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Structure and Properties of Cationic Chitosan Derivative Modified *Bombyx mori*

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Abstract
Cationic modification of silk fabric can highly improve its antibacterial property, but cationic modification may change the microstructure of silk fiber, and further affect its properties, thus O-methyl acrylamide quaternary ammonium salt of chitosan (NMA-HTCC), which is a kind of strong cationic chitosan derivative, was used for the modification on *Bombyx mori* silk fiber. The combination structure between NMA-HTCC and silk fiber was characterized by FT-IR. The surface morphology and structure of silk fiber after being treated by NMA-HTCC were investigated by SEM and XPS analysis. The crystalline structure and thermal stability of silk fibers before and after being treated were determined by XRD and DSC analysis, respectively. Then the breaking strength, breaking elongation and antibacterial properties of the silk yarns were also determined. The results indicated that the NMA-HTCC modified silk fiber clearly showed two characteristic absorption peaks at 1535 cm^{-1} and 1670 cm^{-1} due to the N-H bending and C=O stretch of the secondary amide in the acrylamidomethyl group of the NMA-HTCC molecule. The successful combination of NMA-HTCC and silk fiber was also confirmed by XPS and SEM analysis. Compared with the untreated silk sample, the diffracted intensity of the characteristic absorption peak and crystallinity of the NMA-HTCC modified silk fiber were both increased; the internal aggregation structure of the silk fiber treated with NMA-HTCC was much closer and its thermal stability was enhanced obviously. The breaking strength and elongation of silk fibers after being treated with NMA-HTCC were also significantly increased. Silk fibers treated with NMA-HTCC had excellent durable antibacterial properties against *S. aureus* and *E. coli*, even after 50 repeated launderings, with the bacterial reduction rate of the silk fibers maintained at over 95 %. The results in this research can provide the theoretical basis for the application of NMA-HTCC in the modifications of silk fabric.

Keywords
Chitosan quaternary ammonium salt, NMA-HTCC, B. mori silk fiber, microstructure, antibacterial property.

1. Introduction

Bombyx mori silk is a kind of traditional high-grade garment fabric. It has many excellent properties, including high porosity, good hygroscopicity, affinity to skin, UV resistance and so on. However, silk fabric is often considered to be more vulnerable to microbe attack than man-made fabrics because of its hydrophilic porous structure and moisture transport characteristics. Therefore, the use of antimicrobial agents to prevent the growth of bacteria on silk fabric is becoming a promising method to meet the demands on the commercial silk textile market. Acid dyes and direct dyes are commonly used in silk dyeing, but the washing fastness of dyed silk is very low. In recent years, reactive dyes have been used more and more in silk dyeing, as reactive dye molecules can react with silk fibroin molecules to form a covalent bond; thus, wet treatment fastness is very high, generally reaching level 4 or above [1-3]. But the silk fixing rate of reactive dyeing is very low and a large number of neutral salts is needed to promote the dyeing effect, as a result of which the dyeing wastewater with such a high salt content can cause serious environmental pollution [4]. In order to improve the silk soaping fastness of reactive dyeing and reduce dyeing wastewater pollution, cationic modification of silk fabric is becoming more and more important. Reactive dye is a kind of anionic dye, and cationic modified silk can firmly combine with anionic dye. Consequently, the salt consumption can be greatly reduced, even to realize salt-free dyeing on the basis of not reducing the dyeing fastness, which can greatly reduce the pollution to the environment [5-7]. On the other hand, cationic modification of silk fabric can significantly improve its antibacterial property, because negatively charged bacterium is easily absorbed by cationic substances and then its synthesis of cell wall is disturbed, which makes it die.

NMA-HTCC is a kind of water soluble, strong cationic and highly reactive chitosan derivative. 2-hydroxypropyltrimethyl ammonium chloride chitosan (short for HTCC) is synthesized by the chemical reaction of chitosan and 2,3-epoxypropyltrimethyl ammonium chloride, and then NMA-HTCC is synthesized by the chemical reaction of HTCC and N-(hydroxymethyl) –acrylamide [6-9]. NMA-HTCC has a good antibacterial property, and can be used as cationic surface-active agent, metal ion flocculant ,and so on. Some scholars observed that NMA–HTCC had excellent antimicrobial activity against both *S. aureus* and *E. coli* compared to chitosan, which did not dissolve in pH 7.2 and did not show any antimicrobial activity under this condition, with the highest antimicrobial activity being observed at the lowest concentration (10 ppm) of the NMA–HTCC. In the textile field, it can be used for the modification of fabric, so as to improve its antibacterial property and dyeing fastness [4,10-14].

