Modification of Polyacrylonitrile (PAN) Fiber by Blending with *N*-(2-Hydroxy)propyl-3-trimethyl-ammonium Chitosan Chloride

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ABSTRACT: *N*-(2-Hydroxy)propyl-3-trimethylammonium chitosan chloride (HTCC) was synthesized by the reaction of glycidyltrimethylammonium chloride (GTMAC) and chitosan. The reaction product was a water-soluble chitosan derivative, and showed excellent antimicrobial activity. HTCC was blended with polyacrylonitrile (PAN) using an NaSCN aqueous solution as a common solvent. The blend solution was transparent and stable up to 6 months without phase separation. The PAN/HTCC blend fibers were prepared via a wet spinning and drawing process. Thermal, electrical, and mechanical properties as well as antimicrobial activity were investigated. It was found that the antistatic property and antimicrobial activity of the blend fibers could be achieved by adding only a small amount of HTCC. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2258–2265, 1999

Key words: *N*-(2-hydroxy)propyl-3-trimethylammonium chitosan chloride; polyacrylonitrile; wet spinning; blend fiber; antimicrobial activity

INTRODUCTION

Chitosan, a deacetylated product of chitin, has many interesting properties, such as antimicrobial activity, biodegradability, and nontoxicity. Many attempts have been made to use chitosan in several industrial fields, such as medical, textile, food, cosmetic industry, etc. In particular, several methods were studied so as to apply its antimicrobial property to fiber materials, such as the binding of chito-oligosaccharide to cotton fabric with a crosslinker[1] or blending chitosan with fiber-forming polymers.[2,3] But research on blending of chitosan with other polymers is limited by the difficulty of finding a common solvent for chitosan, which dissolves commonly in aqueous acid solution.

On the other hand, some compounds containing quaternary ammonium groups are water soluble and impart good antimicrobial activity to textiles.[4,5] Therefore, a chitosan derivative containing such a group can be water soluble and exhibit higher antimicrobial activity. *N*-(2-hydroxy)-propyl-3-trimethylammonium chitosan chloride (HTCC) can be synthesized[6] from chitosan and glycidyltrimethylammonium chloride (GTMAC), which enhances water solubility and antimicrobial activity of chitosan. Because many antistatic finishing reagents also contain quaternary ammonium groups,[7] it is expected that HTCC can also be used as an antistatic agent for synthetic fibers. Thus, both antimicrobial and antistatic properties may be obtainable with HTCC.

Polyacrylonitrile (PAN) is one of the most important fiber-forming polymers and has been widely used because of its high strength, abrasion resistance, and good insect resistance. However, it also has some disadvantages, such as strong hydrophobicity, electrostatic accumulation, etc., due to the lack of segmental mobility resulting from intensive molecular orientation of the highly polar nitrile groups. There have been many attempts to improve the electrostatic property of the PAN fiber: blending with other hydrophilic polymers[8,9] and the alkaline hydrolysis of nitrile groups to hydrophilic groups.[10,11] It is expected that the antistatic property and antimicrobial activity of hydrophobic PAN fiber can be improved by introducing HTCC in the wet spinning process.

In this work, HTCC was synthesized and solution blended with PAN using 46% NaSCN aqueous solution as a common solvent. The PAN/HTCC blend fibers were prepared by a two-stage wet spinning process, and the effect of HTCC content on the antimicrobial, antistatic, and mechanical properties of the blend fibers was investigated.

