Study on Structure of Oxidized Raw Bamboo Fiber Treated with Sericin Protein

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Abstract: In order to improve the finishing effect of raw bamboo fiber treated with sericin protein, it was selectively oxidized by $NaIO_4$ and then treated with sericin solution. The morphology and structure of sericin proteinic raw bamboo fiber were analyzed by means of SEM, XRD, TG and DSC. The treatment results show that sericin protein could be directly coated onto the oxidized raw bamboo fiber without any other reagent and a covalence was formed between amido and aldehyde group. After being treated with sericin protein solution, the thermal stability and crystallinity of the oxidized raw bamboo fiber improved and the surface became smoother.

Keywords: Sericin protein, raw bamboo fiber, oxidation, structure, treat.

1. Introduction

Raw bamboo fiber is a new type of natural cellulose fibers extracted from bamboo by mechanical and physical methods. It has attracted extensive attention because it possesses excellent properties such as hygroscopic permeability, regeneration, and antibacterial property. However, raw bamboo fiber is rather rough and harsh and has great rigidity, all of these results in poor wrinkle resistance and scratchy sense in its wearing characteristics. These shortcomings limit its applications and development in high value-added textiles.

Sericin is a kind of water-soluble spherical protein, which possesses soluble, absorbent, antioxidant characteristics, gelation and so on. Sericin is made up of eighteen kinds of amino acids, of which eight kinds are essential for health of human beings. Therefore, sericin possesses affinity and health caring features. If we can graft sericin protein to raw bamboo fiber, we can not only alleviate scratchy sense, enhance crease-resistant property and UV-protective ability, but also get the silk-oriented effect. However, there is a shortage of those groups that can result in covalent crosslinking with cellulose in the sericin protein molecular structure, which will lead to relatively low fixation rate of sericin. In order to improve the modification effect of raw bamboo fiber treated by sericin protein, in this paper we firstly use $NaIO_4$ to implement selective oxidation on raw bamboo fiber. Then we use sericin protein solution to modify oxidized raw bamboo fiber. After the oxidation, the aldehyde groups on the surface of raw bamboo fiber will react with amino-groups in the sericin protein. Thus we can get sericin protein oxidized raw bamboo fiber.

In this paper, we use FT-IR to get the crystal structure of sericin protein oxidized raw bamboo fiber. And we also analyse its form, morphological structure and thermal property with the help of freeze cracking SEM, X-ray diffraction, thermal analysis and so on.

2. Experimental materials

2.1 The preparation of oxidized raw bamboo fiber

Weigh some raw bamboo yarns (29.5 tex) which have been scoured and bleached, put them into brown beaker flask and add a certain density of sodium periodate solution into it. Under a constant condition of 40℃, oxidize them in a shaking water bath pot in the dark for two hours. Then immerse them into glycerin solution (0.1*mol/L*) for one hour so as to remove the Unreacted sodium periodate. After that, we use deionized water to wash them fully and then immerse into deionized water for 24 hours. Thus the oxidized raw bamboo fiber is obtained. Further it is Dried and made to equilibrium and sealed for use.

2.2 The preparation of sericin protein oxidized raw bamboo fiber

Put the oxidized raw bamboo yarn into a certain density of sericin protein solution according to liquor

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ratio 1:30. Treat it under 30-100℃ for 0.5-5 hours, pre-dry it under 80℃ for 5 minutes, dry it under 150℃ for 3 minutes, wash it fully and air-dry it naturally.

3. Experiment test and apparatus

(1) Fourier infrared spectroscopy characterization
Apparatus: Infrared Spectrometer Nicolet 5700;
(2) Microstructure test
Apparatus: Scanning Electron Microscope S-570;
(2) X-ray diffraction test
Apparatus: X-ray Diffraction Apparatus Rint 2027 (made in Japan)
(4) Thermal analysis
Apparatus: Thermal Analysis Apparatus Diamond TG-DTA

4. Results and discussion

4.1 Infrared spectrum analysis of oxidized raw bamboo fiber treated by sericin protein

We use $NaIO_4$ to oxidize raw bamboo cellulose, which can cut the C_2-C_3 Chemical Bond in cellulose glucopyranose units (I), the two adjacent hydroxyl groups in the C_2 and C_3 position can be selectively oxidized into aldehyde groups, then 2,3-dialdehyde cellulose (II) is formed. The aldehyde groups have high activity, which possess the ability of forming covalent interaction with the amino-groups in sericin protein mocleular chain. They can react to form schiff base and coat on the surface of oxidized raw bamboo fiber, so the sericin proteinic raw bamboo fiber is prepared (Ⅲ). The reaction theory is shown in Figure 1.

