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Research Article

Improving the Color Stability of Naturally Colored Silk by Cross-Linking the Sericin with Phytic Acid

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The color of naturally colored silk (NCS) fades easily during home washing due to the loss of pigment accompanied by dissolution of the sericin. In this study, phytic acid was used to cross-link the sericin of NCS and reduce its solubility, aiming at improving the color fastness of NCS to repeated washing. It was found that the sericin-fixing effect increased as the concentration of phytic acid to 1.0 wt% and the cross-linking time to 5 h increased and then reached a constant level. Cross-linking at pH 7.0-8.5 and temperature 30-40°C could obtain relatively good sericin-fixing effects. The cross-linked NCS showed low sericin loss during the degumming and had much better color fastness to repeated washing as compared with the samples before cross-linking. The cross-linking method proposed in this study may be not only a kind of solution for improving the color fastness of NCS with high practicality but also an alternative for cross-linking sericin-based materials in the biomedical field.

1. Introduction

Naturally colored silk (NCS) is referred as a domestic silk variety with natural color and is the product of the color mutant of conventional silkworm *Bombyx mori*. NCS needs not to be dyed and exhibits properties and productivity close to the conventional white silk [1, 2], thus causing considerable attention due to its economic and environmental benefits. However, utilization of NCS is currently limited due to the presence of the hydrophobic pigment substances in the sericin layer rather than in the silk fibroin [1]. Wet processing, such as degumming and repeated washing, can result in a significant loss of the pigment, which is accompanied by the dissolution of sericin [1, 2]. It is reported that the color of NCS fabrics suffers considerable change when washing them for more than 5 cycles [3]. Therefore, improving the color fastness of NCS to repeated home washing is necessary.

Cross-linking the sericin of NCS with a cross-linking agent results in decreasing the solubility of the sericin and could fix both the sericin and pigment [4]. Wang and Yi have reported that cross-linking NCS fabrics with acidic glutaraldehyde can significantly reduce the solubility of sericin and the fabrics show much higher color fastness to repeated washing as compared with the original fabric [5]. Considering the relatively high toxicity of glutaraldehyde, Qiang and Hang modify glutaraldehyde by copolymerizing with ethylene; the modified cross-linker also shows a relatively good color fixing effect [6]. We have also proposed a novel cross-linker, i.e., bis[tetrakis (hydroxymethyl)phosphonium] sulfate, and found that the cross-linked NCS fabrics can maintain a bright color even after 20-cycle washing [7]. However, the cross-linked NCS fabrics release a detectable amount of formaldehyde, thus limiting the application potential of this cross-linker.

There are plenty of cross-linkers for sericin protein been reported, including glutaraldehyde [8], citric acid [9], genipin [10, 11], dimethyloldihydroxyethylene urea [12], and epoxy resin [13]. However, these cross-linkers are not suitable for NCS, because of their toxicity and/or adverse effects on the color of NCS. For example, the cross-linker genipin, which is frequently used for preparing silk protein-based biomaterials, can result in a dark blue color of the materials [14].

Motivated by these considerations, the development of green and effective cross-linking strategies that satisfies the requirements for the high practicality and low cost for NCS fabrics is necessary.

Phytic acid (myo-inositol hexakisphosphate) is an abundant natural product found in plants and has several bioactivities, such as antioxidant and anticancer [15]. Due to the six strongly electronegative phosphate moieties in its structure, phytic acid can interact with amino group-containing polymers via electrostatic forces to form an ionic cross-linked network. Phytic acid shows a strong ability to chelate multivalent cations, such as Fe^{3+}, Ca^{2+}, and cationic polymers [16]. Therefore, it is employed to cross-link chitosan and gelatin materials for biomedical usage [15–17]. Sericin molecules also have plenty of amino group-containing amino acid residues, such as lysine (3.3 wt%) and arginine (3.1 wt%) [18]. This makes cross-linking of the sericin of NCS using phytic acid feasible. In this study, phytic acid was employed to cross-link the sericin of NCS aiming at improving the color fastness of NCS to repeated washing.