EXPERIMENTAL

Materials

The polyacrylonitrile used was a copolymer of 91.3% acrylonitrile, 8.5% methylacrylate, and 0.2% sodium methallylsulfonate with a molecular weight of 50,000 (Taekwang Co. Ltd., Korea). The chitosan (degree of deacetylation 83.9%, molecular weight 476,000) was obtained from Kumho Chemicals Co. Ltd., Korea, and 90.5% deacetylated chitosan was prepared by the method of Mima et al.[12] The raw chitosan was subjected to deacetylation treatment with 50% NaOH, for 2 h at 100°C in a nitrogen atmosphere. The treated chitosan was neutralized by washing with distilled water at 80°C. The molecular weight of the chitosan was measured using a 0.2 M CH_3COOH/0.1 M CH_3COONa as the solvent at 30°C.[13] Chitosan (molecular weight of 336,000) having a 90.5% degree of deacetylation was obtained, then purified by reprecipitation.[14] Glycidyltrimethylammonium chloride (GTMAC, solid content 80%) was obtained from Nagase Co., Ltd., Japan. All the other chemicals were of reagent grade and used without further purification. Nutrient broth and trypton glucose extract agar (DIFCO Laboratories) were used as the bacteria cultivating re-

agents in the antimicrobial activity test of the blend fibers.

Synthesis of HTCC

The purified chitosan was dispersed in water (5% w/w), and GTMAC and $Zn(BF_4)_2$ (0.1% owb) as a catalyst were added to the bath. The mol ratio of GTMAC to amine groups of chitosan was 4. The reaction was continued for 20 h, with stirring at 100°C. After the reaction, the clear viscous solution was poured into an ethanol/acetone (1/1 v/v) mixture and the precipitates were washed by stirring in the same solvent for at least 24 h and filtered. Unreacted reagents were extracted with acetone for 24 h in a Soxhlet apparatus and vacuum dried.

The degree of substitution (DS) of HTCC and the HTCC content in the PAN/HTCC blend fibers were calculated from the chlorine content measured by a combustion flask method.[15] The degree of substitution of HTCC was calculated from the following equation:

$$DS = (203.2 - 42.04x)/[(3545/y(\%) - 151.64],$$

where x is the degree of deacetylation of chitosan, and y is the percent chlorine content of HTCC.

Preparation of PAN/HTCC Blends

The DS of the synthesized HTCC was 0.92, and the molecular weight measured by the Gel Permeation Chromatograph (Shimadzu Co., Ltd.) was 150,000. A 46% (w/w) NaSCN aqueous solution was used as a common solvent. HTCC and PAN were dissolved by stirring at 70°C for 5 h. The total concentration of the blend solution was fixed at 12%, and the relative composition of PAN/HTCC in the blend solution varied from 100/0 to 80/20 (by weight). After blending PAN and HTCC, the solution was treated in an ultrasonic bath to remove bubbles.

The intrinsic viscosity of the blend solution was measured using a Brookfield viscometer (Model LVT, Brookfield Engineering labs. Inc.) in the 0.3 to 12 rpm range.

Wet Spinning

The wet spinning process is shown in Figure 1. The blend solution was extruded with a Zenith Type QM Motor Driver Assembly (Zenith Co. Ltd., USA), fitted with a dope tank, metering pump, spinneret with 12 holes 0.2 mm in diame-
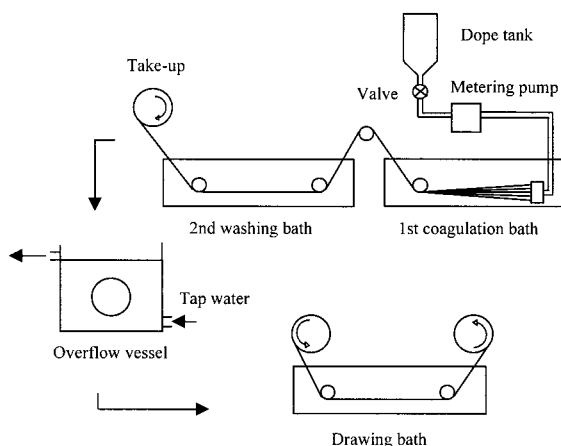
Figure 1 Schematic diagram of wet spinning process.

ter, and a two-stage coagulation bath. Bubble-free blend solutions were poured into the dope tank and passed through 100 mesh and 300 mesh wire filters to remove the impurities. The extrusion velocity was 0.35 cc/min, and the take-up speed varied from 1.2 m/min to 3.0 m/min. Ten percent NaSCN aqueous solution was used as the coagulant in the first bath, and tap water in the second bath. The wet-spun blend fibers were washed in an overflow water vessel for 24 h. The spun fibers were then drawn in a boiling water bath and air dried. The draw ratio varied from 1 to 5.

