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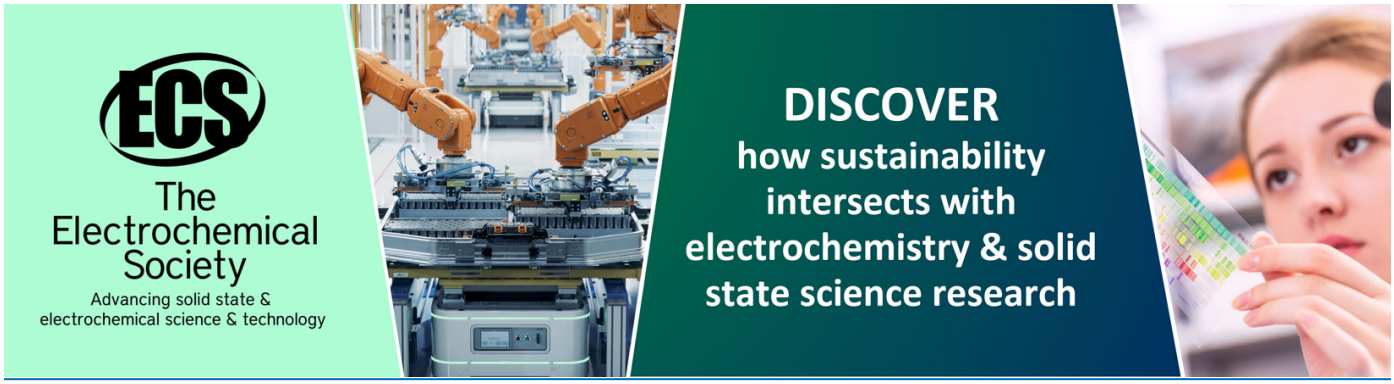


Synthesis of cationic graft modified chitosan and its antibacterial finish on rabbit wool fabric

Yu Han Bai , Yi Zhang, Hao Zhang[1] and Xue Lu

School of Textile Science and Engineering, Tiangong University, Tianjin, China

[1]Email:zhanghaoyangyong@163.com

Abstract. As a natural polymer antibacterial agent, chitosan itself has excellent characteristics, but its application is limited due to its poor solubility. Based on this, using ammonium persulfate ($(NH_4)_2S_2O_8$) and sodium bisulfite ($NaHSO_3$) as redox initiators, a cationic antibacterial monomer was grafted onto chitosan to prepare a new type of modified chitosan. The target product was successfully analyzed by infrared spectrum analysis and XPS energy spectrum analysis. Using polycarboxylic acid as a cross-linking agent and modified chitosan as an antibacterial agent, the rabbit wool fabric was finished, and the finished fabric was tested for antibacterial properties and washing resistance. The effect of graft-modified chitosan with different reaction conditions on the antibacterial finishing fabric, such as the ratio of monomer to chitosan substance, reaction temperature, and the amount of initiator added, was studied. The results showed that the finished rabbit wool fabrics had good antibacterial effects on E. coli, and their antibacterial rates reached 100%, and after 20 washings, the antibacterial rate still reached 100%, with long-lasting antibacterial properties. Considering the cost, the ratio of the amount of the chitosan to the monomer was finally selected as 4: 1 to prepare the modified chitosan.

1. Introduction

Textile antibacterial finishing agents are basically divided into inorganic antibacterial agents, organic antibacterial agents, polymer antibacterial agents, etc [1]. As a natural polymer antibacterial agent, chitosan is favored by people because of its excellent characteristics. Compared with general antibacterial agents, it has the advantages of broad spectrum, high antibacterial activity, and low toxicity to mammalian cells [2], but its application is limited to some extent due to its poor solubility [3-4]. The molecular structure of chitosan contains active hydroxyl and amino groups, and functional functional groups can be introduced into the molecular structure of chitosan through chemical modification to obtain chitosan derivatives, which can improve antibacterial properties and other physical and chemical properties and expand the scope of application [5,6,7].