Cationic modification of silk fabric may change the microstructure of silk fiber, and

further affect its properties. Thus NMA-HTCC was used for the modification of *Bombyx mori* silk fiber in this paper, and then the micro-morphology, aggregation structure, mechanical properties and antibacterial activity of silk fibers before and after treatment were tested, which can provide the theoretical basis for the application of NMA-HTCC in silk finishing.

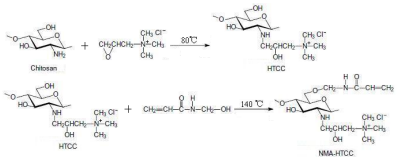
2. Experimental

2.1. Materials

Bombyx mori silk yarn (after degumming) was commercially available. Chitosan (deacetylation degree - 92 % and molecular weight - 2×10^4), 2,3-epoxypropyltrimethyl ammonium chloride, N-(hydroxymethyl) -acrylamide, 4-methoxyphenol and ammonia chloride were provided by Yancheng Chunyu chemical Co. Ltd.. All chemical reagents, including isopropyl alcohol, sodium bicarbonate, ethanol and acetone, used for the following investigations were of analytical grade. Deionized water was used throughout the experiment.

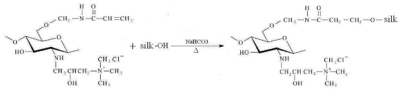
2.2. Synthesis of NMA-HTCC

Chitosan, 2,3-epoxy propyl trimethyl ammonium chloride and isopropanol were put into a 4-mouth flask. The solutions were reacted at 80 °C for 12 h in a water bath, washed with ethanol and acetone after cooling, then filtrated, dried, and the yellow product obtained was HTCC. After that, HTCC, N-methylol acrylamide, 4-methoxyphenol and NH_4Cl were put into the flask and stirred evenly until dissolution. The solutions were reacted at 140 °C for 15 min in the oil bath. Ethyl alcohol and acetone were put into the reaction solutions and stirred to precipitate the product [6,8]. The product was washed in the mixture of ethyl alcohol-acetone and dried. Finally, the white product obtained was NMA-HTCC. The reaction equation was as follows.



2.3. Treatment process of silk fiber with NMA-HTCC

NMA-HTCC contains reactive groups, such as methacrylamide groups. The side double bond of this group can undergo a crosslinking reaction with hydroxyl groups on silk fiber molecules under alkaline conditions. Alkaline sodium bicarbonate as a catalyst can not only catalyze crosslinking reactions but also facilitate effective permeation of NMA-HTCC into fiber by reducing the hydrolysis of NMA-HTCC and promoting the swelling of silk fiber. NMA-HTCC solution was prepared with a bath solution ratio of 1:50 and mass percent of NMA-HTCC, and $NaHCO_3$ was 6 % and 8 %, respectively [1,4,6,13]. The treatment process was as follows: silk fiber→ treated in NMA-HTCC solution at 60°C in the water bath for 1h→ pre-baked in an oven at 80°C for 5 min→ baked in the oven at 160°C for 3 min→ washed with deionized water→ dried at 80 °C. The reaction equation was as follows.



2.4. Fourier Transform Infrared (FT-IR) Spectroscopy

A Nicolet 5700 FT-IR spectrophotometer was used to observe the infrared spectra of the silk fiber with the traditional transmission technique of KBr pellets. The measurements were performed at 20°C and a relative humidity of 65 %.

2.5. Scanning Electron Microscopic (SEM) Analysis

The surface morphology of the silk fibers before and after being treated with NMA-HTCC was observed by a Quanta 200 scanning electron microscope. The measurements were performed at 20°C and a relative humidity of 65 %.

