Antimicrobial Finishing of Wool Fabrics Using Quaternary Ammonium Salts

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ABSTRACT: Durable antimicrobial wool fabrics were prepared by using a simple chemical finishing process. Carboxylate groups in wool protein were employed to form ionic interactions with cationic antimicrobial agents, such as cetylpyridinium chloride (CPC) and other quaternary ammonium salts, under the isoelectric point of wool protein, and such interactions were proven effective. The uptakes of the agents were dependent on their chemical structures, pH values of treatment solutions, concentration of the agents, and treatment temperature. The ionic interactions between the agents and the protein could survive repeated laundering, with CPC showing the best durability among three tested quaternary ammonium salts. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1037–1041, 2004

INTRODUCTION

Microbial growth on textile materials has been considered as a major cause of biodegradation of textile arts, particularly natural products, which has led to development of antimicrobial technologies for preservative purposes.[1–2] More recently, textile materials were identified as media for growth of pathogenic microorganisms in hospitals and could be sources of transmission of diseases.[3] Such results have further stimulated the research on antimicrobial textiles with focuses on development of durable and powerful antibacterial finishing technologies.[4–6] Antimicrobial treatment of wool products has been extensively studied mainly in the areas of preventing wool products from mildew and microorganism damages. Typical treatments include coating wool with resin-bonded 1% copper-8-quinolinolate and using *o*-benzyl-*p*-chlorophenol, 5,5′-dichloro-2,2′-dihydroxydiphenylmethane, 2,4,4′-trichloro-2′-hydroxydiphenylether, sodium dichloroisocyanurate, pentachlorophenol, pentachlorophenyl laurate, quaternary ammonium compounds, chlorinated phenols, metal ions, and organic tin compounds in finishing processes.[1–2,7–9]

Wool fibers consist of karatin proteins that are made of 18 amino acids, and these amino acids bring both free amino and carboxylic acid groups into wool proteins.[10] The free amino groups existing in the proteins have been employed as main sites for interactions in acid dyeing of wool fibers, since the amino groups could form cationic amine salts under acidic conditions. The cationic amine salts could interact with anionic acidic groups in acid dyes to form ionic pairs, thus the wool fibers become colored. Similarly, the carboxylic acid groups existing in wool proteins are also interactive with many other cationic compounds. For instance, metal ions such as Ag^{+} and Cu^{2+} could be absorbed onto wool fibers.[9–10] In this study, the same ionic interactions between carboxylic acid groups and cationic biocidal agents will be employed in producing durable antimicrobial wool fabrics. Such an approach is similar to the recent antimicrobial treatment of nylon and acrylic fabrics; both were employing similar ionic interactions between fibers and biocidal agents[6,11]

In this study, cetylpyridinium chloride (CPC), cetyltrimethylammonium bromide (CTAB), and benzyldimethylhexadecylammonium chloride (BDHAC) were used as antibacterial finishing agents. These agents have been frequently used in textile dyeing and finishing as either softeners and leveling agents or as disinfectants, but have not been employed in antimicrobial finishing of wool fabrics. The chemical structures of the quaternary ammonium salts are shown in Figure 1. The exhaustion of cationic salts on wool fabrics was studied with regards to chemical structures of the salts, the solution concentration, pH, and treatment temperature and time. The durable antimicrobial properties of the treated fabrics were evaluated using standard Launder-Ometer washing and antimicrobial tests.