At present, common chitosan modification methods are: quaternization, acylation, carboxylation, graft copolymerization, etc. [8,9,10]. Chitosan's water solubility can be improved after quaternary ammonium salt modification [11]. Quaternization is mainly an amino group at the C2 position of chitosan. The chitosan quaternary ammonium salt can be synthesized by the halogenation method with an alkyl halide, or it can be directly reacted with the quaternary ammonium compound to generate chitosan quaternary ammonium[12]. Acylation modification is the reaction of amino and hydroxyl groups on chitosan macromolecules with different organic acid derivatives such as acid anhydrides and acid chlorides, and the introduction of aromatic or aliphatic acyl groups with different relative molecular weights on their macromolecular chains [13]. Carboxylated chitosan has good water

solubility, not only has the advantages of strong antibacterial properties, good freshness, etc. but it is also an amphoteric polyelectrolyte [14-15]. Graft copolymerization is the introduction of alkyl chains, polyether chains, and high polymers on the hydroxyl and amino groups of chitosan [16] to change the molecular structure, the type and number of branches of chitosan to improve its solubility and biocompatibility, and to give it new properties [17,18].

In this study, a new type of reactive cationic antibacterial monomer was synthesized, and the chitosan was modified by graft copolymerization method to form a new type of modified chitosan polymer antibacterial agent. the study. And it was applied to the antibacterial finishing of wool fabrics by cross-linking agents, and the antibacterial properties and wash-ability of the finished fabrics were studied.

2. Experimental

2.1. Materials

Reagents: Dimethylaminoethyl acrylate(DMAEA)and tetradecane bromo were provided by Shanghai civic chemical co. LTD; Tianjin fengchuan chemical reagent technology co., LTD. Provides ammonium persulfate ($(NH_4)_2S_2O_8$), sodium bisulfite ($NaHSO_3$), citric acid, acetic acid and sodium hypophosphite(NaH_2PO_2); Chitosan was provided by Shanghai McLean biochemical technology co., LTD., the deacetylation degree of chitosan was 80.0-95.0%; Beijing aoboxing biotechnology co., LTD. provides peptonechlorine Sodium, beef extract and agar. E. coli (ATCC 29522) was provided by Shanghai luwei technology co., LTD.

2.2. Methods

2.2.1. Synthesis of antibacterial monomer. To a double-necked spherical round-bottom flask equipped with a constant-pressure dropping funnel and a condensing reflux device, added 8.4 mL DMAEA in it. Heated in a constant temperature water bath at 40-45℃, and continuously stirred. Added 13.9mL bromotetradecane, and the reaction was performed for 6 hours. Removed it and cooled it.

2.2.2. Synthesis of Graft Modified Chitosan. 0.15g $(NH_4)_2S_2O_8$ and 0.05g $NaHSO_3$ were dissolved in 10mL of distilled water to make an initiator for later use. To the 100 mL flask added 1g of chitosan, 20 mL of distilled water. Then heated in a constant temperature water bath at 45 ℃, and keep stirring. Added 1 mL of monomer, after 15 mins added the initiator dropwise and finish it within 30 min, and react for 3 h. After the reaction, centrifuged the mixture in ethanol (50%) Three times with High speed centrifuge.

2.2.3. Characterization. FTIR: Nicolet 5700 infrared spectrometer was used for testing. KBr tablets were pressed at a constant temperature of 20℃ and a relative humidity of 65%.

XPS: The elemental composition of the modified chitosan was characterized by X-ray photoelectron spectroscopy (XPS, GENESIS 60S, Gemany).

2.2.4. Finishing process of rabbit fur fabric with modified chitosan. To a flask added 40 mL of distilled water, 2 g of citric acid, 0.5 g of modified chitosan, 0.5 mL of 0.5% acetic acid solution. Heated in a constant temperature water bath at 50℃, and continuously stirred. After all the modified chitosan dissolved, added two pieces of 0.75g rabbit fur fabric (one for finishing and one for washing after finishing), 1g of NaH_2PO_2, 0.25mL of JFC (Primary Alcobol Ethoxylate). For 30mins, rolling them with a residual rate of 50%. Dipping them for 30mins, the second rolling was carried out with a residual rate of 200%. Dried it at 80℃ for 5min, then at 130℃ for 10min, took out it and air-dried.

