Antimicrobial Finishing of Acrilan Fabrics with Cetylpyridinium Chloride

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ABSTRACT: Durable antimicrobial properties could be achieved on acrilan fabrics by chemically incorporating biocidal quaternary ammonium salts such as cetylpyridinium chloride (CPC) into the fibers. The chemical interactions between CPC and acrilan fibers were investigated through adsorption isotherm and exhaustion rates of CPC on the fabrics under various conditions. The equilibrium adsorption of CPC on the acrilan fabrics was in good agreement with the Langmuir adsorption isotherm. The study found that CPC concentration, pH value, and finishing temperature and time affected the adsorption process and antimicrobial properties of the acrilan fabrics. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 243–247, 2004

Key words: antimicrobial textiles; modification; acrylic fibers; functionization of polymers

INTRODUCTION

Antimicrobial functions are considered necessary features for certain textile products such as hygienic and medical use textiles and odor-free sportswear. These functions can be incorporated into the textiles by either chemical finishing of fabrics with biocidal agents or physical incorporation of the agents into fibers.[1–6] Washing durability of the antimicrobial properties of the products is always a challenge since the textiles are repeatedly laundered in applications. Two different mechanisms, slow-releasing and regeneration principle, are widely employed in producing durable antimicrobial textiles.[7] According to the slow-releasing mechanism, a sufficient amount of biocides, such as quaternary ammonium salts,[8–10] phenolic compounds,[11,12] polyamines,[13] and silver ions,[14] should be directly imbedded into polymers. The imbedded agents will be slowly released from the polymers to provide durable antimicrobial functions. The durability is fully dependent on the amounts of the agents incorporated during the finishing and released after each use. More specifically, intermolecular interactions between the agents and the polymers determine the amounts of the incorporated agents and the rate of the slow releasing. Recently, ionic interactions between quaternary ammonium salts and polyamides, acrylics, and wool were found capable of providing durable antimicrobial properties on these fabrics, which are intriguing in this study of acrilan fibers with cetylpyridinium chloride (CPC).[15]

Acrilan, one of the main acrylic fibers, is generally made from a copolymer of acrylonitrile and several vinyl comonomers that can improve flexibility and dyeability of the fibers.[16] The comonomers containing carboxylate or sulfonate groups will specifically make acrylic fibers dyeable with cationic dyes. Similarly, cationic compounds such as quaternary ammonium salts can interact with the anionic sulfonate or carboxylate groups on acrylic fibers. In this study, we used CPC as a biocidal finishing agent to form ionic bonds with acrilan fibers so as to increase durability of the antimicrobial functions. The exhaustion behaviors and equilibrium adsorption of CPC on acrilan under conditions with different pHs, temperatures, times, and CPC concentrations in finishing baths will be discussed in detail. The antibacterial properties of the finished fabrics will be explained as well.

EXPERIMENTAL

Materials

Acrylic plain woven fabric S/973, Acrilan no. 16 type acrylonitrile copolymer, was supplied by Testfabrics Inc. (West Pittston, PA). The fabric was thoroughly scoured with AATCC standard detergent 124 before use. CPC (98%) was purchased from Sigma–Aldrich Chemicals (Milwaukee, WI) and was used without further purification.

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CPC finishing and exhaustion

The acrilan fabric samples were immersed in a finishing bath with different CPC concentrations at 100 ± 2°C with a liquor ratio (weight of fabric versus weight of bath) of 1 : 100, at different pH values. The pH conditions of the finishing bath were adjusted by acetic acid for acidic conditions and Na_2CO_3, or Na_2CO_3 + NaOH for alkaline conditions.

The CPC concentrations of dyeing baths were measured by removing 1.00 mL of the solution with a pipette after different dyeing intervals. The UV absorbance of these solutions was then measured at λ_{man} = 259.3 nm in a quartz covet by using a UV–Vis spectrophotometer (U-2000, Hitachi Instruments, Inc.). The percentage exhaustion of CPC on acrylic was calculated according to

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

where E is the percentage exhaustion of CPC at time t, A_0 is the absorbance of CPC solution at the beginning, and A_t is the absorbance of CPC solution at time t. The amounts of CPC remained in the solution and exhausted by the fabrics could be both determined by assuming a mass balance of CPC in the system. The exhaustion time needed to reach 50% of the maximum exhaustion of CPC is defined as a half-uptake time $t_{1/2}$, which is measured from the exhaustion curves.