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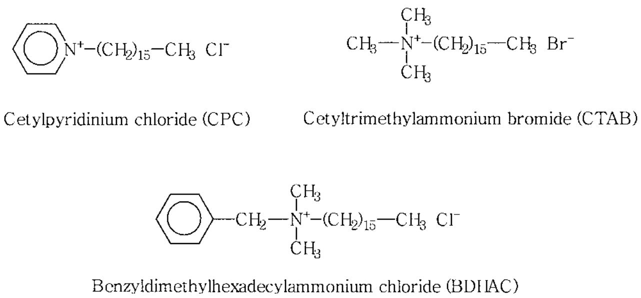

Figure 1 Chemical structures of quaternary ammonium salts

EXPERIMENTAL

Materials

Unbleached worsted wool fabric (#522 TestFabrics, Inc., West Pittston, PA) was laundered using an American Association of Textile Chemists and Colorists (AATCC) standard reference detergent WOB (AATCC Test Method 124-1996) and then thoroughly rinsed. Cetylpyridinium chloride (CPC, 98%) and cetyltrimethylammonium bromide (CTAB) were purchased from Aldrich (Milwaukee, WI), and benzyldimethylhexadecylammonium chloride (BDHAC, 99%) was purchased from Acros Organics (Pittsburgh, PA). All three quaternary ammonium salts were used without further purification.

Methods

Wool fabric samples were immersed in a finishing solution containing a quaternary ammonium salt in a premeasured concentration (2–10% on weight of fabric) and pH (mostly at 7). The pH values of the finishing solution were adjusted by using different pH buffers. The liquor ratio (finishing solution weight : fabric weight) used in the treatments was 50 : 1. The quaternary ammonium salt was exhausted by immersing the fabric in a finishing solution under varied temperatures (at 90°C or as stated) and durations (80 min) of treatments. The concentrations of the salts in the solution during the exhaustion were measured by using a spectrophotometer (Hitachi U-2000, Tokyo, Japan) at λ_{max} values of CPC (260 nm) and BDHAC (208nm) according to their calibration curves. Only CPC and BDHAC were employed in this study since CTAB is invisible in UV spectrometer.

Biocidal properties of the modified fabrics were quantitatively evaluated against a gram negative bacterium, *Escherichia coli* (*E. coli*, American Type Cell Culture #15,597) according to AATCC Standard Test Method 100. About one gram of fabric swatches was contacted with 1.0 ± 0.1 mL of bacterial inoculum in a 250 mL container. The inoculum was a nutrient broth culture containing 1.0×10^5–10^6/mL colony forming units (CFU) of the bacterium. After both testing and control swatches had been contacted with *Escherichia coli* for 90 min, 100mL of sterilized and distilled water was poured into the container, and the mixture was vigorously shaken, and supernatant was diluted to 10^1, 10^2, 10^3, and 10^4. The diluted bacterial solution aliquots were plated on a nutrient agar and incubated for over 15 h at 37°C. The colonies of the bacterium on the agar plate were counted, and the reduction in numbers of the bacterium was calculated using the following equation:

Reduction rate (%) = $(A - B) / A \times 100$

where A is the number of bacterial colonies from an untreated fabric (control) and B is the number of bacterial colonies from the quaternary ammonium salt treated fabrics.

Repeated laundering tests were carried out in a Launder-Ometer® (Atlas Electric Devices Co., Chicago, IL) at room temperature according to AATCC Standard Test Method 61. AATCC standard reference detergent WOB was used in the laundry. Wool fabrics treated in solutions containing 6% (on weight of fabric) of the quaternary ammonium salts at pH 7 and 70°C for 80 min were employed in the laundering test.

RESULTS AND DISCUSSION

Exhaustion of quaternary ammonium salts

Wool protein contains numerous amino and carboxylic groups as a result of existence of acidic and basic amino acids in the protein. The basic amino and acidic carboxylic groups in the same wool protein could form amphoteric ions in water. Normally, wool molecules will be amphoteric under a certain pH, at which the number of positive charges and negative charges carried by the wool protein are equivalent. This pH is called the isoelectric point, which is about 5 for most wool fibers. As the pH of the solution changes, the charge on wool will also be changed. The charges on wool protein under different pH conditions in regard of the isoelectric point can be shown as follows (Equation 1):

$$NH_3^+\text{–W–COOH} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} NH_3^+\text{–W–COO}^- \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} NH_2\text{–W–COO}^- \quad (1)$$