2.2.5. Performance test of finished rabbit fur fabric. Antibacterial performance: According to GB / T 20944.3-2008 "Evaluation of antibacterial performance of textiles-Part 3 shaking method", the shaking

flask method was used to determine the antibacterial performance of E. coli before and after treatment, and the antibacterial rate was calculated according to the following formula:

$$Y=\frac{W_t-Q_t}{W_t}\times 100\% \quad (1)$$

In the formula: Y-the bacteriostatic rate of the sample; W_t -the concentration of live bacteria in the control flask (CFU/mL); Q_t-the concentration of live bacteria in the flask of the experimental group (CFU/mL).

Washing resistance: For the washing method, refer to "GB/T 20944.3-2008 Textiles for the evaluation of antibacterial properties. Part 3: Oscillation method". Compared with the unwashed finished fabric samples, whether the bacteriostatic rate decreased, and the fastness to washing was determined.

3. Results and discussion

3.1. Reaction principle

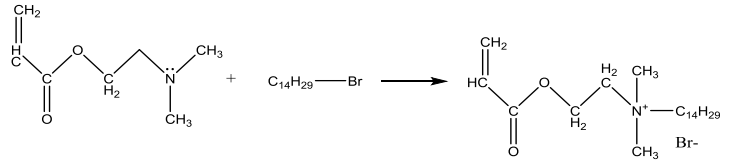


Figure 1. Synthesis process of cationic antibacterial monomer.

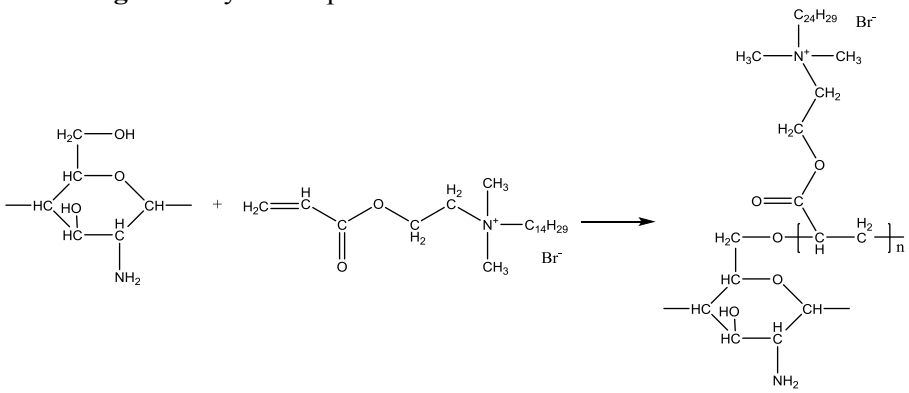


Figure 2. Synthesis process of modified chitosan.

Figure 1 shows the synthesis process of cationic antibacterial monomers. The nucleophilic substitution reaction occurs between dmethylaminoethyl acrylate and bromotetradecane to generate antibacterial monomers with long chain alkyl groups and cationic groups. Figure 2 shows the synthesis process of modified chitosan. The synthesized antibacterial monomer and chitosan undergo graft copolymerization under the initiation of REDOX initiator to synthesize cationic graft chitosan.

3.2. FTIR

Figure 3 is a comparison chart of infrared spectra of modified chitosan and chitosan. It is known that the peak of the carbonyl group is between 1760cm-1-1680cm-1. It can be seen from the figure that the chitosan has no absorption peak between 1760cm-1-1680cm-1, and the modified chitosan has absorption at 1733cm-1. The peak indicates that there is no carbonyl group in the chitosan, but that the modified chitosan contains a carbonyl group, indicating that the carbonyl group is derived from a monomer, indicating that the monomer was successfully grafted onto the chitosan.

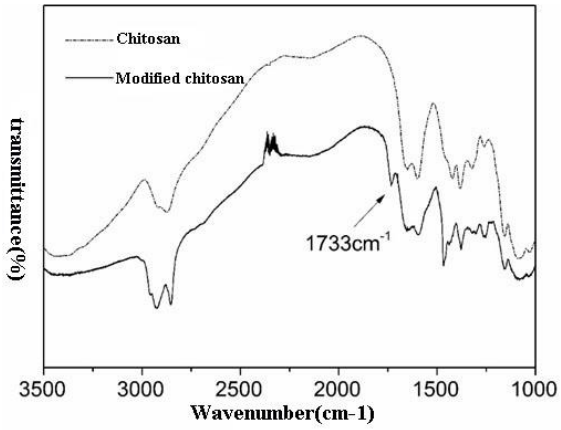


Figure 3. FTIR of modified chitosan and chitosan.

