Antimicrobial Finishing of Acrilan Fabrics with Cetylpyridinium Chloride: Affected Properties and Structures

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ABSTRACT: Durable antimicrobial acrilan fabrics were prepared by using cetylpyridinium chloride (CPC) in a chemical finishing process. The CPC could form ionic interactions with anionic groups on acrilan fibers, which contribute to durable antimicrobial functions. Reaction conditions such as pH, temperature, and time of the chemical treatment affected exhaustion of CPC and antimicrobial properties. However, the pH conditions of the finishing bath also impacted mechanical properties and color of the fabrics, particularly under alkaline conditions. Although a more alkaline condition is preferred for durable antimicrobial functions, high pH reduces tensile strength and results in yellowing of acrilan fibers. The yellowing of the acrilan fibers is caused by the hydrolysis of acrylonitrle groups and induced formation of conjugated C=N systems in the polymers. The conjugated systems were characterized by FTIR. J Appl Polym Sci 97: 1227–1236, 2005

Key words: functionalization of polymers; fibers; FTIR; antimicrobial acrylics; medical textiles

INTRODUCTION

Quaternary ammonium salts such as cationic surfactants can be used as biocides in many applicable areas, with examples of several quaternary ammonium salts finding applications in textiles.[1–3] Recently, cetylpyridinium chloride (CPC), one of the quaternary ammonium salts, was directly employed in antimicrobial treatment of acrylic fabrics.[1,4] Acrylic fibers are one of the popular fibers employed in many apparel and consumer products due to their good elastic and mechanical properties as well as good stability to many chemical compounds and UV light. The direct antimicrobial finishing of acrylic fibers can strengthen applications of the acrylic fabrics in sportswear and hygienic textiles by providing additional odor control functions.[5] Acrilan 16, a typical representative of cationic dyeable acrylic fibers, is a copolymer of acrylonitrile and other vinyl comonomers containing anionic groups.[6,7] Durable antimicrobial functions were conferred to the acrilan through forming ionic bonds between the anionic groups on the fibers and cationic CPC in a batch finishing process.

The antimicrobial functions attributed to the incorporated CPC on the fabrics and the durability of functions is related to the amount of CPC incorporated during finishing and slowly released from the polymers during application according to a slow releasing mechanism.[8] The incorporation of CPC onto the fiber was implemented through the formation of ionic bonds between CPC and the fiber. Such an ionic bond formation is preferred under alkaline conditions as revealed in previous papers.[1,4] Acrilan polymer contains anionic acid groups that can react with cationic dyes. These groups become more negatively charged and thus are more reactive with cationic species under alkaline conditions, which is a major reason for increased CPC exhaustion on CPC at high pH. However, a strong alkaline condition would also cause certain negative impacts on mechanical properties and colors of the fiber due to a potentially alkaline-induced reaction of acrylic polymers.[7] The physical property changes such as the loss of tensile strength and yellowing of the finished fabrics during the antimicrobial finishing of the acrilan fabrics are discussed in this paper. Acrylic polymers can be hydrolyzed under strong alkaline or acidic conditions.[5,7] The yellowing and loss of tensile strength of the fabrics indicate that the CPC might play an important role in the reaction with the polymer under alkaline conditions. The yellowing effect of the materials is possibly due to the formation of chromophores in the system, while chromophores in polymers can be characterized by using a photospectrometer. Thus, we employed FTIR and conducted a quantitative analysis of the acrylic fabrics

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treated under different pH values, CPC concentrations in the finishing bath, and finishing times. The results indicated that a conjugated system containing C=N bonds could be formed in the acrylic polymer with the presence of CPC and a strong alkaline condition.

EXPERIMENTAL

Materials

Acrilan 16 (acrylic plain woven) was supplied by TestFabrics Inc. (West Pittston, PA). The fabric was thoroughly scoured before use. Cetylpyridinium chloride was supplied by Aldrich Chemicals (Milwaukee, WI) and was used directly without further purification.

CPC finishing

The acrilan fabric samples were immersed in a finishing bath in a liquor ratio (weight of solution to weight of fabric) of 100 : 1. The exhaustions of CPC on the fabrics were conducted at different pH values, finishing temperatures and times, and CPC concentrations. The finishing bath was adjusted to acidic condition with acetic acid or basic condition with Na_2 CO_3 or Na_2CO_3 + NaOH. The finishing baths were gradually heated up to the desired temperatures (normally 100°C or specified in text) and maintained at the temperatures for a duration of 120 min. (or specified in text). After the treatments, the fabrics were rinsed and dried.

Tensile strength test of fabric

Tensile strength of the fabric was examined according to ASTM method D-5035. The fabrics were cut into 10.16 cm × 2.54 cm (4 in ×1 in) pieces along warp direction and three specimens were measured for each sample group. The tests were conducted using an Instron Series IX Automated Materials Testing System with a 5 kN capacity load cell at a constant strain rate of 1.5 cm/min and a gauge length of 2.54 cm. All tests were carried out at 21°C and 65% relative humidity. The results of the fabric tests were analyzed using one-way analysis of variance (ANOVA) and Fisher's pair-wise comparisons with an individual error rate of 0.05.

K/S value estimation

K/S values of fabrics were measured using a CM-2002 Spectrophotometer (Minolta Camera Co., LID, Japan) based on eq. 1:

$$\frac{K}{S} = \frac{(1 - R)^2}{2R} \quad (1)$$

where R is the measured reflectance of the fabric samples. The maximum wavelength of the reflectance at 400 nm was used through out the tests.

