking of fibrous membranes was 32.51 ± 3.52, 28.96 ± 4.78, and 27.23 ± 1.98, respectively. The water generated during the cross-linking process would make the fibers adhere slightly to each other and would restrict the fibers from sliding somewhat in the stretching process of fibrous membranes. Thus, there was more fiber breakage but not in the form of

Table 2. Thermal Parameters of Cross-Linked Fibers

| cross-linking conditions | T_{peak} (°C) | W % (w/w) |
|--------------------------|--------------|-----------|
| 60 °C/10 h                | 51.19        | 15.57     |
|                          | 247.38       | 63.66     |
|                          | 240.57       | 58.90     |
| 80 °C/80 h               | 53.70        | 13.98     |
|                          | 254.45       | 64.89     |
|                          | 255.45       | 64.89     |
| 100 °C/6 h               | 52.87        | 16.46     |
|                          | 254.45       | 64.89     |
|                          | 255.45       | 64.89     |
| 120 °C/4 h               | 52.88        | 14.32     |
|                          | 254.45       | 64.89     |
|                          | 255.45       | 64.89     |
| 140 °C/2 h (without cross-linker) | 72.25 | 7.58 |
|                          | 270.37       | 65.41     |
sliding during the stretching process, which resulted in the increase in tensile strength. The decrease in strain at break for both cross-linked and cross-linked (immersed) water fibrous membranes further suggested the result (Table 4).

When the nano silver was added into fibers, the tensile strength and strain at break began to decrease (Figure 6). These results were induced by the increase in intermolecular distance that resulted from nano silver. As listed in Table 4, the tensile strength and strain at break of fibrous membranes were decreased from 1.51 ± 0.34 to 1.24 ± 0.21 MPa and from 27.21 ± 4.87 to 21.34 ± 3.48%, respectively. These changes reflected that the mechanical properties of fibrous membranes would be further decreased and therefore further increasing nano silver was not conducive to the application of fibers.

2.6. Antibacterial Analysis of Ag-Loaded Fibers.

Figure 8 shows the antibacterial properties against *E. coli* and *S. aureus* of ST/PVA fibers loaded with different nano silver contents. From Figure 8a, we could observe that the
antibacterial performances of fibrous membranes were increased when the nano silver was increased from 15 to 25%. The diameters of the bacteriostatic zone were increased from 1 to 3.5 mm, which suggested relatively high antibacterial properties against E. coli. The antibacterial properties against S. aureus for the obtained fibers were not obvious (Figure 8b). The diameter of the bacteriostatic zone was just about 2 mm for the fibers with nano silver of 25%, and the fibers with nano silver of 15 and 20% showed almost no antibacterial properties. According to the previous papers, the nano silver showed excellent antibacterial properties against both E. coli and S. aureus, while the growth inhibition of bacteria for E. coli was usually larger than that for S. aureus. 37

3. CONCLUSIONS
The water stability of centrifugally spun ST/PVA ultrafine fibers was greatly improved by vapor phase cross-linking. Optimum parameters for the cross-linking temperature and time were obtained on the basis of the water stability combined with mechanical properties. The resultant Ag-loaded fibrous membranes cross-linked at optimum parameters could be used for antibacterial property testing. The results suggested that the fibrous membranes had antibacterial properties against E. coli and S. aureus. In conclusion, we may provide some help in developing biocompatible, biodegradable, and low-cost antibacterial fiber materials.

4. MATERIALS AND METHOD
4.1. Materials. The food-grade native potato starch was self-prepared. The amylopectin ratio and weight-average molecular weight ($M_w$) were determined to be 73.35 ± 0.76% and 1.173 × 10^6, respectively. 14c,21 The PVA powder (average polymerization degree of 1799 and hydrolysis degree of 95%), nano silver (1000 ppm, diameters: 10-15 nm), sodium hydroxide (AR), glutaraldehyde, and formic acid (AR) were purchased from Aladdin (Shanghai, China). Additionally, the nano silver was prepared in the same way as in commercial applications and directly obtained by dispersing the nano silver powder in water. Therefore, the applied nano silver was safe, nontoxic, and environmentally friendly.

