

PREPARATION AND PROPERTIES OF PVA/SS COMPOSITE NANOFIBERS

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A blending solution of 8 wt% polyvinyl alcohol (PVA) and different mass fraction of silk sericin (SS) was prepared by using deionized water as solvent. Polyvinyl alcohol/silk sericin (PVA/SS) composite nanofiber materials with different mass ratios were spun by electrospinning technology, and the properties of PVA/SS composite nanofibers were studied. Under the experimental conditions, the results shows that when the PVA is 8 wt%, the SS is 2 wt%, the PVA/SS composite nanofiber with smooth surface and uniform thickness can be prepared. FTIR curve of PVA/SS has both the absorption peak of PVA and SS; XRD shows that the intensity of the diffraction peak of the PVA/SS composite nanofiber membrane increases at 2θ of 19.4° with the SS content increasing. DSC showed the temperature of the decomposition peak of PVA/SS decreased at about 220°C and weakened at 320°C with the SS content increasing. The TG curve shows that PVA/SS composite nanofibers are thermally stable. The research results regenerate the wasted SS into a functional new material.

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1. Introduction

Silk Sericin (SS) is a silk protein secreted by silkworm in the central silk gland with molecular weight ranging from 65 kDa to 400 kDa [1-3]. SS is widely used in medical and cosmetic fields because SS contains a large number of hydrophilic amino acids and is easy to absorb and release water [4-5]. However, in order to achieve the gloss and handle of silk products, it is necessary to degum silk. Wasted SS will pollute the environment [6]. Therefore, SS has been studied repeatedly in recent years as a research hotspot. Polyvinyl alcohol (PVA) is a synthetic, non-toxic, biodegradable polymer that can be easily electrospun [7-8] or blended with other materials [9-11].

Electrospinning is a new processing technology for the simple and efficient production of nanofibers. The nanofibers prepared by this technology have broad application prospects in filtration, textile, medical, catalyst and composite materials [12-14]. Electrospun nanofiber mats have a controlled fiber diameter, a significant specific surface area, a highly open porosity, and interconnected porous structures [15-16]. Therefore, it is a simple and economical method to prepare nanofibers having a micron to nanometer diameter range, a controllable composition, and a porous structure by electrospinning. The PVA/SS mixed solution was prepared, and the PVA/SS nanofibers were electrospun. According to the surface morphology and diameter of the PVA/SS composite nanofibers, the optimal concentration and ratio of the PVA/SS blend solution was compared and chosen. The PVA/SS composite nanofibers were tested for performance.

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2. Experiment

2.1. Materials

Sericin (SS): Favorsun Pharmaceutical Co., Ltd (Shanghai); PVA1797: (melanol degree 96.0-98.0%, Aladdin); deionized water (H₂O): Zhengzhou Erqi District Changhe distilled water sales department.

2.2. Experimental instruments

Electronic balance (UX620H), constant temperature heating magnetic stirrer (DF-101S), electronic high voltage generator (D-ES50PN-10W/DDPM), electric blast drying oven (101A-3E), syringe pump (LSP01 -1A).

2.3. The preparation of PVA/SS blended solution

Weigh 6 parts of 8 g PVA powder into six blue cap bottles, and add 91.5g, 91g, 90g, 88g, 87.5g and 84g of deionized water respectively, swell for 1 hour at room temperature, then stir at 95 °C for 4 hours until the PVA is completely dissolved, at last cool to below 60 °C. Add 0.5g, 1g, 2g, 4g, 6g and 8g SS powder to the PVA solution, and dissolve at a constant temperature of 60 °C for hour. 8 wt% PVA and different mass fraction SS mixed solution can be obtained and cooled for use.

2.4. Electrospinning

A 10 ml syringe was used to draw a certain amount of PVA/SS blended solution. The syringe was mounted on the syringe pump and connected to the positive electrode. The negative electrode of the receiving screen was placed in front of the needle. The spinning distance was 12 cm, the voltage was 15 KV, and the spinning speed was 0.35 ml/h. The nanofibers are received on a receiving screen.

2.5. The characterization of PVA/SS nanofibers

The PVA/SS composite nanofibers material was observed at room temperature with a FEI Quanta 250 scanning electron microscope. To further investigate the effect of SS content on the diameter of the composite nanofiber, the fiber diameter in the SEM image was measured by Image J software, and 100 times of per category were measured. The average diameter and diameter standard deviation of the nanofibers were calculated using Excel.

The Thermo Fisher Nicolet 6700 conversion infrared spectrometer was used to test the total reflection infrared spectrum of PVA/SS composite nanofibers. The structure and composition of the PVA/SS composite nanofibers were studied according to the absorption characteristics of infrared wavelengths. The wavenumber range is 250-4500 cm⁻¹ and the resolution is 0.09 cm⁻¹.