Antimicrobial properties

The antimicrobial properties were examined against *Escherichia coli* (*E. coli*, ATCC 15597), a Gram-negative bacterium, according to a modified AATCC test method 100-1993. The fabric samples (~ 0.5 g) were challenged with 0.5 ± 0.05 mL of bacterial inoculums containing 10^5-10^6 colony-forming units (CFU)/mL of *E. coli*. The inoculated fabric samples were then placed into a 250-mL container for a measured duration of 6 h (defined as the contact time). Then, 100 mL of sterilized distilled water was added into the container; the mixture was vigorously shaken, and then the supernatant was diluted to 10, 100, 10^3, and 10^4 in series. Aliquots of the diluted bacterial solutions were placed onto a nutrient agar plate and incubated for 18 h at 37°C. The colonies of the bacterium on the agar plate were counted. The percentage reduction of the bacterium was calculated following

$$R = \frac{N_0 - N_1}{N_0} \times 100 \quad (2)$$

where R is the percentage reduction of the bacterium; N_0 is the number of bacterial colonies from an untreated fabric, and N_1 is the number of bacterial colonies from the CPC finished fabrics.

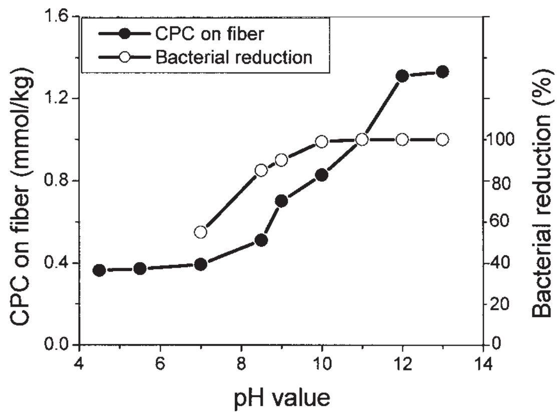

Figure 1 Effect of pH on exhaustion of CPC and biocidal functions of acrilan fabrics. Initial CPC concentration, 1.4 m*M*; liquid-to-goods ratio, 1 : 100; finishing temperature, 100°C. Biocidal functions were measured after the samples were washed 10 times in a launder-ometer at room temperature following AATCC test method 61.

The finished acrilan fabric specimens were subjected to a launder-ometer washing test according to AATCC standard method 61-1994. The antimicrobial effects of the washed samples were then measured after the launder-ometer washing.

RESULTS AND DISCUSSION

Effects of pH values

In a previous study, ionic intermolecular interactions between cationic quaternary ammonium salts and anionic sulfonate groups in acrylic fibers could produce durable antimicrobial functions on acrylic fabrics. The ionic interactions are dependent on pH conditions of finishing bath.[15] In this study, impacts of pH values of the finishing baths on CPC exhaustion and antimicrobial efficacy of resulting products are further investigated. Figure 1 shows CPC exhaustions on acrilan fabrics and their antimicrobial efficacies under different finishing pH conditions. Similar to the reported results,[15] the acrylic fabrics exhibited almost no adsorption on CPC under acidic conditions. After the pH value of the finishing bath reached 8.5, the exhaustion of CPC on the fabrics started to increase dramatically. The more alkaline the conditions, the higher exhaustion rates were for the fabrics demonstrated.

The exhaustion of CPC on acrylic fabrics involves three major steps:[16–18] (1) adsorption of CPC on fiber surfaces; (2) diffusion of CPC from the surface into the fibers; and (3) interaction of CPC with reactive sites in the fibers. When acrilan fibers are immersed in water, an electrokinetic potential, so-called the zeta-potential, is established between fiber surfaces and the water, and provides attraction to cationic ions. Acrilan fiber is made of a copolymer containing both weak and strong anionic groups, about 31 mequiv/g strong acidic and 21 mequiv/g weak acidic groups.[16] The dissociation of strong anionic groups is not affected significantly by more alkaline conditions, whereas the weak anionic groups dissociate more easily at higher pH, which leads to increased exhaustion rates. Such a result is in good agreement with Rosenbaum results.[19]