2. Materials and Methods

2.1. Materials. Phytic acid with a purity of over 98% was purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). A NCS single filament, a yarn with 6 single filament fibers, and a plain-weave fabric with a basic weight of 108 g/m^2 were undegummed samples and were supplied by Xinyuan Cocoon Silk Group Co. Ltd (Nantong, China). A neutral nonbleach liquid detergent, Blue Moon Silk & Wool NET care detergent, was purchased from Guangzhou Blue Moon Industry Co. Ltd., Kwangtung, China.

2.2. General Cross-Linking Procedure. The samples were cross-linked by soaking them in the phytic acid aqueous solution at pH conditions from 3.2 to 11.5 and temperatures from 20°C to 60°C. The concentrations of phytic acid varied from 0.05 wt% to 1.00 wt%. The bath ratio was 50 : 1. After cross-linking, the samples were rinsed with water and dried at room temperature. The effects of cross-linking conditions on the fixing fastness of sericin were investigated by evaluating the weight loss of the samples during 1-hour boiling in 0.3 wt% sodium carbonate solution.

In order to obtain sericin for evaluating the cross-linking effects, the degumming solution was dialyzed by using an 8000 Da dialysis membrane for 48 h against distilled water. The sericin solution was then concentrated at 60°C with a rotary evaporator; a sericin solution with a concentration of 2.2 wt% was finally obtained. The sericin solution (5 mL) was added with 2 mL of 0.8 wt% phytic acid. After 12 h, the solution was used for sodium dodecyl sulfate-polyacrylamide gel electrophoresis (SDS-PAGE) analysis.

2.3. SDS-PAGE Analysis. SDS-PAGE was performed to evaluate the molecular weight of the sericin with and without cross-linking. The samples were dissolved in sodium phosphate buffer at a concentration of 6 mg/mL, and 20 μL of the sample solution was loaded onto the gel consisting of 5% stacking gel and 8% acrylamide separating gel. After electrophoresis, the gels were dyed with 0.1% Coomassie Brilliant Blue R250 solution (dissolved in 50% methanol, 6.8% acetic acid, and 43.2% distilled water) for 2 h, and then, the electrophoresis images were observed.

2.4. Thermogravimetric Analysis. A thermal test was performed using a Perkin–Elmer thermal analyzer (TGA-7) at a heating rate of 10°C/min with a temperature range from ambient to 800°C.

2.5. Mechanical Property Measurement. The single filament samples before and after cross-linking were tested according to the Standard Testing Method for Breaking Strength and Breaking Elongation of Synthetic Staple Fibers in China (GB/T 14337-1993) using an XQ-1 laboratorial fiber tensile tester. A gauge length of 20 mm and a strain speed of 20 mm/min were used.

2.6. SEM Analysis. The NCS yarns consisting of 6 single filaments were cross-linked and then subjected to degumming; the samples were analyzed by using a JEOL JCM 6000 microscope after the samples were coated with Au.

2.7. Machine Washing. The fabric samples were washed in an Electrolux-ews 850 rotary drum washing machine with a standard mode at 30°C. Samples and AATCC Dummy I Ballast with a total weight of 1 kg, as well as 15 L and 2.5 g/L of detergent-water mixtures, were used. The samples were dried at 35°C after washing.

2.8. Color Measurements. The color value of the samples, including K/S (shade depth), L^* (brightness), a^* (red, +; green, -), b^* (yellow, +; blue, -), and ΔE (total color change), were evaluated according to AATCC Evaluation Procedure 6 and 7 using a Datacolor SF600X spectrophotometer with a D65 illuminant and 10° observer. Each sample was measured for five times at different positions.

2.9. Fabric Hand Measurement. Fabric hand properties of NCS were measured by a PhabrOmeter Model 3 fabric evaluation system (Nu Cybertek Inc., Davis, CA, USA) according to AATCC test method 202-2014. Three specimens for each sample were tested. Relative hand values of NCS fabrics, including stiffness, smoothness, softness, and wrinkle recovery rate, were obtained and reported as the mean ± standard deviation.

