

Synthesis of a Polyurethane–Chitosan Blended Polymer and a Compound Process for Shrink-Proof and Antimicrobial Woolen Fabrics

Chung-Yang Shih, Kuo-Shien Huang

Department of Applied Fiber Style, Kun Shan University of Technology, Yung Kang, Tainan, Taiwan 71016, Republic of China

Received 27 November 2001; revised 18 June 2002; accepted 20 June 2002

ABSTRACT: The purpose of this study was to develop a finishing process to improve the shrinkage and anti microbial properties of woolen fabrics. First, polyurethane (PU) prepolymers were synthesized from poly(ethylene glycol) (PEG) of different molecular weights. Next, the PU prepolymers were mixed with chitosan to form blended polymers. Then, these blended polymers were used to treat woolen fabric in a compound process to determine if they could modify the fabric, making it more resistant to shrinkage and bacteria. Our experimental results indicate an improvement in both the shrink-proof and antimicrobial properties of the fabric with an increase in the temperature or duration of the heat treatment, as well as with an increase in the concentra-

tion of the processing agent. However, the yellowing and softness tendency of the fabric shifted towards the opposite, unfavorable direction. The treatment also seems to somewhat improve the strength of the fabric. Furthermore, our results show that the addition of chitosan remarkably increased the shrink-proof and antimicrobial properties of the treated fabric. Finally, the blended polymer made of PEG with a molecular weight of 600 and chitosan gave the best results of the polymer combinations tested. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2356–2363, 2003

Key words: polyurethanes; blends

INTRODUCTION

Woolen fabrics are quite unstable and tend to shrink or crimp easily and lose the original shapes after washing and heating. It is traditional to clean all woolen fabric items by dry cleaning methods or careful hand washing with certain special care lotions or detergents. Woolen fabrics are basically composed of protein fibers, the little pieces of which may break from time to time. The numerous little loose segments can easily mix with human sweat, becoming an ideal culture medium in which bacteria and molds can grow. If the latter happens, the fabric can easily be affected by all kinds of microorganisms (e.g., bacteria and mildew) that might spread diseases and deteriorate the fabric, causing discoloration, disintegration, and emission of foul smells. Therefore, shrink-proof and antimicrobial properties are two very important issues for the utility of woolen garments.

Currently, shrink-proof finishing of woolen fabrics is accomplished with chemicals containing activated chlorine or peroxides, which oxidize scale fiber, or resin, which reacts with and reinforces the fiber. The process changes the directional friction, thereby affecting or altering the contracting character of the wool,

and resulting in the shrink-proofing of the fabric. Antimicrobial properties are afforded wool fabric with processes that use the following chemicals: organosilicon quarternary ammonium salts, halogenated dibenzyl ether derivatives, nitrophenide, organic nitrogen, etc. Organosilicon quarternary ammonium salts are by far the most frequently used chemicals in these processes. The antimicrobial principle of these salts is based on the fact that the quarternary ammonium cation attracts the negatively charged bacteria and damages the cell wall, which in turn allows the cell contents to leak out and kills the bacterium.² The drawback to the chemicals used in these shrink-proofing treatments is they easily pollute the environment. In particular, the halogenation reactions can produce absorbable organic halides (AOX). The metal salts or quarternary ammonium salts, used as surfactants in antimicrobial finishing processes, not only cause pollution problems, but are also unsuitable for skin-friendly requirements.^{3–5} Therefore, a compelling goal is the search for a degradable replacement chemical for multifunctional finishing processes that can ensure both shrink-proof and antimicrobial properties for woolen fabrics.

In dyeing and finishing studies, hydrated polyurethane (PU) has customarily been used for hydrophilic finishing, anti-soiling finishing, and anti-static finishing of synthetic fibers.^{6–10} There is an isocyanic group ($-\text{N}=\text{C}=\text{O}$) in the PU prepolymer chemical struc-

Correspondence to: C-Y. Shih (scy-f@mail.ksut.edu.tw).