The wool molecule contains negative charges when the pH of the solution is above the isoelectric point of the wool. The higher the pH of the solution, the more negative the wool will become in the solution. On the other side, when the pH of the solution is below the isoelectric point, the wool protein will carry positive charges. So the charge status on wool protein can be

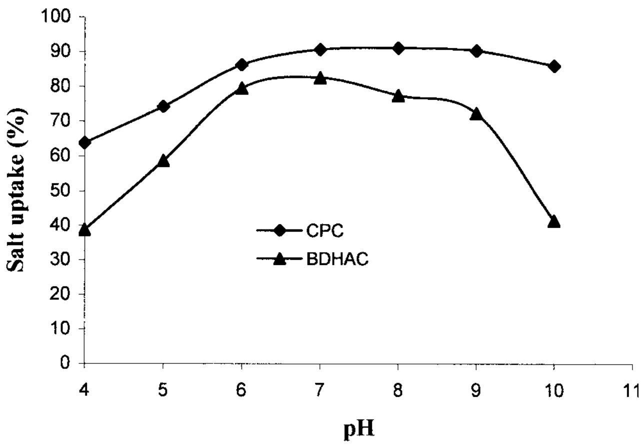

Figure 2 Effect of pH values on salt uptakes on wool fabrics (liquor ratio 50 : 1, salts concentration 6% (owf), temperature 90°C, time 80 min.)

controlled by adjusting pH condition of a finishing or dyeing bath. Furthermore, quaternary ammonium ions carry positive charges in aqueous solution after dissociation of the quaternary ammonium salts. Ionic attractions between the wool molecules and salts could be promoted at a pH above the isoeletric point of the wool. To study the effect of the pH on the exhaustion of the salt cations, a broad range of pH varied from below to above isoelectric point of the wool was examined. The results are shown in Figure 2.

Two quaternary ammonium salts, CPC and BDHAC, were used in the experiments due to their visibility under UV spectrophotometers. As shown in Figure 2, the salt exhaustions by the wool fabric increased continuously as pH values of the salt solutions were raised from 4 to 7, which is consistent with our expectation according to the charge status on the wool around the isoelectric point. The exhaustion of the agents below the isoelectric point may attribute to the zeta potential of the fibers in aqueous solution, which makes the surface of the fibers carrying partially negative charges. Then the salt uptakes become flattened after 7; however, under more alkaline conditions, they were reduced. The wool proteins are unstable and become hydrolyzed under strong alkaline conditions.[12] The hydrolysis of the wool protein results in weight losses of the finished fabrics at pH above 7, as well as causing a yellowing effect. In the BDHAC treatment of the wool fabrics, the BDHAC uptakes started to drop at pH conditions above 7, and stronger yellowing effect on the fabrics was also observed (from visual observation of the fabrics). Thus, a mild pH condition, such as pH at 7, was selected in the treatment of the wool fabrics. This pH is above the isoelectric point of the wool and therefore is capable of generating negative charges on the wool protein and promoting ionic interaction between wool and the quaternary ammonium salts but without causing a significant hydrolysis of the protein.

Effect of agent concentration

The exhaustions of both CPC and BDHAC on wool are determined by both adsorption and diffusion processes of the agents in the wool. The adsorption of the agents is dependent on the coulombic interactions between the quaternary ammonium salts and wool proteins, while the diffusion rate of the agents is controlled by their concentrations. Figure 3 shows the uptakes of both CPC and BDHAC on the wool under varied concentrations. The uptakes of CPC were always higher than that of BDHAC on the wool and were almost unchanged in the solutions with varied concentrations from 2 to 10% at pH 7. Surprisingly, the uptakes of BDHAC were increased as its concentration was raised in the finishing baths, which is quite abnormal. BDHAC is bulkier than CPC, therefore, is relatively more difficult to diffuse into wool protein, which results in lower uptakes under the same concentration. The bulky BDHAC also contains large hydrophobic groups, and its solubility in water may be affected by other electrolytes existing in the solution. Under increased concentrations of BDHAC in solutions, sodium chloride ions are increased as a major by-product of ionic interaction between BDHAC and wool fibers, which can consequently reduce the solubility of the ionic BDHAC in water and suppress it to move into wool protein. Such an effect is similar to the common ion effect of sodium chloride in reactive dyeing, resulting in the increased exhaustion of reactive dyes with increased NaCl concentrations in dyeing baths. However, CPC has a high solubility in water and is not affected dramatically by the concentration