2.6. X-Ray Diffraction (XRD) Patterns Analysis

XRD patterns of silk powder samples were obtained by D/MAX-IIIC type X-ray diffraction with a tube voltage of 40 kV, tube current of 30 mA, and scan speed of 2º/min. The X-ray diffraction intensity curves of the three kinds of silk fibers were fitted by peakfit software, and their crystallinity was calculated by the peak separation method.

2.7. X-Ray Photoelectron Spectroscopy (XPS) Analysis

XPS spectra were observed by an XSAM 800 electron spectrometer. The samples were analyzed using MgK_α radiation (1253.6 eV) operating under a working pressure of 2×10^{-7} Pa in 0.1 eV steps with 100 eV analyzer pass energy. The X-ray anode was run at 180 W and the high voltage was kept at 12.0 kV. The position of the carbon peak (284.8 eV) for C1s was used to calibrate the XPS scale for all substrates. XPS data fitting was performed using the software with 100 % Gaussian curve fitting.

2.8. Differential Scanning Calorimetry (DSC) Analysis

Differential scanning calorimetry curves of silk powder samples were obtained by a CDR-4 type differential thermal analyzer with a heating rate of 5°C/min, a scanning temperature range from room temperature to 450°C, air with nitrogen, and a flow rate of 120 ml/min.

2.9. Determination of Breaking Load and Elongation

The breaking strength and breaking elongation of the silk yarn were determined on a YG020 type electronic single yarn strength tester at an effective gauge length of 250 mm and extension rate of 250 mm/min. The samples were put in a room with a temperature of 20°C and relative humidity of 65 % for more than 2 days before measurement. Each

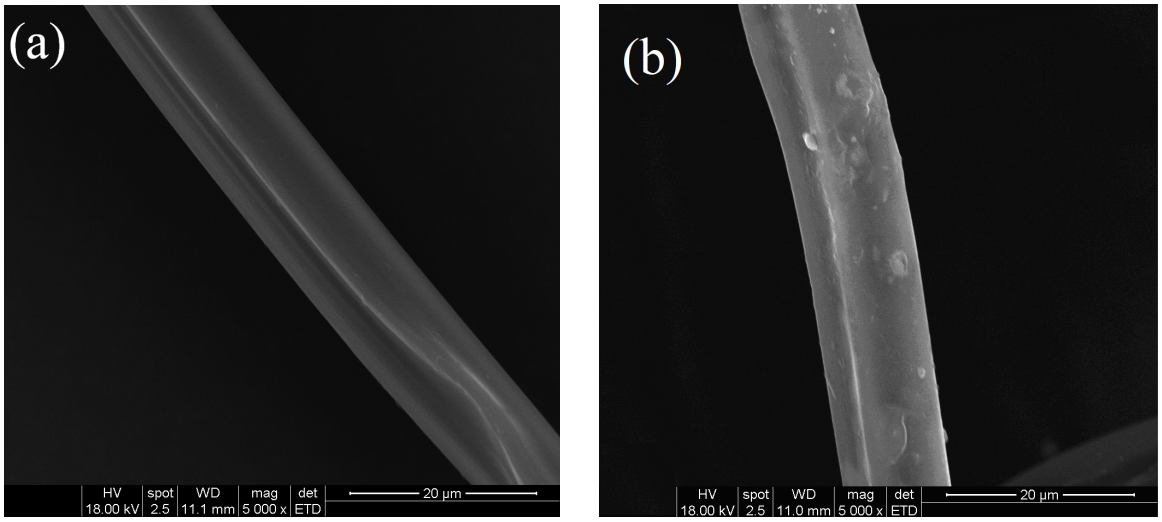


Fig. 1. Longitudinal surface photomicrographs of (a) untreated silk fiber and (b) modified silk fiber treated with NMA-HTCC (×5000)

sample was tested 10 times and the result was averaged with 10 data.