3. Results

3.1. Cross-Linking Conditions. Usually, pH conditions dramatically affect the binding strength of electrovalent bonding. Phytic acid is considered "a strong organic acid polyelectrolyte" whose electronegative character is mainly due to six phosphate moieties of phytic acid. The phosphate moieties are known to be limitedly undissociated at acidic conditions and mostly ionized at pH >7 [19]. The ionized phosphate moieties become electronegative and bind ionically to the electropositive amino groups of sericin. The effects of pH conditions on the cross-linking of raw NCS filament with phytic acid were examined by evaluating the sericin solubility of NCS in degumming bath. As shown in Figure 1(a), the weight loss of the cross-linked fiber decreased

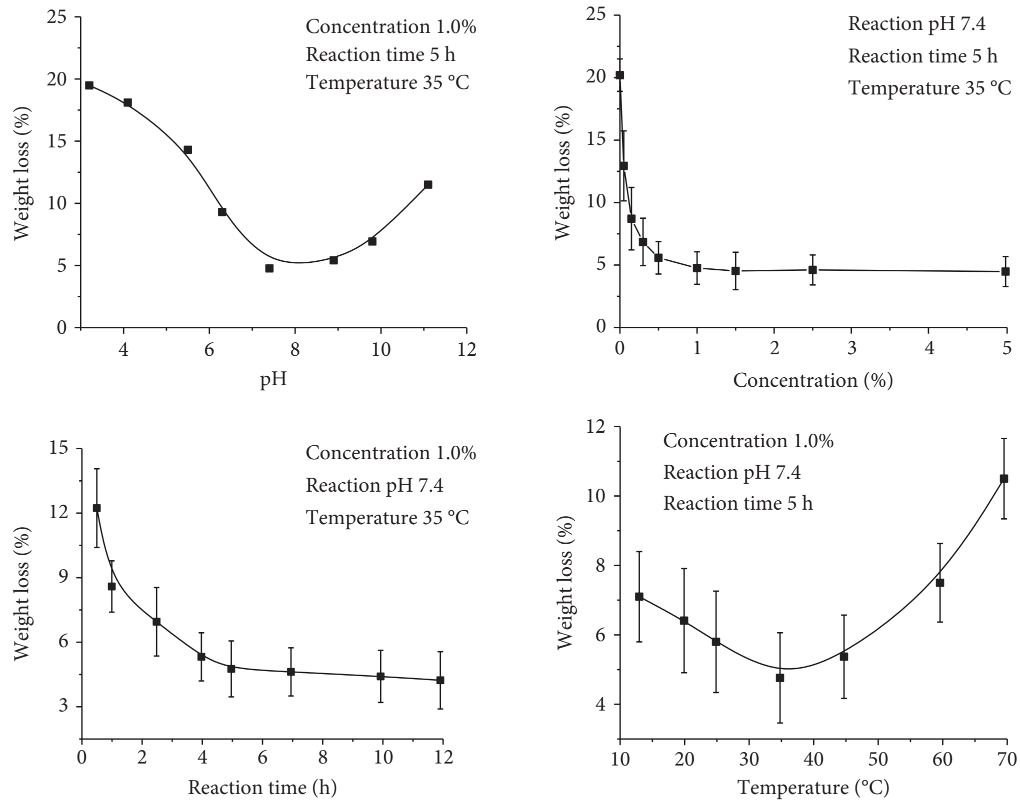


Figure 1: Weight loss of cross-linked fiber during degumming as a function of the cross-linking pH, the concentration of phytic acid, reaction time, and temperature.