Analysis and Measurements

Infrared (FTIR) spectra were obtained from a KBr pellet using an MIDAC M series FTIR spectrometer (MIDAC Co.). Thermogravimetric analysis was carried out on a Seiko TG/DTA 6200 in a nitrogen atmosphere heating from 25 to 600°C at 10°C/min.

The mechanical properties were measured using an Instron tensile tester (model 4301) at 20°C, 65% R.H. The gauge length was 20 mm, and the crosshead speed was 20 mm/min. The figures quoted are the averages of 10 tests.

To estimate the release of water-soluble HTCC from the blend fibers in water, the weight loss was measured after extraction with water at 25 and 60°C. The moisture content of the blend fibers was calculated from the following equation:

$$\text{Moisture content } (\%) = (m_c - m_d)/m_c \times 100,$$

where m_c is conditioned weight at 20°C, 65% R.H. for 24 h, and m_d is dried weight at 100°C for 30 min. The surface electric resistance was mea-

sured using the Static Voltmeter R-4021 (Rothschild, Schweiz). The samples conditioned at 20°C, 40% R.H. for 12 h, were clamped with 10 cm-long electrodes. They were charged to 150 V, and the half discharge time was measured. The surface electric resistance value was calculated according to the following equation:

$$\text{Surface electric resistance} = t \times 10^{11} \text{ (in ohms)},$$

where t is the measured time (in seconds) to reach the half value of the charged voltage.

Antimicrobial activities were evaluated according to the Shake Flask CTM 0923 test method (Dow Corning, USA).[4,16] A gram-positive bacterium, *Staphylococcus aureus* (American type culture collection No. 6538), was used for testing. The blend fibers were placed in a diluted culture medium containing *Staphylococcus aureus*, and then shaken for 1 h at 37°C. After shaking, the medium was cultivated on an agar plate and the percent reduction in bacteria was evaluated.

RESULTS AND DISCUSSION

Synthesis of HTCC

The reaction between the amine groups of chitosan and GTMAC is represented in Scheme 1. The epoxy ring of GTMAC is opened by the catalyst, and the activated glycidyl group reacts with the amine groups of chitosan. Figure 2 shows the FTIR spectra of chitosan and HTCC. In the spectrum of the synthesized HTCC, the amine scissoring band at 1570 cm^{-1} of chitosan disappeared,
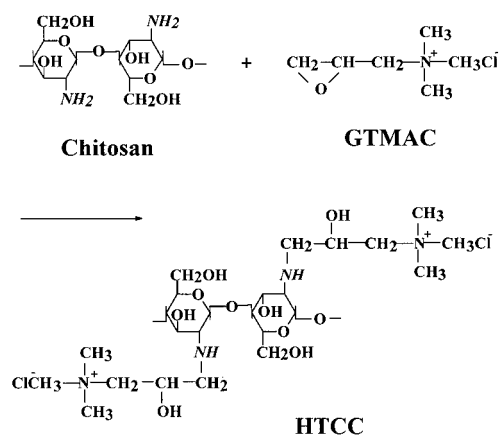
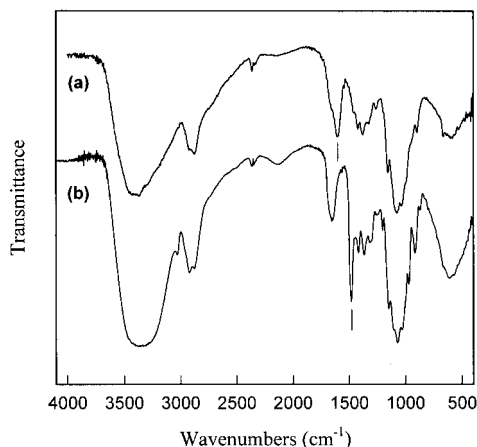**Scheme 1** Reaction scheme for the synthesis of HTCC.