2.10. Antibacterial Activity Test of Silk Fiber

AATCC 100-2012 (Assessment of antibacterial finishes on textile materials) was conducted to evaluate the antibacterial activities of the silk fibers before and after being treated with NMA-HTCC. *Staphylococcus aureus* (ATCC 6538) and *Escherichia coli* (ATCC 25922) were chosen as the tested bacteria. The shake flask method was adopted and the bacteria reduction rate was calculated. The washing durability of NMA-HTCC modified silk fibers was evaluated according to AATCC 124-2010(Smoothness appearance of fabrics after repeated home laundering).

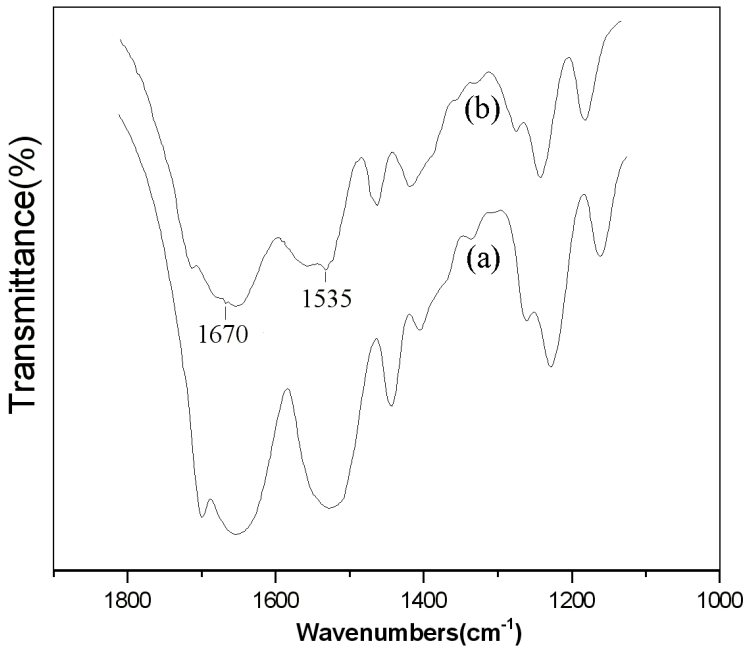


Fig. 2. FT-IR spectroscopy of (a) B. mori silk fiber and (b) modified silk fiber treated with NMA-HTCC

3. Results and Discussion

3.1. SEM Analysis

The longitudinal surfaces of the silk fibers before and after treatment with NMA-HTCC were morphologically observed by SEM. The longitudinal surface of the silk fiber before treatment, shown in Figure 1(a), was smooth, while many adhesive substances appeared on the surface when it was treated with NMA-HTCC, shown in Figure 1(b). This was mainly because NMA-HTCC had the fiber reactive methyl acrylamide group, whose side double bond could directly crosslink with the silk fiber under the alkaline condition. It indicated that NMA-HTCC had undergone a crosslinking reaction with the silk fibers[7-8].

3.2. FT-IR Spectroscopy

FT-IR spectra of the silk fibers before and after being treated with NMA-HTCC solution are shown in Figure 2. Two new peaks at 1535 cm^{-1} and 1670 cm^{-1} appeared after treatment with NMA-HTCC, which corresponded to the N-H bending and C=O stretch of the secondary amide in the acrylamidomethyl group of the NMA-HTCC molecule, respectively. On the other hand, the peak at 1630 cm^{-1} corresponding to the C=C stretch of the conjugated vinyl group did not appear after treatment with NMA-HTCC, because the C=C bond was a reactive group of NMA-HTCC [6,8,14], which disappeared when NMA-HTCC reacted

