Properties of Polyacrylonitrile-*N*-(2-hydroxy) propyl-3-trimethylammonium Chitosan Chloride Blend Films and Fibers

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ABSTRACT: A water-soluble chitosan derivative namely, *N*-(2-hydroxy) propyl-3-trimethylammonium chitosan chloride (HTCC) was synthesized by the reaction of chitosan with glycidyltrimethyl ammonium chloride in a neutral aqueous condition and solution blended with polyacrylonitrile (PAN) in an organic solvent. Polymeric films were made by casting, and they were dyed with an acid dye, a basic dye, and mixture of them. Results obtained from differential scanning calorimetry, scanning electron microscopy, and dyeing show that these polymers are immiscible even at low percentage of HTCC (lower than 20%). However, at higher ratio, the phase separation takes place. Fibers obtained from this blend system by wet-spinning technique show a good mechanical properties and increasing the amount of HTCC causes an increment in the mechanical strength of the fibers up to 20% of HTCC and beyond that due to phase separation mechanical strength reduces. Blending PAN with HTCC improves the dyeing behavior of the films and fibers. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 545–554, 2008

Key words: *N*-(2-hydroxy) propyl-3-trimethylammonium chitosan chloride; polyacrylonitrile; polymer blend; miscibility

INTRODUCTION

Polyacrylonitrile (PAN) is a semicrystalline vinylic homopolymer with the repeating unit —(CH_2—CHCN)—, usually in atactic form. This polymer is widely used for making membranes, which leads to good resistance against a wide range of solvents. PAN shows good mechanical strength as a film.[1] It is one of the most important fiber-forming polymers and has been widely used because of its high strength, abrasion resistance, and high elasticity, resistance to pilling, and good resistance to insect, air, sun shine, and micro organisms. Despite these benefits, it also has some disadvantages, such as low dye uptake, poor hydroscopicity and low moisture regain, and high static charge, due to the lack of segmental mobility resulting from intensive molecular orientation of the high-polar nitrile groups.[2–5]

There have been many attempts to improve the electrostatic property of PAN fiber by methods such as blending with other hydrophilic polymers like fibroin, collagen in 5%–15%, polyvinyl methyl formamide, poly-*N*-vinyl pyrrolidone, and acrylonitrile-dimethyl acryl amide copolymer, the alkaline hydrolysis of nitrile groups with alkaline reagents such as sodium carbonate, sodium hydroxide, and potassium hydroxide at room temperature to 85°C,[6] the hydrolysis of acrylonitrile copolymers with 75% sulfuric acid at 5°C and 45–65% nitric acid at −10 to 60°C[5] or hydrolysis of PAN with water at 180–210°C under the pressure with acidic reagents such as acetic acid, benzene sulfonic acid, and sulfuric acid at 85°C to convert hydrophilic groups and finally copolymerization of PAN with various comonomer.[3,5,6]

Chitin and its acetylated derivative, chitosan, are natural amino polysaccharides, which are the most abundant biopolymers next to cellulose. As a natural renewable resource, chitosan is a new functional material has high potential in various fields and lots of unique properties such as antimicrobial activity, biodegradability, nontoxicity, biocompatibility, non-antigenicity, wound healing and/or clot blood, polyoxysalt formation, ability to form films, chelate metal ions, and optical structural characteristics.[2,3,7,8]

Chitosan undergoes typical reactions of amines, which *N*-acetylation and Schiff reaction are the most important. Chitosan derivatives are easily obtained under mild conditions and also can be considered as substituted glucans.[8,9]

The antimicrobial activity of chitosan against a variety of bacteria and fungi arises from its polycationic nature. However, this activity is limited to acidic conditions due to its poor solubility in when pH is more than 6.5, because of lose cationic nature of chitosan,[7,10] thus water-soluble chitosan deriva-

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tives that soluble to both acidic and basic physiologic circumstances may be good candidates for the polycationic biocides.[10] Many studies have performed on the chitosan as an antimicrobial agent in textile industry such as linkage of chitooligo saccharide to cotton fabric, cospinning or cocoating of low molecular weight chitosan with textile fiber and blending of chitosan with the other polymers such as polyvinyl alcohol, polyacrylic acid, polyethylene oxide, and polyamide with an aqueous acid as a common solvent.[11–16]

It is anticipated that polymer blends will show new, desirable physical, and/or physicochemical properties not to be expected in conventional homopolymers. Compatibility and phase separation behavior, morphological characteristics, mechanical properties, permeability, and adsorption have been extensively investigated in many systems of multicomponent polymers.[17] To overcome inherent weakness of some polymers, they have been merged with chitosan, or blending may be performed to introduce useful properties of chitosan.[3]

N-(2-hydroxy) propyl-3-trimethylammonium chitosan chloride (HTCC), a chitosan derivative, is a hydrophilic material and is likely to impart hydrophilicity to a polymer blend, which prepared by blending of HTCC with another mechanically stronger and hydrophobic material such as PAN. Therefore, it would be interesting to investigate the formation of polymer blend using the unique properties of HTCC and PAN.