The amount of CPC exhausted on the fabrics determines their antimicrobial efficacy, and more importantly, affects washing durability of the products. Only the CPC diffused into the polymer and formed ionic bonds with internal reactive acidic sites can be slowly released to outside and provide durable functions. Increased exhaustion of CPC on the fabrics is a result of both increased adsorption and diffusion of CPC into the acrylics, which then obviously will improve durability of the antimicrobial properties. Figure 1 also shows antimicrobial efficacies of the fabrics treated under different pH conditions after 10 launder-ometer washes. At pH values > 9, the antimicrobial functions of the fabrics could survive 10 launder-ometer washings without noticeable reduction. This further reveals the importance of intermolecular interactions between the agents and the fibers and the diffusion of CPC into the fibers.

Although an alkaline condition is preferred for increased exhaustion CPC on the acrylic fabrics, higher pH, particularly at values > 10, could cause hydrolysis of the acrylic fibers, indicated by the appearance of a yellowish color. Thus, high pH should be avoided in dyeing and finishing of acrylic fibers. So, in this study, only pH conditions of 10 and 11 are used in the rest of the study.

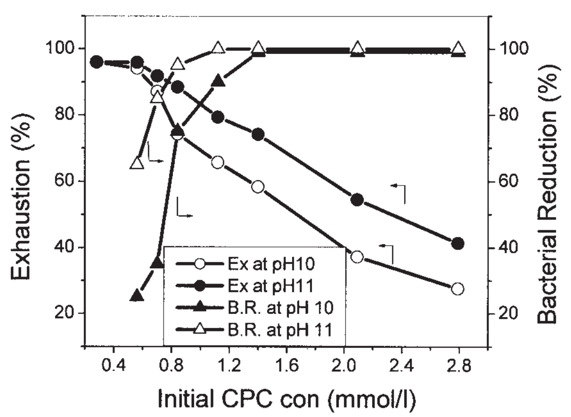

Figure 2 Effect of initial concentrations on exhaustion of CPC on and biocidal functions of acrilan fabrics. Liquid-to-goods ratio, 1 : 100; finishing temperature, 100°C; time, 120 min.

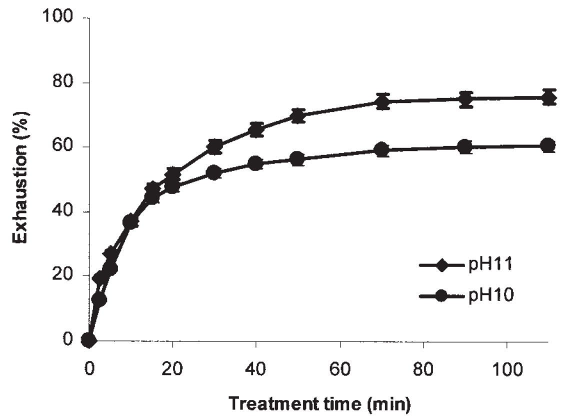

Figure 3 Effect of finishing time on exhaustion of CPC on acrilan fabrics. CPC concentration of 1.4 m*M*; liquid-to-goods ratio of 1 : 100; finishing temperature, 100°C.

Effects of CPC concentration

Diffusion of CPC in acrylic fibers is dependent on its concentration in the finishing bath according to Fick's Laws. Figure 2 shows the maximum exhaustion rates of CPC on and bacterial reductions of the fabrics under different initial CPC concentrations. Acrilan fibers contain a limited amount of reactive sites to interact with the quaternary ammonium salt. Increase of the CPC concentration can increase the diffusion rate of the salt into the fibers, but cannot raise the overall amount of ionic reactive sites between the agent and the fibers. Thus, under both pH values of 10 and 11, the maximum exhaustion rates of CPC on the fabrics decline as the initial concentrations of CPC increase. However, when the initial concentration of CPC was >0.8 m*M*, the overall exhausted amounts of CPC (percentage of the maximum exhaustion multiply the initial concentration) on the fabrics were almost a constant at different pH values. Meanwhile, the higher exhaustion of CPC on the fabrics at higher pH was a result of increased accessible reactive sites under more alkaline conditions, similar to Figure 1. In addition, the antimicrobial functions of the fabrics depend on the CPC in the fibers, and a complete reduction of the bacterium may need an initial CPC concentration in the finishing bath above 1.4 m*M*.