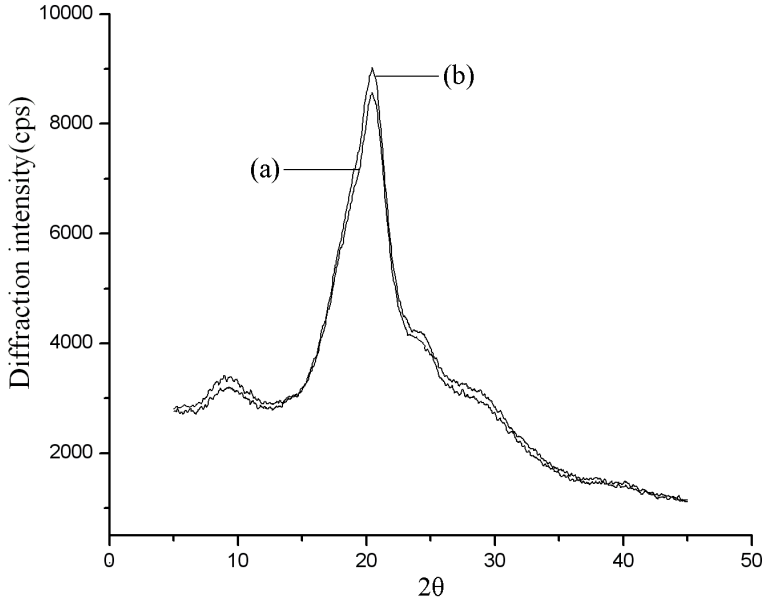


Fig. 3. XRD curve peak fitting of (a) Bombyx mori silk fiber, (b) NMA-HTCC modified silk fiber

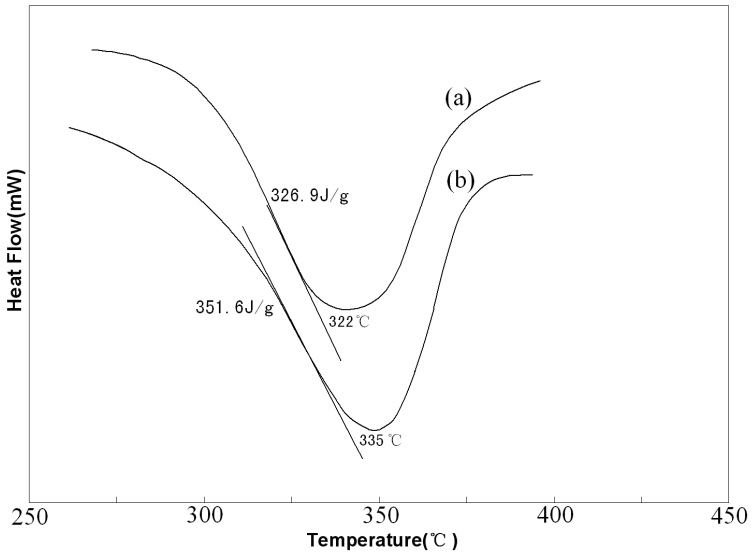


Fig. 4. DSC diagram of (a) Bombyx mori silk and (b) modified silk treated with NMA--HTCC

with the silk fibers. All of these displayed that NMA-HTCC had undergone a cross-linking reaction with the silk fiber and successfully entered into the fiber.

3.3. XRD Patterns of Silk Fiber

Figure 3 shows the XRD curves for the silk fibers before and after NMA-HTCC solution treatment. The 2θ of two characteristic absorption peaks on curve (a) was very close to that on curve (b), illustrating that treatment with NMA-HTCC could not change the crystalline structure of silk fiber. The crystallinity of silk samples before and after NMA-HTCC treatment were calculated by the peakfit method, with the results showing that the crystallinity of the silk fiber was 48.26 %, while it increased greatly to 61.37 % after treatment with NMA-HTCC [15]. It illustrated that the crystallinity of the silk fiber could be increased significantly by treatment with NMA-HTCC. The reason was that the high temperature baking provided more chances for silk fiber to react with the active group in the NMA-HTCC molecule, and it was easy for NMA-HTCC to enter into the silk fiber; thus, the internal structure of the silk fiber was enhanced, and the diffracted intensity of the characteristic absorption peak and the crystallinity of the silk fiber were both increased.

3.4. Differential Scanning Calorimetry Analysis

Figure 4 shows the DSC curves for the silk fibers before and after NMA-HTCC solution treatment. Similar characteristics are shown on two curves, where the thermal decomposition of the endothermic temperature was 322°C and 335°C, respectively, and the thermal decomposition and absorption of heat was 326.9 J/g and 351.6 J/g, respectively. It illustrated that the thermal decomposition of the endothermic temperature and absorption of heat of the silk fiber were significantly increased after the NMA-HTCC treatment [6]; thus, the internal aggregation structure of the silk fiber treated with NMA-HTCC was much closer and its thermal stability was obviously enhanced.

