Antimicrobial Finishing of Wool Fabrics with Quaternary Aminopyridinium Salts

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ABSTRACT: Quaternary aminopyridinium salts were employed in antimicrobial finishing wool fabrics. The effects of alkyl chain length in the salts, pH conditions of finishing baths, finishing time and temperature, and salt concentrations were investigated. The incorporated quaternary aminopyridinium salt molecules on wool were characterized by FTIR. The quaternary ammonium salt could form ionic interactions with anionic groups on wool, which contribute to the durable antimicrobial functions. All the finished wool fabrics exhibited antimicrobial efficacy against *Escherichia coli*. The washing durability of antimicrobial functions on the finished wool fabrics was also studied. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 482–486, 2007

Key words: fictionalization of polymers; structure and relationship; surfactants; fibers

INTRODUCTION

Many processes of incorporating antimicrobial functions into textile materials have been developed elsewhere.[1–5] Antimicrobial agents used so far include quaternary ammonium salts, phenolic compounds, polyamines, halamine, metal ions, and antibiotics.[1–9] Incorporating chemicals into fibers rely on intermolecular interactions of polymer molecules and the antimicrobial finishing agents, including covalent bonds and secondary interactions such as van der Waals forces, dipole–dipole interactions, and hydrogen bonds. These secondary interactions can increase durability of antimicrobial functions on textiles, however, ionic bonds and covalent bonds can produce much more durable functions on the materials. These intermolecular interactions have been used in dyeing and chemical finishing of textiles as well.[7–11] For example, acid dyeing protein fibers and cationic dyeing acrylic fibers use ionic bonds formed between fibers and dyes to achieve good washing fastness. Ionic bonds are also used in antimicrobial treatments of nylon and acrylic fabrics with quaternary ammonium salts.[7–9] Despite their high degree of water solubility, which limits their use as textile finishing agents, some quaternary ammonium salts still have durability in their antimicrobial function because of the ionic interactions of fibers and agents.[7–10]

Wool protein fibers contain free carboxylic acid and amino groups. Cationic compounds such as quaternary ammonium salts could interact with the free carboxylic acid groups to form ionic bonds. Extensive studies have been carried out in the acidic dyeing of wool fibers, but less work has been done in the antimicrobial finishing. Recently, cetylpyridinium chloride (CPC) was proven effective in antimicrobial finishing of acrylics, nylon, and wool fabrics. More recently, several quaternary aminopyridinium salts (QAPS) have been successfully designed, synthesized, and characterized (Fig. 1).[12] In this article, we used these salts as antimicrobial finishing agents to form ionic bonds with wool fibers so as to prepare durable antimicrobial wool fabrics. The exhaustion of QAPS on wool fibers under conditions of different pH, treatment temperatures, and time were discussed. The durability of antimicrobial properties of the treated wool fabrics were also evaluated and explained.

EXPERIMENTAL

Materials

Unbleached worst wool fabric (#522 Testfabrics, West Pittston, PA) was thoroughly scoured with AATCC standard detergent WOB (AATCC Test Method 124-1996), and then rinsed thoroughly in tap water and dried in open air. Acetic acid (99%, EM Science, USA) and sodium carbonate (99.5%, EMD, USA) were used as received. 4-Amino-butylpyridinium bromide (ABPB), 4-amino-octylpyridinium chloride (AOPC), and 4-amino-laurylpyridium chloride (ALPC) were prepared according to the described method.[12]

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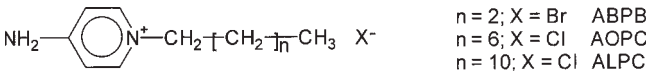


Figure 1 Structures of QAPS.

Finishing of fabrics

The wool fabrics were immersed into a finishing bath containing a quaternary aminopyridinium salt (QAPS) under fixed temperature (85°C) at different pH conditions. The bath liquor ratio (weight of finishing solution versus weight of fabric) was 50 : 1. The pH values of the finishing bath were adjusted by acetic acid for acidic conditions and sodium carbonate for alkaline conditions. The QAPS concentration changes during finishing were measured by taking 1.00 mL of the solution from the baths at different intervals. The UV absorbance of these solutions was then measured at λ_{max} values of ALPC (270.5 nm) by using a UV–vis spectrophotometer (U-2000, Hitachi Instruments, Japan). The percentage exhaustions (uptakes) of the salt ALPC on wool fabric was calculated by eq. (1).

$$E = \left(\frac{A_0 - A_t}{A_0}\right) \times 100\% \quad (1)$$

where E is the percentage exhaustion (uptake) of the salt at time t, A_0 is the absorbance of the salt solutions at the beginning of finishing, and A_t the absorbance of ALPC solution at time t.