Kim et al. applied HTCC on cotton fabric to obtain an antimicrobial fabric and found that at very low concentrations, such as 0.025% owb, HTCC shows superior antimicrobial activity, indicated by an almost 100% reduction in bacteria, whereas, 1% owb chitosan provides only a 30% reduction in bacteria.[18] Nam et al. modified PAN fiber by blending with HTCC in sodium thiocyanate solution.[2,3] Kim and coworkers investigated antimicrobial activity of HTCC against Streptococcus mutans and found that cationic character of HTCC form an impermeable layer around the bacterial cell wall by the formation of polyelectrolyte complexes with acidic macromolecules produced at the cell surface.[19] Lim and Hudson modified HTCC by reacting with *N*-methylolacrylamide to prepare a chitosan derivative, *O*-acrylamidomethyl-HTCC, which can form covalent bonds with cellulose under alkaline conditions.[7] Qin et al. performed calorimetric studies of the action of HTCC on the growth of microorganisms. They found that the antimicrobial activity of the HTCC in alkaline condition was stronger than acidic condition.[20]

In this work, HTCC was synthesized and was solution blended with PAN using dimethyl solfoxide (DMSO) an organic solvent as a common solvent. Then PAN/HTCC blend films were prepared and the effect of HTCC content on the antimicrobial activity, miscibility, and dyeability of PAN/HTCC blend films were investigated. Finally, the blended solution was used for production of fiber by wet-spinning technique.

EXPERIMENTAL

Materials

The PAN used was a copolymer containing 93% acrylonitrile, 6% methylacrylate, and 1% 2-acrylamide-2-methyl propane sulfonic acid (SAMPS) with a molecular weight of almost 70,000, which was obtained from Polyacryl, Iran. Glycidyltrimethyl ammonium chloride (GTMAC) was supplied by Fluka. Irgasol Red 2GL, an acid dye, Maxilon Blue, a basic dye, also Irgasol NA, as a disperse agent to prevent the complex formation, were provided by Ciba, Switzerland. All the other chemicals were of reagent grade and were supplied by Merck, Germany.

FTIR spectroscopy

Fourier transform infra red (FTIR) spectra were obtained by using a Nicollet Nexus 670 FTIR spectrophotometer. Powder samples were made into using KBr pellets and were scanned. Film samples were directly scanned.

Degree of acetylation

Degree of the chitosan acetylation was determined by FTIR spectroscopy using the following equation[21]:

$$DA = 97.67 - [26.486 \times (A_{1655}/A_{3450})]$$

Molecular weight of chitosan

To determination of chitosan molecular weight (MW), 0.5 g chitosan was weighted and dissolved in 100 mL of 0.1*M* CH_3COONa-0.2*M* CH_3COOH solution. The relative viscosity was measured with an Ubbelohde viscometer at 30°C in a constant temperature bath using different concentrations of chitosan solution. M_W was calculated based on the Mark-Houwaink equation as follows[7]:

$$[\eta] = KM_v^{\alpha}$$

where K is 5.261×10^{-3} and α is 0.8796.

Synthesis of HTCC

HTCC was prepared by the method of Lang et al.[22] The degree of quaternization (DQ) of HTCC was measured by conductometeric titration. Solution con-

TABLE I
Percent of Moisture Adsorption in Blend Films

PAN/HTCC	Moisture content (%)
100/0	1.18
95/5	1.73
90/10	2.58
85/15	3.12
80/20	3.82
0/100	18.17

ductivities were monitored with conductometer 644 Metrohm, Swiss. To measure the amount of Cl^- ions on the HTCC, $AgNO_3$ aqueous solution was used. The degree of substitution in HTCC was calculated by chloride content.[18] It was a function of the reaction temperature and mole ratio of GTMAC and NH_2 in chitosan. DQ is defined as the ratio of reacted GTMAC (mole) per glucosamine (mole) calculated from the original mass of chitosan used. Then 0.100 g of dried HTCC was dissolved in 100 mL of deionized water and titrated with 0.017*M* $AgNO_3$ aqueous solution. The conductivity is a function of temperature, so during the titration, the temperature of the solution was kept constant (20°C ± 0.5°C). The calculated value of DQ was 0.989.

Preparation of PAN/HTCC blends

Polymer blends were prepared by dissolving the HTCC and PAN in DMSO as a common solvent with stirring at 54°C ± 0.5°C for 4 h. Relative composition of PAN/HTCC in the blend solution varied from 100/0 to 80/20 by weight. Final products were yellowish transparent viscose solution.

Preparation of polymeric films

The PAN/HTCC blend films were prepared by casting a thin layer with thickness 250 μm of the mixture 12%(w/v) blend solution onto glass plates and allowing the solvent to evaporate at room temperature. After 10 h, the plates were immersed in distilled water for 3 s, and polymeric films were dried at room temperature.

Moisture absorption

To calculate the moisture content of the blend films, the following equation was used:

$$\% \text{ Moisture content} = \frac{m_c - m_d}{m_c} \times 100$$

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 results are presented in Table I.

Dyeing procedure

Polymeric films were dyed with an acid dye, a basic dye and mixture of them. To compare the substantivity of both dyes to blend films and effectiveness of the HTCC existence on dyed films, dyeing were performed according to the Table II. The wavelength of minimum reflectance of dyed films was defined by a reflectance spectrophotometer Coloreye XTH Gretag Macbeth, USA 400–700 nm that λ_{max} = 510 nm for acid dye and λ_{max} = 630 nm for basic dye were obtained. To obtain the color strength of dyed films, K/S value was calculated with the following Kubelka-Munk equation[23]:

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

where R is the observed reflectance of a dyed film at λ_{max}, S is the scattering coefficient at λ_{max}, and K is the absorption coefficient of the dye at λ_{max}.