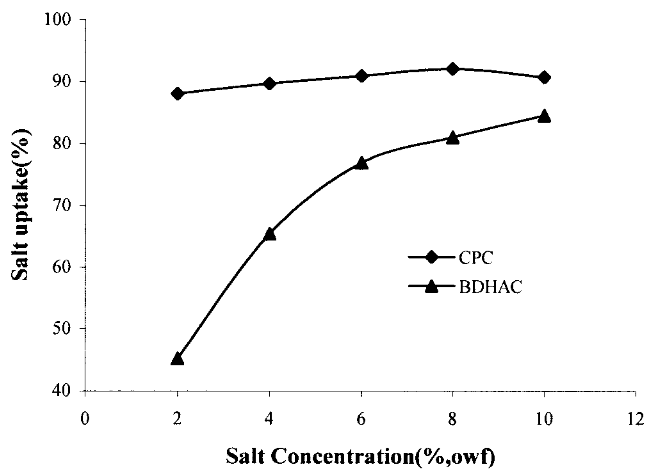

Figure 3 Effect of salt concentrations on salt uptakes on wool (liquor ratio 50 : 1, pH = 7, temperature 90°C, time 80min.)

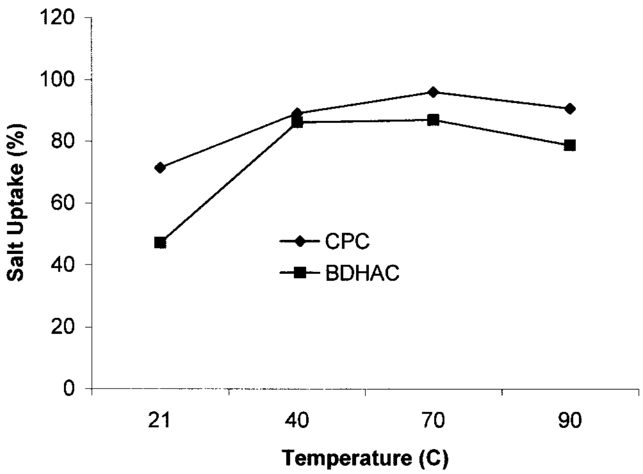

Figure 4 Effect of treated temperature on salt uptakes on wool (liquor ratio 50 : 1, salts concentration 6% (owf), pH = 7, time 80min.)

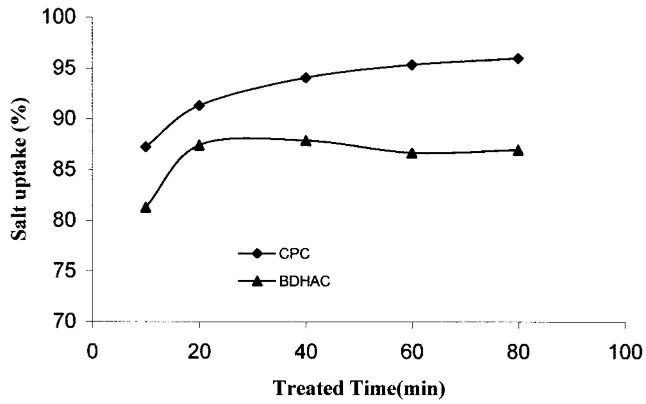

Figure 5 Effect of treated time on salt uptakes on wool (liquor ratio 50 : 1, salts concentration 6% (owf), pH = 7, temperature 70°C)

of sodium chloride in solution. Thus, the common ion effect on CPA is not so significant.