Figure 2   FTIR spectra of chitosan (a) and HTCC (b).

Figure 3   Effect of HTCC weight ratio on the viscosity of PAN/HTCC blend solutions at 20°C.

implying that the epoxide groups of GTMAC have reacted with the NH_2 groups rather than the OH groups of chitosan. Also, a new intensive peak at 1490 cm^{-1} appeared, probably due to the methyl groups of the quaternary trimethylammonium groups of HTCC.

Preparation of PAN/HTCC Blend Fibers

The PAN/HTCC blend solution was prepared by dissolving PAN powder and HTCC in NaSCN aqueous solution at 70°C. The solution was transparent, and stable up to 6 months without phase separation, showing that the stability of the blend solution is excellent.

The solution viscosity is one of the important factors in the wet-spinning process. Therefore, we measured the viscosity of the blend solutions, and investigated the effect of HTCC content on the solution viscosity. Figure 3 shows the viscosity of the 12% PAN/HTCC blend solutions. As the HTCC content increased, the viscosity increased. It is believed that the viscosity of the blend solutions increased due to the higher molecular weight and the bulkier structure of HTCC compared with PAN. The maximum viscosity was about 210 poise at the 80/20 blend ratio, which was nearly four times compared to that of pure PAN solution. But the increased viscosity upon addition of HTCC was not significant in wet spinning because the appropriate extrusion viscosity of the spinning solution is known to be between 20 and 5,000 poise.[17]

Figure 4 shows the FTIR spectra of the wet-spun PAN/HTCC blend fibers. As the HTCC content increased, the absorption peaks at 3350 cm^{-1} for OH stretching vibration and 1490 cm^{-1} for
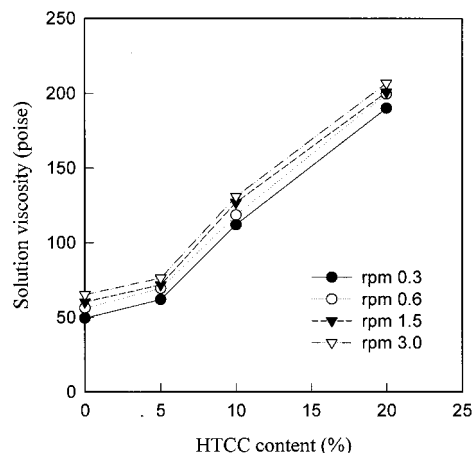
methyl groups increased, both of which did not exist in the PAN fiber. Therefore, the presence of HTCC in the blend fibers could be confirmed. On the other hand, the position of the —C≡N absorption peak at 2245 cm^{-1} does not vary with the increase in HTCC content, implying that there are no significant interactions between HTCC and the nitrile groups of PAN.

The PAN/HTCC blend fibers were successfully produced by a two-stage wet-spinning process. During the spinning process, some HTCC may diffuse into the coagulation and washing bath due to its high water solubility. Therefore, we measured the chlorine contents in the blend fibers to determine the HTCC contents, and the results were shown in Table I. Most of the HTCC incorporated remained in the blend fibers, with 99%
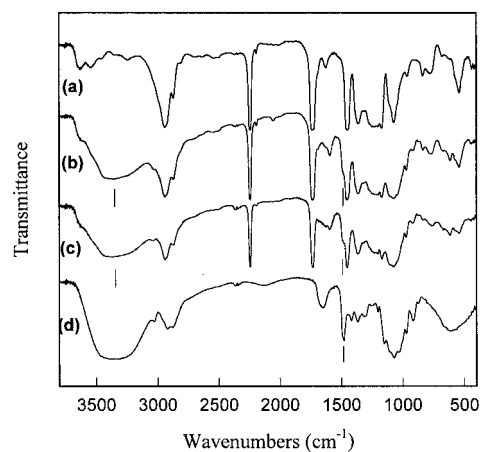

Figure 4   FTIR spectra of the PAN/HTCC blend fibers: (a) PAN, (b) 90/10, (c) 80/20, (d) HTCC.