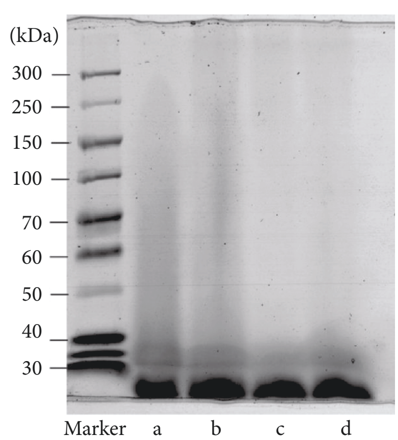


Figure 2: SDS-PAGE of the NCS sericin before and after being cross-linked with phytic acid. Samples a, b, and c represent the sericin cross-linked at pH 9.8, pH 7.4, and pH 4.1, respectively; Sample d was the uncross-linked sericin.

with increasing pH to 7.4 from 3.2, indicating increased fixing fastness of the sericin. However, as the pH was further increased, the weight loss increased significantly. This probably resulted from the hydrolysis of the sericin molecules under alkaline conditions. The result indicated that cross-linking at the pH in the range from 7.4 to 8.9 showed good sericin-fixing effects with the sericin solubility lower than 5.5%. The concentration of phytic acid also significantly affected the fixing fastness of sericin. The sericin solubility was decreased until the phytic acid concentration reached 1.0 wt% and then stayed almost constant with increasing concentrations of phytic acid (Figure 1(b)). This is probably due to that the positively charged amino groups became increasingly saturated with the electronegative phosphate ions at relatively high phytic acid concentrations and could not supply more opportunity for the ionic cross-linking to take place.

A relatively short-term reaction can give a significant sericin-fixing effect; for example, cross-linking for 1 hour, the weight loss of NCS dropped from 18.7% to 12.9% during the degumming. The sericin-fixing effect was improved with increasing cross-linking time and reached a constant state after 5 hours. The cross-linking reaction occurring at room temperature could give relatively good sericin-fixing effects. It is showed that the NCS cross-linked at 13-25°C only lost 4.8%-7.1% of weight during degumming and 35°C seemed to be the optimal temperature for the reaction. As further increasing the cross-linking temperatures from 35°C, the sericin-fixing effect decreasing gradually may be due to the exothermal reaction of this ionic bonding [20]. It is a great advantage for this cross-linking method used at such low temperatures. As well known, many cross-linkers for protein fiber act at high temperature (140-180°C) curing and even in the presence of catalyzer, such as polycarboxylic acids [21].

3.2. Verification of Cross-Linking. Cross-linking undoubtedly results in forming higher molecular weight complex. Figure 2 shows the molecular weight distribution of the uncross-linked sericin and the sericin cross-linked at different pHs

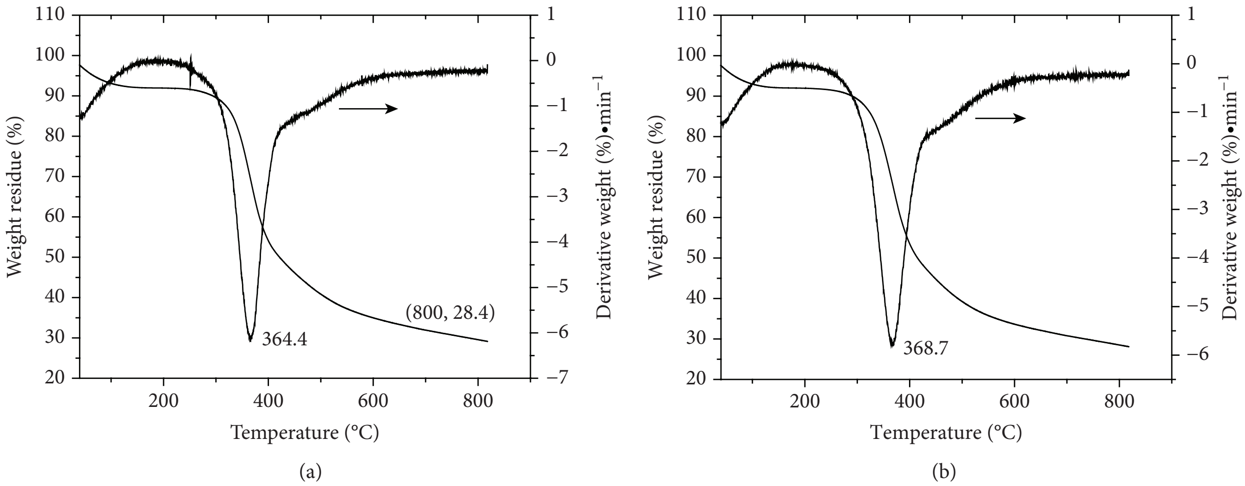


Figure 3: TG and DTG of the (a) original NCS and (b) cross-linked NCS.