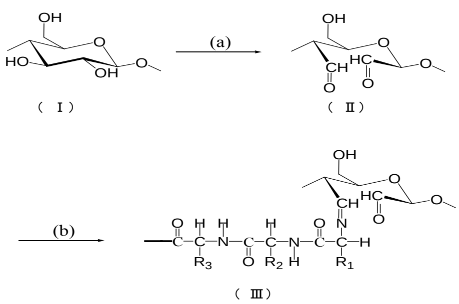

Figure 1 The reaction model of sericin protein and oxidized raw bamboo fiber.
(*a*) The selective oxidation of raw bamboo fiber
(*b*) The reaction of sericin protein and oxidized raw bamboo fiber

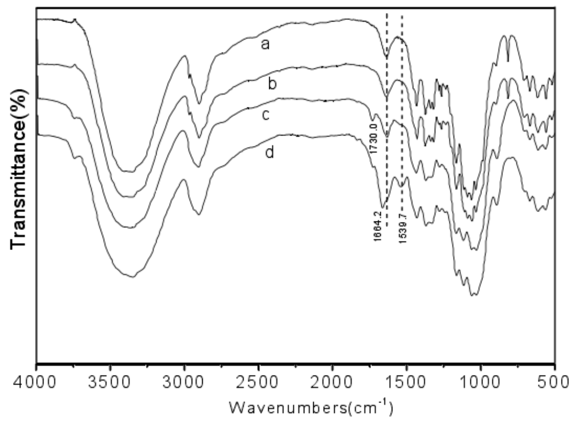

Figure 2 FT-IR spectra of raw bamboo fiber.
(*a*) raw bamboo fiber
(*b*) raw bamboo fiber treated by sericin protein (3*wt%*)
(*c*) oxidized raw bamboo fiber(4*g/L* $NaIO_4$, 2*h*)
(*d*) oxidized raw bamboo fiber treated by sericin protein(3*wt%*)

FT-IR spectra of raw bamboo fiber samples before and after treatment are shown in Figure 2. We can see that curve (b) is similar in shape to curve (a) and there is no obvious change in characteristic peak, which show that non- oxidized raw bamboo fiber has no chemical cross-linking with sericin protein. This is because raw bamboo fiber does not have the groups that can react with sericin protein macromolecules directly, thus there can not take place any chemical cross-linking reaction. Only a little sericin protein can be attached to the fiber by the way of physical absorption and will shed readily. While raw bamboo fiber is oxidized by $NaIO_4$, its infrared spectrum changes greatly. Comparing curve (*c*) with curve (*a*), we can see that characteristic peak of aldehyde group appears at the point of $1730cm^{-1}$, which indicates that we can know raw bamboo fiber has been oxidized into dialdehyde cellulose. After being treated by sericin protein solution, characteristic peak of aldehyde groups (C=0) weakens, and a new characteristic peak appears at the point of $1539cm^{-1}$(C-N) and $1664cm^{-1}$(C=N). It shows that raw bamboo fiber is oxidized into active aldehyde groups, and the active aldehyde groups can combine with the amino-group on the sericin protein globin chain and form imine structure. Meanwhile, the corresponding wavenumber of stretching and vibrating absorption peak (O-H) in infrared curve (*d*) changes from $3350.9cm^{-1}$ to $3348.8cm^{-1}$, it moves to the direction of lower wavenumber and the absorbance peak becomes sharp. All of these show that part of the aldehyde groups and hydroxyls in the oxidized raw bamboo fiber molecule can combine with polar groups on the sericin protein globin chain to form hydrogen bonds and ionic bonds, which can enhance the combining ability between oxidized raw bamboo fiber macromolecules coated by sericin, and can make the molecule structure compact and regular. They can also improve the orientation of molecular chain.

