Durable Antimicrobial Nylon 66 Fabrics: Ionic Interactions with Quaternary Ammonium Salts

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ABSTRACT: Acidic or basic dyeing of fibers involves ionic interactions between reactive groups on the polymers and dye molecules. Such interactions can be utilized in the functional finishing of fabrics. This article discusses a new approach of employing the ionic interactions between anionic carboxylic end groups of polyamides and cationic quaternary ammonium salts in the chemical finishing of nylon fabrics to achieve desired durable antimicrobial functions. The finishing conditions such as pH, finishing temperature, and time were studied, and the pH of the finishing bath was very critical in affecting the ionic interactions and thus exhaustion of the salts on the fabrics. The finishing process should be carried out at a temperature above the glass transition temperature of nylon 66. The finished products demonstrated excellent durability of antimicrobial functions. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2194–2199, 2003

Key words: polyamides; modification; fibers; adsorption

INTRODUCTION

Functional finishing of fabrics is a process of incorporating new functional agents into fibers, which can be implemented by chemically or physically modifying the textile materials.[1,2] To achieve durable functions on textiles, chemical modification methods have been proven to be more effective than physical ones in providing excellent washing fastness of the functions. Durable wrinkle-free cotton,[3,4] durable fire-resistant cotton,[5,6] and durable and regenerable antimicrobial cottons[7,8] are examples of chemical modifications of cotton cellulose. However, most of such successful modifications on cellulose were accomplished using chemical grafting or chemical modifications of the hydroxyl groups on the polymer. Many other textile materials, particularly synthetic polymers, lack such reactive groups or sites on their polymer chains and thus are difficult to be chemically modified by functional agents.

While chemical modifications are difficult to implement on synthetic fabrics, coloration of these textile polymers is very practical, and the resulting colors are durable to repeated laundering. There are several options of chemical treatments employed in dyeing synthetics. For example, acrylic fibers become dyeable by incorporating a comonomer containing sulfonate or carboxylate groups that are interactive with cationic dyes.[9] Coloration of nylon fabrics with acid dyes uses the same ionic interactions between protonated amino end groups of the polyamides and sulfonate or carboxylic acid groups of the dyes.[10] A similar approach in developing durable antimicrobial nylon was attempted in this research group by subsequently adding reactive agents that are interactive with the incorporated acidic dyes.[11] The results were very encouraging, with the antimicrobial functions surviving 10 Launder-Ometer washes. But the additional treatment on the dyed fabrics is not suitable to undyed fabrics and thus is limited to certain applications. It is worth noting that antimicrobial nylons could be prepared by incorporation of halamine structures with other chemical modification technologies.[12,13] However, nylon polymers have two different ends, amino and carboxylic groups, if they were polymerized properly. The carboxylic groups are able to react with cationic functional agents and thus can be utilized in durable functional finishing processes. In this article, a novel functional finishing approach, focusing on how to briefly demonstrate the feasibility of using this ionic interaction in the incorporation of quaternary ammonium salts to nylon 66 and some related finishing conditions, is discussed.

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EXPERIMENTAL

Materials

Nylon 6,6 filament taffeta (#306A), purchased from Testfabrics Inc. (West Pittston, PA), was scoured in a

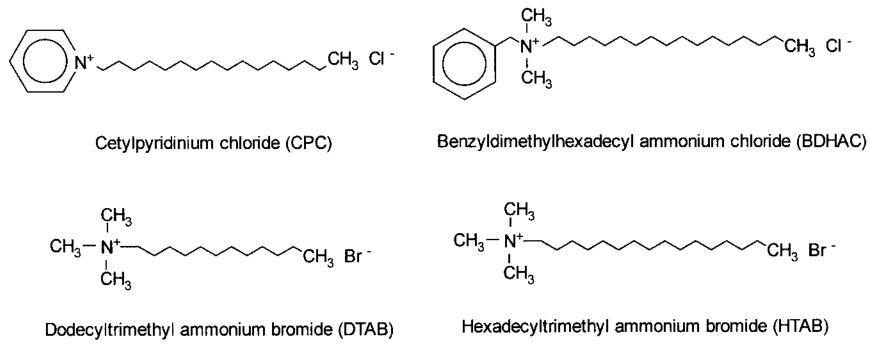


Figure 1 Structures of quaternary ammonium salts.