Assessment of antimicrobial properties

The antimicrobial activities of the treated wool fabric were evaluated against *Escherichia coli* (*E. coli*, gram-negative) according to AATCC test method 100-1999. Following this method, about 1.0 g of circular fabric samples was challenged with 1.0 ± 0.1 mL of bacterial inoculums containing 10^6–10^7 colony-forming units (CFU) of the bacterium (*E. coli*). The inoculated fabric samples were then placed into a 250-mL container for a measured duration of 5 h (defined as the contact time). Afterward, 100 mL of sterilized distilled water was added into the container; the mixture was vigorously shaken, and then the supernatant was diluted to 10^1, 10^2, 10^3, and 10^4 in series. Then, 100 μL of each dilution was placed onto a nutrient agar plate, which is incubated for 18 h at 37°C. Finally, viable bacteria colonies on the agar plate were counted, and the percentage reduction of the bacterium was calculated using eq. (2).

$$R = \left(\frac{A - B}{A}\right) \times 100\% \quad (2)$$

where R is the percentage reduction of the bacterium, A represents the number of bacterial colonies in control (an untreated fabric), and B the number of bacterial colonies in the QAPS finished wool fabrics.

The treated wool fabric was washed in a Launder-Ometer (Atlas, USA), according to AATCC standard method 61-2005, to evaluate the washing durability of the treated fabrics. According to this method, one cycle of a Launder-Ometer washing is considered equivalent to five machine washes in a home laundry. The antimicrobial effects of the washed samples were then measured after the Launder-Ometer washing.

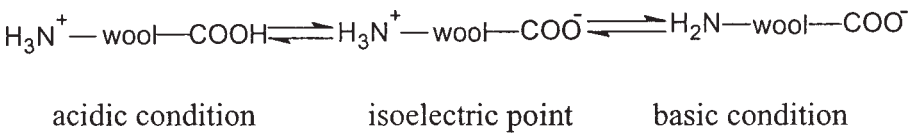
RESULTS AND DISCUSSION

Effects of pH values

Wool protein contains numerous amino and carboxylic groups, and when wool is immersed in water, the amino and carboxyl groups will exist in ionized or zwitterionic forms under different pH conditions (Scheme 1).[8]

At the isoelectric point (pH value is about 5), the wool is electronically neutral because the numbers of positively charged ammonium groups are equal to that of negatively charged carboxyl anions. When pH of a finishing solution is above the isoelectric point, the wool will become negatively charged, and carboxylate anionic groups become more reactive with ammonium groups by ionic interactions. The higher the pH of the solution, the more negatively charged carboxylate anions will form on the wool and the more reactive the wool will be. On the other hand, when the pH of the solution is below the isoelectric point, the wool will carry positively charged ammonium groups and is less attractive to QAPS. Therefore, pH conditions of finishing baths become critical in controlling the exhaustion of QAPS on the wool fabrics. The maximum reactive site on wool is about 0.82 m equiv/g.[11]

Dissociated aminopyridinium salts in aqueous solution carry positive charges, which can interact with negative carboxylate anions in wool fibers. Thus a pH above the isoelectric point of wool fibers can result in more negative charges on wool and consequently promote interaction with QAPS or exhaustion of QAPS.



Scheme 1

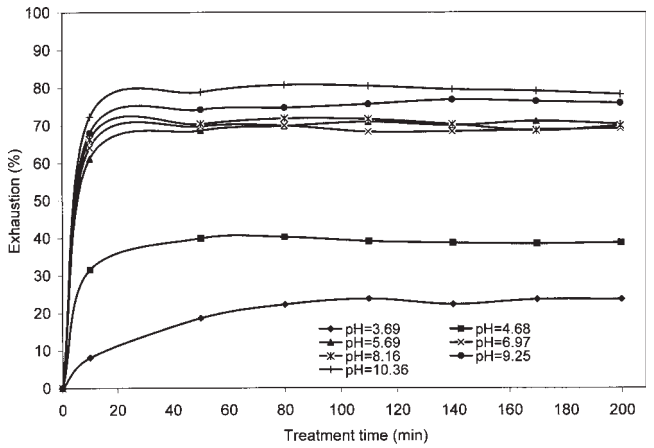


Figure 2 Effect of pH conditions on ALPC uptake on wool (liquor ratio: 50 : 1; ALPC concentrations: 5.0% (owf); temperature: 85°C).