4.2 The SEM analysis of oxidized raw bamboo fiber treated by sericin protein

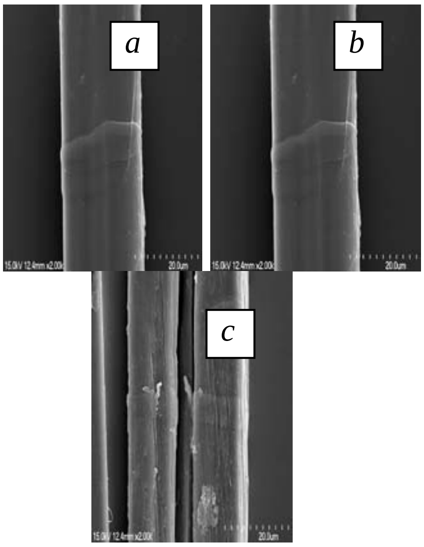

Figure 3 SEM micrographs of raw bamboo fiber with different oxidized concentration treated by sericin protein.
(*a*) raw bamboo fiber;
(*b*) oxidized raw bamboo fiber (6*g/L* $NaIO_4$) treated by sericin protein (3*wt%*);
(*c*) oxidized raw bamboo fiber (24*g/L* $NaIO_4$) treated by sericin protein (3*wt%*).

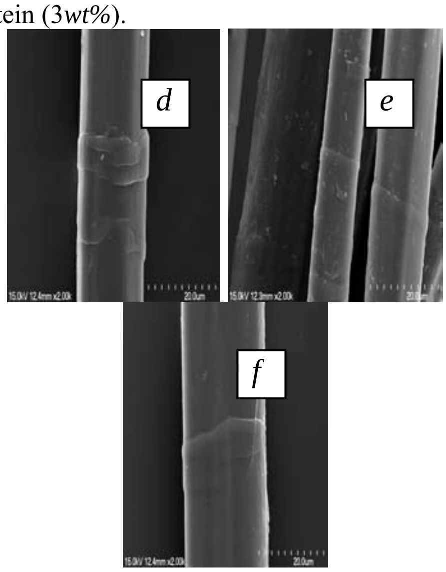

Figure 4 SEM micrographs of oxidized raw bamboo fiber treated by sericin protein solution with different concentrations.
(*d*) oxidized raw bamboo fibers treated with sericin protein (3*wt%*)
(*e*) oxidized raw bamboo fibers treated with sericin protein (6*wt%*)
(*f*) oxidized raw bamboo fibers treated with sericin protein (12*wt%*)

Figure 3 and 4 show the SEM photographs of native and the modified raw bamboo fiber samples. The former is under different oxidized concentration and the latter is under different sericin protein concentration. From these photographs, it can be concluded that with the continuous oxidation, stripping loss streaks become deeper; but after being treated with sericin protein solution, minor streaks of oxidized raw bamboo fiber disappear, and the surface becomes smoother. The reason for this is that sericin macromolecules can not only form the film in the deep cannelure on the surface of fiber, but also get into the inner fiber to form covalent bond with active aldehyde so as to deposit on the oxidized raw bamboo fiber to get a uniform layer of sericin film; but if the damage on fiber is great because of the high concentration of oxidation, the steaks still remain. And with the increase of the concentration of sericin protein solution, sericin particles fixtures can be seen on the surface of raw bamboo fiber. With the concentration of sericin protein solution improving, the probability of its contact and reaction with the aldehyde group will also increase, but the amount of aldehyde groups on the oxidized raw bamboo fibers that can react with sericin protein is limited, and the protein macromolecule will agglomerate with the concentration of sericin protein solution increasing, besides, solution viscosity will also raise, in such case the sericin protein may be adsorbed physically on the surface of raw bamboo fiber.