solution of AATCC standard detergent 124 before use, then rinsed thoroughly in tap water and dried in open air. Four quaternary ammonium salts employed in this work were purchased from the Aldrich Chemical Co. (Milwaukee, WI) and are listed in Figure 1. All other chemicals used were laboratory-grade reagents.

Procedures

Samples of nylon 6.6 fabrics were treated, separately, with 2% on mass of fabric (omf) of each of the cetylpyridinium chloride (CPC) and benzyldimethylhexadecylammonium chloride (BDHAC), hexadecyltrimethylammonium bromide (HTAB), and dodecyltrimethylammonium bromide (DTAB) solutions. Fabric samples were stirred for 60 min in a finishing bath with a liquor ratio of 50:1. The finishing temperature was increased gradually to 90°C. To determine an optimum pH condition, an initial treatment was carried out to evaluate the effect of the application pH on the exhaustion of quaternary ammonium salts and their corresponding antibacterial functions. The applied methods are as follows:

- Acidic condition: At pH 3–3.5 provided by the addition of 1 g dm^{-3} acetic acid;
- Neutral condition: With no addition of acid or alkali to the bath;
- Alkaline condition: At pH 11, with the addition of 1 g dm^{-3} sodium carbonate.

At the end of the finishing process, the treated sample was removed, rinsed thoroughly in tap water, and allowed to dry in the open air.

Treated nylon 6.6 fabrics were subjected to a Launder-Ometer washing test using AATCC standard method 61-1994 to determine the washing durability of antibacterial activities. In general, one cycle of a Launder-Ometer washing using this AATCC test method is considered equivalent to five machine washes in a home laundry. The antimicrobial properties were quantitatively evaluated using *Escherichia coli*, ATCC 2666, a Gram-negative bacterium, according to AATCC test method 100-1993. Fabric swatches were contacted with 1.0 ± 0.1 mL of bacterial inoculum in a 250-mL container. The inoculum was a nutrient broth culture containing 1.0×10^4–10^6/mL colony-forming units (CFU) of the bacterium. After both testing and control swatches had been contacted with *E. coli* for over 18 h, 100 mL of sterilized and distilled water was poured into the container, and the mixture was vigorously shaken, and the 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 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:

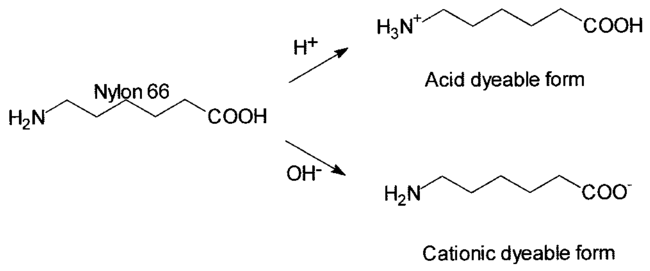
$$\text{Reduction rate (\%)} = (A - B)/A \times 100$$

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

RESULTS AND DISCUSSION

Effect of pH condition

Polyamides have two different end groups, amino and carboxylate, due to the polymerization reactions employed in preparing the polymers. Both groups are chemically active, and the amino ends have been widely employed in the dyeing of nylon fibers under acidic conditions. To promote ionic interaction between anionic acid dyes with the polyamide fibers, acidic conditions were very necessary to protonate amino groups of the polyamides to their salt forms. Thus, the resulting ionic interaction will lead to adsorption and exhaustion of acid dyes by the polymers, producing colored nylon fabrics (Scheme 1). But carboxylic acid ends of the polymers have never been utilized in either dyeing or chemical finishing of the nylon fabrics. Ideally, a similar interaction between anionic carboxlate and cationic dyes such as basic dyes