The D8 ADVANCE X-ray diffractometer (XRD) was used with an operating voltage of 40 kV and a current of 30 mA using a CuK α source ($\lambda=1.5418$) through a continuous scan mode at a scan rate of 2 °/min. The angle range is 10 ~ 80°.

Using a synchronous thermal analyzer from Netzsch, Germany, the instrument model STA449 F3 was used to test the thermal performance of the PVA/SS composite nanofibers. The temperature range was 35-600 °C, the heating rate was 10 °C/min, and nitrogen was used as an inert shielding gas. More than 5 mg of test sample was accurately weighed and empty pan was used as the comparison sample.

3. Results and analysis

3.1. Morphology analysis of PVA/SS composite nanofibers

In order to study PVA/SS composite nanofibers, different mass ratio PVA/SS blend solutions were prepared, and PVA/SS composite nanofibers were spun by electrospinning technology.

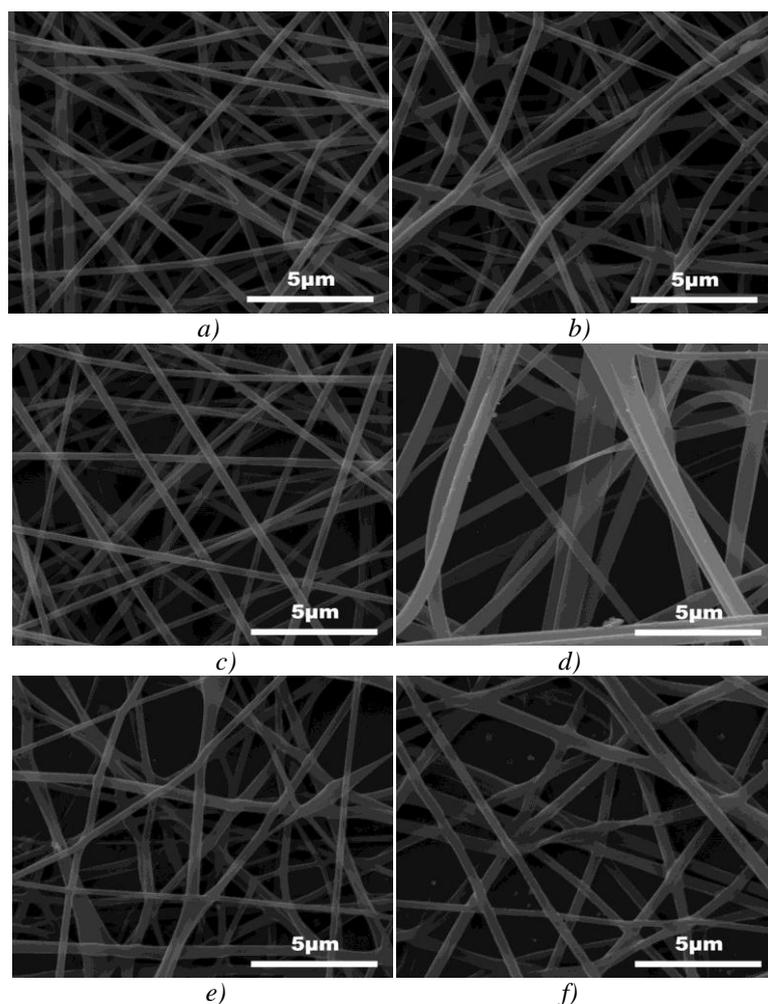


Fig. 1. Electron micrograph of PVA/SS composite nanofibers with different mass ratios. a: PVA: SS (8:0.5); b: PVA: SS (8:1); c: PVA: SS (8:2); d: PVA: SS (8 :4); e: PVA: SS(8:6); f: PVA: SS(8:8).

Fig. 1 shows scanning electron microscope of the PVA/SS composite nanofibers to observe the surface microscopic morphology. When the PVA is 8 wt%, PVA:SS is less than 1:1, the smooth nanofibers can be obtained. When the PVA:SS is 8:0.5 and 8:1 (Fig. 1a and 1b), although the visible spindle and the tapered structure are not present, the surface roughness of the fiber is pronounced. When PVA:SS is 8:4, the composite nanofibers begin to adhere and become more serious, and the fiber thickness is uneven (Fig. 1d). When PVA:SS is 8:6 and 8:8 (Fig. 1e and 1f), the fiber has a large amount of adhesion, irregular columnar shape, a large degree of fiber roughness, and the fiber diameter is extremely uneven. Only when PVA:SS is 8:2 (Fig. 1c), the fibers are smooth, little rough, and have no adhesion and irregular shapes.

Table 1. Average diameter and standard deviation of PVA/SS composite nanofibers.