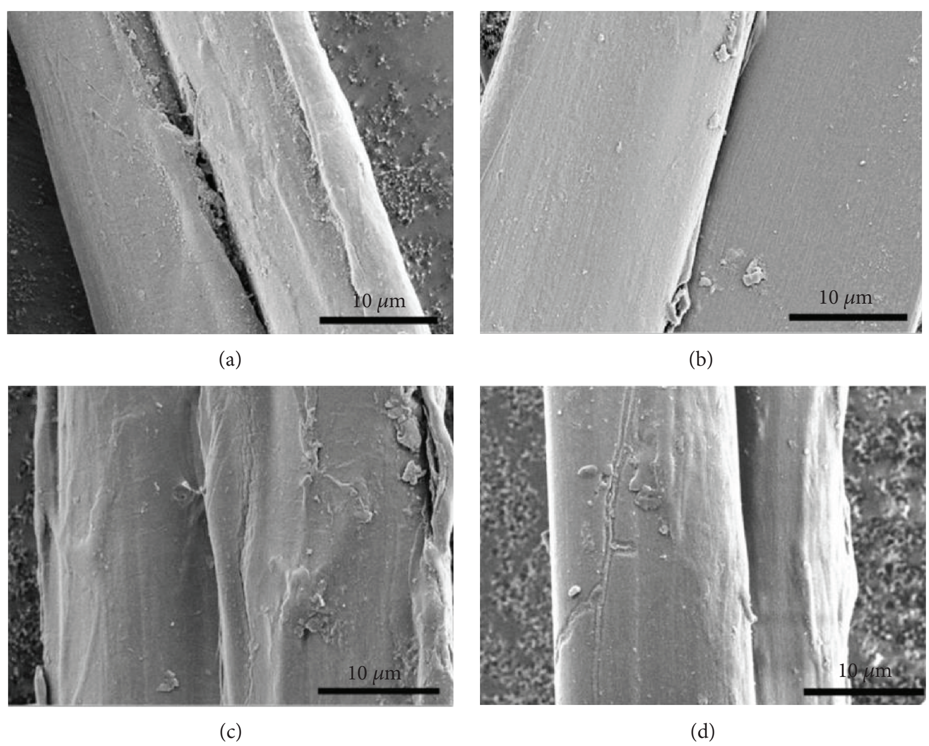
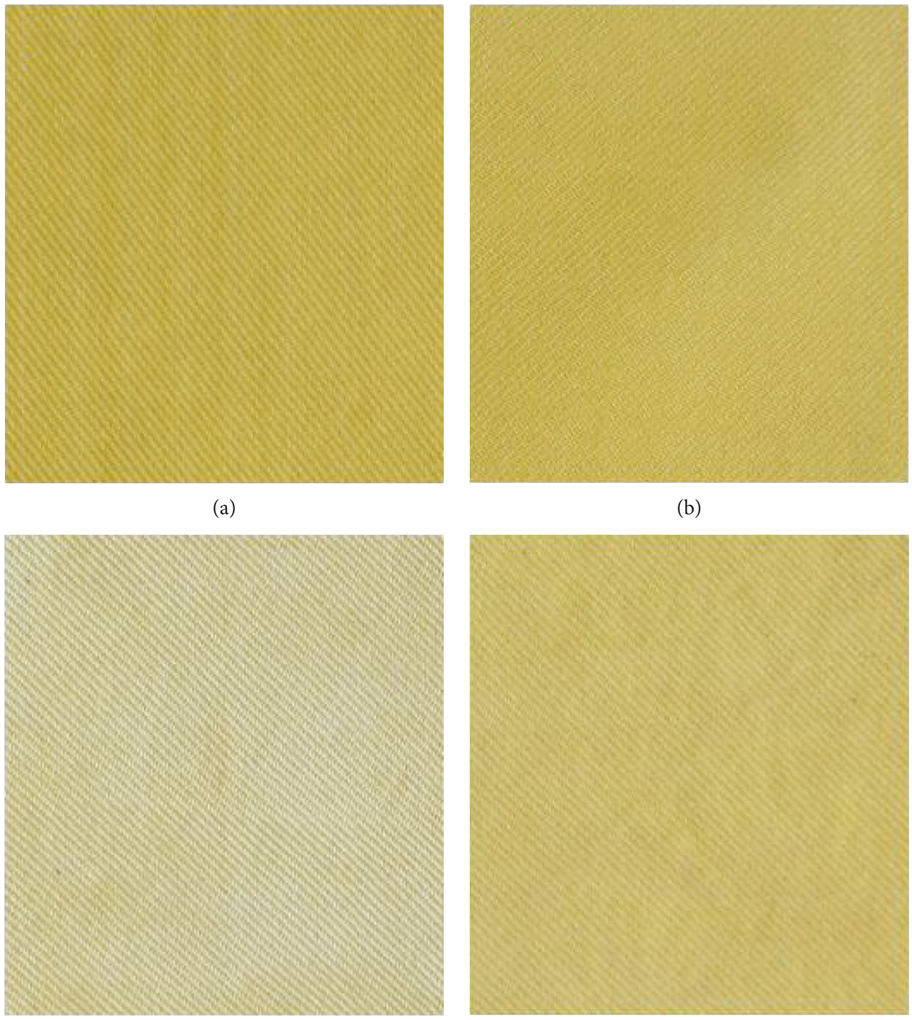