Table I HTCC Content in the PAN/HTCC Blend Fibers

PAN/HTCC Blend Ratio	Cl Content (%)		HTCC Content in Fiber (%)	Measured/Calculated
	Calculated	Measured		
95/5	0.535	0.530	4.95	0.99
90/10	1.071	0.894	8.35	0.84
80/20	2.142	1.712	15.99	0.80

Cl content of HTCC: 10.71%.

HTCC remaining in the case of the 95/5 blend and 84 and 80% in the case of the 90/10 and 80/20 blends. It is thought that HTCC is fairly stable against dissolving into water at a low blend level, presumably due to the entanglement of two polymer chains. The HTCC is released less than 20% from the blend fibers during coagulation and washing; however, most of the HTCC incorporated remain in the blend fibers despite the high water solubility of HTCC.

Textile materials are subjected to laundering, so it is possible that some of HTCC may be released during laundering. Table II shows the weight loss of PAN/HTCC blend fibers after water treatment at 25 and 60°C for 24 and 16 h, respectively, from which the LOST amount of HTCC can be inferred. Park[18] reported that more than 8% was extracted by water treatment at 60°C for 12 h from PAN/hydrophilic modified protein (80/20) composite membrane. As can be seen from Table II, the weight loss on treating PAN/HTCC (80/20) blend fiber at 60°C for 16 h was only 4.1%. Furthermore, the weight loss in water treatment at 25°C was much lower. The increased weight loss at the higher temperature may be explained by the higher solubility of HTCC at higher temperature. These results suggest that the water stability of the blend fibers is sufficient for textile end uses.

Properties of PAN/HTCC Blend Fibers

The PAN/HTCC blend fibers are likely to show a thermal behavior dissimilar to PAN. However, it

Table II Weight Loss of the PAN/HTCC Blend Fibers by Water Treatment

PAN/HTCC Blend Ratio	Weight Loss (%)	
	25°C, 24 h	60°C, 16 h
95/5	0.2	0.7
90/10	0.6	1.4
80/20	1.8	4.1

is difficult to determine the melting point of PAN because it is decomposes before melting, and HTCC also does not melt before degradation. PAN undergoes a degradation reaction involving cyclization at elevated temperatures in which the adjacent nitrile groups on the polymer chain react to form six-membered rings.[19] We measured the thermal degradation behavior instead of measuring the melting point, and the results are shown in Figure 5. HTCC, which starts to decompose at 210°C, is less stable compared with PAN fiber. The PAN fiber shows maximum decomposition at 360°C, and the maximum decomposition temperature gradually decreases with increasing HTCC content.

To assess the interaction between PAN and HTCC in the blend fiber, the degradation behavior of a physical mixture prepared by mixing PAN and HTCC powder was measured, and compared with that of the blend fibers. The physical mixture of PAN/HTCC (80/20) decomposes more heavily around 210°C than the blend fibers of the same composition, and the residue content of the former is lower than the latter. In addition, while
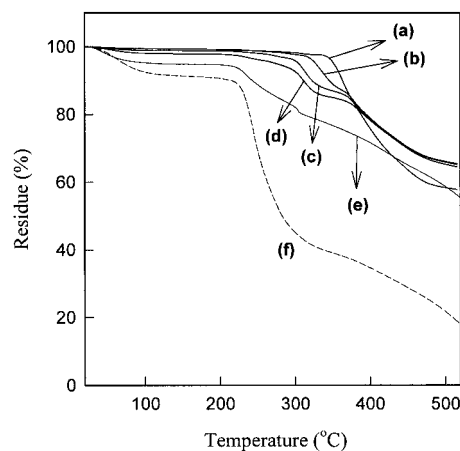

Figure 5 Thermograms of the PAN/HTCC blend fibers: (a) PAN, (b) 95/5, (c) 90/10, (d) 80/20, (e) 80/20 powder mixture, (f) HTCC.