Study of dyeing effluent

Amount of absorbed dyes could be defined from measuring the absorption of dyeing effluents by transfer spectrophotometer. The wavelength of maximum absorption of dyes were defined by a transfer spectrophotometer Jenway 6105 on 380–720 nm that λ_{max} = 505 nm for acid dye and λ_{max} = 617 nm for basic dye were obtained. Amount of absorption were obtained from blank bathes of both dyes at λ_{max} and in different concentrations, then calibration curves were drown. Dyeing effluents were diluted, and absorption of them at λ_{max} was measured. Concentrations of effluents were calculated by interpolation method. For mixture of dyes, the absorptions of each dye were measured at λ_{max} of both dyes. Con-

TABLE II
Recipe of Dyeing Processes

	Dye concentration (%)	L.R	Acetic acid (g/L)	Nonionic agent (g/L)	Disperse agent (g/L)	Boiling time (min)
Acid dye	5	30 : 1	0.8	0.5	–	30
Basic dye	5	30 : 1	0.8	–	–	30
Mixture	2.5 + 2.5	30 : 1	0.8	–	2	30

centration of each dye could be calculated by solving the following equations:

$$\begin{cases} A_{mix,\lambda_{max}\text{Acidic}} = \varepsilon_1 C_{\text{Acidic}} + \varepsilon_2' C_{\text{Basic}} \\ A_{mix,\lambda_{max}\text{Basic}} = \varepsilon_1' C_{\text{Acidic}} + \varepsilon_2 C_{\text{Basic}} \end{cases}$$

where ε_1 and ε_1' are molar absorptivity of the acid dye at λ_{max} of acid dye and basic dye respectively. Also ε_2 and ε_2' are molar absorptivity of the basic dye at λ_{max} of basic dye and acid dye.

Antimicrobial tests

Antimicrobial activities of the blend films were evaluated using AATCC 147-1999 and AATCC 100-1999. The Staphylococcus aureus as a gram-positive bacterium was used. One loop full of the bacteria was inoculated in 150 mL of nutrient broth at 37°C for 24 h in a test tube. Nutrient broth containing 1.4×10^4 colony forming unit per milliliter was used to test antimicrobial activity. After 24 h, according to AATCC 100-1999 antimicrobial test method, 1 mL of the same culture was added to 9 mL of distilled water. Hundred milliliters of each dilution removed and spread on the nutrient agar. The blend films were contacted with bacterial and incubated for 24 h at 37°C to assess their bactericidal activities. To assess antimicrobial activities of the blend films, the diameter of ring around the colonies was measured and amount of colonies culture between the films with different amount of HTCC after incubation was compared. For measuring the antimicrobial activity of samples according to AATCC 100-1999 after diluting the culture ratio to one-tenth, five streaks on films with dimension 3×7 cm^2 was created and incubated for 24 h at 37°C. The decrease in the number of living microorganisms was estimated from the number of living microorganisms on the film according to the following equation:

$$\text{Reduction of bacteria } (\%) = [(B - A)/B] \times 100$$

where A is the number of bacteria after 24 h of shaking and B is the number of bacteria before shaking. The results are shown in Figures 7 and 8.

Scanning electron microscopy

The cross section of blend strings fractured in liquid nitrogen was observed by XL30 SEM, Philips, Holland.

Differential scanning calorimetry

Thermal properties of the blends were studied by a thermal analysis instrument TA Instrument 2010, USA, at a heating rate of 10°C/min and under N_2 atmosphere from room temperature to 350°C.

Wet spinning

Wet-spinning process was carried out using a laboratory wet spinning line with a spinneret having mono hole with 0.1 mm diameter. Dope with 12% solid content was used and a two-stage coagulation bath. The extrusion velocity was 20 mL/min and take-up speed was 3 m/min. Temperature of the blend solution was fixed at 40°C ± 1°C and temperature of the first bath was 10°C ± 1°C and in the second bath was 16°C ± 1°C. The solvent/nonsolvent ratio of the first bath was 60/40 and for the second bath it was 40/60. DMSO was used as a solvent, and water was used as a nonsolvent in coagulation bath. The fibers were washed after stretching in the consequent bath by tap water. Finally, fibers were dried and collected.

Physical properties of fibers

Instron 5566 with gauge length of 2 cm and cross head speed 10 mm/min was used to measure the strength and elongation at break of fibers and denier of the samples was measured by Vibromat M Textechno, Germany at 20°C, 65% R.H. The data are the average of 10 tests.