Figure 2 shows ALPC exhaustions on wool fabrics under a broad range of finishing pH conditions. The maximum ALPC exhaustions by the wool increased continuously as the pH value of the finishing bath were raised from 3.69 to 10.36. The pH increase from 3.69 to 4.68 did not result in significant increase in the exhaustion of the quaternary salt. But, the pH change from 4.68 to 5.69, above the isoelectric point of wool, dramatically increased the maximum exhaustion of ALPC on the fabrics. The more alkaline the conditions, the higher exhaustions rates the fabrics demonstrated.

The exhaustion of ALPC on wool involves adsorption, diffusion, and interaction of ALPC with reactive sites in the wool. Under most different pH conditions, the time to reach saturation in exhaustion was quite short, mostly below 30 min, except at pH 3.69. The ionic bond is a strong intermolecular interaction, which generally leads to quick interaction, such as adsorption between the two species. The rapid exhaustion of ALPC, the QAPS with longest alkyl chain, may also indicate quick diffusion of the molecules into wool protein. Such a result is quite important for wool finishing, since short exhaustion time will make the process more economical.

Although an alkaline condition is preferred for increased exhaustion ALPC on the wool, the wool proteins are quite vulnerable to higher pH condition, particularly at pH values above 10. The hydrolysis of wool protein results in the appearance of a yellowish color and a decrease of tenacity. Most likely, a pH value of 7–8 is sufficient in this finishing treatment, since this pH range is already above the isoelectric point of wool protein and could not cause damages to wool fibers.

Effects of alkyl chain length in QAPS

The length of alkyl chain is an important factor to antimicrobial functions of quaternary ammonium salts. Longer in length, particularly longer than 8 or 12 carbons, the antimicrobial functions will be better.[13] However, longer alkyl chain may affect adsorption and diffusion of the QAPS in the wool. The exhaustion of QAPS in different chain lengths was investigated and the results are shown in Figure 3. The increase of alkyl chain length in QAPS resulted in increased exhaustion of the salts in wool fibers. These results may be explained by the characteristics of structures and interactions of wool protein and amphipathic QAPS. Wool protein is hydrophilic in nature, but is quite hydrophobic when compared with water. The three QAPS are generally hydrophilic as well. However, ALPC is most hydrophobic due to the longest alkyl chain, while ABPB is most hydrophilic among three QAPS. Thus, the affinity of ALPC to wool in an aqueous solution is higher than that of ALPC to water. The interactions of three QAPS to wool are in the order of ALPC > AOPC > ABPB, i.e., the ALPC-wool interaction is the strongest, and followed by AOPC-wool and then ABPB-wool. Two other quaternary ammonium salts, CPC and benzyldimethylhexadecylammonium chloride, were employed in antimicrobial finishing of wool, and their exhaustion rates on wool were in the range of 80–95% in a rapid mode.[9] CPC has a similar pyridinium structure, but longer alkyl chain comparing to ALPC. The maximum exhaustion of CPC on wool was about 95%, higher than that of ALPC, consistent with the observation presented here.

Effects of ALPC concentration

Finishing bath concentration affects add-on of the finishing agent on wool fibers, and consequently impact antimicrobial efficacy of the treated fabrics. But, over concentrated finishing bath may not be economical. Thus, the concentration of ALPC was changed from

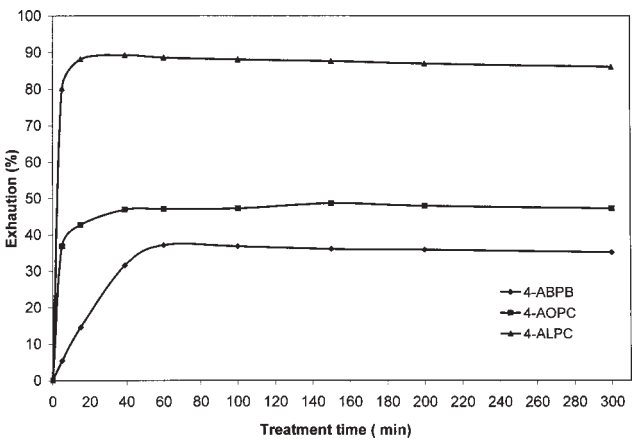


Figure 3 Effect of alkyl chain length on exhaustion of QAPS on wool (liquor ratio: 50 : 1; QAPS concentrations: 5.0% (owf); temperature: 85°C; pH: 8.45).