FTIR analysis

Infrared spectra were recorded with a Nicolet Magna 560 FT-IR spectrometer (Madison, WI), using potassium bromide pellets prepared by using 300 mg KBr and 3 mg fabric samples. The fabric samples were grinded into powder and passed through 25-mesh sieves. The pellets were conditioned for 72 h at 80°C before IR analysis. All of the IR data were collected from 32 scans with a resolution of 4.0 cm^{-1}.

RESULTS AND DISCUSSION

Effect of finishing pH on properties

The finishing of CPC on acrilan fabrics was preferably conducted at basic conditions since alkaline conditions facilitate the formation of more anionic carboxylic groups in acrylic fibers, which can then interact with more cationic quaternary ammonium ions.[9] But, a strong basic condition may induce some reactions on the acrylic polymers since nitrile groups are vulnerable to alkaline conditions.[7] Such reactions will be accelerated particularly when the pH value of the finishing solution is above 10. In previous papers we have discussed the pH effect on power and durability of antimicrobial properties of the treated acrilan fabrics.[1,4] The treated acrilan fabrics showed that, when the pH value of the finishing bath was above 8.5, the exhaustion of CPC on the fabrics started to accelerate, and the durable antimicrobial performance began to improve. Following the same finishing conditions, the treated acrilan fabrics were evaluated in tensile strength and color changes (K/S value) in accordance with the pH changes from 4.5 to 13. The tensile strengths and K/S values of the treated fabrics are shown in Figure 1. Coincidently, the tensile strengths of the finished acrilan fabrics were almost unchanged in the pH range of 4.5 to 8.5 and then were reduced as the pH value was further increased in the finishing baths, particularly in the range of pH 10 to 13. The K/S values (at a wavelength of 400 nm) of the fabrics were increased gradually before the pH value reached 10 and then dramatically after the pH value was above 10. The slope of the K/S curve in Figure 1 indicates the yellowing degree of the finished fabrics. The reduction of both strength and whiteness of the fabrics is considered to be a result of structural changes of acrilan caused by CPC-induced reactions during the finishing process. The reacted acrylic polymer may reduce polymer chain orientations in the fibers, which will lower tensile strength of the fibers, while the yellowing of the fibers might be a result of the formation of some

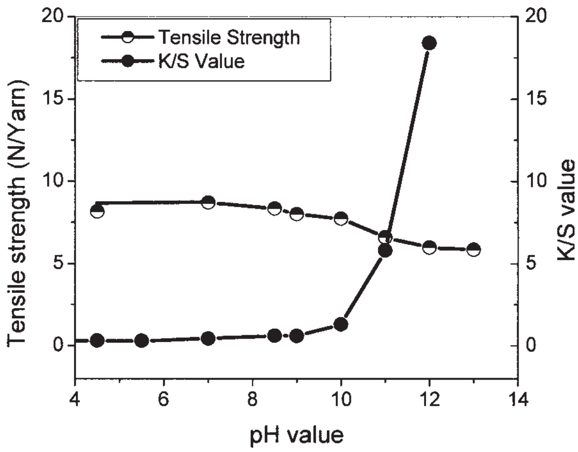


Figure 1 Tensile strength and K/S values of acrilan fabrics verses pH values of the finishing bath. Finishing conditions: initial CPC concentration = 1.4 m*M*; liquor ratio = 100 : 1; finishing temperature = 100°C; finishing time = 120 min.

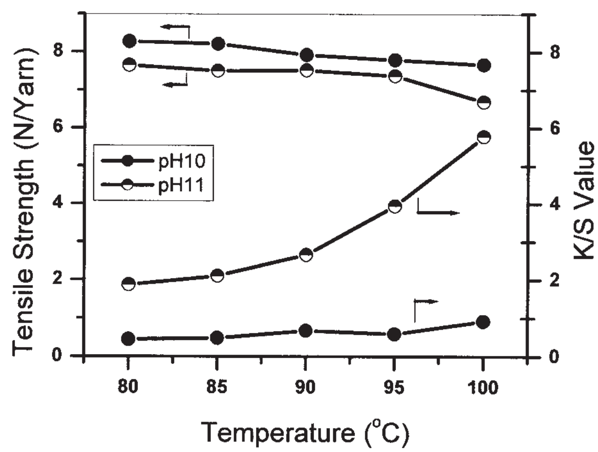


Figure 3 Tensile strengths and K/S values of acrilan fabrics verses finishing temperature. Finishing conditions: initial CPC concentration = 1.4 m*M*; liquor ratio = 100 : 1; finishing time = 120 min.

conjugated system in acrylic polymers induced by both hydroxide ions and CPC.