RESULTS AND DISCUSSION

Htcc synthesis

Degree of the chitosan acetylation was calculated to be 17.5% and molecular weight of chitosan was 480,000. HTCC was prepared by the reaction of chitosan with GTMAC in a neutral aqueous condition. Reaction of chitosan with epoxide compounds involves nucleophilic substitution and cleavage of the epoxide ring. Hydroxyl groups of chitosan are not sufficiently nucleophilic to induce ring opening

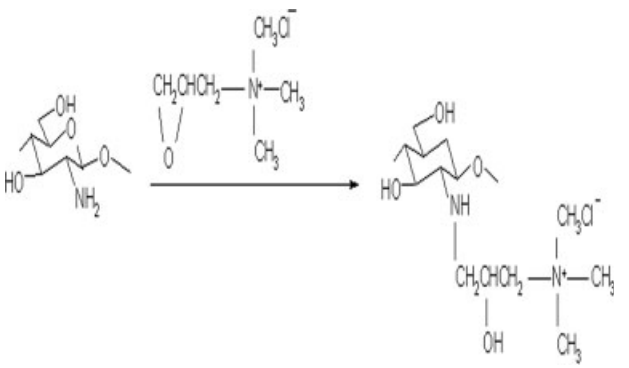

Figure 1 Reaction of chitosan with GTMAC for synthesis of HTCC.

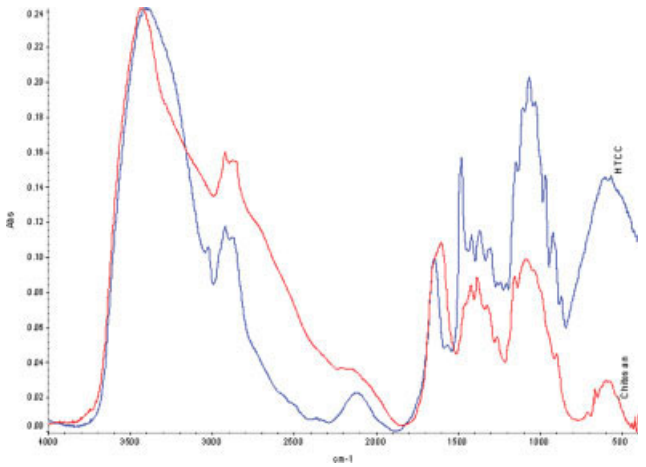

Figure 2 FTIR spectra of chitosan and HTCC. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of GTMAC, whereas the amino groups of chitosan are enough nucleophilic to fulfill this purpose. This reaction is represented in Figure 1. The nitrogen of ammonium groups is an electronegative element and cannot bear the positive charge in its vicinity therefore to overcome the lack of electron charge; it attracts electron from neighboring alkyl. This lack of electron charge is transmitted in the alkyl chain by conduction and makes a positive charge on C-1 and negative charge on C-2. Therefore, C-1 is a suitable electrophilic site. The nucleophilic amino group that is a Lewis base attack to the epoxy rings (C-1) and opens the ring. One proton is separated from amino group and gets attracted by negatively charged oxygen, which is formed after ring opening.

Figure 2 shows the FTIR spectra of chitosan and HTCC. The FTIR spectra of chitosan shows absorption bands at 3500–3300 cm^{-1}, the absorption bands at 3425 cm^{-1} are due to OH stretching and at 3300–3360 cm^{-1} were assigned to the NH_2 bending. Also the absorption bands at 1646 and 1589 cm^{-1} are assigned to the C=O stretch of the secondary amide and $—NH_2$ bending of the primary amine, respectively. The absorption band at 1151 cm^{-1} was assigned to the antisymmetric stretching of C—O—C bridge and 1074 and 1032 cm^{-1} are due to the skeletal vibrations involving the C—O stretching.

The FTIR spectra of HTCC indicate that the characteristic bands of amine NH vibration of chitosan at 1595 cm^{-1} disappears in HTCC due to the formation of quaternary ammonium salt at C-2 in the chitosan and the primary amine changes to the secondary amine. Also, it points that the epoxide groups of GTMAC have reacted with the NH_2 groups rather than the OH groups of chitosan and *N*-alkylation in chitosan occurred. A new intensive peak at 1479 cm^{-1} appeared, which is probably due to the methyl groups of the quaternary trimethylammonium salt and peak at 1642 cm^{-1} referring to C—O stretching vibrations of HTCC.

Synthesized HTCC showed good water solubility and can be easily dissolved in water, whereas chitosan did not have such ability and only dissolved in acidic conditions (pH < 6.5). By changing pH of HTCC solution from acidic to neutral and finally basic conditions, solution was transparent, whereas chitosan losses its positive charge and its antimicrobial activity in neutral and basic conditions.

The degree of quaternization (DQ) of HTCC was measured by conductometeric titration of Cl^- with $AgNO_3$ aqueous solution. The amount of $AgNO_3$ used at the end point equals the amount of Cl^- ions present on the HTCC. The value of DQ calculated was 0.98, which means that amino groups of chitosan were fully substituted by quaternary ammonium salt groups.

Preparation of blend solution

HTCC due to bulkier groups has a higher molecular weight compare to PAN, therefore addition of HTCC to PAN results an increase in the molecular weight of the blend and its viscosity. When the amount of HTCC in the (DMSO) solution was 15% the viscosity of the solution was very high and the stirrer could not mix the solution. However, the maximum amount of two polymers used in solution was kept at 12%. Solution blends (12%) of HTCC and PAN were prepared by varying the ratio of HTCC from 0 to 20%. Higher than 20% the phase separation took place, and the films made were rigid and brittle. The DSC data showed the presence of two separate T_g for HTCC and PAN at higher ratio of HTCC in the blend.

During fiber formation, when the ratio of HTCC in the blend is higher than 20% the spinning solution does not coagulate easily in the coagulation bath and even after extrusion of dope from spinneret it remains unchanged in the bath for sometime; in other words, the coagulation process is very slow.