CPC adsorption isotherm on acrilan

The CPC adsorption behaviors on the acrilan fabric samples were further investigated through kinetic exhaustion and adsorption isotherm. Figure 3 illustrates the percentage exhaustions of CPC finished acrilan samples in varied durations under pH 10 and 11. Table I summaries the results of time of half uptake ($t_{1/2}$) and maximum equilibrium exhaustions obtained from Figure 3. Again, acrilan adsorbed more CPC under more alkaline conditions. The kinetic adsorp-

TABLE I
Half Uptake Time, Equilibrium Exhaustion, Langmuir Parameters of CPC Adsorption on Acrilan Fabrics at pH 10 and 11[a]

	$t_{1/2}$ (min)	Exhaustion (%)	S (mmol/kg)	K_L (L/mmol)
pH 10	28.3	58.3	0.4	51.3
pH 11	19.1	74.2	1.1	28.6

[a] CPC con of 1.4 mmol/L; liquid-to-goods ratio of 1 : 100; finishing temperature of 100°C.

tion curves indicate that the slopes of both curves at the beginning of adsorption were similar, but after 20 min of adsorption, they became different. Under more alkaline conditions, the acrilan would open more reactive sites inside the fibers, which will lead to a gradual and slow diffusion of CPC from the outside to the inside of the fibers. This step is slow and thus delays reaching the maximum of adsorption. However, at pH 10, the $t_{1/2}$ and the time to reach the maximum were shorter than that at pH 11. This should be a combined result of fewer sites available for CPC to bind but mostly on the fiber surface areas at pH 10.

Figure 4 shows the adsorption isotherm of the CPC on the acrilan samples at both pH 10 and 11, indicating that the equilibrium adsorption of CPC at pH 11 is greater than that at pH 10. A Langmuir plot of the equilibrium adsorptions of CPC at pH 10 and 11 on acrilan according to eq. (3) shows linear correlations of the adsorption through the tested concentration range (Fig. 5), proven that the adsorption of the CPC on the acrilan fibers follows Langmuir adsorption pattern, a monolayer adsorption. This result is completely consistent with the ionic interaction mechanism. In eq. (3), C_f and C_s are the equilibrium CPC concentrations on the fiber and in the finishing bath, respectively; K_L and S are the Langmuir affinity constant and the Langmuir

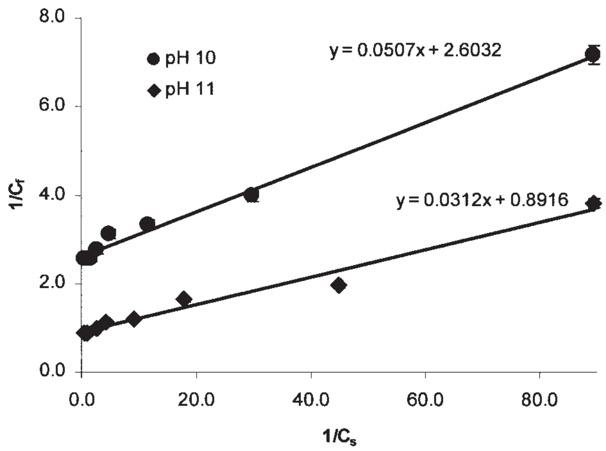

Figure 5 Langmuir plot of equilibrium adsorption of CPC on acrilan fabrics.

capacity constant, respectively. The CPC uptake parameters calculated from isotherms according to eq. (3) are also summarized in Table I. Clearly, the Langmuir adsorption capacity (S) of the acrilan fiber on CPC at pH 11 was almost three times higher than that of at pH 10

$$\frac{1}{C_f} = \frac{1}{K_L S}\frac{1}{C_s} + \frac{1}{S} \quad (3)$$

Effects of temperature

Chemical treatment temperature is a very important factor affecting adsorption and then ionic interactions between CPC and the reactive sites on the fibers. Figure 6 illustrates the CPC uptakes on acrilan fibers and biocidal functions of the fabrics finished at temperatures that varied from 80 to 100°C in the baths under pH values of 10 and 11, respectively. The CPC