3.3. XPS

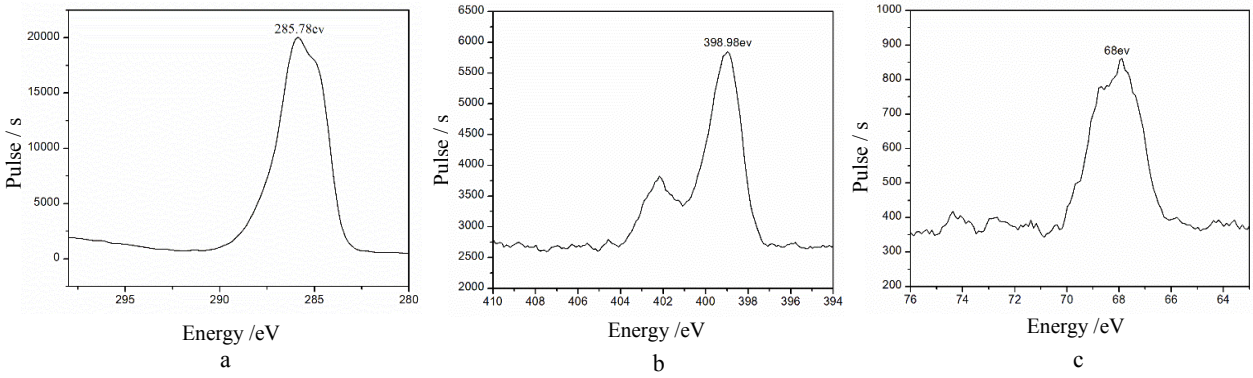


Figure 4. XPS of modified chitosan (a: C atom; b: N atom; c: Br atom).

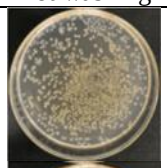
In Figure 4, 'a' corresponds to the C atomic electron spectrum in the modified chitosan, 'b' to the N atomic electron spectrum in the modified chitosan, and 'c' to the Br atomic electron spectrum in the modified chitosan. As can be seen from figure a, it presents a peak with a binding capacity of 285.78eV, corresponding to the C atom in $MeCH_2NH_2$, which indicates that the C atom in the modified chitosan is connected between the methyl and the N atom, and the N atom is the N atom in the quaternary ammonium salt. In addition, we can also see from other peaks that C is connected to O and H. In figure b, the electron spectral line of N atom in the modified chitosan is corresponding, where the binding energy is 398.98eV peak, and the corresponding N is connected between C atoms. The other peak of binding energy of 401eV corresponds to that the N atom is connected between the ethyl and the halogen atoms, which is the N in the monomer, which also further indicates that the monomer is grafted to the chitosan. In figure c, the XPS electron spectra of Br atom in the modified chitosan showed a peak value of 68eV, indicating that the Br atom was connected to methyl and N atoms. The XPS test results showed that the effective bromine content was 0.48%, and the grafting rate was 2.75% based on the molecular weight of the bromine group.

3.4. Antibacterial performance analysis of rabbit fur fabric

3.4.1. Antibacterial finishing of fabrics with modified chitosan made from different amounts of monomers. Single factor control method was used to change the amount of monomer added. According to the ratios of 2:1, 3:1 and 4:1 between chitosan and monomer, the monomers used were calculated to be 1.3g, 0.85g and 0.65g, and three modified chitosan were prepared, which were

denoted as A, B and C. The rabbit wool fabric was treated according to the above finishing technology. Three kinds of chitosan A, B and C were used to conduct antibacterial finishing on the rabbit hair fabric respectively. Other conditions remained unchanged, and the antibacterial test and washing fastness were carried out on the rabbit hair fabric. The results were shown in Table 1 compared with the blank (the antibacterial property of the unfinished fabric).