PVA wt%	SS wt%	Average diameter (nm) /nm	Standard deviation
8	0.5	333	98
8	1	355	91
8	2	346	90
8	4	578	145
8	6	433	191
8	8	425	117

From Table 1 and Fig. 1 we know that the Change of the average diameter and diameter standard deviation of PVA/SS composite nanofibers is not obvious as the SS increases to 2 wt% compared with the nanofibers with SS of 0.5 wt%. At the same time, by comparing the PVA/SS composite nanofibers with different ratios, it can be seen that the average diameter of the nanofibers increases from 346 nm to 578 nm and the standard deviation increases from 90 to 191 as the SS increases from 2 wt% to 4 wt%. As the SS continues to increase to 8 wt%, the average diameter decreases to 425 nm and the standard deviation of diameter decreases to 117. It may be that the added SS affect the properties of the blended solution. From Tab. 2 and Fig. 2 we know that when PVA:SS is 8:2, the PVA/SS composite nanofibers obtained have uniform thickness and the best morphology.

3.2. Infrared spectroscopy

Fig. 2 shows the infrared spectrum of PVA/SS (8:0.5, 8:2 and 8:6) composite nanofibers. By observing the infrared spectrum curve, it can be found that the PVA/SS infrared spectrum curves with different mass ratios are similar. The peak at 3296 cm^{-1} is the stretching vibration frequency of $-\text{NH}$, the infrared characteristic peak at 2924 cm^{-1} is caused by the stretching vibration of $-\text{CH}_2$, and the strong absorption peak of 1420 cm^{-1} is the characteristic peak of $-\text{OH}$ induced by $-\text{CH-OH}$ bending vibration. $-\text{CH}_2$ and $-\text{CH-OH}$ are the main functional groups of the PVA polymer. SS is the outer layer protein of silk fiber. The absorption peaks of protein secondary structure amide I, amide II and amide III are at 1650 , 1537 and 1241 cm^{-1} , respectively. The structure of SS is due to random coil, consistent with the study^[17]. The intensity of these three peaks increase as the SS content increases. In addition, the bending vibration absorption peak of the main chain methine $\equiv\text{CH}$ is at 1322 cm^{-1} , the asymmetric stretching vibration absorption peak of hydroxy OH is at 1083 cm^{-1} , 919 cm^{-1} is O-H in-plane bending vibration peak, 837 cm^{-1} is an out-of-plane twisting peak of $-\text{CH}_2$. It can be seen from the above that the PVA/SS infrared spectrum curve has both an absorption peak of PVA and an absorption peak of SS.

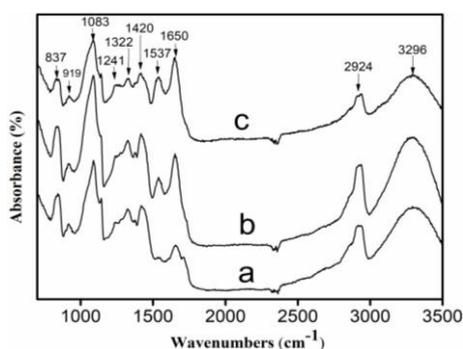


Fig. 2. Infrared spectrum of PVA/SS composite nanofibers with different mass ratios.
a: PVA:SS (8:0.5); b: PVA:SS (8:2); c: PVA:SS (8:6).

3.3. X-ray diffraction analysis

It can be seen from Fig. 3 that the X-ray diffraction (XRD) patterns of PVA/SS composite nanofibers with different mass ratio are similar. The diffraction angles at the 29.4° and 41.7° are the diffraction peaks of the PVA, and the intensity of these two peaks is substantially unchanged. The peaks with diffraction angles of 12.8° and 19.4° are due to the addition of SS. At 12.8° , the diffraction peak intensity of PVA/SS composite nanofibers with different mass ratios showed no obvious regularity. With the increase of SS content, the intensity of diffraction peaks of PVA/SS composite nanofiber membranes increased at 2θ of 19.4° .

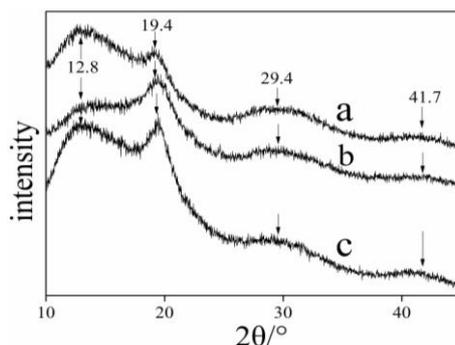


Fig. 3. XRD spectrum of PVA/SS composite nanofibers with different mass ratios.
a: PVA:SS (8: 0.5); b: PVA:SS (8: 2); c: PVA:SS (8: 6).