Effect of CPC concentration on properties

Concentration increase of the antimicrobial agent (CPC) in the finishing bath enhanced the exhaustion of CPC on the acrylics fibers and improved antimicrobial functions.[1,4] The finishing agent (CPC) concentration was raised from 0.28 to 2.79 m*M* under two pH conditions, 10 and 11, respectively. The finished fabrics showed quite interesting changes in both tensile strength and color (Fig. 2). The tensile strengths of the fabrics were slightly reduced as the concentration of CPC was increased in the finishing baths, with the tensile strengths of the fabrics treated at pH 11 were always lower than those of pH 10, consistent with the results showed in Figure 1. The K/S values of the fabrics treated at pH 10 were almost unchanged throughout the varied concentrations. However, the K/S values (at a wavelength of 400 nm) of the fabrics treated at pH 11 were dramatically increased as the concentration of the CPC was raised in the finishing baths. This result indicates that higher CPC concentration produces more yellowing effect on the fabrics, revealing a potential interference of CPC in the hydrolysis of acrylic polymers. More interestingly, such interference was not present when the pH was at 10.

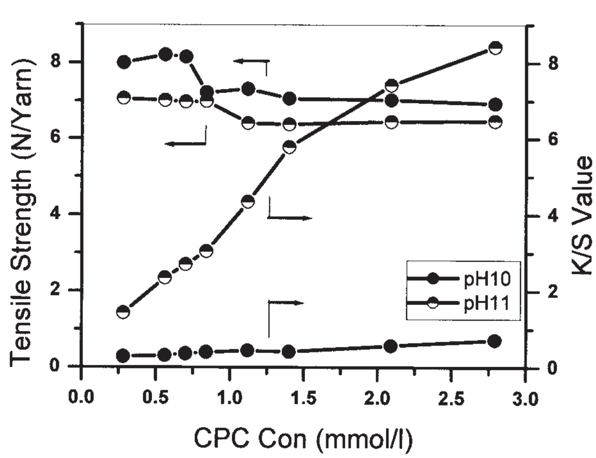


Figure 2 Tensile strengths and K/S values of acrilan fabrics versus CPC concentration. Finishing conditions: liquor ratio = 100 : 1; finishing temperature = 100°C; finishing time = 120 min.

Effect of finishing temperature on properties

In the chemical finishing of acrilan fabrics, temperature is another critical factor. Chemical modification of the polymers occurs in amorphous regions. But chemicals can only enter amorphous regions of fibers when the finishing temperature is above the glass transition temperature of the polymer. Acrylic polymers have a glass transition temperature range of 70–80°C. So the finishing of the acrilan fabrics was conducted > 80 to 100°C. Higher temperatures also promote diffusion of the CPC into the polymers and increase exhaustion of the CPC and antimicrobial properties of the fabrics.[4] Figure 3 shows tensile strength and color changes of the treated acrilan fabrics as the treatment temperature was raised from 80 to 100°C. The tensile strength of the fabrics changed very little in the temperature range, though there was a general trend of slight decline in the tensile strength. More basic conditions still caused lower tensile strength due to the increased CPC-induced reactions on acrylic polymers. But the color changes in two different alkaline conditions were significantly different. At pH 10, the color was

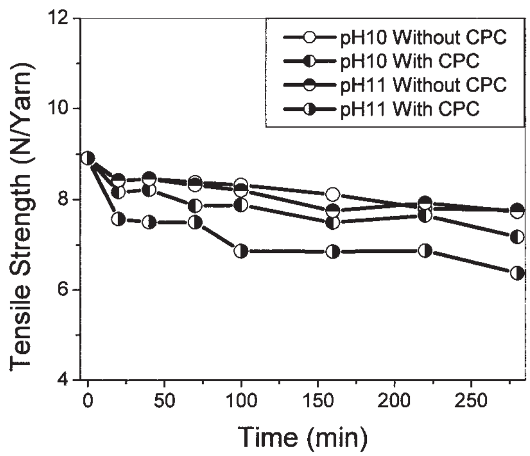


Figure 4 Tensile strengths of acrilan fabrics verses finishing time in solutions containing or without containing CPC at different pH values. Finishing conditions: initial CPC concentration = 1.4 m*M*; liquor ratio = 100 : 1; finishing temperature = 100°C.

almost unchanged throughout the temperature range. However, at pH 11, the yellow color started to intensify after the temperature was above 90°C. It seems that the high temperature may accelerate the reactions on the nitrile groups of the polymer, particularly when the temperature was above the glass transition temperature of the polymer. More interestingly, this accelerated reaction occurred only under strong alkaline conditions.

Effect of finishing time on properties

Finishing time certainly affects the results of the chemical modifications, especially when the polymer may have other side reactions, such as hydrolysis of nitrile groups. We have found that a longer finishing time increased the exhaustion of CPC on acrilan fabrics, resulting in better antimicrobial functions. But, increased finished time obviously can cause more reactions on nitrile groups of the polymer, which may lead to lower tensile strength and an increase yellow color. Indeed, from Figures 4 and 5, the variations of tensile strength and color of the acrilan fabrics at different finishing durations could be viewed. The tensile strength changes were not very significant. As a general trend, more alkaline conditions and the presence of CPC resulted in lower tenacity. The color changes of the treated fabrics with increased finishing time were similar to those of the increased finishing temperature. At pH 11 the yellowing effect was growing more rapidly as the finishing time was increased. However, this effect was not present when there was no CPC in the finishing solution.