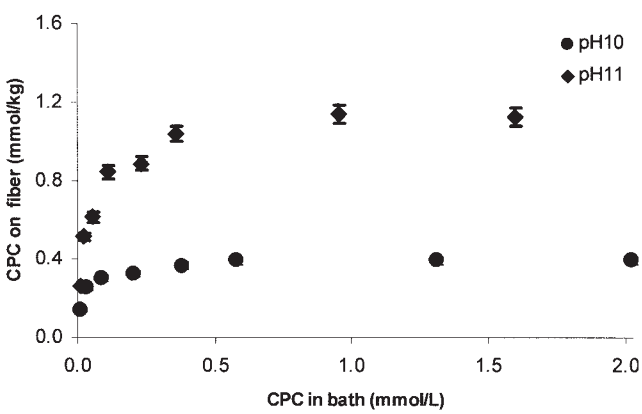

Figure 4 Equilibrium adsorption isotherm of CPC on acrilan fabrics. Temperature, 100°C; pH, 10 and 11; liquid-to-goods ratio, 1 : 100.

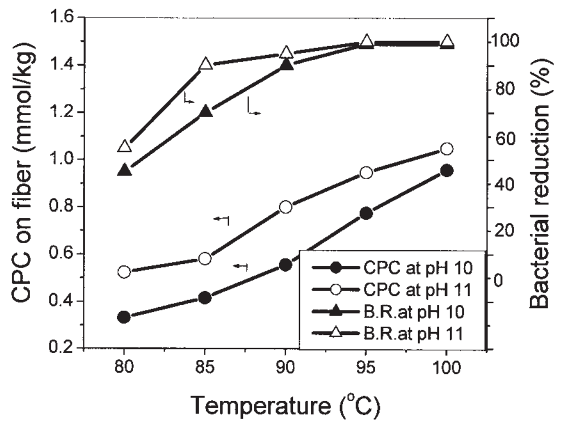

Figure 6 Effect of finishing temperature on CPC concentrations on acrilan fabrics. CPC concentration, 1.4 mM; liquid-to-goods ratio, 1 : 100; finishing time, 120 min.

uptakes on the fabrics increased with the temperature rising, but the increase rates were accelerated at temperatures > 85°C, which is around the glass transition temperature (T_g) of the acrylic fiber. At a pH of 10, the CPC uptakes on the samples were 0.332 mmol/kg at 80°C, 0.415 mmol/kg at 85°C, and 0.556 mmol/kg at 90°C, and the corresponding changing rates were 24.8% from 80 to 85°C and 34% from 85 to 90°C. Similarly, at pH 11 the changing rates were 11 and 37.7%, corresponding to 80–85 and 85–90°C, respectively. This trend continued at temperatures above 85°C, or above the T_g of the acrilan fibers. During the whole process of exhaustion of the CPC on the fibers, diffusion of CPC through the fiber is a slow but mostly critical step that can be affected by the T_g. At a temperature above T_g, the polymer chain segmental movement occurs; the glasslike amorphous region changes into a rubbery one, allowing more CPC to migrate into the inner fiber easily and resulting in higher CPC uptake values at temperatures above T_g. In addition, the weak acidic groups, carboxylic acid groups in acrilan, were pH dependent to interact with cationic ions. This is another reason that the CPC uptakes were higher at pH 11 than those at pH 10. Increased exhaustions of CPC on the fibers obviously could increase their antimicrobial power. Thus high-temperature treatment, particularly above T_g, is preferred in this antimicrobial finishing.

CONCLUSION

Powerful antimicrobial functions could be conferred to acrilan fabrics by using a simple exhaustion method with CPC. The finished fabrics demonstrated good efficacy against *E. coli*. The washing durability of the antimicrobial functions of the finished fabrics was excellent, surviving 10 launder-ometer washes. The CPC uptake on the acrilan fibers was dependent on pH condition of the finishing, concentration of the finishing agent, and finishing temperature. High pH and temperature are preferred in the finishing process. However, higher pH > 10 should be limited in practice due to hydrolysis of the polymer.

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