

Blend Fibers of Polyacrylonitrile and Water-Soluble Chitosan Derivative Prepared from Sodium Thiocyanate Solution

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ABSTRACT: A water-soluble chitosan derivative of *N*-(2-hydroxy)propyl-3-trimethylammonium chitosan chloride (HTCC), synthesized by the reaction of chitosan and glycidyltrimethyl ammonium chloride, and polyacrylonitrile (PAN) were blended using 46% (w/w) NaSCN aqueous solution as a common solvent. The total polymer concentration of blend solution was fixed at 12% (w/w), and the relative composition of PAN/HTCC in the blend solution varied from 0/100 to 80/20 by weight. The PAN/HTCC blend fibers with the appropriate physical property were prepared by a wet spinning and drawing process. The effect of HTCC content on the structural change, miscibility, and ability to be dyed of the blend fibers was investigated. The optical and scanning electron microscopic observation gave no indication of phase separation up to 20% HTCC content. Differential scanning calorimetry and dynamic mechanical measurements of the blend fibers show single glass transition temperatures that increase with increasing blend ratio of HTCC. All the experimental results exhibit that the blends are miscible on the molecular scale. The blend fibers could be dyed with an acid dye. This enhanced ability of the blend fibers to be dyed with acid dyes could be useful for one-step dyeing when mixed with other fibers, such as wool and nylon. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1620–1629, 2001

Key words: *N*-(2-hydroxy)propyl-3-trimethylammonium chitosan chloride (HTCC); polyacrylonitrile (PAN); blend fiber; miscibility; ability to be dyed

INTRODUCTION

Chitosan, a deacetylated product of chitin, is a high molecular weight heteropolysaccharide composed mainly of β -(1,4)-2-deoxy-2-amino-D-glucopyranose units and partially of β -(1,4)-2-deoxy-2-acetamido-D-glucopyranose. It has been used for the preparation of fibers and films. The driving force in the development of new applications for chitosan lies in the fact that it is not only naturally abundant but also has many novel properties such as antimicrobial activity, biodegradability, and nontoxicity. Therefore, many studies have been made to use chitosan in various industrial fields, such as medical, textile, food, cos-

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metic, and other industries.¹⁻⁴ Chitosan has been incorporated into other polymers to overcome their inherent weakness or to introduce useful properties of chitosan.^{5, 6} Among them, attempts to obtain chitosan blends with other polymers have been made using an aqueous acid solution as a common solvent, such as poly(vinyl alcohol) (PVA),⁷⁻⁹ poly(acrylic acid) (PAA),¹⁰ poly(ethylene oxide) (PEO),¹¹ and polyamide (PA).¹² However, blending of chitosan with the other polymers that are insoluble in aqueous acid solution has not been fully studied.

A chitosan derivative containing the quaternary ammonium group becomes water soluble and exhibits higher antimicrobial activity.¹³ *N*-(2-Hydroxy)propyl-3-trimethylammonium chitosan chloride (HTCC) can be synthesized from chitosan and glycidyltrimethylammonium chloride (GT-MAC), which enhances the water solubility and antimicrobial activity of chitosan.

Polyacrylonitrile (PAN), manufactured by wet spinning using organic solvent or aqueous solution of inorganic salt, is one of the most important fiber-forming polymers and has been widely used because of its outstanding physical and chemical properties. However, it also has some disadvantages, such as low dye affinity, low moisture regain, and high static charge 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 PAN fiber by blending with other hydrophilic polymers^{14, 15} or by the alkaline hydrolysis of nitrile groups to convert hydrophilic groups.^{16, 17} However, to the best knowledge of the present authors, the studies of PAN blends with chitosan or chitosan derivatives have not been reported in the literature. In our previous paper,¹⁸ we prepared the PAN/HTCC blend fibers by a two-step wet spinning process. The electrostatic charge of PAN fiber was reduced by the blending with HTCC and the blend fibers also showed excellent antimicrobial activity. However, there was no detailed examination of the structural changes of PAN caused by blending with HTCC and the miscibility of the two polymers.

This study is mainly concerned with the miscibility characterization of PAN/HTCC blend fibers. We prepared the PAN/HTCC blend fibers up to 20% HTCC content by a two-step wet spinning process. The effect of HTCC content on the structural change, miscibility, and ability to be dyed of the blend fibers was investigated. Microscopic ob-

servations and determination of glass transition temperature (T_g) indicate that PAN and HTCC are miscible within the experimental range. This result and the presence of specific interactions between two polymers are discussed.