Effect of CPC in finishing bath on properties

Carefully analyzing the above results, we found an interesting phenomenon, i.e., the presence of CPC induced the reactions on the acrilan polymers. Figures 4 and 5 revealed that, without CPC in the finishing solution, the fabric color was almost unchanged under different pH conditions and prolonged finishing time; the fabric tenacities were consistently reduced with the increased finishing time. The yellowing of the fabrics only occurred in the presence of CPC and under more alkaline conditions. The yellowing effect of the fabrics is mostly caused by a formation of chromophores in the polymers, which could be some conjugated systems containing C=N bonds. The formation of the system was facilitated by CPC under higher pH values. Without the presence of CPC the chromophore was not easily formed in the acrylic polymers. In fact, we have found that other quaternary ammonium salt surfactants also facilitate the formation of the conjugated C=N bonds. The pure alkaline condition may only hydrolyze nitrile bonds to amide structures that are colorless.

FTIR analysis of treated acrilan

To explore structural changes of acrylic fibers after the CPC treatment, FTIR spectra of acrilan fabrics treated in finishing baths with and without CPC are compared with those of the untreated acrilan fabric (control) (Fig. 6). Table I lists major FTIR bands and their assigned functional groups.[10] When the acrilan fabric was only treated in a basic solution at pH 13, several FTIR bands, such as 3,500–3,600 and 1,630 cm^{-1} become intensified (spectrum A, Fig. 6) compared with those of the control fabric (spectrum C, Fig. 6). These

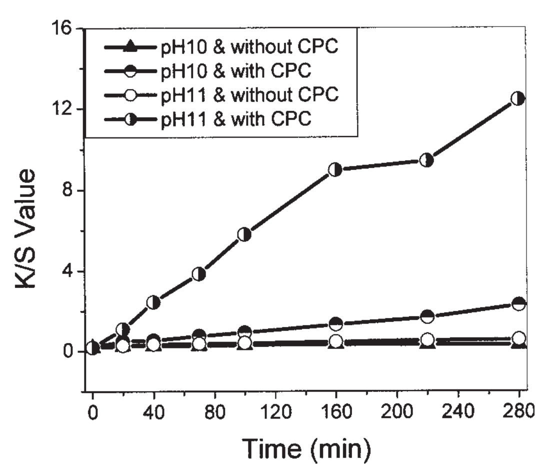


Figure 5 K/S values of acrilan fabrics verses finishing time in solutions containing or without containing CPC at different pH values. Finishing conditions: initial CPC concentration = 1.4 m*M*; liquor ratio = 100 : 1; finishing temperature = 100°C.

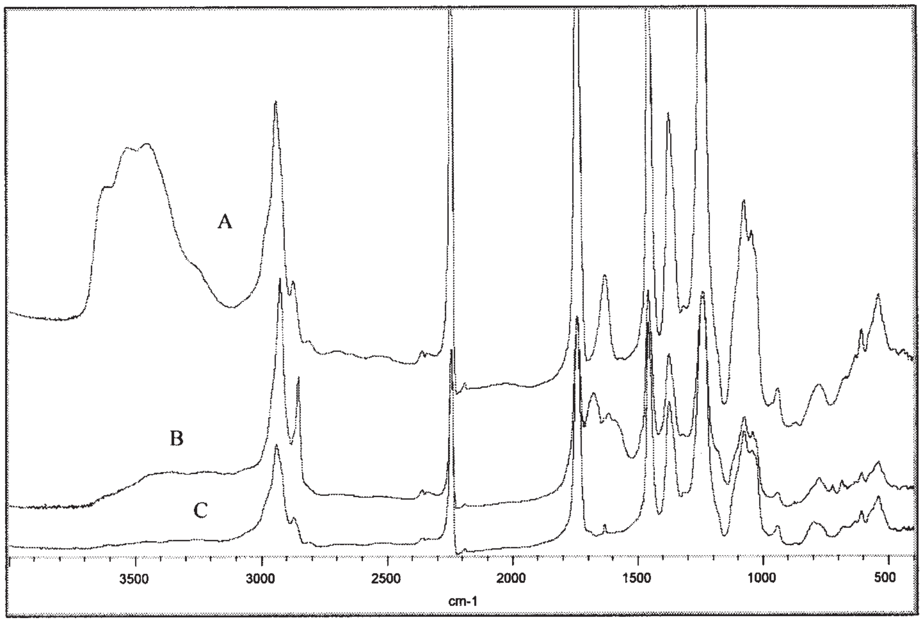


Figure 6 FTIR spectra of the acrilan fabrics treated at pH 13, without CPC (spectrum A), with initial CPC concentration of 1.4 m*M* (spectrum B) and control fabric (spectrum C). Treatment conditions: liquor ratio = 100 : 1; finishing temperature = 100°C; finishing time = 120 min

bands may indicate formation of a $CONH_2$ structure in the polymer, revealing a hydrolysis of the nitrile (CN) bonds. The FTIR of the acrilan fabric that was treated with the CPC (initial concentration = 1.4 m*M*) in a finishing bath under the same pH showed a different pattern (spectrum B, Fig. 6). The NH_2 bending bands at around 3,400 cm^{-1} were slightly increased, but the stretching band of C=N at 1,680 and 1,617 cm^{-1} becomes stronger than the band at 1,630 cm^{-1}. The new bands at 1,680 and 1,617 cm^{-1} might be the infrared absorbance of conjugated C=N bonds formed due to the nucleophilic addition of hydroxyl groups to nitrile bonds. The $C{=}N^-$ could continue to attack the vicinal nitrile groups to lead to the formation of a conjugated system in polyacrylonitrile (path b shown in Scheme 1). The conjugated C=N bonds could absorb light in the visible range, thus, producing a yellowing effect on the fabrics. This conjugated structure is similar to but might not be as long as that of the preoxidized acrylic fibers because the surface resistivities of the fabrics were not significantly reduced.