4.3 X-ray diffraction curve of oxidized raw bamboo fiber treated by sericin protein

X-ray diffraction curves of raw bamboo fiber samples are shown in Figure 5. From curve(*b*), (*c*)and (*d*) we can see that the shape of X-ray diffraction curves of oxidized raw bamboo fiber before and after being treated with sericin protein solution is similar with that of raw bamboo fiber in curve (*a*). And the diffraction angles for main diffraction characteristic peaks are also similar to each other. The 2θ angles of raw bamboo fiber are 14.94, 22.76 and 34.52, and the 2θ angles of oxidized raw bamboo fiber before and after being treated with sericin protein solution are 14.97, 22.86, 34.59 and 15.07, 22.99, 34.76 respectively. All of those are X-RAY diffraction peaks of cellulose I. From the above, it can be concluded that neither the oxidation by $NaIO_4$ nor the coating with sericin protein can change the microstructure of raw bamboo fiber significantly. The crystallinity of oxidized raw bamboo fiber treated by sericin protein solution increases because there are active aldehyde groups in oxidized raw bamboo fiber molecules, which can form imine primary bonds and non-chemical bonds such as hydrogen bonds with sericin protein to restructure some weak structures of raw bamboo fiber and improve the orientation and regularity of molecular chain so that the inner structure of raw bamboo fiber can get compact.

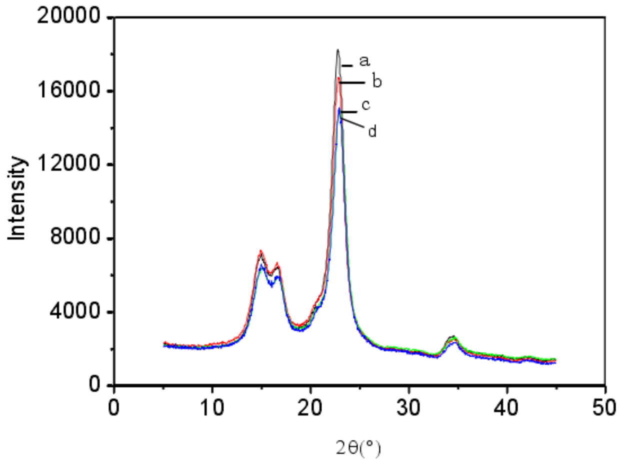

Figure 5 X-ray diffractograms of raw bamboo fiber.
(*a*) raw bamboo fiber; (*b*) oxidized raw bamboo fiber (6*g/L* $NaIO_4$); (*c*) oxidized raw bamboo fiber (6*g/L* $NaIO_4$) treated with sericin protein(3*wt%*); (*d*) oxidized raw bamboo fiber (6*g/L* $NaIO_4$) treated with sericin protein (6*wt%*).

4.4 Thermal analysis of oxidized raw bamboo fiber treated by sericin protein

Figure 6 and 7 are TG curves and DAT curves of oxidized raw bamboo fiber treated with sericin protein solution respectively. It can be seen from Figure 6, that the temperature change of thermogravimetic is not distinct when the raw bamboo fiber is under low oxidized concentration, while the thermogravimetic temperature became higher when it is under high oxidized concentration. The reason for this is that the oxidation reaction of low concentration was mainly conducted on the surface of the fiber so that fewer aldehyde groups were formed; thus sericin protein has less impact and damage on raw bamboo fiber. While under high oxidized concentration, with the increase of aldehyde groups, the combination between oxidized raw bamboo fiber and amino-groups is reinforced so that sericin protein can enter into the inner surface of the fiber to conduct chemical reactions.