ture that can readily react with the amino group in the woolen fabric and form a thin membrane on the surface of fiber. On the one hand, this membrane covers the scales of the fibers so they lose the freedom of relative mobility, and on the other hand, the membrane forms multispot linkages between fibers, preventing them from moving against each other and thus achieving shrink-proofing. Chitin is a substance extracted mainly from the exoskeleton of crustaceans, such as shrimps and crabs, and (next only to cellulose) it is the second most abundant natural polysaccharide resource on earth. One of its major derivatives, chitosan, has many beneficial and useful properties that include antimicrobial activity, biocompatibility, biodegradability, biological function, and anti-inflammatory, hemostatic, nontoxic, moisturizing, and tissue regenerative effects.^{11,12} So, chitosan is often used as one of the important ingredients in the manufacturing of fabric items for hygiene and health care purposes, such as antimicrobial clothes, gauze, bandage, and artificial organs. For the protection of the environment, the use of chitosan eliminates the need to synthetic resins in shrink-resistance finishing processes for wool fabrics.^{13,14} In addition, chitosan facilitates the dyeing ability of woolen fabrics.^{15,16}

Takeshi, in his study of the application of chitin and its derivatives to the antimicrobial finishing of cotton and silk fabrics, reports that these compounds have very strong bacterial toxicity against *Staphylococcus aureus*, in cotton and *Escherichia coli* in silk.¹⁷ Erra et al. used chitosan in a finishing process for woolen fabrics pretreated with plasma and discovered that this treatment not only added shrink-resistance to the fabrics, but also was remarkably helpful in easing the ecological problems.¹⁸ Other scientists have also found, as far as shrink-proof finishing of woolen fabrics is concerned, that soaking wool in a 2–5% chitosan solution and heat-treating the fabric at a proper temperature results in a shrink-resistant character to the treated woolen fabric.¹⁹

These results in the literature indicate that both hydrated PU and chitosan have shrink-proofing and bacteria-resisting effects on various fabrics. However, to date, we have found few reports specifically about the combination of these two compounds being used for these purposes for woolen fabrics. Therefore, the objective of this study was to devise a shrink-proofing and antimicrobial compound finishing process for woolen fabrics, using PU and chitosan blended polymers, that would enhance both of these favorable characteristics to a new level at the same time.

EXPERIMENTAL

Materials

The chemicals used in this study included 4,4'-methylene-bis(isocyanatocyclohexane) (H_{12} MDI), poly(eth-

ylene glycol) (PEG; MW, 400 or 600 Da.), 2,2-bis(hydroxymethyl)propionic acid (DMPA), triethylamine (TEA), di-*N*-butyltin dilaurate (DBTDL), 1-methyl-2-pyrrolidone (NMP), $NaHSO_3$, and chitosan (supplied by OHKA Enterprises, Company, Ltd., Kaoshiung, Taiwan; degree of deacetylation, 85%; $M_r = 400$ kDa). *Staphylococcus aureus* was purchased from Sigma Chemical Company, and Baird-Parker medium was purchased from Scharlau Chemie, Spain. All chemicals were reagent grade except H_{12} MDI, which was industrial grade. The PU prepolymer was synthesized in our laboratory. The woolen fabrics employed as the test products were pretreated by the washing and grabbing process [supplied by Shun Fu Tai Industrial Company, Ltd., Taiwan; $48 N_w \times 48 N_w$, ends (52) and picks (44); 66-inch width].