Scheme 1 Effect of pH on nylon polymers.

can be used in the dyeing of nylon fabrics. Carboxylic acid groups will become more interactive with cationic groups under basic conditions, at which these groups can form carboxylate anions (Scheme 1). However, many basic dyes are not stable at high pH, which might be one reason that such a reaction has not been employed in cationic dyeing of nylon fabrics. But such an ionic interaction can be a good access for durable antimicrobial finishing of nylon fabrics if selected antimicrobial agents, for example, long-chain quaternary ammonium salts, are stable under the pH variations. Therefore, an antimicrobial finishing of polyamide fibers with quaternary ammonium salts is chemically feasible based on the above analysis.

To prove the feasibility of utilizing ionic interactions between carboxylic ends of polyamides with cationic reagents, the chemical adsorption of the agents on the polymers under different pH values was studied. Chemical exhaustion of two quaternary salts (CPC and BDHAC) that are ultraviolet visible were conducted, separately, on nylon 66 fabrics under three different pH conditions. Acidic solutions were prepared in an aqueous system containing 1 g/L of acetic acid, and the pH of the solution was 4.0; alkaline solutions were prepared by dissolving 1 g of sodium carbonate in 1 L of deionized water, and its pH was 11. The results of the salt exhaustion on the fabrics are shown in Figure 2. As predicted, both acidic and neutral treatment conditions did not result in significant exhaustion of CPC and BDHAC on the nylon 6.6 fabrics. In contrast, the higher pH solution led to a higher exhaustion since the cationic quaternary ammonium salts are more attractive to the negatively charged carboxylate groups under the basic condition. Due to the ionic interactions, the quaternary ammonium salts were quickly absorbed onto and then diffused into the nylon fibers. Such a result further reveals that the promoted interactions between the polymers and the functional regents can be achieved by varying the pH values of the finishing solutions.

Higher exhaustion of quaternary ammonium salts on fabrics should result in better antimicrobial functions on the treated fabrics. Indeed, antibacterial tests of the finished nylon 6.6 fabrics demonstrated this trend (Table I). In addition, the increased exhaustion

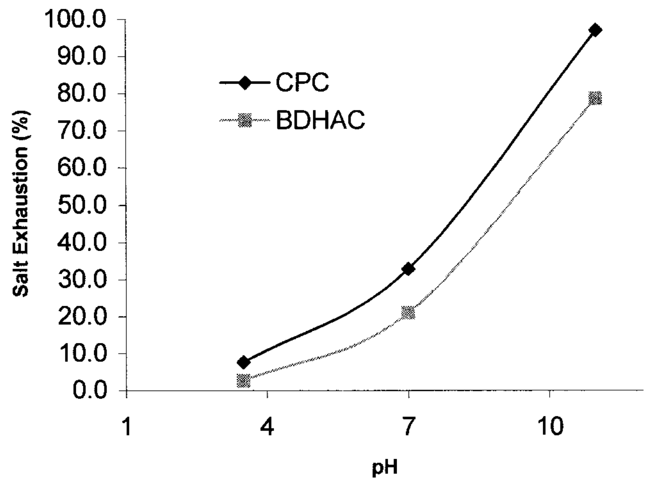


Figure 2 Effect of pH on quaternary ammonium salt exhaustion (percent) (2% salt solution at 90°C for 60 min).

of the salts by the nylon under the basic condition could lead to increased diffusion of the salts into the polymer, and, as a result, the increased ionic bonds formed inside fibers would improve the washfastness of the functions. As the fabrics were laundered repeatedly in a Launder-Ometer, the antimicrobial efficacy of the samples treated under different pH conditions became significantly different. After 10 Launder-Ometer washes, the fabrics treated under neutral and acidic conditions, specifically the BDHAC-treated ones, dramatically lost their biocidal properties. Surface-absorbed quaternary ammonium salts are usually less durable compared to those that can diffuse into nylon polymers since they can be washed out easily. The size of the quaternary ammonium salt plays an important role in the difference of exhaustion and the durability of the antimicrobial functions between the nylon fabrics treated by two quaternary ammonium salts. Bulky BDHAC showed low exhaustion ratios on and, thus, poor durability from the treated fabrics compared with the CPC-treated ones. A large molecular size reduces the strength of the interactions between the ions and the diffusion velocity of the bulky salt. The limited sizes and spaces in amorphous re-