4.2. Cross-Linking of ST/PVA Fibers. The ST/PVA fibers with a starch/PVA mass ratio of 60/40 were prepared by using the centrifugal spinning setup designed by our group (Figure 1), and the spinning solution was obtained by blending a starch solution of 12% (w/w) and a PVA solution of 8% (w/w) with a mass ratio of 50/50 according to our previous report. 14c In addition, the parameters of nozzle diameters, rotational speed, and perpendicular distance of the spinneret to the collector were kept at 25 gauge (inner diameter: 0.26 mm) and 12 mm long, 1000 rpm, and 80 mm, respectively. The obtained fibers were then cross-linked by using a mixture solution of formic acid/glutaraldehyde, and experiments were operated in the form of vapor phase. The cross-linker parameters were mainly the parameters listed in Table 1. After cross-linking, the fibers were further dried in the oven at 90 °C for 1 h to remove the unreacted cross-linker. A control experiment was operated by thermal treatment of as-spun ST/PVA fibers at 140 °C for 2 h.

4.3. Preparation of Ag-Loaded ST/PVA Fibers. Nano silver was directly added into the composite ST/PVA solution and continuously magnetically stirred until evenly mixed to obtain the spinning solution. The Ag-loaded fibers with different Ag ratios were then prepared by using the same spinning conditions of the ST/PVA fiber preparation, and the cross-linking experiments were operated according to the optimum parameters obtained from former cross-linking experiments.

4.4. Fiber Morphological and Structural Characterization. The morphologies and element analysis of obtained fibers were investigated by scanning electron microscopy (EDS/EBSD, Carl Zeiss, Germany) after coating with Perkin. The samples with 4 mm² fibrous membranes were prepared and then mounted on the SEM stub to test at 2 kV. The
diameter distribution of fibers was analyzed by the ImageJ2x software (ImageJ2X 2.1.4.7, National Institutes of Health, Bethesda, MD) by measuring about 100 fibers. FTIR spectra of the ST/PVA fibers were characterized by an infrared spectrometer (Nicolet is50, Thermo Electron Corp., New York, USA) in the range of 4000 to 500 cm\(^{-1}\). To reduce spectral noise, 32 scans were collected for the samples under a resolution of 4 cm\(^{-1}\). X-ray diffraction (Thermo ARL Corp., Ecbulens, Switzerland) with Cu Ka radiation (\(k = 1.5406 \text{Å}\)) was used to characterize the crystal structure changes of fibers. The data were continuously collected with a scanning rate of 2\(^\circ\)/min and 20 range from 5 to 45\(^\circ\).

4.5. Fiber Properties. The thermal behaviors before and after cross-linking fibers were determined using a TGA (Mettler Toledo, Zurich, Switzerland) in N\(_2\) from 30 to 500 \(^\circ\)C at a heating rate of 15\(^\circ\)/min. The tensile strength of fibrous membranes was determined by using a multi-function stretching instrument (KES-FI, Aichi, Japan). The fibrous membranes were cut into a size of 20 mm long and 5 mm wide and then tested at a tensile rate of 0.1 cm/s under 25 \(^\circ\)C. The thicknesses of fibrous membranes ranged from 0.15 ± 0.03 to 0.26 ± 0.11 mm. Each specimen was tested five times, and stress was calculated according to eq 1:\(^{16c}\)

\[
\sigma = \frac{F}{S} \tag{1}
\]

where \(F\) is the measured force and \(S\) is the measured cross-section of samples (width \(\times\) thickness).

4.6. Antibacterial Property. The antibacterial property of Ag-loaded ST/PVA fibers against both E. coli (ATCC25922) and S. aureus (ATCC29213) was tested according to the bacteriostatic zone test.\(^{38}\) In brief, the fibrous membranes were cut into circles with diameters of 10 mm. All of the samples were sterilized under 121 \(^\circ\)C for 20 min and then placed on an agar plate. Then, the agar plates were incubated for 24 h at 37 \(^\circ\)C.

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### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

We acknowledge the financial support by the Natural Science Foundation of Zhejiang Province (grants LQ21E030011 and LY21E030021). The authors would like to thank the anonymous reviewers for their valuable comments.

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