3.4. DSC performance analysis

Fig. 4 is DSC graph of PVA/SS composite nanofibers of different mass ratios. Below 100 °C is the endothermic peak of moisture. The decomposition peak of PVA/SS composite nanofibers is about 220 °C, and the temperature of the decomposition peak of SS decreases with the SS content increasing. There is a decomposition peak around 320 °C, but this peak weakens with the increase of SS.

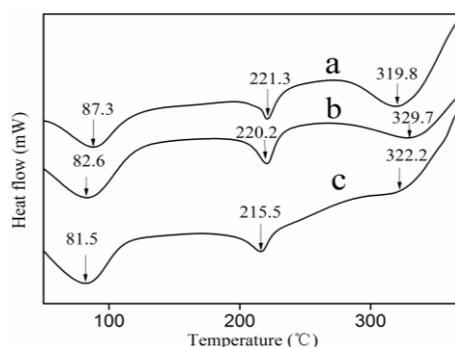


Fig. 4. DSC graph of PVA/SS composite nanofibers with different mass ratios.
a: PVA: SS (8:0.5); b: PVA: SS (8:2); c: PVA: SS (8:6).

3.5. TG performance analysis

Fig. 5 is a TG diagram of PVA/SS composite nanofibers with different mass ratios for further analysis of the thermal properties. Below 100 °C is the evaporation of water. The initial weight loss of the PVA/SS composite nanofibers with different mass ratios appears at 271 °C, 278 °C and 262 °C, the weight loss rates are 4%, 8% and 9%, respectively (Fig. 5a, 5b and 5c). At 297 °C, the weight loss of composite nanofibers of PVA/SS (8:0.5) (Fig. 5a) and PVA/SS (8:2) (Fig. 5b) was 12%; and after 297 °C, the weight loss rate of the PVA/SS (8:0.5) (Fig. 5a) composite nanofibers is faster than that of the PVA/SS (8:2) (Fig. 5b) composite nanofibers. The weight loss rate of the PVA/SS (8:0.5) (Fig. 5a) and PVA/SS (Fig. 5c) composite nanofibers is 22% at 310 °C. However, the weight loss rate of PVA/SS (8:0.5) (Fig. 5a) composite of nanofibers is faster than that of PVA/SS (8:6) (Fig. 5c) after 310 °C. At 350 °C, the weight loss rate of PVA/SS (8:2) (Fig. 5b) and PVA/SS (8:6) (Fig. 5c) composite nanofibers was 40%. The weight loss rate of PVA/SS (8:6) (Fig. 5c) composite nanofibers is slower than PVA/SS (8:2) (Fig. 5b) composite nanofibers exceeding 350 °C. The weight loss rate of PVA/SS (8:0.5) (Fig. 5a), PVA/SS (8:2) (Fig. 5b) and PVA/SS (8:6) (Fig. 5c) composite nanofibers becomes slower after 375 °C, 381 °C and 369 °C, respectively.

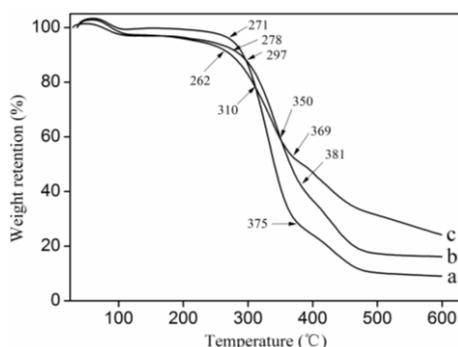


Fig. 5. TG diagram of PVA/SS composite nanofibers with different mass ratios.
a: PVA: SS (8:0.5); b: PVA: SS (8:2); c: PVA: SS (8:6).

4. Conclusions

The PVA/SS composite nanofibers were prepared by electrospinning technology by dissolving PVA and SS in deionized water. The effects of different mass ratios of PVA/SS on the morphology and diameter of nanofibers were studied. Under the experimental conditions, when PVA is 8 wt% and SS is 2 wt%, the PVA/SS composite nanofibers with smooth surface and uniform thickness can be prepared. The average diameter of PVA/SS composite nanofibers is 346 nm and the standard deviation of diameter is 90. The infrared spectra of PVA/SS with different mass ratios have similar regularity. There are both absorption peaks of PVA and SS in the curves, and the intensity of absorption peaks of amide I, amide II and amide III increases with the increase of SS content.

In XRD, the diffraction peak strength of PVA/SS composite nanofibers with different mass ratios does not show obvious regularity at 12.8° , but with the increasing of SS content, the diffraction peak strength of PVA/SS composite nanofibers gradually increases at 19.4° . DSC showed the decomposition peak of PVA/SS, and with the increase of SS content, the decomposition peak temperature tended to decrease at about 220 C, while the decomposition peak weakened at about 320 C. TG curve shows the thermal stability of PVA/SS composite nanofibers. The results show that waste sericin can be regenerated into new functional materials.

Acknowledgements

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