Figure 4: SEM observation of uncross-linked and cross-linked NCS filament before and after degumming ((a) and (b): uncross-linked fiber before and after degumming; (c) and (d): cross-linked fiber before and after degumming).

Table 1: Effects of repeated washing on the color of cross-linked and uncross-lined NCS fabrics.

Washing cycles	$\triangle L^*$		$\triangle a^*$		$\triangle b^*$		K/S		$\triangle E$	
	U	CL	U	CL	U	CL	U	CL	U	CL
1	-1.53	-1.01	-0.62	-0.93	-0.54	-2.33	3.22	3.05	1.74	2.70
5	-2.62	0.28	-2.04	-1.42	-4.01	-4.22	2.57	2.83	5.21	4.46
10	0.27	0.46	-2.19	-1.75	-6.09	-5.05	2.15	2.55	6.48	5.46
15	1.06	0.75	-2.65	-1.88	-9.64	-5.54	1.63	2.21	10.05	5.90
20	1.76	1.22	-3.46	-2.07	-15.92	-7.37	0.90	2.04	16.39	7.75

U: uncross-lined sample; CL: cross-linked sample; $\triangle L^*$, $\triangle a^*$, $\triangle b^*$, and $\triangle E$ are the difference of L^*, a^*, b^*, and E value of the samples before and after washing. The L^*, a^*, b^*, and K/S value of control were 74.91, 7.81, 51.47, and 3.68, respectively.



(a) (b) (c) (d)

Figure 5: Picture of cross-linked and uncross-linked NCS fabrics before and after washing for 20 cycles.

as measured by SDS-PAGE. The sericin cross-linked at acidic condition (e.g., pH 4.1) showed low and narrow-distributed molecular weight similar to that of the original sericin, which was around 20 kDa. The sericin cross-linked at both pH 7.4 and pH 9.8 exhibited high molecular weight chains continuously and was broadly distributed from 20 kD to 300 kD. Furthermore, the sericin cross-linked at pH 7.4 showed darker smear at a high molecular weight range (70-250 kD) than the sericin cross-linked at pH 9.8, indicating that a better cross-linking effect could obtain at neutral condition. This is in accordance with the sericin fastness of the NCS filament cross-linked at different pHs as shown above.