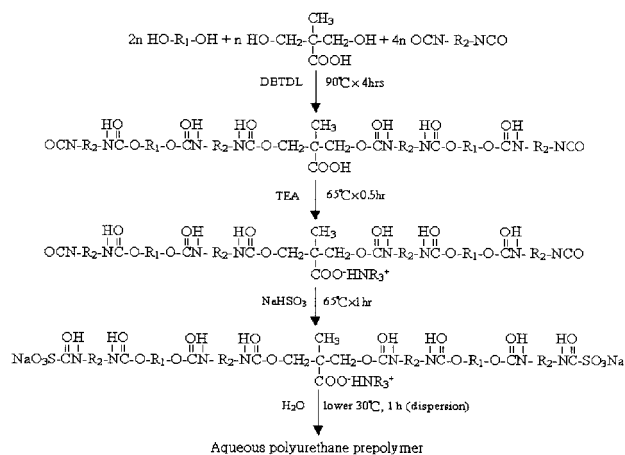
Methods

Syntheses and analyses of PU prepolymer and its blended polymer with chitosan

In this synthesis, a rigid chain, a soft chain, and an anion center (i.e., H_{12} MDI, PEG, and DMPA, respectively) in a ratio of 4:2:1 were mixed together with a proper amount of NMP as solvent and two drops of catalyst (DBTDL). The mixture was put under a nitrogen atmosphere at 90°C and left there for 4 h. After cooling the mixture to 65°C, 1 mol of TEA was added to neutralize the mixture. At a temperature of ~30°C, 2 mol of $NaHSO_3$ were added, and the mixture was blended for another hour. Then, at a temperature of ~30°C, an appropriate amount of chitosan was added, and the reacting mixture was allowed to blend for 1 h. Next, distilled water for emulsion dispersion was added and blended for 1 h. This synthesis yielded the blended polymer of hydrated PU and chitosan. The synthesis and reaction of PU–chitosan blended polymer are shown in Figure 1. It can be assumed that chitosan sorption on wool is due to the ionic interaction between the negative charges of carboxylate groups in the keratin molecule and the protonated amino groups of chitosan, and to hydrogen bonding between hydroxyl or amide groups of wool and similar groups in chitosan. In addition some authors believe that treatment with chitosan produces a fast and uniform layer on the surface of wool fibers.^{13–15}

The PU prepolymer and its blended polymers with chitosan were analyzed by Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC). The PU prepolymers synthesized from PECS with molecular weights of 400 and 600 Da are designated PU(400) and PU(600), respectively. The PU(400) and PU(600) blended polymers with chitosan are referred to as PU(400) + C and PU(600) + C blended polymers, respectively.

1) Synthesis of PU prepolymer



Where HO-R₁-OH : PEG HO(CH₂CH₂O)_nH

OCN-R₂-NCO : H₁₂MDI OCN-◇-CH₂-◇-NCO

2) Blending of Chitosan and PU prepolymer

There may be hydrogen bonds on chitosan and PU blend polymer because they were blended at 30°C.

3) PU-Chitosan blended polymer reaction between fiber

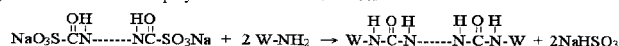


Figure 1 Synthesis and reaction of the PU-chitosan blended polymer.

Compound finishing process for woolen fabrics and testing the properties of the treated fabric

First, several processing solutions of different concentrations (2–10%) were prepared. The test was started by putting pieces of test fabric into each solution to soak twice, with a pressing step after each soaking and with a press-absorption ratio of 85%. After drying at 120°C for 1 min, each soaked fabric was then heat-treated at a specific temperature in the range 130–170°C for a specific length of time in the range 15–90 s. Finally, the finished (treated) fabrics were analyzed separately for their shrink-proofing property according to the AATCC TM 187–2001 method, as described in Table I.

The antimicrobial property of the fabrics was tested by the standard procedure set by the JAFET (Japanese Association for Functional Evaluation of Textiles).²⁰ This method is employed to assess the antibacterial

property of the fabric by counting the number of bacteria present. *Staphylococcus aureus* was used as the testing bacterium. The procedure was as follows: First, we prepared a bacterial culture with the Baird-Parker medium and diluted the grown culture into a test suspension with a concentration of $5\text{--}30 \times 10^5$ cell/mL. Then we took the piece of cloth to be tested 0.2 g and placed it in a sterile vial along with 0.2 mL of the test suspension already mentioned as inoculum. The vial was then incubated at rest at 35–37°C for 18 h. After the incubation period, 20 mL of sterile physiological saline was added into the vial, and the mixture was vortexed 25–30 times at a moderate speed of 100 rpm. The well-mixed bacterial suspension was then further serially diluted into several samples. For each such sample, 1 mL of diluted solution was transferred into a sterilized Petri dish to make a 15-mL standard agar disc. Such disc making was duplicated. After the discs had been incubated at 35–37°C for 24 h, the number of bacterial colonies on each disc was counted. This count was used to determine the bacterial population in the test sample by multiplying by the respective diluting factor. To determine the antibacterial effect, we tested the same specimen in triplicate, took the average result, and used eq. 1 to obtain the differences between the fabrics with and without antibacterial properties. We defined that any value >1.6, determined with eq. 1, was an indication of positive antibacterial property.

The antimicrobial index was determined by the discrepancy of the two items according to the following equation:

$$\text{Discrepancy } (\Delta BC) = \log(B/A) - \log(C/A) \quad (1)$$

where *A* is the original bacteria count, *B* is the bacteria count on the treated fabrics after a 18-h incubation period, and *C* is the same post-incubation count on the treated fabric. Normally, if the calculated ΔBC value is >1.6, the fabric is considered to have the antimicrobial property.^{20,21}

We also measured the strength of a single yarn by the regulation CNS 11263 (Chinese National Standard 11263), the softness by CNS 1481, and the tendency of yellowing by the magnitude of the yellowing index (YI) of the treated fabric. The definition of YI is²²

TABLE I
Accelerated Machine Program Settings^a

| Program operation | Number of cycles | Time per cycle, s | Temperature, °C |
|-------------------|------------------|-------------------|-----------------|
| Wash | 1 | | 60 |
| Agitation time | | 165 | |
| Rinse/dry | 3 | | 60 |
| Agitation time | | 45 | |
| Spin time | | 35 | |
| Dry time | | 240 | |

^a The air pressure was 3.8 bars, and the water level was 3 L.