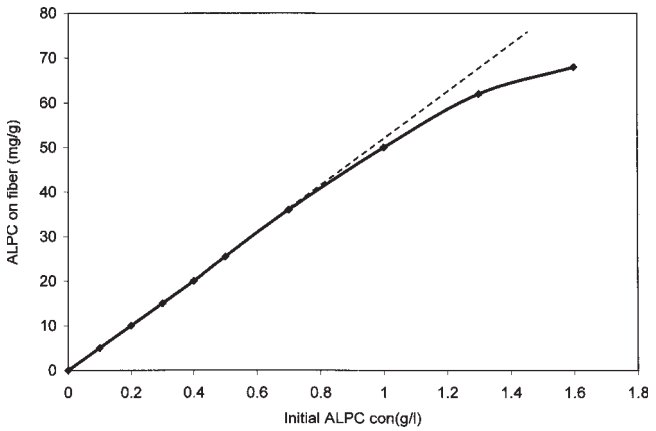


Figure 4 Effect of initial concentrations on exhaustion of ALPC on wool (liquor ratio: 50 : 1; temperature: 85°C; pH: 8.23; time: 120 min).

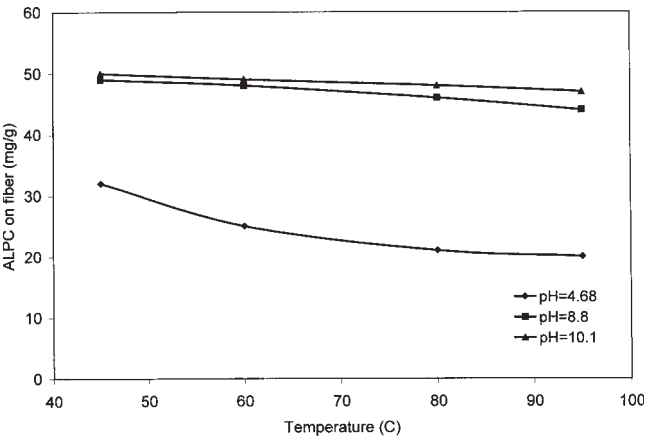


Figure 5 Effect of temperature on the uptake of ALPC on wool (liquor ratio: 50 : 1; ALPC concentrations: 5.0% (owf); time: 90 min).

0.1 to 1.6 g/L, and the uptake values of ALPC are shown in Figure 4. It can be seen that the increased initial concentration of ALPC in the bath raised the uptake of the reagent gradually. When the initial concentration was below 0.7 g/L, the relationship between the uptakes of ALPC on wool and its initial concentrations in bath was almost linear, indicating that the amount of ALPC exhausted by wool increased proportionally to the increase of the initial concentration in the finishing bath. Above the concentration of 0.7 g/L, the linear relationship no longer existed, showing that the adsorption rate of ALPC on the fabrics began saturated. As wool fibers contain a limited amount of reactive sites to interact with the ALPC, ALPC will not be able to be adsorbed on the wool infinitely.

Effect of finishing temperature

Treatment temperature is also a very important factor affecting the diffusion, adsorption, and affinity of the antimicrobial agent on the fibers. Figure 5 shows the uptake of ALPC on the wool fibers at temperatures varied from 45 to 95°C under pH values of 4.68, 8.80, and 10.1, respectively. The uptake of the agent on the fabrics decreased consistently with the temperature increase under all three different pH conditions. At the pH of 4.68, the ALPC uptakes on the wool were 32.2 mg/g at 45°C, 25.1 mg/g at 60°C, 22 mg/g at 80°C, and 19.8 mg/g at 95°C, respectively. At higher pH such as 8.8 and 10.1, the ALPC uptake on the wool were further reduced, but the reduction rate was lower than that at pH 4.68. The decrease of the uptakes at higher temperature is due to the reduced intermolecular interactions under higher temperature. Molecules such as amphipathic quaternary ammonium salt probably have low standard affinity with wool protein, a polyampholyte.[14] The affinity of the QAPS to wool will decrease when kinetic energy of the molecules increases. The quaternary ammonium salts with long alkyl chains would have relatively reduced ionic strength to interact with wool protein comparing to the regular cationic ions.

