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Modification of Antheraea Pernyi Silk with Reactive Quaternary Ammonium Salt of Chitosan

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Abstract: Reactive quaternary ammonium salt of chitosan (RQC) with quaternary ammonium salt and reactive carbon double bonds were synthesized in two steps in order to improve the solubility and reactive properties of chitosan. Quaternized chitosan was first obtained by heterogeneous reaction of chitosan and 2, 3-epoxypropyltrimethyl ammonium chloride using isopropyl alcohol as dispersing solvent. Then RQC was prepared using the quaternized chitosan and N-(hydroxymethyl)-acrylamide. FTIR was used to characterize the structure of the synthesized RQC, and the results show that H of $-NH_2$ in chitosan molecules was substituted with $-CH_2CH(OH)CH_2N^+(CH_3)_3$ and H of OH in RQC molecule was substituted with $-CH_2NHCOCH=CH_2$. *Antheraea pernyi* (*A. pernyi*) silk was then modified with RQC by padding and curing method. The results revealed that the dyeing depth of treated *A. pernyi* silk dyed with reactive dyes increased greatly in comparison with the untreated and chitosan treated ones, and the bacterial reduction against *S. aureus* and *E. coli* of the treated *A. pernyi* silk fabric was more than 98% even after 20 launderings.

Keywords: Modification, biopolymers, functionalization of polymers, crosslinking reaction, dyeing property, anti-bacterial activity.

1. Introduction

Chitosan, as an environment protective material, has the advantage of being abundant in resources, non-toxic, pollution-free, renewable, having excellent biocompatibility and biodegradation. It had been widely applied in the fields of environmental protection, medicine and agriculture, as well as in cosmetic and food industries [1, 2]. In textile industry, it is expected to look for eco-friendly processes that substitute for some toxic textile chemicals. In this point of view, chitosan is an excellent candidate for an eco-friendly textile chemical treatment. The various applications of chitosan in textile dyeing and finishing were reviewed in a recent paper. For example, chitosan has been used as a pretreatment agent in dyeing of cotton, textile printing, wool dyeing and shrink proofing and durable press finish [3-5]. However, the application and development of chitosan is limited to poor solubility above pH of 6.5. Thus, water soluble chitosan derivatives which are soluble in both acid and basic aqueous solution might be good candidates for a polycationic anti-bacterial agent and other uses.

Chitosan can be formed into its soluble derivatives by quaternized modification, N-acylation reaction, carboxy methylation reaction, and hydroxylethyl reaction by introducing some functional groups such as quaternary ammonium salt to its molecules [6, 7]. As for as quaternized chitosan was concerned, it was reported to have a favorable antibacterial property, water solubility, hygroscopicity and moisture retention [8, 9]. In textile fields, quaternized chitosan was used to improve anti-bacterial property and increase dyeing property of natural fabrics [10, 11].

This study attempts to prepare RQC in two steps: 2, 3-epoxypropyltrimethyl ammonium chloride was first applied to prepare quaternary ammonium salt of chitosan by heterogeneous reaction in isopropanol medium, then N-(hydroxymethyl)-acrylamide was applied to react with quaternary ammonium salt of chitosan to prepare RQC with reactive double bonds. RQC was then allowed to react directly with *A. pernyi* silk fiber in the absence of crosslinking agents. As a result, *A. pernyi* silk fabric modified with the RQC can provide good anti-bacterial property and enhanced dyeing property.

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2. Experimental

2.1 Materials

A. pernyi silk fabric (type 5023, 100 g/m^2, degumming rate of 14.0%) was purchased from Dandong Software Silk Co. Ltd. in China; Chitosan (the viscosity-average molecular weight is 15000, degree of deacetylation is 92.0 %) was prepared by degrading commercial chitosan (the viscosity average molecular weight is 40 0000) according to the reference [12]. N-(2,3-glycidyl) trimethyl ammonium chloride was purchased from Sangong Chemical Industry Co. Ltd.(Yantai, China); Acid red B (C. I. Acid Red 14), acid brilliant blue G (CI Acid blue 90), Cibacron red FN-R (C.I. Reactive red 238) and Cibacron blue FN-G (C.I. Reactive blue 235) were selected for the typical dyestuffs in the experiment. N-(hydroxymethyl)-2-propenamide, sodium sulphate, acetic acid, 4-methoxyphenol, ammonium chloride, sodium hydroxide, methyl alcohol, ethanol, acetone and isopropanol were all chemically pure reagents.