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 g/mol (Taekwang Company, Ltd., Ulsan, Korea). The chitosan (degree of deacetylation, 83.9%; molecular weight, 476,000 g/mol) was obtained from Kumho Chemicals Company Ltd., Seoul, Korea. Glycidyltrimethylammonium chloride (GTMAC, solid content 80%) was obtained from Nagase Company, Ltd., Japan. $Zn(BF_4)_2$ was used as a catalyst for synthesis of HTCC. Irgalan Red 2GL, an acid dye, was obtained from Ciba Chemicals, Ltd. (Basel, Switzerland).

Synthesis of HTCC and Preparation of PAN/HTCC Blends

HTCC was synthesized by the method of previous paper.¹⁸ The degree of substitution (DS) of the synthesized HTCC, determined by the modified combustion flask method,¹⁹ is 0.92 and the molecular weight, measured by gel permeation chromatograph is $\sim 150,000$ g/mol.

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 polymer 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 of PAN and HTCC, the blend solution was treated in an ultrasonic bath to remove bubbles. The HTCC content was limited to 20% because the main purpose of blending HTCC with PAN is to improve some disadvantages of PAN. Less than 20% of blending is considered to be sufficient for the modification of PAN without significant change of other properties. Another reason to limit the HTCC content is the difficulty of fiber formation in the case of high HTCC content. HTCC alone did not form a fiber in the coagulation bath used in this study. Therefore, all the experiments in this study were carried out for the blend fibers with up to 20%

HTCC content, and HTCC powder or film was used for the comparison of HTCC with PAN or PAN/HTCC blend fibers.

Wet Spinning of PAN/HTCC Blend Solutions

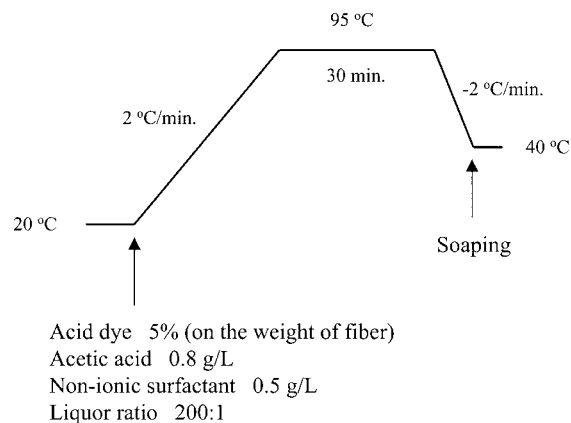
The blend solution was extruded with a Zenith Type QM Motor Driver Assembly fitted with a dope tank, metering pump, spinneret with 12 holes of 0.2-mm diameter, and a two-step coagulation bath. The bubble-free blend solutions were poured into the dope tank and passed through 100- and 300-mesh wire filters successively. The extrusion velocity was 0.35 cm³/min, and the take-up speed varied from 1.2 to 3.0 m/min. A 10 % NaSCN aqueous solution was used as a coagulant in the first bath and tap water was used in the second bath. The wet-spun blend fibers were washed in an overflowed tap water vessel for 24 h to remove the residual solvent. Subsequently, the spun fibers were drawn in a boiling water bath and air dried. The draw ratio was varied from 1 to 5.

A PAN/HTCC blend string with 0.5-mm diameter was prepared by extruding the blend solution using a syringe-type extruder. The blend string was used to observe the distribution state of the HTCC in the blend fibers by scanning electron microscope (SEM).

Analysis and Measurements

Fourier transform infrared (FT-IR) spectra were obtained from KBr pellet using a Midac M series FT-IR spectrometer (Midac Company, Irvine, CA). Wide-angle X-ray diffraction (WAXD) patterns were recorded on an X-ray diffractometer (MAC science, M18X HF) using nickel-filtered CuK α radiation from a generator operated at 45 kV and 200 mA. The cross-section of blend strings fractured in liquid nitrogen was observed with a JEOL JSM-840A SEM.

Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC-7. The scans were run at a heating rate of 10 °C/min under nitrogen atmosphere. The results of the first run are not described because the thermograms were often disturbed due to the presence of trace amounts of water. The results of the second run, which was done after rapid cooling by liquid nitrogen following the first heating, are reported. Dynamic mechanical thermal analysis (DMTA) for PAN/HTCC blend fibers was carried out with a Seiko DMA model DMS 210. The measuring



Scheme 1 Dyeing profile of blend fibers.

frequency was 10 Hz, and the heating rate was 2 °C/min with the temperature range of -40 to 210 °C.

Dyeing of the blend fibers were performed according to the dyeing profile shown in Scheme 1. Reflectance of the dyed blend fibers was measured at the wavelength of maximum absorption of the given dye. The K/S values, which represent the color strength of dyed materials, were calculated with the following Kubelka–Munk equation²⁰ with a reflectance spectrophotometer (Macbeth, New Windsor, NY):

$$\left(\frac{K}{S}\right)_{\lambda} = \frac{(1 - R_{\lambda})^2}{2R_{\lambda}} \quad (1)$$

where R is the reflectance of a dyed material at wavelength λ , S is the coefficient of scattering at λ , and K is the coefficient of absorption of the dye at λ .