It is well known that chemical cross-linking results in forming a stable network of the chains and therefore increases the thermostability of polymers. The TG and DTG curves of the NCS fiber before and after cross-linking are shown in Figure 3. After cross-linking, the NCS fiber became more thermostable due to the formed network chains. Furthermore, the peak at 364.4°C which is attributed to the thermolysis of the side chains of sericin molecules has shifted to 368.7°C after cross-linking. The weight residue of the cross-linked sample at 800°C was 1.1% more than that of the uncross-lined sample. These results both confirmed that the cross-linking took place between NCS and phytic acid. It should be noted that the amount of amino-containing amino acid residues of silk fibroin is very less [18]; thus, the cross-linking mainly took place with sericin rather than silk fibroin.

Figure 4 shows the surface morphology of combined NCS filaments before and after degumming. It is clearly seen that both the uncross-linked and cross-linked NCS have a rough surface with sericin bonding several raw filaments together (Figure 4(a) and 2(c)). After degumming, the sericin of the uncross-linked NCS fiber has been completely removed and left the fiber with a smooth surface and apart from each other (Figure 4(b)). However, there was still a considerable amount of sericin presented on the surface of the cross-linked NCS (Figure 4(d)), indicating a considerable sericin-fixing effect by cross-linking with phytic acid. Due to the considerable amount of residual sericin and the pigment in the sericin layer, the cross-linked NCS still showed an acceptable depth of color (picture not shown), as compared with the uncross-linked NCS which completely lost the color.

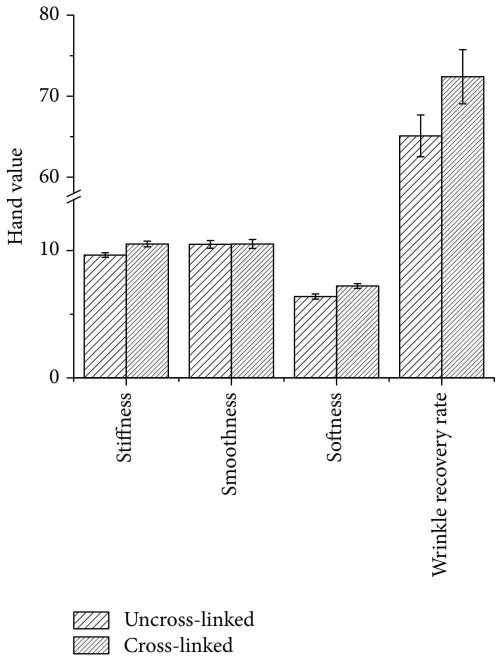


Figure 6: Fabric hand values of NCS before and after cross-linking.

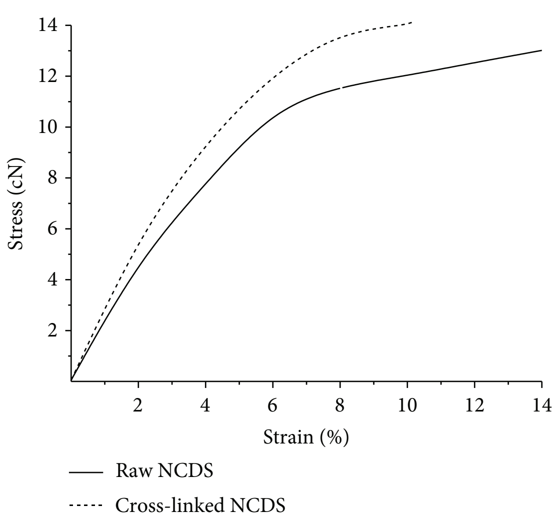


Figure 7: Typical stress and strain curve of NCS fiber before and after cross-linking with phytic acid.