FTIR spectra of films

Figure 3 shows the FTIR spectra of films. The absorption peak at 3350 cm^{-1} is referred to OH stretching vibration, which did not exist in PAN film. Its intensity increases with increasing the content of HTCC. Also, band at 1490 cm^{-1} corresponds to absorption of methyl groups, which increases with increasing the HTCC content in films. The band at 2242 cm^{-1} was assigned to the nitril group, which did not change with increasing HTCC content in the film. It indicates that there are no reactions between

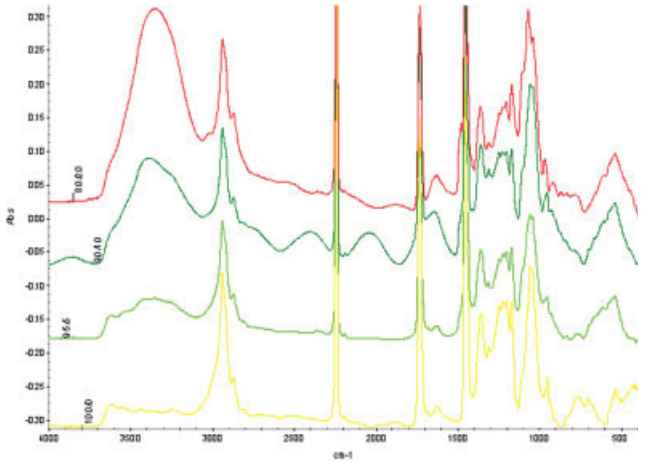

Figure 3 FTIR spectra of blend films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

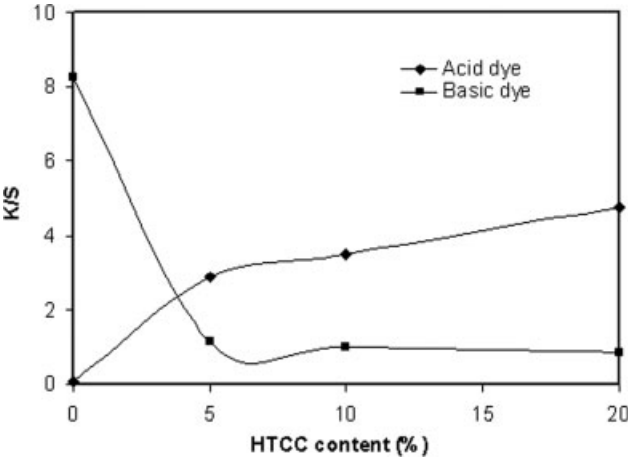

Figure 5 Absorption of acid and basic dye on the blend films.

HTCC and nitril groups of PAN. This peak may be considered as a reference peak.

Moisture absorption

Table I shows the amount of moisture absorption of polymeric films. Films prepared from PAN show 1.18% moisture absorption. However, addition of HTCC to PAN, moisture absorption of films prepared from the blends increases the moisture absorption of film prepared from 80/20 (PAN/HTCC) ratio was 3.82%. This could be due to the hydrophilicity of HTCC.

Dyeing results

The reflectance of opaque blank and dyed films was measured, and the data of dyed films was normalized based on the data of blank films in the various HTCC contents, and so the effect of surface reflectance was deleted. Then the normalized reflectance of dyed films versus wavelength was plotted in Figure 4 and found that the wavelength of the minimum reflectance for basic dye was 630 nm and for acid dye was 510 nm. In comparison with the data obtained from transfer spectrophotometer (λ_{max} = 505 nm for acid dye and λ_{max} = 617 nm for basic dye), there were slight shifts in the λ_{max} of both dyes probably due to interaction between dye molecules and polymer chains. Dyeing shows that the samples were uniformly dyed, which indicate that the chains of HTCC and PAN though being immiscible seem to be compatible at low concentration of HTCC. Physical interaction between the two polymer's chains seems to be strong enough to prevent the solubilization of HTCC in boiling water. Figure 5 shows the *K/S* versus HTCC content of the blend films at λ_{max} of each dyes. PAN film was not dyed with acid dye because both acid dye and PAN have negative charge, whereas, ionic charge of HTCC in aqueous media is positive and increasing amount of this