Table 1. Antibacterial effect of modified chitosan-treated fabrics prepared with different monomer amounts.

Sample	Antibacterial effect(10^{-3})		Bacteriostatic rate Y	
	Not washing	Washing 20 times	Not washing	Washing 20 times
Blank		-	-	-
A. 2 : 1			100%	100%
B. 3 : 1			100%	100%
C. 4 : 1			100%	100%

3.4.2. Antibacterial finishing of fabrics with modified chitosan prepared at different reaction temperatures. The single-factor control method was used to change the reaction temperature. The temperatures of the modified chitosan were 40℃, 45℃ and 50℃, and other conditions remained unchanged. Three kinds of chitosan I (40℃), II (45℃) and III (50℃) were used to conduct antibacterial finishing on the rabbit hair fabric respectively. The Antibacterial results were shown in Table 2 compared with the blank (the antibacterial property of the unfinished fabric).

3.4.3. Antibacterial finishing of fabrics with modified chitosan made with different amounts of initiator. Single factor control method was used to change the amount of initiator. Different initiators were added in the preparation of modified chitosan, Other conditions remained unchanged. the chitosan a($(NH_4)_2S_2O_8$:$NaHSO_3$=0.18g:0.06g), b($(NH_4)_2S_2O_8$:$NaHSO_3$=0.3g:0.1g) and c($(NH_4)_2S_2O_8$:$NaHSO_3$=0.45g:0.15g) were used to conduct antibacterial finishing on the rabbit wool fabric, other conditions remained unchanged, and the antibacterial testing and washing fastness were carried out. The results were shown in Table 3 compared with the blank (the antibacterial property of the unfinished fabric).

The single factor control method was used to modify the modification conditions. Three groups of modified chitosan-treated fabrics were tested for antibacterial activity, and the washing group was used as a control. From the number of colonies in the petri dish, the bacteriostatic rate reached 100% in both the washed group and the unwashed group, indicating that the modified chitosan has a good antibacterial effect and has a longer-lasting effect than ammonium. After 20 times washing with standard washing method, the bacteriostatic effect was not affected. Considering the cost, a finishing

process with the least amount of monomer is used, that is, the amount of monomer is 0.65g. Modified chitosan can be widely used in various fields and has development value.

Table 2. Antibacterial effect of modified chitosan treated fabrics prepared at different reaction temperature.

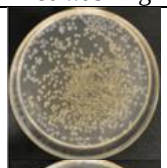
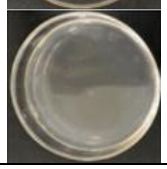
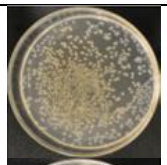
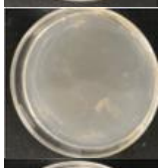
sample	Antibacterial effect(10^{-3})		Bacteriostatic rate Y	
	Not washing	Washing 20 times	Not washing	Washing 20 times
blank		-	-	-
I:40℃			100%	100%
II:45℃			100%	100%
III:50℃			100%	100%

Table 3. Antibacterial effect of modified chitosan treated fabrics prepared with different initiators.

sample	Antibacterial effect(10^{-3})		Bacteriostatic rate Y	
	Not washing	Washing 20 times	Not washing	Washing 20 times
Blank		-	-	-
a			100%	100%
b			100%	100%
c			100%	100%

4. Summary

In this study, we used ammonium persulfate ($(NH_4)_2S_2O_8$) and sodium bisulfite ($NaHSO_3$) as redox initiators to graft polymerize cationic antibacterial monomers onto chitosan to prepare a new type of modified chitosan. The grafting rate was 2.75%.

Different modified chitosan was prepared by changing the reaction conditions of graft copolymerization, such as the amount of monomer, reaction temperature, and initiator. Using polycarboxylic acid as a cross-linking agent and modified chitosan prepared under three conditions as bacteriostatic agents, rabbit wool fabrics were finished, and the finished fabrics were tested for antibacterial properties. The results showed that the finished rabbit wool fabric had a good antibacterial effect on E. coli, and the antibacterial rate reached 100%, and after 20 washings, the antibacterial rate still reached 100%, with long-lasting antibacterial properties.

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