RESULTS AND DISCUSSION

In the reaction of chitosan and GTMAC, the epoxy ring in GTMAC opened by the catalyst and the activated glycidyl group reacted with the amino groups of chitosan. In the FT-IR spectrum of the synthesized HTCC, the amine scissoring band of chitosan at 1570 cm⁻¹ disappeared and a new intensive peak at 1490 cm⁻¹ appeared due to the methyl groups of the quaternary trimethylammonium group of HTCC. The FT-IR spectrum of HTCC indicated that the quaternary ammonium group had been successively introduced in the chitosan and the epoxide groups of GTMAC had reacted with the NH₂ groups rather than the OH

groups of chitosan. Detailed results about the synthesis from FT-IR, nuclear magnetic resonance (NMR), and other analyses can be found in other papers.^{13, 18}

The PAN/HTCC blend solution prepared by dissolving PAN powder and HTCC in aqueous NaSCN solution at 70 °C was transparent and stable for >6 months without phase separation, showing that the stability of the blend solution is excellent. The PAN/HTCC blend fibers were produced successfully by a two-step wet-spinning process. During the spinning process, some HTCC may diffuse into the coagulation and the washing bath because of its high water solubility. However, it has been shown that <20% of HTCC in the blend fibers was released during the process of coagulation and washing.¹⁸ Most of the incorporated HTCC remained in the blend fibers. Although it is water soluble, HTCC in the blend fibers is fairly stable to washing because of the entanglement of two polymer chains. HTCC may be mixed completely with PAN molecules (i.e., they form a miscible blend system) or finely distributed in the PAN matrix. In Park's study²¹ on the blend system of PAN and modified proteins, the proteins were aggregated in the PAN matrix and the domains of modified proteins were identified with an optical microscope when they were stained with an acid dye. Similarly, in this work we carried out optical and electron microscopic observations to assess the distribution of HTCC in the blend fibers. The blend films, not fibers, prepared via the coagulation, washing, and drawing process, were dyed with Irgalan Red 2GL and observed by an optical microscope with 200× magnification. The results are shown in Figure 1. By the addition of HTCC, the shade depth of the films increased due to the reaction of the dye with ammonium groups in the HTCC component. No heterogeneity was observed.

The cross-sectional SEM photographs of fractured blend strings are shown in Figure 2. The domain size in polymer blends depends on a number of factors, such as the type of solvent, polymer-solvent interactions, and composition of coagulation bath etc., and is largely governed by the level of polymer miscibility. In the PAN/HTCC blend system, no heterogeneity was shown in SEM photographs. HTCC, therefore, was distributed homogeneously in the PAN matrix or perfectly mixed with PAN on the molecular scale. From these results of SEM and optical microscopy, we can suggest that the HTCC and PAN were blended without phase separation.