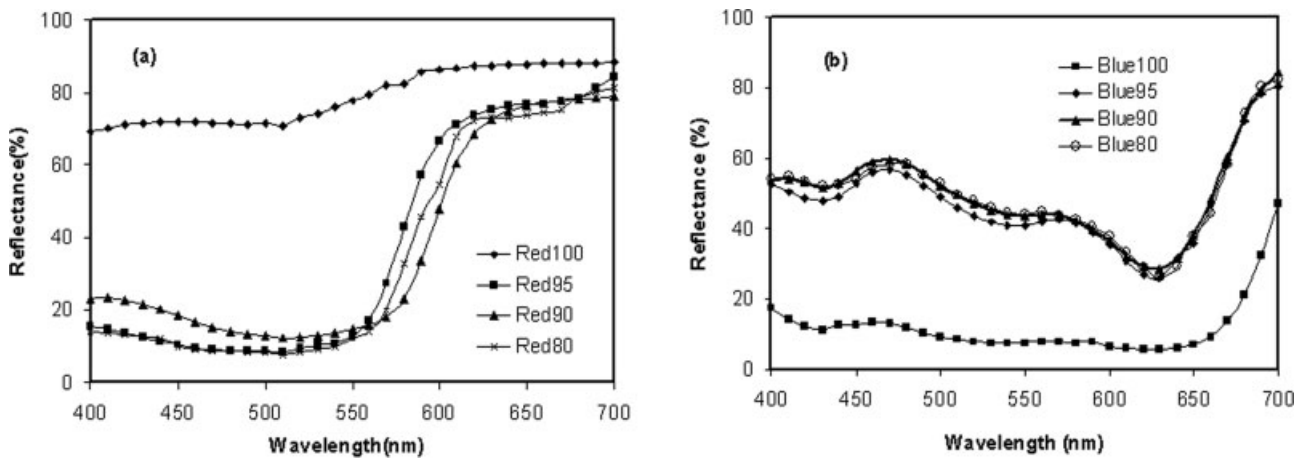

Figure 4 Determination the λ_{max} of dyed films, (a) acid dye and (b) basic dye.

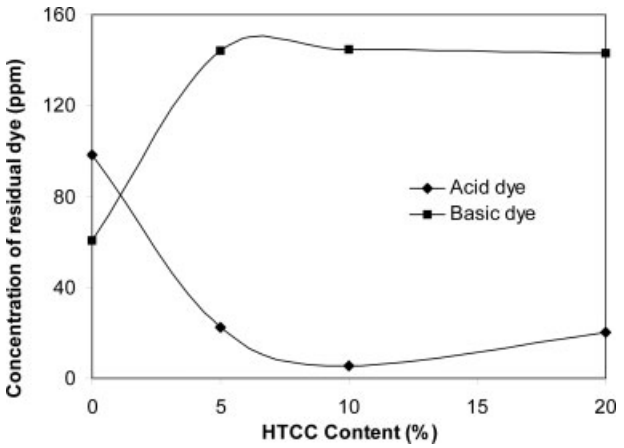

Figure 6 Concentration of residual acid and basic dye in dyeing bath.

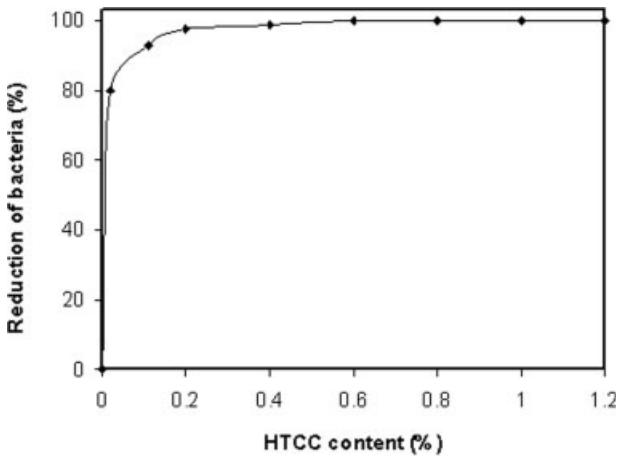

Figure 8 Reduction of bacterial versus content in the blend.

polymer in the blend films causes increasing the dye uptake percentage of acid dyes on the samples. On the other hand, PAN film completely dyed with basic dye and appear an intense blue. Because of similar ionic charge of basic dye and HTCC chains by increasing the amount of HTCC in the blend the basic dye uptake will decrease. Dyeing the samples in a dye bath containing mixture of acid and basic dye showed that PAN film only absorbed basic dye, whereas blend films absorbed both dyes and a purple color appeared. Uniformity dyed samples (95/5 and 90/10 PAN/HTCC films) indicate two polymers are miscible enough. But in 80/20 PAN/HTCC dyed film slight poor uniformity obtained shows that in higher than 20% of HTCC in the blend films results poor miscibility and compatibility. Investigation of the dye effluent confirms the above results. Figure 6 shows the concentration of residual dyes in effluent versus HTCC content. The concentration of acid dye decrease with increasing the HTCC content of blend films and the concentration of basic dye increase respectively. Figure 7 shows the concentration of each dye in the mixture bath. Initial concentration of dye in dyeing bath was 5000 ppm, and Figure 7 confirms that there is no interaction between PAN film and acid dye due to their same charges and by increasing the HTCC content in blend films, the concentration of acid dye in effluent will increase.

Antimicrobial results

The capability of HTCC to inhibit the growth of the *S. aureus* in PAN/HTCC polymeric films is shown in Figures 8 and 9. From the antimicrobial activity of PAN/HTCC blend films, it was found that the viable cell number decreased with increasing amount of HTCC in polymeric blends. The PAN film has small diameters of inhibition zone, whereas with increasing amount of HTCC in polymeric blend, the diameters of inhibition zones are increasing and extending. Because of low moisture regain of PAN, it only is a

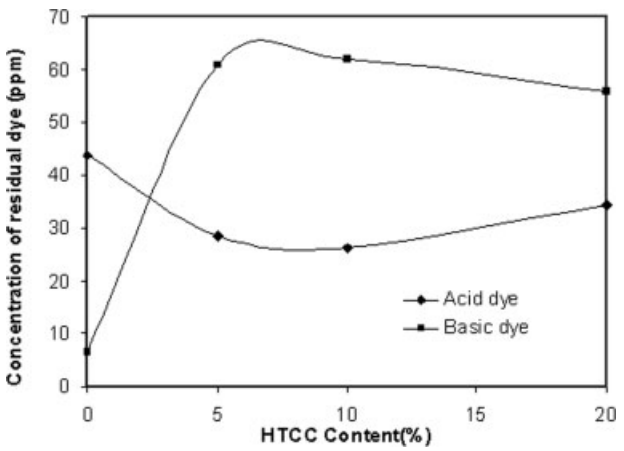

Figure 7 Concentration of residual acid and basic dye in mix dyeing bath.