TABLE I
Effect of pH on Bacterial Reduction (%) to Nylon 6.6 Fabrics

	Bacterial reduction, *E. coli* (%)					
	CPC			BDHAC		
pH	1[a]	5	10	1	5	10
3.5	99.6	22.1	11.5	98.1	7.7	0
7	99.9	38.3	15.0	99.9	36.2	0
11	100	100	95.7	100	99.5	65.0

[a] After 1, 5, and 10 times Launder–Ometer washing; fabrics were treated with 2% salt solution at 90°C for 60 min; AATCC test method 100.

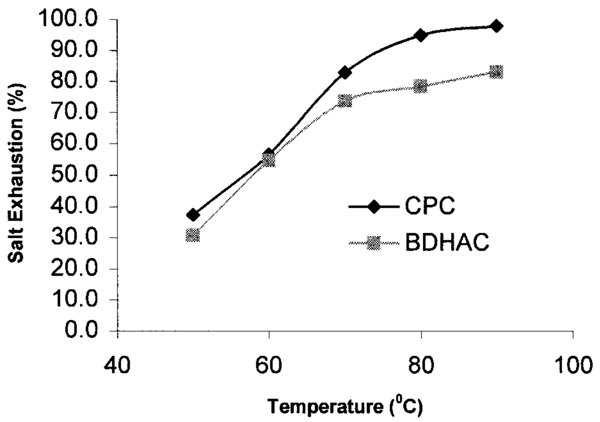


Figure 3 Effect of finishing temperature on exhaustion (percent) (2% salt solution for 60 min).

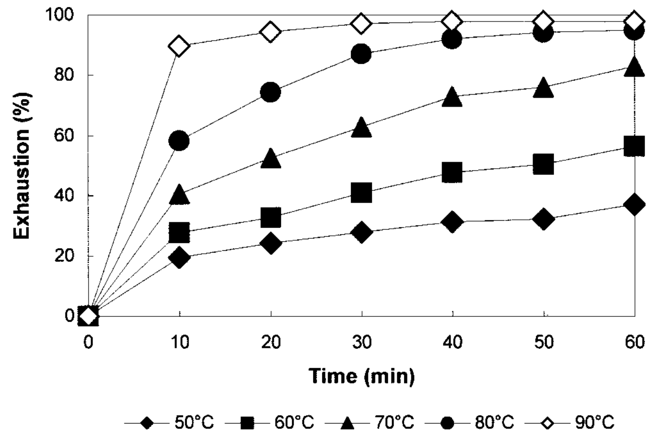


Figure 4 Effect of temperature on exhaustion of CPC (percent) (2% salt solution).

gions of nylon may also restrict or slow the diffusion rates of the large salts into the fibers. The mostly affected carboxylic end groups by the diffusion process are these inside, not those on the surface of the fibers. The internally bounded quaternary ammonium salts contribute mostly to the washing durability; thus, the durability of the antimicrobial functions on the BDHAC-treated nylon was relatively lower than that of CPC-treated samples. However, both salts still could verify the feasibility of using carboxylic groups in the chemical modification of nylon polymer.

Effect of finishing temperature

Having successfully shown that the quaternary ammonium salts could be employed in the antimicrobial treatment of nylon 66 fabrics under alkaline conditions (pH 11), another set of experiments was designed to examine the effect of finishing temperatures on the exhaustion of quaternary ammonium salts on the fabrics. The results displayed in Figure 3 show that the exhaustion of both salts was increased as the temperature was increased from 50 to 90°C. The increase of the exhaustion was more significant in the temperature range around the glass transition temperature of the fiber than in the higher range. At 90°C, the exhaustion of CPC on the fiber almost reached 100%. We selected 90°C as the temperature used in subsequent experiments since it could be easily controlled in a water-bath shaker and provides high exhaustion rates.