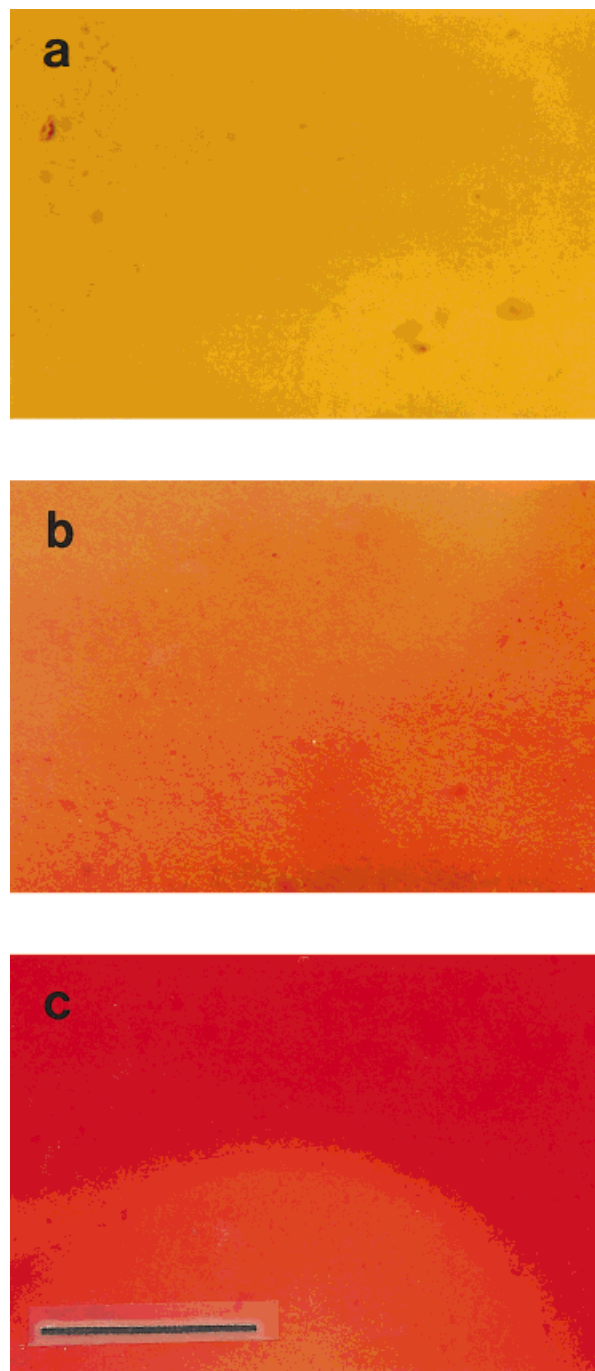


Figure 1 Microscopic pictures of PAN/HTCC blend films dyed with Irgalan 2GL (200×): (a) PAN, (b) 95/5, (c) 90/10. The scale bar corresponds to 100 μm . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Although microscopic observations suggest no phase separation, further experimental results are needed to clarify the miscibility of these two polymers. There are some popular methods to

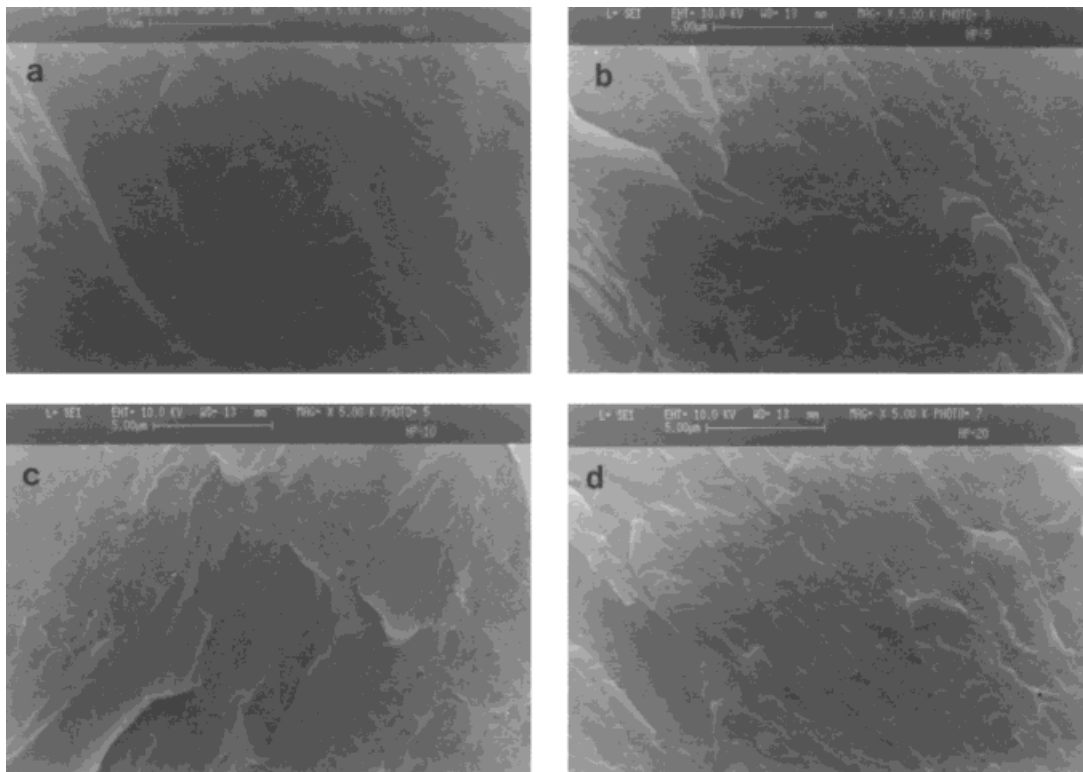


Figure 2 Scanning electron microscopy (SEM) photographs of PAN/HTCC blend fibers (5000 \times): (a) PAN, (b) 95/5, (c) 90/10, (d) 80/20.

evaluate the miscibility of the polymer blend systems. One of them is to observe the transparency of films and another is to measure the glass transition temperature (T_g) of the blends; a single T_g peak might indicate the blend pairs are miscible. The other method is to measure the melting point (T_m) depression. If the T_m of the blend pair decreases with blend ratios, the blend pairs could be miscible. We cannot measure the melting points of both PAN and HTCC by the aforementioned methods because both compounds decompose before melting.