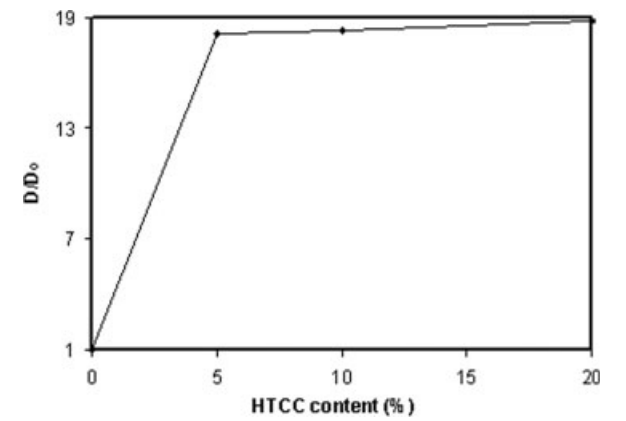

Figure 9 Diameter inhibition index (D/D_0) versus HTCC content.

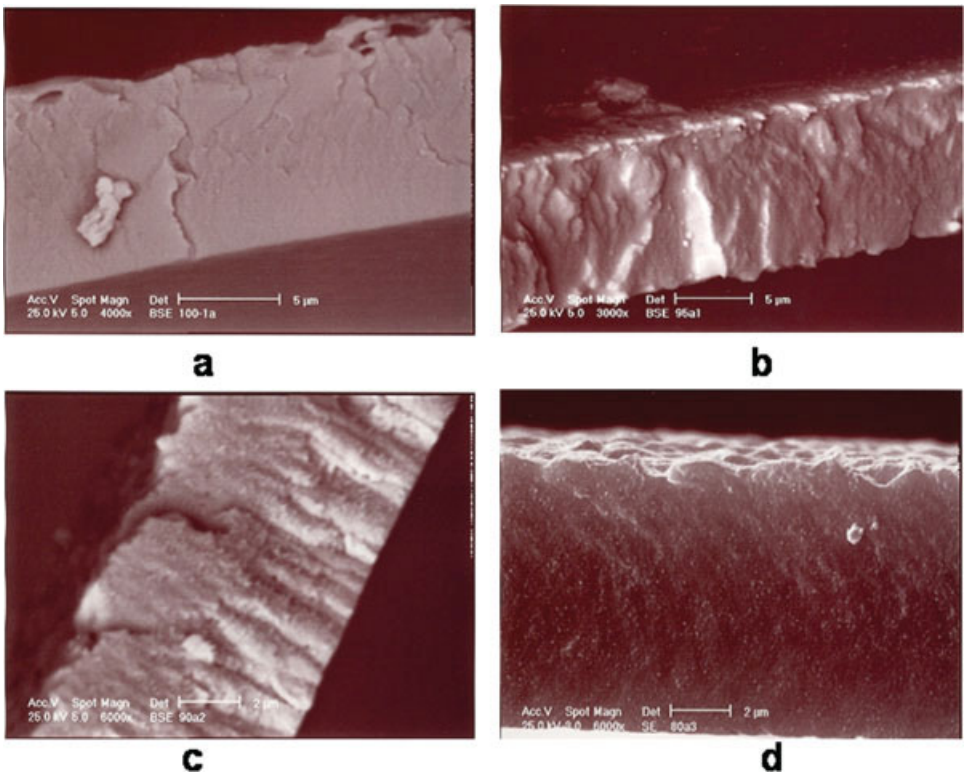

Figure 10 Scanning electron micrographs of the blend films. (a) 100/0 PAN/HTCC, (b) 95/5 PAN/HTCC, (c) 90/10 PAN/HTCC, and (d) 80/20 PAN/HTCC. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

bacteristatic material and not capable of killing the bacteria.

SEM

Figure 10 shows the cross-sectional SEM micrographs of fractured blend films in liquid N_2. The domain size in polymer blends depends on the interaction between polymer and solvent and miscibility of the used polymers. PAN is a hydrophobic polymer, whereas, HTCC is a hydrophilic polymer; therefore, in a chemical view, there is no attraction between two polymers and both seems to repel each other. But as can be seen from Figure 10 homogeneous structures of blend films denote that there are good entanglements between chains of polymers. When the amount of HTCC in the blend is less the dominating phase, that is, PAN acts as a medium in which the HTCC gets dispersed and shows a uniform structure. However, when the amount of HTCC increases, it cannot be dispersed easily and shows two distinguished phases, which can be seen on its SEM photos.