FTIR analysis of treated wool

The incorporation of QAPS on wool can be observed by infrared spectroscopy. Figure 6 shows the FTIR spectra of untreated and ALPC treated wool fabrics in the range of 500–4000 cm^{-1}. In the spectrum of untreated wool fabric (spectrum A), several characteristic FTIR bands, such as 3300–3500 and 1650 cm^{-1}, can be observed. The spectrum of ALPC treated wool fab-

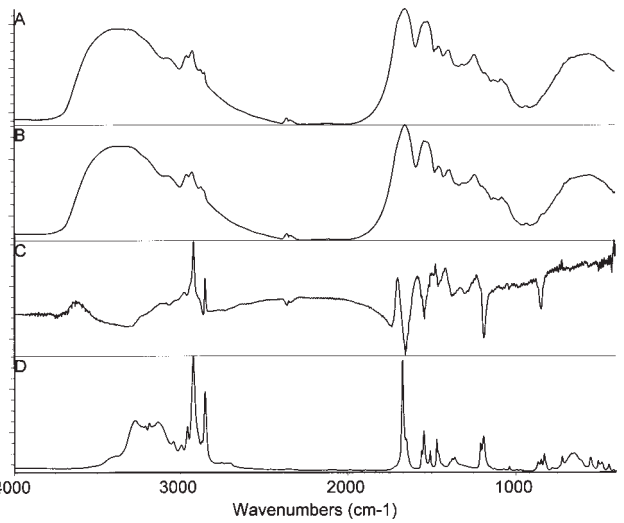


Figure 6 FTIR spectra of (A) untreated wool, (B) ALPC treated wool (ALPC concentration: 1 g/L; pH: 8.2; liquor ratio: 50 : 1; finishing temperature: 80°C; Time: 120 min), (C) difference spectrum of B and A (subtracting A from B), and (D) pure ALPC.

TABLE I
Antimicrobial Functions and Durability of Treated Wool Fabrics

Washing time	Percentage reduction of *E. coli*								
	45°C			65°C			85°C		
	ALPC	AOPC	ABPB	ALPC	AOPC	ABPB	ALPC	AOPC	ABPB
0	100	99.8	93.3	100	99.9	94.7	100	99.8	93.8
1	99.9	99.3	93.1	100	99.5	93.5	100	99	92.9
5	99.4	96.3	92.8	99.9	97.6	92.7	99.9	98.2	92.2

QAPS concentrations were 5% on weight of wool fabrics; pH = 8.25; liquor ratio, 50 : 1; treatment temperature, 45, 65, and 85°C; treatment time, 120 min; *E. coli* concentration, 10^6–10^7 cfu/mL; contact time, 5 h.

ric (spectrum B) is similar to the untreated wool fabric. However, after subtracting spectrum A from B, their difference spectrum can be obtained as spectrum C. The wool characteristic bands of 3300–3500 and 1650 cm^{-1} disappeared, and three new peaks centered at 2918, 2849, and 1698 cm^{-1} appeared, which are similar to FTIR spectrum of pure ALPC, as shown in spectrum D. The peaks of long alkyl chain of ALPC can be seen clearly, although the pyridinium ring stretch band (1680 cm^{-1}) is shifted probably due to ionic interaction with wool.

The wool fabrics treated by ABPB and AOPC show very similar results as the one treated with ALPC in FTIR spectra. Therefore, it can be concluded that all the synthesized antimicrobial QAPS can be incorporated into wool during the finishing process.

Antimicrobial assessment

Antimicrobial functions of three QAPS-treated wool fabrics were evaluated against *E. coli* following AATCC Test Method 100. The results are shown in Table I. It can be seen that with the increase of the alkyl chain of salts the QAPS showed higher antimicrobial activities. These results agree well with our findings in our earlier work.[15] The washing durability of the treated wool fabrics were different, which can be observed by the antimicrobial results after accelerated Launder-Ometer washing tests. After five times of Launder-Ometer washing, equivalent to 25 times of regular launderings, ALPC treated wool fabrics could still provide about 99.9% bacterial reduction, while other two compounds demonstrated relatively lower antimicrobial efficacy. Such a result could be caused by several factors, such as increased add-on of ALPC on wool and higher hydrophilicity of AOPC and ABPB. High add-on of ALPC on wool could add more available biocides, while high hydrophilicity of AOPC and ABPB could facilitate wash-off of the agents from the wool fabrics. More interestingly, the wool fabrics treated under different temperature ranges showed quite similar antimicrobial functions even though the uptake of the salts may be slightly reduced under higher temperatures.

CONCLUSIONS

QAPSs were incorporated into wool fibers in a finishing process using ionic interactions between the salts and the protein. The finishing bath pH is critical in affecting the uptakes of the quaternary ammonium salt and should be above the isoelectric point of wool protein. The maximum exhaustion of the salts on wool is dependent on length of alkyl chain. Longer alkyl chain results in stronger intermolecular interactions and higher uptakes. The exhaustion process is quite rapid, reaching the maximum in 30–60 min. High temperature is not favored in this finishing process. The treated wool fabrics demonstrated durable and powerful antimicrobial functions.

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