3.5. XPS Analysis

The chemical composition of the silk fiber surfaces was determined by X-ray photoelectron spectroscopy. The N1s XPS spectra of the silk fibers before and after being treated with NMA-HTCC are shown in Figure 5. From Figure 5(a), we observe that N1s XPS spectra of the silk fiber only had one peak at 399.7 eV, while that of the silk fiber after treatment had two peaks at 400.50eV and 399.50eV in Figure 5(b). It implies that the nitrogen binding mode of the silk fiber had changed after treatment with NMA-HTCC, which was the result of the cross-linking reaction between the NMA-HTCC molecule and silk fibroin[16]. A composition analysis of N(1s) is shown in Table.1 from which we can calculate that the peak area of 399.50 eV accounted for 46.1 % and the peak area of 400.50 eV for 53.9 %.

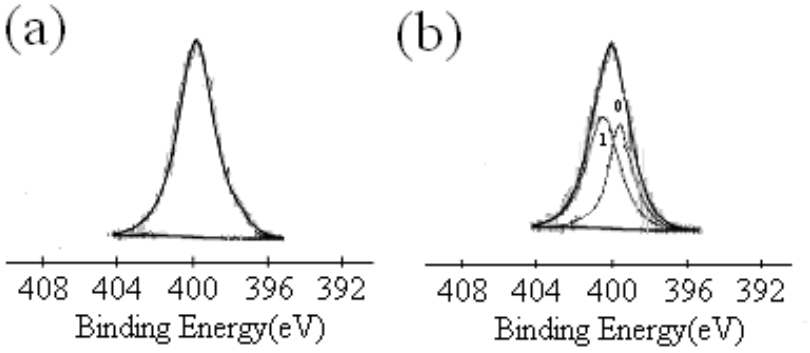


Fig. 5. XPS spectra of N1s peaks for silk fibers: (a) before treatment, (b) after treatment with NMA-HTCC

Parameter of peak	Before treatment	After treatment	
		0 peak	1 peak
Binding energy/eV	399.70	399.50	400.50
Half peak width/eV	2.13	1.89	1.99
Peak area	251.67	68.16	79.68

Table 1. Composition analysis of N(1s)

Element composition	Surface element content of silk fiber (%)		Change rate (%)
	Before treatment	After treatment	
C	83.44	86.19	+3.30
O	9.42	8.79	-6.69
N	5.20	2.19	-57.88

Table 2. Elements on the surface of silk fiber

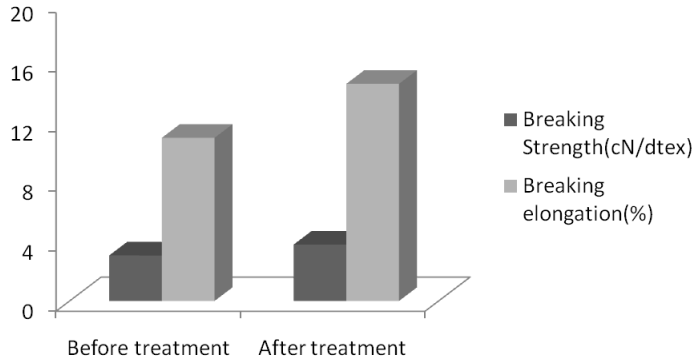


Fig.6. Breaking strength and breaking elongation of silk fibers

Element content on the surface of the silk fiber before and after NMA-HTCC treatment is shown in Table.2, from which we observe that the content of the N element was significantly reduced. This is mainly because that the content of the N element in the NMA-HTCC macromolecule is obviously lower than that in the silk fiber. When a certain amount of NMA-HTCC reacts with silk fibroin fiber, the overall content of the N element will drop, which implies that the NMA-HTCC molecule has undergone a cross-linking reaction with the silk fibroin.