Effect of treatment temperature and time

Treatment temperature and time are both critical in the diffusion of the antimicrobial agents into wool protein, and thus will affect their exhaustions and consequently washing durability of the antimicrobial functions on wool. The durable antimicrobial effect on the treated fabrics depends on the amount of the quaternary ammonium salts incorporated and released during functioning and laundering. More antimicrobial agents could prolong the durability of the antimicrobial functions. Normally high temperature is preferred in textile finishing since it can enhance diffusion rates of the agents into fibers so as to increase uptakes of the chemicals. The treatment time depends on the temperature, and shortened time is preferred by industry. The treatment temperatures were varied from 21 to 90°C in this study, and treatment times were changed from 20 to 80 min. CPC always showed higher exhaustion rate than that of BDHAC on the wool protein due to its smaller size and higher diffusion coefficient (Fig. 4). However, higher treatment temperature was not optimal in the exhaustion of the agents, especially for BDHAC. The decrease of BDHAC uptakes at 90°C might be an overall impact of slight hydrolysis of wool since BDHAC has a strong surface active effect on hydrophobic fibers. Prolonged treatment time helped the exhaustion of CPC but did not improve that of BDHAC, possibly due to the same hydrolysis induced by the compound (Fig. 5). Economically speaking, a treatment time of 30 min will be sufficient for the uptakes of the agents. This finding also supports the mechanism of the coulombic interactions between the agent and wool protein.

Antimicrobial functions and durability

Antimicrobial functions of wool fabrics treated by CPC, BDHAC, and CTAB (cetyltrimethyl ammonium bromide) were examined against *E. coli* following AATCC Test Method 100. CTAB was not involved in the exhaustion tests since it is invisible under UV. As shown in Table I, all three quaternary ammonium salts could produce excellent antimicrobial functions on the wool fabrics. The normal contact time to result in the maximum reduction of the bacterium was in a range of over 90 min, and the antimicrobial effect against *E. coli* was similar to the textiles treated by quaternary ammonium salts,[6] but weaker than biocidal halamine materials.[5] Thus, this antimicrobial function is more suitable for consumer products that can provide odor control or hygienic functions. The washing durability of the treated fabrics was different, which can be observed by the antimicrobial results after accelerated Launder-Ometer washing tests. After 10 times of Launder-Ometer washing, CPC treated fabrics could still provide about 70% bacterial reduction, while BDHAC and CTAB treated samples showed no or little effect. It is believed that desorptions of quaternary ammonium salts from the finished wool sub-

TABLE I
Antibacterial Activity of Wool Fabric Treated with Quaternary Ammonium Salts

Washing time	Percentage reduction of *E. coli* (%)		
	CPC	BDHAC	CTAB
0	99.33	97.33	100
1	99	99.33	96.67
5	83	98.33	97.67
7	73.33	26.67	20
10	79.31	10.34	0

Salt concentrations were 6% on weight of fabrics. pH = 7, treatment temperature = 70°C and treatment time = 80 min.

strates occurred progressively as the number of washes increased, which causes reduced antimicrobial effect after repeated laundry. Exhaustion of CPC on wool was always higher than that of BDHAC under all different conditions, which should result in more CPC on the fabric and provide better antimicrobial functions. However, CTAB is more soluble in water but less interactive with wool protein than CPC due to the lack of hydrophobic aromatic ring, which might make it easier to be washed off from the fabric and thus less durable in laundry.

CONCLUSION

Antimicrobial wool fabrics were prepared by directly incorporating quaternary ammonium salts such as cetylpyridinium chloride (CPC), benzyldimethyl-hexadecylammonium chloride (BDHAC), and cetyltrimethylammonium bromide (CTAB) onto wool fabrics. Ionic interactions between the protein and the agent molecules contribute to the durability of the functions. The pH condition of the finishing bath should be above the isoelectric point of the protein, but strong alkaline condition may cause damage to wool fibers and should be avoided. The achieved antimicrobial functions on wool fabrics were durable in laundering, and some samples, particularly the CPC treated ones, could survive extensive Launder-Ometer washing cycles.

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