Table III   Effect of HTCC Content on the Mechanical Properties of the PAN/HTCC Blend Fibers

| HTCC Content (%) | Denier | Mechanical Properties | | |
		Tenacity (g/den)	Elongation (%)	Initial Modulus (g/den)
0	85	1.01	15.8	31.6
1	94	1.05	15.7	32.3
5	81	1.05	15.3	31.3
10	83	1.03	8.8	36.2
20	92	1.16	7.9	42.9

Wet spinning conditions: take-up speed 2.4 m/min; draw ratio 2.

the blend fibers have only one major derivative peak, the physical mixture curve shows two peaks. Therefore, it may be said that interaction between PAN and HTCC is present in the case of solution blending, contrary to the physical mixing.

The effect of HTCC content and spinning conditions on the mechanical properties of the PAN/HTCC blend fibers was studied. Poor compatibility of the component polymers may result in extremely low tenacity, which would disallow the utilization of these blend fibers. The change on the mechanical properties of the blend fibers with HTCC content, shown in Table III, is nominal up to 5%. As the HTCC content increases, the tenacity changes little, the elongation decreases, and the initial modulus increases. Especially, the tenacity of PAN/HTCC blend fibers did not decrease, implying compatibility between PAN and HTCC.

Table IV shows the mechanical property changes with the take-up speed and draw ratio. It is generally known that the tenacity increases and the elongation decreases in proportion to draw ratio and take-up speed. The tenacity increases only slightly with take-up speed, because the range of take-up speed studied was very low. On the other hand, the draw ratio greatly affects the tenacity. The maximum tenacity value (2.09 g/den) was obtained at a draw ratio of 5. As the tenacity of Acrilan (Monsanto Co.), commercial PAN fiber, is 3.6 g/den for textiles fiber, and 2.2 g/den for carpet fiber, it is thought that the blend fibers have sufficient tenacity for normal textile applications.

As many antistatic reagents contain quaternary ammonium groups, there is a possibility that HTCC can also be used to impart antistatic property to synthetic fiber. It is expect that the PAN/HTCC blend fibers may show good antistatic properties due to the cationic groups in HTCC. Table V shows the moisture contents and surface electric resistance of the blend fibers. HTCC has a moisture content of more than 17%, similar to

Table IV   Effect of Take-Up Speed and Draw Ratio on the Mechanical Properties of the PAN/HTCC Blend Fibers

| Spinning Conditions | | | Mechanical Properties | | |
Take-Up Speed (m/min)	Draw Ratio	Denier	Tenacity (g/den)	Elongation (%)	Initial Modulus (g/den)
1.2	2	180	0.90	19.4	20.4
1.8	2	121	0.98	21.0	21.4
2.4	2	94	1.05	15.7	32.3
3.0	2	59	1.17	18.2	32.2
2.4	1	182	0.52	17.4	20.3
2.4	2	94	1.05	15.7	32.3
2.4	3	65	1.44	16.3	37.4
2.4	4	45	1.82	13.7	45.3
2.4	5	36	2.09	12.8	49.2

HTCC content: 1%.