3.6. Breaking Strength and Elongation

Figure 6 shows the breaking strength and breaking elongation of silk fibers before and after NMA-HTCC treatment. Compared with the untreated sample, the breaking strength and elongation of silk fiber after being treated with NMA-HTCC were significantly increased. This is principally because when NMA-HTCC molecules enter into the internal structure of silk fiber, the binding force between the silk fibroin molecules is enhanced, and the internal structure of silk fibers is closer thus, the mechanical properties of silk fibers are improved.

3.7. Antibacterial activity and laundering durability of silk fiber

Figure 7 shows the bacterial reduction rate of silk fibers treated by NMA-HTCC against *S aureus* and *E. coli*, respectively. It shows that the antibacterial activity of

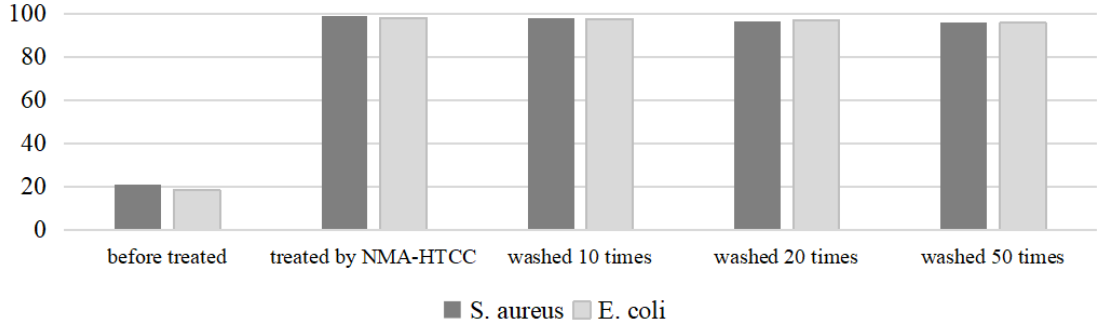


Fig. 7. Antibacterial activities of silk fibers

silk fiber could be improved significantly after NMA-HTCC treatment. NMA-HTCC is a strongly cationic compound with positive charge, which can combine with negatively charged bacteria to inhibit the propagation of bacteria and kill them. The bacterial reduction of silk fibers treated by NMA-HTCC after 10, 20 and 50 launderings was tested, respectively. The results showed that the bacterial reduction of the modified silk fiber for *S. aureus* and *E. coli* was maintained at over 95 % for both even after 50 repeated launderings. This was because that NMA-HTCC could undergo a cross-linking reaction and combine firmly with silk fibers. Thus, the antibacterial activity and laundering durability of silk fiber after treatment with NMA-HTCC were excellent.

4. Conclusion

In order to prepare cationic silk fiber, NMA-HTCC, which is a kind of strong cationic chitosan derivative, was used for the modification of *Bombyx mori* silk fiber in this paper. In order to research the microstructure of silk fiber treated with NMA-HTCC, FT-IR was used to characterize the combination structure between NMA-HTCC and silk fiber. The result indicated that the NMA-HTCC modified silk fiber clearly showed two new characteristic absorption peaks due to the N-H bending and C=O stretch of the secondary amide in the NMA-HTCC molecule. SEM and XPS were used to investigate the surface morphology and structure of silk fiber, with the result showing that the longitudinal surface of the silk fiber before treatment was smooth, while many adhesive substances appeared on the surface when it was treated with NMA-HTCC. The N1s XPS spectra of untreated silk fiber only had one peak at 399.7 eV, while those of the NMA-HTCC modified silk fiber had two peaks at 400.50 eV and 399.50 eV, and the N element content of the silk fiber after treatment was significantly reduced. XRD and DSC were used to determine the crystalline structure and thermal stability of silk fibers before and after being treated, the results of which showed that the diffracted intensity of the characteristic absorption peak and the crystallinity of the NMA-HTCC modified silk fiber were both increased, the internal aggregation structure of the silk fiber treated with NMA-HTCC was much closer, and that its thermal stability was obviously enhanced. The mechanical properties of the silk fiber were also determined, where the breaking strength and elongation of silk fibers after being treated were significantly increased. The antibacterial activity of silk fiber against *S. aureus* and *E. coli* could be improved significantly after NMA-HTCC treatment, and for both was maintained at over 95 % even after 50 repeated launderings.

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