To investigate the miscibility of two polymers, we measured the T_g of the blend fibers by DSC and DMTA. The DSC thermograms are shown in Figure 3. In the case of PAN fiber, there was an apparent change in slope in the temperature range 84–110 $^{\circ}\text{C}$, and T_g was obtained as the midpoint of the discontinuity of heat flow. However, the T_g of HTCC could not be detected. The T_g values of the blend fibers obtained by DSC, summarized in Table I, increase with increasing HTCC content. As far as the detection of T_g is concerned, dynamic mechanical thermal analysis (DMTA) may be more sensitive than calorimetric

measurement in many cases of blend studies. The temperature dependence of mechanical loss tangent ($\tan \delta$) for samples containing 100–80 wt %

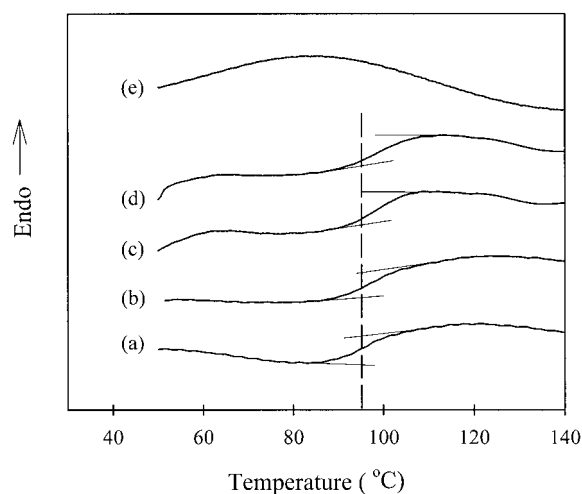


Figure 3 Differential scanning calorimetric thermograms of PAN/HTCC blend fibers with various blend ratios: (a) PAN, (b) 95/5, (c) 90/10, (d) 80/20, (e) HTCC (powder, 2nd heating).

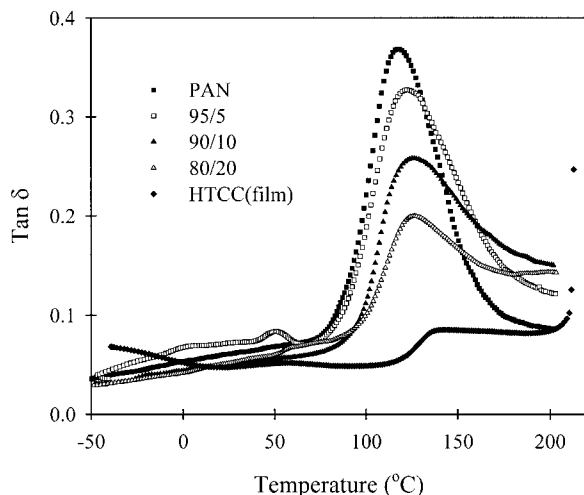
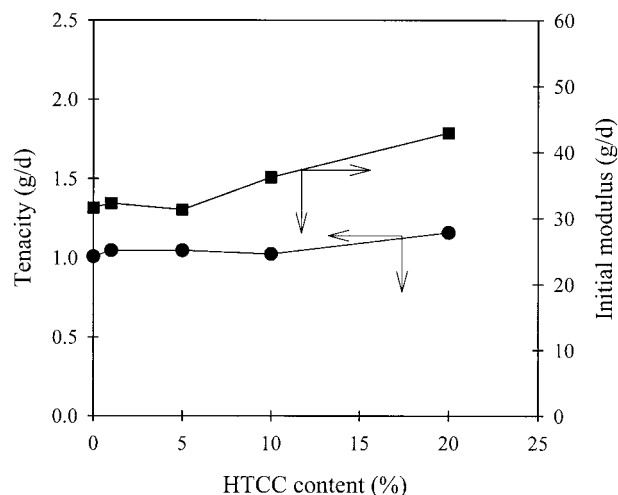
Table I Glass Transition Temperature (T_g) of the PAN/HTCC Blend Fibers

PAN/HTCC	Glass Transition Temperature (°C)		
	DSC ^a (2nd heat)	Dynamic Mechanical Analysis	
		Tan δ	E''
PAN (fiber)	92.8	116.8	102.5
95/5 (fiber)	94.9	120.7	104.8
90/10 (fiber)	97.3	124.2	106.8
80/20 (fiber)	99.4	125.1	112.6
HTCC (film)	ND ^b	142.3	139.9

^a From the midpoint of the discontinuity of specific heat.