The significant exhaustion of the salts did not occur until the finishing temperature was above the glass transition temperature of nylon 66 (57°C),[14] a similar effect that can be observed from the dyeing of the fabrics. Above the glass transition temperature, the amorphous regions in the polyamide will provide more free volume to accept the salts and, as a result, higher exhaustion of the salts. In addition, a swelling effect resulted from the higher temperatures and basic conditions should facilitate diffusion of the quaternary ammonium salts into the nylon substrate. Consequently, there would be an increased amount of the salts present within the substrates, which provide good washing durability of the antibacterial efficacy.

Effect of finishing time

The quaternary ammonium salt molecules usually can only enter into amorphous regions in the polymer by diffusion, while nylon 66 fibers contain about 30% of the amorphous areas and 70% of the crystalline ones. The majority of the polymer structure is crystalline, which is tightly packed and difficult to penetrate for the salts. Thus, the finishing time is quite critical to the exhaustion of the salts on nylon. The effect of the treatment time under different temperatures on the exhaustion of the quaternary ammonium salts is demonstrated in both Figures 4 and 5. Clearly, the extent of salt exhaustion gradually increased with increase of the finishing time of the treatments. At a lower finishing temperature, a longer reaction time is needed to

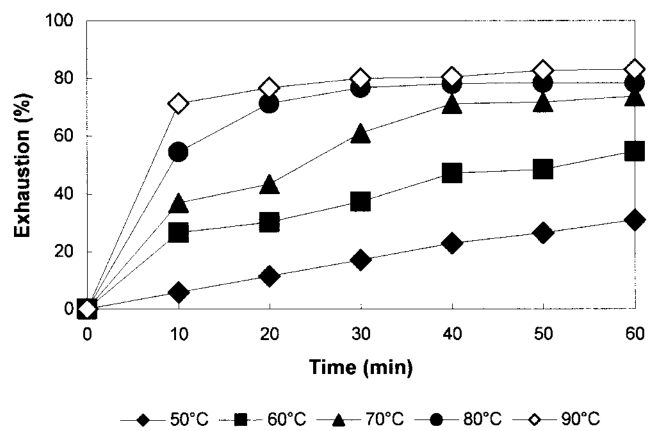


Figure 5 Effect of temperature on exhaustion of BDHAC (percent) (2% salt solution).

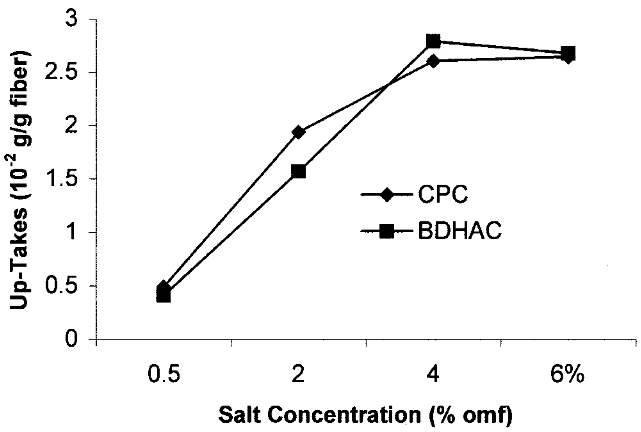


Figure 6 Salt uptake on nylon 66 at different concentrations (90°C and 60 min).

result in a higher exhaustion of the salts. At 90°C, an exhaustion time of 10 min is proper to reach maximum exhaustion. As the treatment time increased, the diffusion of quaternary ammonium salts on the fabrics could be improved significantly, which will result in high durability of the antimicrobial functions.