Table V Moisture Content and Surface Electric Resistance Value of the PAN/HTCC Blend Fibers

Blend Fibers	Moisture Content (%)	Surface Electric Resistance ($\times 10^{-12}$ Ω)
100% PAN	1.07	400
PAN/HTCC		
99/1	1.21	75
95/5	1.48	31
90/10	2.24	8
80/20	3.43	1
HTCC	17.11	—
PET	0.40	580
Nylon 6	4.50	290

Wet spinning conditions: take-up speed 2.4 m/min; draw ratio 1.

that of wool fiber. The moisture contents of the blend fibers show a slight change with increasing HTCC content. However, the surface electric resistance value decreased sharply upon blending with only 1% of HTCC. The antistatic property generally depends on the moisture content of fiber materials,[20] but the PAN/HTCC blend fibers show a very low electric resistance value contrary to their low moisture content. At the blend ratio of 80/20, the moisture content is only 3.43%, which is a lower value compared with that of Nylon 6 having 4.5%. But the 80/20 blend fiber shows a much lower surface electric resistance than that of Nylon 6. The former has 1.0×10^{-12} Ω of surface electric resistance, and the latter has 290×10^{-12} Ω. The better antistatic property may be due to the increased electric conductivity, resulting from the cations of HTCC. Therefore, it is possible to impart excellent antistatic property to a PAN fiber by blending small amounts of HTCC.

Antimicrobial Activity

HTCC shows excellent antimicrobial activity.[6] It is expected that HTCC has a stronger antimicrobial activity than chitosan, owing to the effect of chitosan and quaternary ammonium groups. Therefore, we can expect that the blend fibers have good antimicrobial activity. Figure 6 shows the effect of the HTCC content on the antimicrobial activity of the blend fibers. As can be seen in Figure 6, they show nearly 100% reduction in bacteria by the addition of only 0.5% HTCC. Ko et al.[21] reported that at chitosan contents of above 2%, the cellulose/chitosan blend fibers showed

nearly 100% reduction in bacteria. However, the antimicrobial activity of the PAN/HTCC blend fiber is superior to the cellulose/chitosan blend fibers. Only 0.5% HTCC is required for nearly 100% reduction in bacteria under the same environment.

CONCLUSION

HTCC was synthesized from the reaction of chitosan and GTMAC having quaternary ammonium groups, and then blended with PAN by 46% NaSCN aqueous solution as a common solvent. Mechanical properties, electrical property, and antimicrobial activity of the PAN/HTCC blend fibers were investigated in relation with the HTCC content and conditions of wet spinning. The following conclusions may be proposed.

The PAN/HTCC blend fibers having appropriate mechanical properties can be prepared by a two-stage wet-spinning process. The blend solution was transparent and stable up to 6 months without phase separation. Not only did most of the HTCC remain in the blend fiber after wet spinning, but the stability to water treatment was also good.

As the HTCC content increased, the elongation decreased slightly, with little difference in tenacity. The tenacity value sharply increased with an increasing draw ratio.

Although the moisture content increased only slightly with increasing HTCC content, the surface electric resistance decreased sharply with addition of only 1% HTCC. The antimicrobial ac-
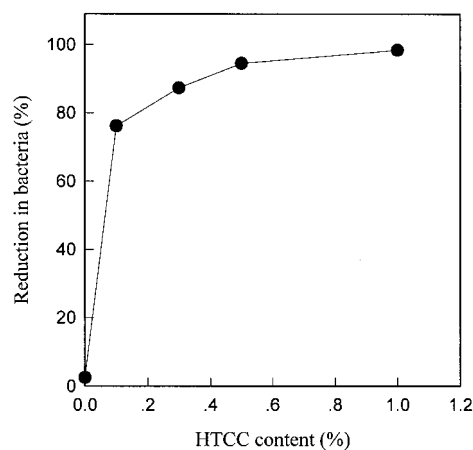

Figure 6 Effect of HTCC content on the antimicrobial activity of the PAN/HTCC blend fibers.

tivity of the blend fibers was excellent showing nearly 100% reduction in bacteria at 0.5% HTCC content. It has been shown that HTCC can be used as an antistatic and antimicrobial agent for the PAN fiber.

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