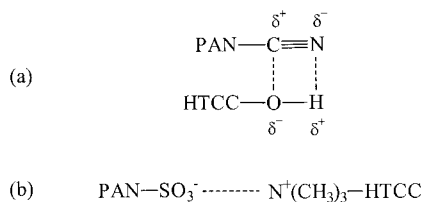
^b Not detected.

PAN is shown in Figure 4. The detailed dynamic mechanical analysis of solution-spun PAN fibers showed that there were three relaxations, α_x (140–160 °C), α_a (85–115 °C), β (40–70 °C).²² In this work, PAN fiber exhibited a peak of tan δ with its maximum at 116.8 °C, as shown in Figure 4. Although the PAN used is not 100% pure, the major tan δ peak can thus be designated as α_a relaxation, reflecting the glass transition of PAN. We also measured the tan δ curve of HTCC using film rather than fiber because of the difficulty of fiber formation. For HTCC, the tan δ curve showed a maximum at 142.3 °C and increased sharply above 210 °C because of thermal degradation. As HTCC content in blend fibers in-

**Figure 4** Temperature dependence of loss tangent (tan δ) measured at 10 Hz for PAN/HTCC blend fibers.**Figure 5** The effect of HTCC content on the mechanical properties of the PAN/HTCC blend fibers.

creased, the intensity of tan δ peak decreased and the maximum tan δ moved toward a higher temperature. The maximum tan δ temperatures of the blend fibers are also summarized in Table 1. Generally, T_g of PAN determined by DSC is reported to be 80–110 °C; it varies with the sample preparation methods and goes up to \sim 110 °C depending on stretching and heat treatment. The T_g of PAN determined by DMTA was higher than that determined by DSC because of the different measuring conditions. As can be seen in Table 1, the T_g of the blend fibers measured by both DSC and DMTA increased with the addition of HTCC. From the fact that a single T_g exists and it moves toward higher temperature with higher HTCC content, it is concluded that the PAN/HTCC blend pairs are miscible when the HTCC content is <20%.

Mechanical properties are important for the practical use of the blend fibers. Usually, poor compatibility of the component polymers may result in extremely low tenacity of the blend fibers. The changes in the mechanical properties of the blend fibers, shown in Figure 5, are negligible up to 5% HTCC content. As the HTCC content increases, the tenacity and initial modulus even improves slightly. Hasegawa et al.²³ reported that the tenacity of cellulose/chitosan blend films increased up to 20% chitosan content, which was explained by the occurrence of specific interaction between cellulose and chitosan molecules. The improvement of tenacity and initial modulus of blend fibers, therefore, may be attributed to the presence of the interaction between PAN and HTCC molecules in the fibers.



Scheme 2 Schematic representation of interactions between PAN and HTCC.

From the results of no heterogeneity by microscopic observation, single T_g of blend fibers by DSC and DMTA analyses, and no mechanical property depression in the PAN/HTCC blend fibers, we can suggest that the two polymers are miscible within the experimental range; that is, up to 20% HTCC content.

For more explanation of the miscibility behavior, it is instructive to consider the possibility of specific chemical interactions between HTCC and PAN. HTCC molecules contain two hydroxyl groups and a quaternary ammonium group in the repeating unit, which can contribute to such a specific interaction. The PAN used in this study is a copolymer of acrylonitrile, methylacrylate, and sodium methallylsulfonate. PAN contains a lot of $-\text{C}\equiv\text{N}$ side groups that have large dipole moments and a small amount of anionic groups. Therefore, there may be two possible interactions between HTCC and PAN, which are shown in Scheme 2. One interaction is a dipolar one between a hydroxyl group and a nitrile group, and another interaction is an ionic one between a quaternary ammonium group and a sulfonate group, a minor component of PAN. According to Manley et al.,¹⁵ the cellulose and PAN molecule are miscible blend pairs in the DMAc-LiCl solvent system and they achieve their miscibility by specific interaction between a hydroxyl group of cellulose and a nitrile group of PAN. Although there is no direct evidence for the interactions, we could suppose the specific interaction between the hydroxyl group of HTCC and the nitrile group of PAN.