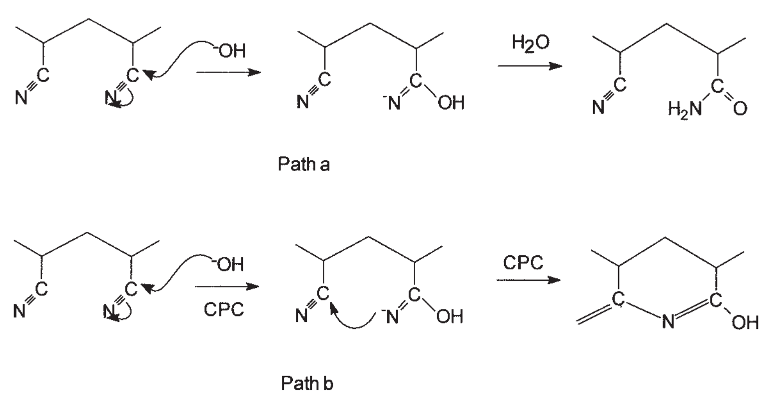
To understand the role of CPC in facilitating the formation of conjugated C=N systems, two additional quaternary ammonium salts, benzyldimethylhexadecyl ammonium chloride (BDHAC) and cetyltrimethyl ammonium bromide (CTAB), were employed in the treatments of the arilan fabrics as well. The findings were similar to the CPC-treated fabrics, and the FTIR spectra show identical bands at both 1,680 and 1,615 cm^{-1} (Fig. 7). We believe that such an effect is probably caused by coverage of quaternary ammonium surfactants on surfaces of acrylic fibers.[11] The cationic quaternary ammonium salt is interactive with the formed anionic species on acrylic fibers, which prevents the access of water molecules and facilitates formation of conjugated systems (path b, Scheme 1). If water can access to intermediate structure the nitrile group could produce an amide structure (path a, Scheme 1), which is supported by the FTIR results.

TABLE I
Assignment of FTIR Spectra of Acrilan Fiber

Range (cm^{-1})	Assignment
3,400–3,600	NH_2 bending
2,927	CH_2 stretching
2,244	CN triple bond stretching
1,740	C=O stretching
1,680	C=N stretching
1,630	NH_2 deformation
1,617	C=N in ring stretching
1,455	CH_2 scissors vibration

Effect of pH on structure

Antimicrobial treatment of acrilan fabrics with CPC was affected by different pH conditions. FTIR spectrometry was employed to analyze the fibers finished at pH values from 4.5 to 13 with the same initial CPC concentration (1.4 m*M*) shown in Figure 8. No significant changes were observed in FTIR spectra of the fabrics treated under a pH range of 4.5 to 9 compared



Scheme 1 Hydrolysis of acrylic fibers.

with the control sample. But when the pH values were increased to 10–13 in the finishing baths significant changes in the FTIR spectra were found in the area of 1,580–1,690 cm^{-1}. Several new bands were formed in this region, and bands at 1,680 and 1,588 cm^{-1} were intensified, but the one corresponding to nitrile (CN) group (2,244 cm^{-1}) was weakened as the pH value was increased. If the absorbance values of 2,244 and 1,680 cm^{-1} are both divided by that of 2,927 cm^{-1} (CH_2 stretching), the results are found to be related to the increased pH values. The relationships are plotted in Figure 9. The increase of the peak ratio of 1,680 versus 2,927 indicates the increased content of C=N bonds in the system, while the decreased peak ratios of 2,244 versus 2,927 reveal the loss of nitrile (CN) bonds. Both of them demonstrated that significant structural changes occurred in the pH range of 10–13. These changes are consistent with the yellowing and tensile strength loss of the acrilan fabrics.

These results are completely consistent with the potential mechanisms proposed in Scheme 1; i.e., the alkaline condition is the key to induce the reactions. Only when the pH value was higher than 9 would the finishing bath contain sufficient hydroxyl groups to attack nitrile groups in polyacrylonitrile. A strong alkaline condition itself was unable to