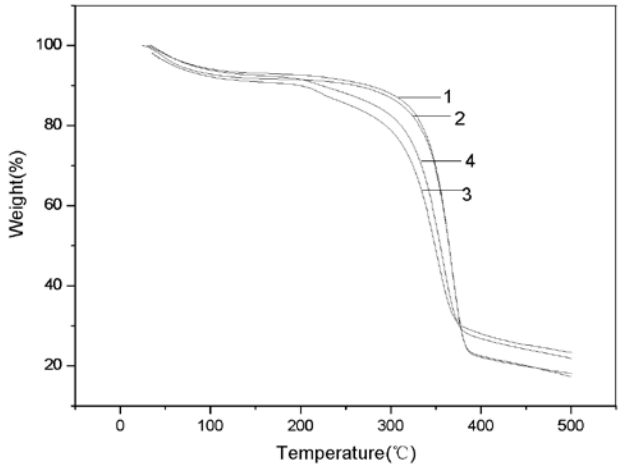

Figure 6 TG curves of oxidized raw bamboo fiber treated with sericin protein solution.
1# oxidized raw bamboo fiber (2*g/L* $NaIO_4$)
2# oxidized raw bamboo fiber (2*g/L* $NaIO_4$) treated with sericin protein (3*wt%*)
3# oxidized raw bamboo fiber (12*g/L* $NaIO_4$)
4# oxidized raw bamboo fiber (12*g/L* $NaIO_4$) treated with sericin protein (6*wt%*)

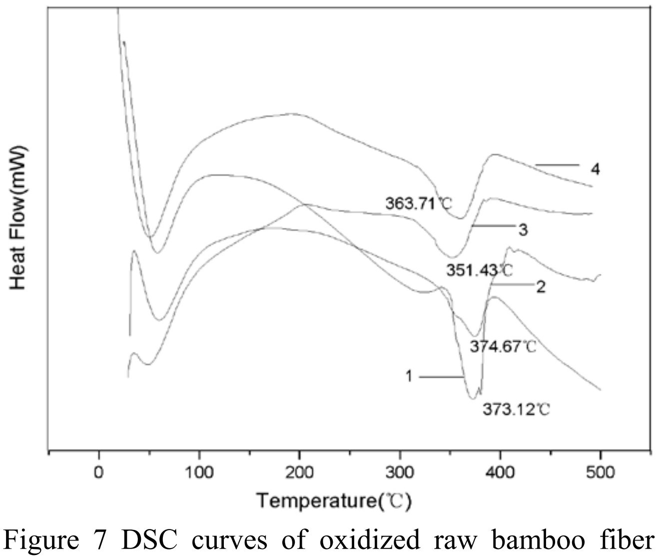

Figure 7 DSC curves of oxidized raw bamboo fiber treated with sericin protein solution.
1# oxidized raw bamboo fiber (2*g/L* $NaIO_4$)
2# oxidized raw bamboo fiber (2*g/L* $NaIO_4$) treated with sericin protein (3*wt%*)
3# oxidized raw bamboo fiber (12*g/L* $NaIO_4$)
4# oxidized raw bamboo fiber (12*g/L* $NaIO_4$) treated with sericin protein (6*wt%*).

Figure 7 shows that the endothermic and decomposition peak of oxidized raw bamboo fiber with 2*g/L* $NaIO_4$ has fewer changes after being treated with sericin protein solution while that of oxidized raw bamboo fiber with 12*g/L* $NaIO_4$ changes from 351.43℃ to 363.71℃. In the later case, the raw bamboo fiber (under high oxidized concentration) and sericin protein are combined by covalent crosslinking reaction and sub-valence bond structures increase, and more heat is required when thermal decomposing occurs. So we can see that the thermal stability of oxidized raw bamboo fiber will be improved after being treated with sericin protein.

5. Conclusion

(1) When raw bamboo fiber is oxidized selectively by $NaIO_4$**,** the aldehyde group on the surface of it can react with the amino-group in sericin protein and combine securely by chemical bonds, which can attach sericin protein to raw bamboo fiber hence we can produce sericin protein raw bamboo fiber.

(2) Non-oxidized raw bamboo fiber and raw bamboo fiber oxidized by $NaIO_4$ with low concentration can be stripped and reduced after the sericin solution treatment; appropriately increasing the oxidation degree of raw bamboo fiber is beneficial to the fixation of sericin protein.

(3) After the sericin protein solution treatment, minor streaks of oxidized raw bamboo fiber will disappear, and the surface of oxidized raw bamboo fiber becomes smoother. The thermal properties and crystallinity have litter change if raw bamboo fiber is treated with sericin protein solution under low oxidized concentration. However, the thermal stability and crystallinity will be improved if the raw bamboo fiber is treated with sericin protein solution under high oxidized concentration.

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