The crystalline structure of PAN in the blend fibers may be affected by the HTCC component. The X-ray diffraction patterns of the blend fibers with various blend ratios are shown in Figure 6. The X-ray pattern of PAN fiber shows two peaks, one is an intensive peak at $2\theta = 17^\circ$ and the other is a less intensive peak at $\sim 2\theta = 30^\circ$. The intense peak at $2\theta = 17^\circ$ corresponds to a lateral repeat distance of 5.4 Å and has been attributed to the (100) reflection of a hexagonal lattice.²⁴ HTCC

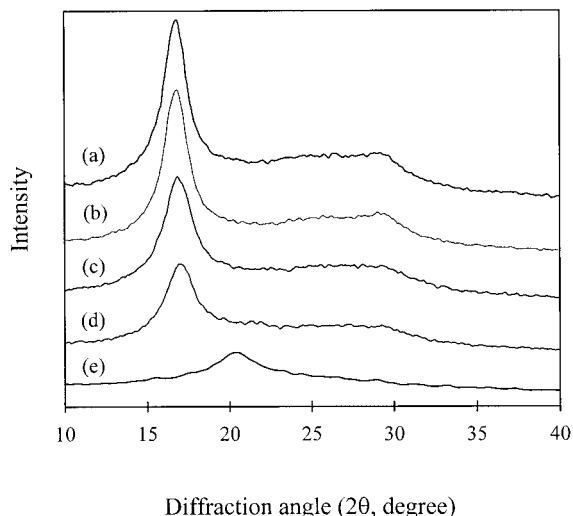
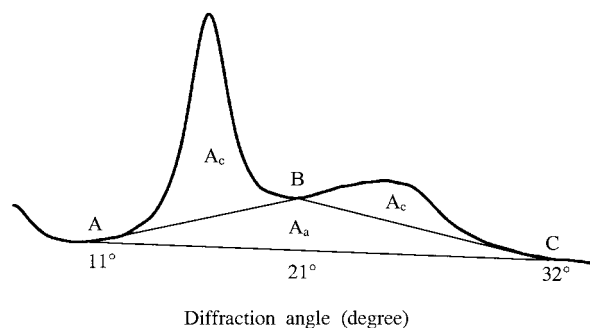


Figure 6 Equatorial X-ray diffractograms of the PAN/HTCC blend fibers with various blend ratios: (a) PAN, (b) 95/5, (c) 90/10, (d) 80/20, (e) HTCC (film).

shows only amorphous halos. All the blend samples show the PAN crystalline profiles with no other additional peaks. But the peak intensity at $2\theta = 17^\circ$ decreased gradually as HTCC content increased, implying that the crystallinity of PAN decreased. The crystallinity of the blend fibers can be calculated in terms of a crystallinity coefficient (CC) proposed by Hinrichsen.²⁵ The CC determination involves the separation of intensities due to the ordered and disordered phases by joining the intensities at $2\theta = 11^\circ$, 21° , and 32° with straight line segments, as shown in Scheme 3, and the calculation from the following equation:

$$\text{CC} = \frac{A_a}{A_a + A_c} \quad (2)$$



Scheme 3 Schematic representation of extrapolation of crystalline and amorphous component in the X-ray diffraction pattern of PAN (Hinrichsen's method).

Table II Parameters for X-ray Diffraction of PAN/HTCC Blend Fibers with Various Blend Ratios^a

PAN/HTCC	Crystallinity Coefficient	Diffraction Angle (degree)	Bragg Spacing (Å)	Peak Width at Half Maximum (degree)	Crystallite Size (Å)
PAN	71.0	16.76	5.279	1.82	44.1
95/5	62.9	16.80	5.273	1.78	45.1
90/10	59.1	16.90	5.242	2.00	40.2
80/20	52.9	17.00	5.211	2.04	39.4

^a Take-up speed, 2.4 m/min; draw ratio, 2.

where A_c is the total area above the line AB and line BC, and A_a is that between the lines and the line AC in Scheme 3. This CC parameter shows higher values than usual polymer crystallinity because of the simple determination method. The Bragg spacing (d) and the crystallite size can also be calculated from the Bragg equation and Scherrer line-broadening formula, respectively.²⁶ The calculated CC values and other parameters of the samples are shown in Table II. The CC values decreased considerably with increasing HTCC content, whereas the Bragg spacing changed slightly. Park²¹ reported that the CC of PAN decreased by the blending of organic-soluble amorphous protein with no Bragg spacing change, suggesting that amorphous proteins do not participate in the crystal formation of PAN. The higher crystallinity in the PAN fiber is accompanied by a narrower peak width at half the maximum or a higher crystallite size.²⁷ In this work, a broader half width and a smaller crystallite size in the blend fibers, which are generally observed with a decrease in crystallinity of polymers, were obtained with increasing blend ratio of HTCC. The X-ray diffractograms of the blend fibers with a 95/5 blend ratio and various draw ratios are shown in Figure 7. As draw ratio increased, the peak intensities at $2\theta = 17^\circ$ increased gradually. The CC, Bragg spacing, and other parameters are shown in Table III. The CC increases with an increment of draw ratio, but the Bragg spacing (d) does not change. The drawing affects only the crystallinity rather than the crystalline structure. The half width (D_ω) decreased and the crystallite size (t) increased with draw ratio, which are the same results as the other study.²⁷

The crystallite orientation factor (f_c) was calculated by the following equation and the results are also shown in Table III:

$$\text{Crystallite orientation factor } (f_c) = \frac{180 - \omega}{\omega} \quad (3)$$

where ω is the half width obtained by azimuthal scans of the blend fibers at $2\theta = 17^\circ$. The crystallite orientation was generally affected by spinning conditions such as take-up speed and draw ratio. The f_c increased with increasing draw ratio.