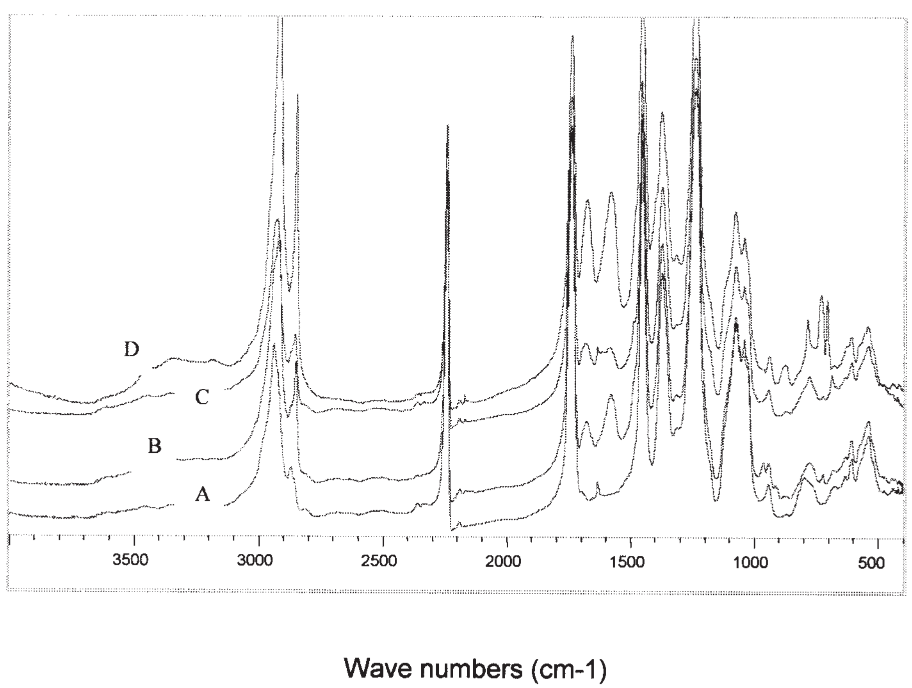


Figure 7 FTIR of acrilan fabrics treated with control (A), CTAB (B), CPC (C), and BDHAC (D). Treatment conditions: initial concentration of quaternary ammonium salt = 1.4 m*M*; liquor ratio = 100 : 1; finishing temperature = 100°C; finishing time = 120 min.

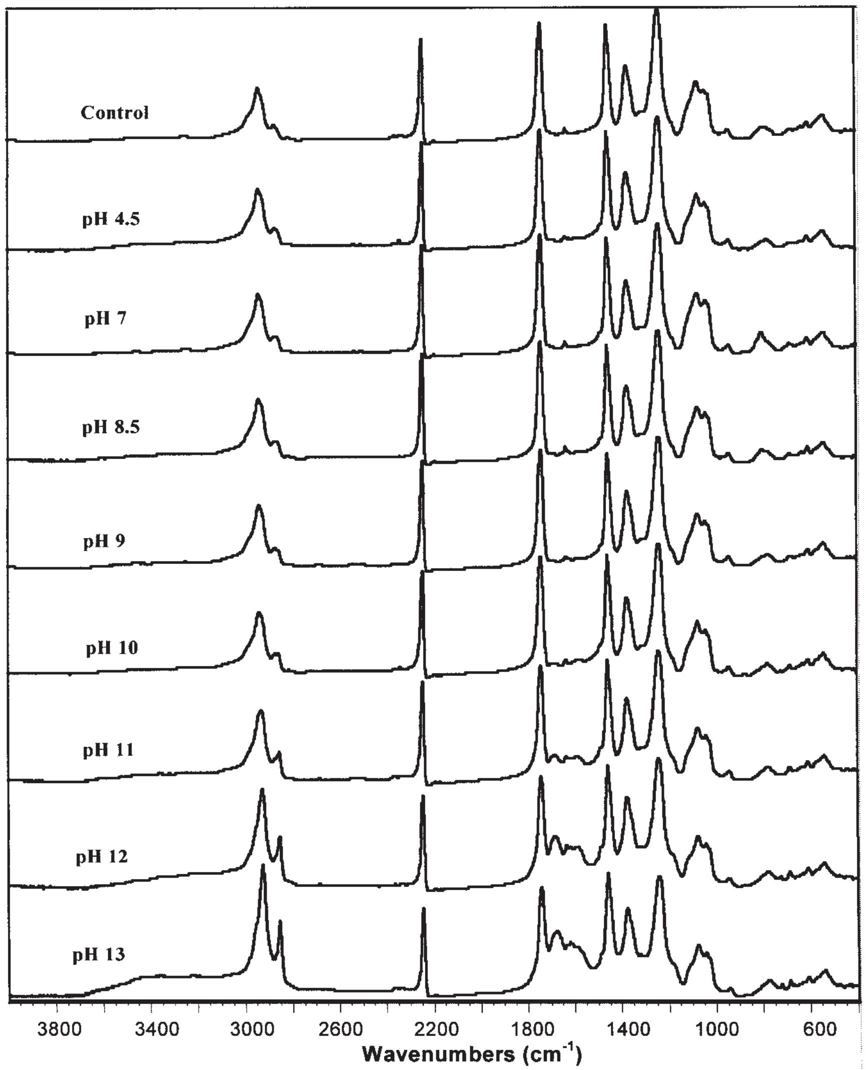


Figure 8 FTIR spectra of the acrilan fibers finished in CPC baths under different pH values. Finishing conditions: initial CPC concentration = 1.4 m*M*; liquor ratio = 100 : 1; finishing temperature = 100°C; finishing time = 120 min.

produce a yellowing effect on acrilan due to the formation of an amide structure instead of a conjugated C=N system.