3.3. Improvement in Color Fastness to Repeated Washing. As previously reported, NCS fabrics suffer significant changes in color when exposing to the temperatures higher than 105°C and the pH exceeds 11.0 [2]. Owing to the moderate pH and temperature conditions, cross-linking the sericin with phytic acid did not cause a visible color change of NCS. The cross-linking resulted in slight yellowing of NCS fabrics; as shown in Table 1, the L^* value decreased by 0.1 from 74.9 and b^* value increased by 2.2 from 51.5. However, the yellowing was not significant as observed by the naked eyes (Figure 5). The cross-linked and uncross-linked samples both gradually became lighter in color as the washing cycles increased. After washing for 20 cycles, the K/S value of the uncross-linked sample decreased from 3.68 to 0.9. However, the cross-linked sample had much higher retention in color depth, still having a final K/S value of 2.04. Repeated machine washing made NCS fabrics dull. The color of cross-linked and uncross-linked NCS fabrics had a tendency of greening and bluing as the a^* and b^* value decreased gradually. However, as compared with the uncross-linked samples, the cross-linked samples had much better retention in color hue. After washing for 20 times, the cross-linked sample showed a total color change ($\triangle E$) of 7.75, which was much lower than the $\triangle E$ value (16.39) of the uncross-linked sample. It is clearly seen that the cross-linked sample exhibited the color much deeper and brighter than that of the uncross-linked sample after 20 washing cycles (Figure 5). These results indicated that cross-linking of sericin with phytic acid significantly improved the color fastness of NCS to repeated washing. Clothing use is a major application of NCS products; cross-linking NCS with phytic acid undoubtedly improves the application performance of this green textile material.

3.4. Effects of Cross-Linking on the Fabric Hand and Mechanical Properties. Cross-linking of a textile material decreases the flexibility of the polymer chains and usually leads to a poorer fabric hand [21, 22]. There are three basic parameters for evaluating the fabric hand, i.e., stiffness, smoothness, and softness, which refer to the resistance offered by a fabric to bending, slipping, and compressing, respectively. Figure 6 shows the fabric hand values of the NCS fabrics before and after cross-linking. The stiffness value of NCS increased to 10.52 from 9.65 after cross-linking, indicating a slight increase in stiffness. The smaller the softness value, the softer the fabric will be. The cross-linked sample showed a softness value of 7.22 which was higher than that of the uncross-linked samples (6.39). This indicates a limited decrease in softness. The smoothness of NCS was kept almost constant before and after cross-linking. Similar to other chemically cross-linked textiles [21, 22], the NCS showed a significant improvement in the wrinkle recovery rate after being cross-linked with phytic acid, which was increased to 72.4 from 65.1. Silk fabrics are known for their relatively bad wrinkle recovery properties. Cross-linking of NCS using phytic acid did not cause a significant negative change in the fabric hand but improved the resistance of NCS to wrinkling.

Cross-linking with phytic acid changed the mechanical properties of the NCS fiber significantly. As shown in Figure 7, the breaking tenacity and initial modulus of the NCS fiber increased by 6.9% and 18.5%, but the elongation at break decreased by 27.2%. This could be attributed to the fact that cross-linking of NCS resulted in the formation of the cross-linking network structure and decreased the mobilization of the polymer chain under stress [21]. As well as we have known, silk is a kind of a flexible textile fiber as compared with other natural fibers; limited change in flexibility will not remarkably affect its fabric hand as shown in Figure 6.

4. Discussion

Cross-linking of the sericin of NCS with phytic acid could significantly decrease the water solubility of the sericin and improve the color fastness of NCS to repeated washing. The cross-linking did not cause a significant change in color and sensible change in the fabric hand of NCS. The green cross-linker phytic acid developed in this study is of potential interest not only for fixing the color of NCS products but also for sericin-modified textiles or biomaterials, because (1) the cross-linking occurs in aqueous solution at moderate conditions, such as at pHs around 7.0, low temperatures (30-40°C), and relatively short time (5 h), (2) the reaction did not produce any byproduct and the cross-linker phytic acid is a nontoxic natural product, (3) cross-linking the sericin does not cause any adverse effects on the fabric hand and color, and (4) the cross-linker is cheap (approximately 6.0 US dollar/kg) and available easily.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

No conflict of interest was declared by the authors.

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