Tested micro-organism included gram positive bacteria *Staphylococcus aureus* (*S. aureus*, ATCC 6538) and the gram negative bacteria *Escherichia coli* (*E. coli*, ATCC 8099).

2.2 Preparation of RQC

Quaternary ammonium salt of chitosan was synthesized using heterogeneous method [13]. The heterogeneous system contained 5g chitosan and 20g N-(2, 3-glycidyl) trimethyl ammonium chloride with 250 ml isopropanol as the dispersion medium, under stirring at 80 ℃ for 10 hrs. Then the product of the above reaction was washed in the mixture of acetone and alcohol (1:1), subsequently filtered and dried in a vacuum drying oven at 40 ℃.

The synthesis of RQC was carried out as described in the earlier method [14]. Briefly, the prepared quaternary ammonium salt of chitosan (10g), N-(hydroxymethyl)-2-propenamide (25g), 4-methoxyphenol (0.1g) and ammonium chloride (5g) were dissolved in 50ml aqueous solution at room temperature by stirring. The above solutions were reacted at 140℃ for 15 min. To the reaction solution, methyl alcohol (100mL) was added and stirred for 10 seconds. The product was precipitated in acetone and then washed thoroughly with a mixture of 1:1 acetone-ethanol and finally with ether. The nearly white reaction product was dried at 40 ℃ for 48hrs in a vacuum drying oven.

2.3 FT-IR measurement of RQC

Infrared spectra of RQC and chitosan were recorded on a Nicolet 5700 FT-IR spectrophotometer by using KBr disk. The measurements were performed at 20 ℃ and a relative humidity of 65% with scanning times of 32 and a resolution of 4 cm^{-1}. The ranges of determination were 4000～400cm^{-1}.

2.4 Solubility of the RQC in water

Solubility in water, also known as aqueous solubility, is the maximum amount of RQC that can dissolve in water at equilibrium at a given temperature 25℃. It was tested in water in a broad range of pH (4-10). The pH value of RQC aqueous solution was adjusted using 5g/l acetic acid and 5g/l sodium hydroxide.

2.5 Treatment of *A. pernyi* silk fabric with RQC aqueous solution

A. pernyi silk samples were immersed in treatment solution (RQC 5g/l, sodium bicarbonate 1% o.w.f.) at 60 ℃ for 30 min, using a laboratory padder (AO type, Taiwan Labortex Co., Ltd.) at 90% wet pick-up. The *A. pernyi* silk samples were then dried at 80 ℃ for 5 min and cured at 160 ℃ for 3 min. Next, the treated samples were washed with tap water until neutral to pH paper and further washed in deionized water in ultrasonic cleaner for 5 min to remove unfixed materials. Finally, the samples were dried at 80 ℃ in a laboratory oven.

2.6 Dyeing process of *A. pernyi* silk fabric

Depending on the class and particular kind of dyestuffs used in the study, different dyeing recipes and dyeing technologies were used. All dyeing processes were carried out at 2% (o.w.f.) dyestuff shade. Acetic acid was used to maintain pH values during the dyeing process of acid dyestuffs. Sodium sulphate (15 g/l) was used in reactive dyeing for acceleration. Dyeing cycles for the acid dyestuffs and reactive dyestuffs used in this experiment are presented below. The dyeing process of the acid dyestuffs and reactive dyestuffs were all carried out using exhaustion method at a liquor ratio of 1:40 in a laboratory water bath. Dyeing process for *A. pernyi* silk fabric with two acid dyes and two reactive dyes were performed according to the cycles shown in Figures 1 and 2 respectively.