Effect of CPC concentration on structure

K/S values and antimicrobial functions of the fabrics were increased dramatically with CPC concentrations increased from 0.28 to 1.40 m*M*. FTIR analysis of the CPC-treated fabrics exhibited a similar pattern, i.e., when the initial CPC concentration was raised to 1.4 m*M* from 0.28 m*M*, the band at 1,680 increased significantly. But further increase of the CPC could not raise the intensity of the same band. The FTIR spectra of the acrilan fabrics treated with different CPC concentrations under pH 11 are shown in Figure 10. This result further supports the proposed mechanism of CPC-facilitated hydrolysis of CN and formation of the conjugated C=N system. Since CPC only serves as a

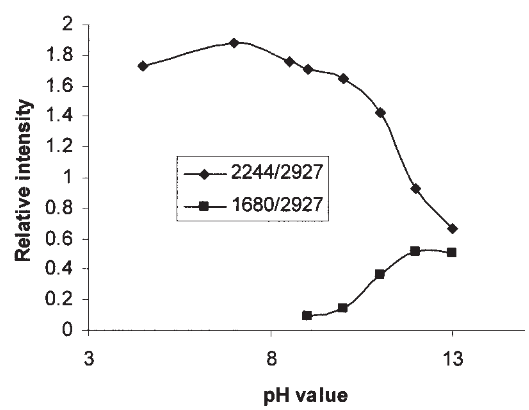


Figure 9 Relative intensities of band ratios of 2,244 : 2,927 and 1,680 : 2,927 cm^{-1} versus pH values of finishing baths. Finishing conditions: initial CPC concentration = 1.4 m*M*; liquor ratio = 100 : 1; finishing temperature = 100°C; finishing time = 120 min.

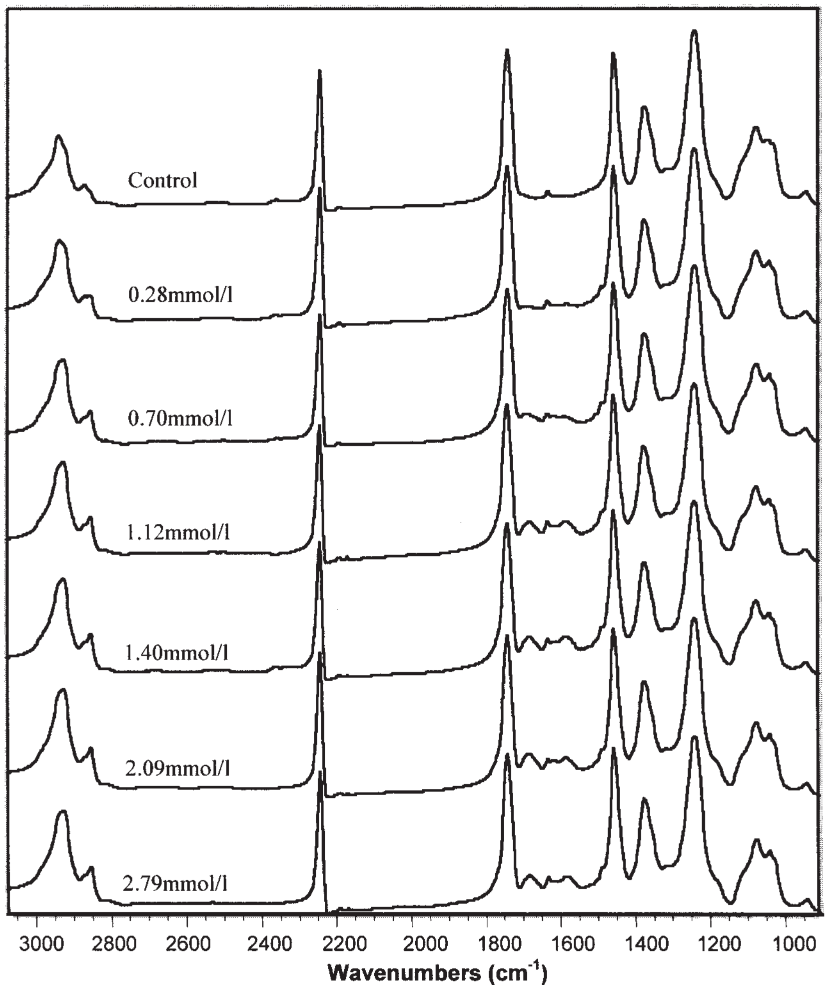


Figure 10 FTIR spectra of the acrilan fibers finished with different CPC concentrations at pH 11. Finishing conditions: liquor ratio = 100 : 1; finishing temperature = 100°C; finishing time = 120 min.

surface active agent, after reaching the critical micelle concentration of the surfactant, increased concentration of CPC would not be able to further cover the surface of the fibers and improve the formation of the conjugated C=N system.

Effect of finishing time on structure

Figure 11 shows IR spectra of the fibers treated in different durations varied from 20 to 280 min under pH 11 and at a CPC concentration of 1.4 m*M*. Again, similar FTIR band changes are observed with the increase of the reaction time. The band at 1,680 cm^{-1} becames intensified as the chemical treatment time was over 70 min, indicating the beginning of the formation of conjugated C=N systems in the polymer. The relative intensities of band ratios of 2,244 : 2,927 cm^{-1} and 1,680 : 2927 cm^{-1} are plotted against the finishing time in Figure 12. Both lines show a consistent linear relationship to reaction time. The formation of conjugated C=N systems and hydrolysis of CN groups correlate with each other in the presence of CPC. The formation of amide structures was less important under this condition. Since the formation of the conjugated C=N system is time dependent, to avoid yellowing of the treated acrilan fabrics, a finishing time shorter than 100 min is preferred. However, most cationic dyeing of acrilan fabrics could be completed within 100 min;[5] thus, this antimicrobial treatment of acrilan fabric is still applicable using current dyeing facilities.