Most of the PAN fibers are used as fiber mixtures with other fibers, such as wool and nylon instead of PAN fiber alone. These fiber mixtures can usually be dyed with a one-step or two-step dyeing process using both cationic dye and acid dye.²⁸ However, the one-step dyeing process using different types of dye has some disadvantages such as cross staining by each dye. PAN fiber alone could not be dyed with acid dye, but PAN/HTCC blend fibers can be dyed with acid dye because HTCC behaves as cationic dyeing sites. The color strength of dyed samples is usually compared by the K/S value, which is proportional to the dye concentration on the sample. Dyeing results of the blend fibers dyed with an acid dye are shown in Table IV. The K/S values at 520 nm

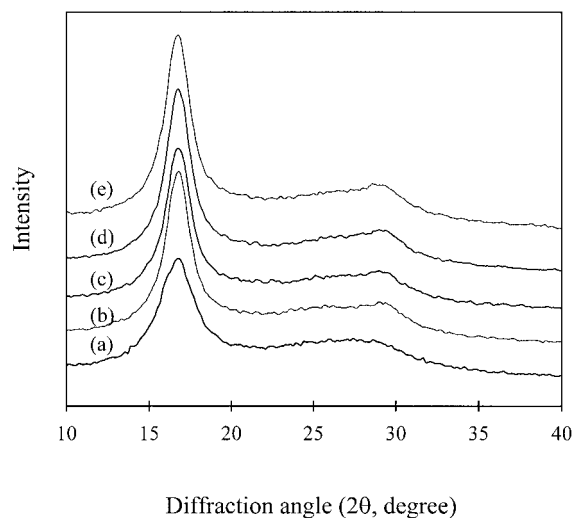


Figure 7 Equatorial X-ray diffractograms of the PAN/HTCC (95/5) blend fibers with various draw ratios (DR): (a) DR 1, (b) DR 2, (c) DR 3, (d) DR 4, (e) DR 5.

Table III Parameters for X-ray Diffraction of PAN/HTCC (95/5) Blend Fibers with Various Draw Ratios^a

Draw Ratio	Crystallinity Coefficient	Diffraction Angle (degree)	Bragg Spacing (Å)	Peak Width at Half Maximum (degree)	Crystallite Size (Å)	Crystallite Orientation Factor (f_c)
1	57.4	16.80	5.273	2.38	33.7	0.59
2	62.9	16.80	5.273	1.78	45.1	0.65
3	66.9	16.78	5.279	1.74	46.2	0.70
4	74.0	16.78	5.279	1.74	46.2	0.73
5	73.9	16.78	5.279	1.68	47.8	0.74

^a HTCC content, 5%; take-up speed, 2.4 m/min.

increased with increasing HTCC content. When the blend fibers are mixed with other fibers, such as wool or nylon, they can also be dyed with a one-step process using acid dyes, which is more convenient and economic than using two kinds of dyes.

CONCLUSIONS

HTCC and PAN were blended using 46% (w/w) NaSCN aqueous solution as a common solvent. The PAN/HTCC blend fibers with appropriate physical properties were prepared by a wet-spinning and drawing process. Crystallinity coefficients (CC) of the blend fibers, measured from wide-angle X-ray diffraction patterns, gradually decreased by addition of HTCC, whereas the draw ratio increased. The optical microscopic and scanning electron microscopic observations gave no indication of phase separation and heterogeneity up to 20% HTCC content.

The blend fibers showed single glass transition temperatures that gradually shifted to higher temperatures with increasing blend ratio of HTCC. From the estimation of the glass transi-

tion temperature and the microscopic observations, it could be considered that the blends up to 20% HTCC content exhibit miscibility on the molecular scale. The blend fibers can be dyed with an acid dye, so the textile products made of mixture fibers (i.e., mixture of PAN/HTCC fiber with other fibers such as wool and nylon) can be dyed by a one-step dyeing process.

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Table IV Color Strength of PAN/HTCC Blend Fibers Dyed with Acid Dye^a

PAN/HTCC	K/S_{520nm}
100/0	0.931
99/1	1.905
95/5	4.230
90/10	6.250
80/20	7.679

^a Dye, Irgalan Red 2GL (acid dye); dye concentration, 5% (on the weight of fiber); liquor ratio, 200:1.

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