Effect of quaternary ammonium salt concentration

Diffusion of quaternary ammonium salts into nylon fibers depends on the concentration of the salts in the finishing baths. Thus, the concentration of the salts plays an important role in loading a sufficient amount of the salts into the fabrics for the required antimicrobial functions. To study the effect of the salt concentration on the finishing of the nylon fabrics, the exhaustion of the quaternary ammonium salts on the fabrics was examined with varied concentrations of the salts under the optimized pH condition and temperature based on the previous findings. Figure 6 displays the amount of the salt uptake on the fabrics corresponding to different concentrations of the quaternary ammonium salts. Obviously, the concentration of quaternary ammonium salt solutions directly affects the uptake rates of the salts on fabrics due to the ionic interactions between the carboxylate groups on nylon polymers and quaternary ammonium salts. Figure 6 also indicates that the equilibrium exhaustion was achieved using a salt concentration of 4% omf for both CPC and BDHAC. Polyamides have limited carboxylic end groups, and an excess amount of quaternary ammonium salts in the finishing baths could not produce a higher exhaustion than the maximum amount of the end groups and, instead, it will be washed off after finishing. Thus, at a concentration of 6% in the finishing solutions, the uptake of the salts by the fabrics was not higher than that of those treated by 4% of the salts, where the maximum exhaustion of the salts was reached. The washing durability of the antimicrobial property depends on the strength of the ionic bonding and the amount of the quaternary ammonium salts within the polyamide substrates.

Antimicrobial assessment

In the above exhaustion tests, two quaternary ammonium salts, CPC and BDHAC, were employed since they could be detected using a UV spectrophotometer. In the antimicrobial tests, another two quaternary ammonium salts, HTAB and DTAB, were also used. Table II shows the extent of bacterial reduction functions demonstrated on the finished samples treated by four different quaternary ammonium salts and the washing durability of the fabrics subjected to five and 10 repeated Launder-Ometer washing tests. All four salts could provide effective antimicrobial functions to the nylon 66 fabrics, and the washing durability of the functions exceeds more than 10 Launder-Ometer washes. It is believed that the desorption of quaternary ammonium salts from the finished nylon substrates occurred progressively as the number of washes increased and that the extent of bacterial reduction on nylon 6.6 fabrics decreased with an increasing number of washes. The functions on the treated fabrics was reduced to certain level after 10 Launder-Ometer washes, and the fabrics treated with the concentrations of 2, 4, and 6% omf quaternary ammonium salts could still provide more than 60% bacterial reduction against *E. coli*. A higher extent of bacterial reduction was still obtained from both 4 and 6% omf salt treatment. These results show that, re-

TABLE II
Effect of Quaternary Ammonium Salt Concentration on Bacterial Reduction (%)

	Bacterial reduction, *E. coli* (%)							
	CPC		BDHAC		HTAB		DTAB	
% omf	5[a]	10	5	10	5	10	5	10
0.5	97	29.7	57.9	30.6	82.5	24.6	92.5	51.4
2	100	91.3	99.8	69.5	100	82.6	100	80.3
4	100	98.4	100	97.1	100	98.7	100	95.4
6	100	99.5	100	99.4	100	99.4	100	97.3

[a] No. washings; AATCC test method 100; fabrics were treated with the salt solution at 90°C for 60 min.

gardless of the finishing concentrations used in the study, the existence of quaternary ammonium salts on nylon 6.6 fabrics will provide antibacterial functions.

CONCLUSIONS

Chemical modification of polyamide could be achieved by reacting carboxylic end groups with biocidal quaternary ammonium salts under alkaline conditions. Such a reaction could be implemented in the exhaustion treatment of nylon 66 fabrics with several quaternary ammonium salts. The interactions between carboxylic end groups and quaternary ammonium salts could provide improved durable antimicrobial functions over repeated washing tests. The treatment is usually conducted at elevated temperatures above the glass transition temperatures of the polymers. The achieved antimicrobial functions on the fabrics are durable in repeated laundering processes. This new finishing method is very simple and practical to the textile finishing industry.

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