CONCLUSIONS

Durable antimicrobial acrilan fabrics were prepared by a chemical finishing process with a quaternary ammonium salt, CPC. Alkaline conditions, concentration of CPC, and finishing temperatures and times could affect the desired antimicrobial functions, but also impact physical properties of the fabrics, especially when the pH was at or higher than 11. Without the presence of CPC, the alkaline condition could not

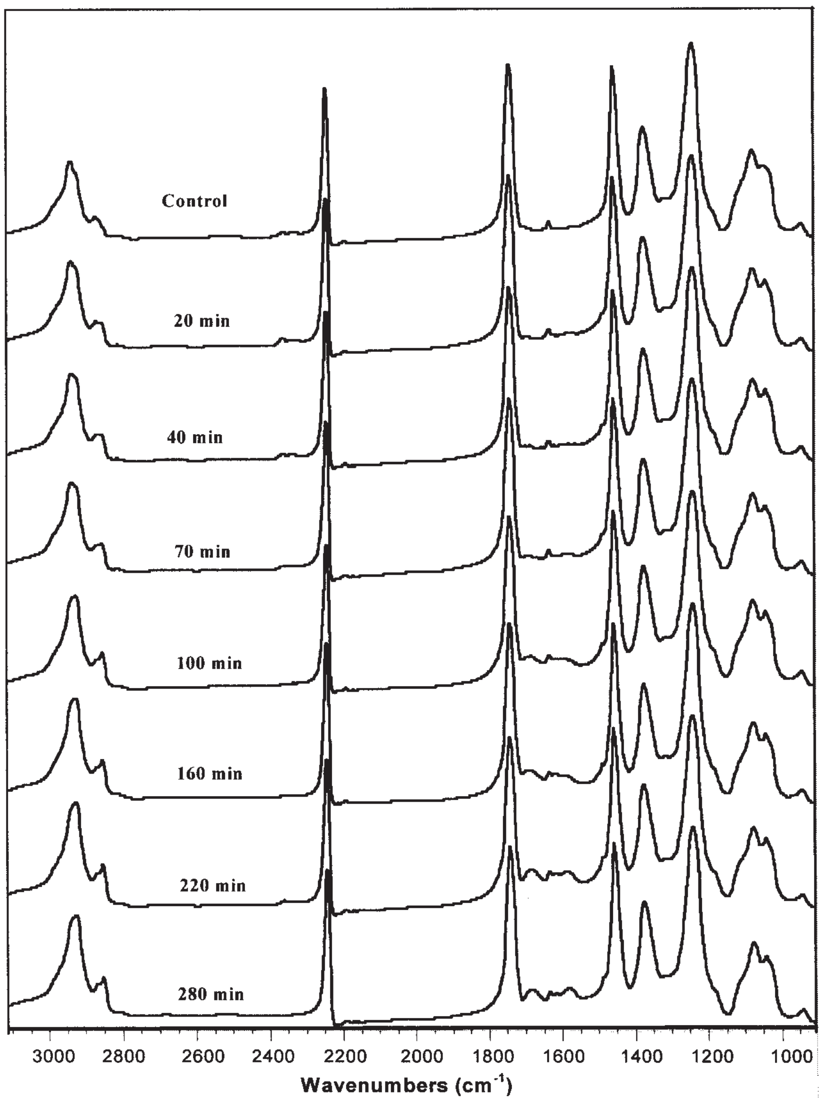


Figure 11 FTIR spectra of the acrilan fibers finished with CPC at different times. Finishing conditions: initial CPC concentration = 1.4 m*M*; liquor ratio = 100 : 1; finishing temperature = 100°C; bath, pH 11.

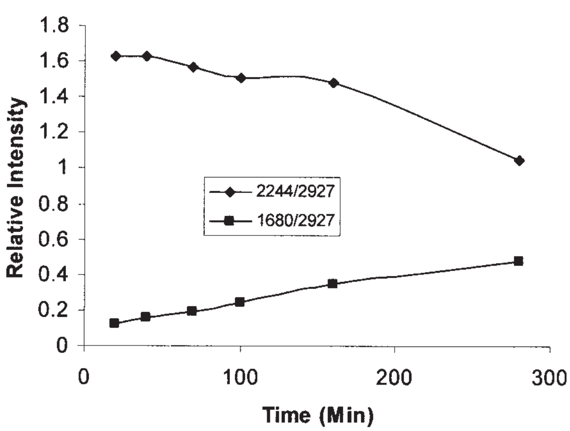


Figure 12 Relative intensities of band ratios of 2,244 : 2,927 and 1,680 : 2,927 cm^{-1} versus finishing time. Finishing conditions: initial CPC concentration = 1.4 m*M*; liquor ratio = 100 : 1; finishing temperature = 100°C; pH 11.

result in similar damage to the finishing fabrics, indicating the quaternary ammonium salt may facilitate reaction on the acrylic polymer.

A FT-IR study of the treated acrilan fibers indicated that a potential chemical reaction forming a conjugated C=N system might be responsible for the yellowing effect and loss of tensile strength of the treated fabrics. This reaction could be facilitated by the presence of CPC when its concentration was increased under a specific concentration, possibly its critical micelle concentration under alkaline conditions. Above this concentration, increasing CPC concentration could accelerate the formation of the conjugated C=N system. With the presence of CPC, the formation of conjugated systems in acrilan polymers could be strengthened as the pH value of the finishing solution was raised above 10. This formation of the conjugated

C=N is not a rapid reaction, which may take around 1.5 h to begin under conditions of pH 11 and 100°C.

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