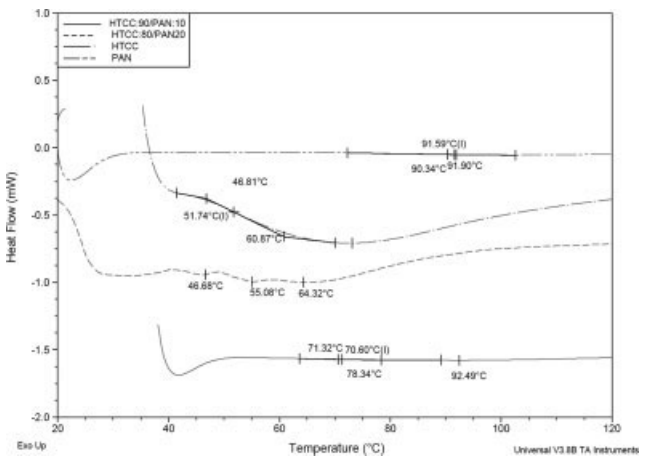

Figure 11 Differential scanning calorimetry thermograms of PAN and HTCC.

TABLE III
Thermal Properties of Polymer Blends

Blend ratio			Decomposition temp. (°C)		
PAN	HTCC	T_g (°C)	T_i	T_p	T_f
100	0	82	270	310	350
95	5	78	260	290	320
90	10	75	248	286	300
85	15	72	240	260	289
82	18	70	230	252	278
80	20	60–80	210	240	258
0	100	55	220	235	250

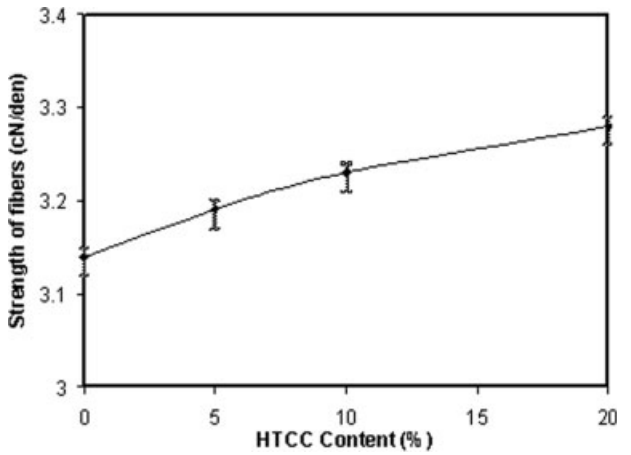

Figure 12 Change in the tensile strength of fibers with increasing HTCC content.

DSC

Results from DSC thermograms of PAN and its blends with HTCC are shown in Figure 11 and Table III. When two polymers are miscible in molecular scale, the resulting blend will show a single glass transition temperature (T_g) on heating. This would be independent of volume fraction of each polymer. The immiscible polymers will show separate and distinguished T_gs. PAN shows a glass transition temperature at 82°C and on further heating it does not show a melting point but its decomposition starts from temperature above 270°C. The HTCC shows a T_g at 55°C, and decomposition starts at above 210°C. When two polymers are blended together with different composition the DSC data shows a single T_g for 95/5 PAN/HTCC composition at 78°C. When the ratio of HTCC increases, the T_g shifts to a lower temperature (Table III). At 18% HTCC content though a single T_g is observed at 70°C, but it is not sharp and it occurs at a wider range of temperature. When the blend ratio is 80/20, a clear two T_g appears while indicates that the polymer blend systems is no longer compatible and miscible. These data support observations made by SEM photographs.

Physical properties

The strain–stress behavior of the fibers shows that the tensile strength of PAN fibers is 3.14 cN/den with 23% elongation at break. However, with incorporation of HTCC, the strength of the fibers increases. Figure 12 shows that with increasing HTCC content in the blend, the tensile strength of the fibers increases and reaches to 3.28 cN/den when HTCC content is 20%. This may be due to the fact that HTCC chains are bulky and can interlock the PAN chains, which results in an increase in the mechanical strength of the blend fibers; however, when the HTCC content increases more than 20% and because they are not compatible, the phase separation takes place and the strength reduces after this blend ratio.

CONCLUSIONS

HTCC was prepared by reaction of chitosan with GTMAC in a neutral aqueous condition. The FTIR spectra of HTCC indicate that the characteristic bands of amine NH vibration of chitosan at 1595 cm^{-1} disappears in HTCC, caused by the formation of quaternary ammonium salt at C-2 in the chitosan and a new peak appears at a high wave number. In the synthesized HTCC, the amine scissoring band at 1595 cm^{-1} of chitosan almost disappeared due to the change of the primary amine to the secondary amine. Solution blends (12%) of HTCC and PAN were prepared by varying the ratio of HTCC from 0 to 20%. Higher than 20%, the phase separation takes place, and the films made were rigid and brittle. The FTIR spectra of film show absorption peak at 3350 cm^{-1}, which is due to OH stretching vibration, which did not exist in PAN film. Its intensity increases with increasing the content of HTCC. Addition of HTCC to PAN increases the moisture absorption of film due to the hydrophilicity of HTCC.

The samples were uniformly dyed, which indicates that at low concentration of HTCC chains of HTCC and PAN though being immiscible seems to be compatible and interaction between the two polymer's chains seems to be strong enough to prevent the solubilization of HTCC in boiling water.

From the antimicrobial activity of PAN/HTCC blend films, it was found that the viable cell number decreased with increasing amount of HTCC in polymeric blends. With increasing HTCC content in the blend, the tensile strength of the fibers prepared increased.

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