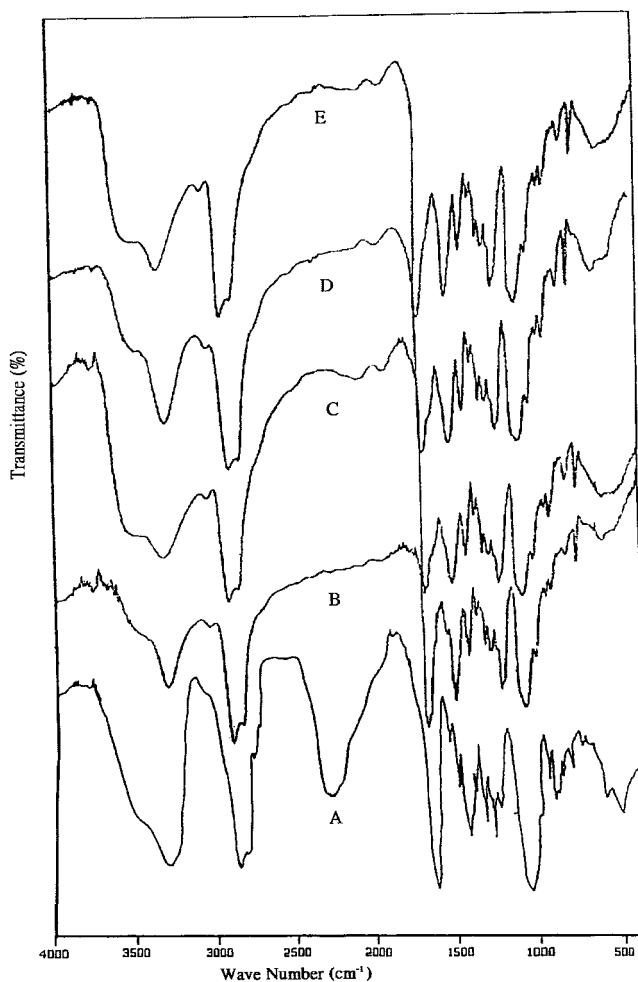


Figure 2 FTIR spectra of PU and PU-chitosan blended polymer: (A) before NaHSO₃ blocking; (B) PU(400); (C) PU(400) + C; (D) PU(600); (E) PU(600) + C.

$$YI = 100(1.28X - 1.06Z)/Y \quad (2)$$

where X , Y , and Z are three activation values.

RESULTS AND DISCUSSION

FTIR and DSC analysis of PU-chitosan blended polymer

The FTIR spectra shown in Figure 2 indicate that the characteristic absorption at 2281 cm⁻¹ for the NCO functional group in PU(400) and PU(600) disappeared after the reaction. In the broad OH group absorption region of 3300–3500 cm⁻¹, there emerged a typically narrow and sharp —NH absorption peak. Peaks located at 3322, 1708, and 1449 cm⁻¹, which correspond to the absorptions of —NH, —CO, and —CNH, respectively, revealed that the new synthesized product contains an NHCOO—group. In addition, there are absorption peaks for —C—O—C— soft linkage at 1101 cm⁻¹ and for —COO— at 1529 cm⁻¹. These peaks confirmed that ionized groups were present.

Similarly, the characteristic absorption at 2270 cm⁻¹ for the NCO functional group disappeared in the post-reaction spectra of PU(400) + C and PU(600) + C. Again, there is a rather narrow and sharp —NH absorption peak in the region 3300–3500 cm⁻¹, and there is a broad absorption peak corresponding to the many OH groups contributed by chitosan. It is obvious that the addition of chitosan would result in more OH groups than PU alone. Also, there are peaks for —NH, —CO, and —CNH at 3319, 1708, and 1449 cm⁻¹, respectively, suggesting that the new synthesized product contains —NHCOO—group. Finally, there is an absorption peak for —C—O—C— soft linkage at 1103 cm⁻¹ and a —COO— absorption peak at 1531 cm⁻¹. These results confirm that the blended polymer contains ionized groups as well. As shown in Table II, the glass transition temperatures (T_g) of the soft segment for various PU prepolymers decrease by increasing the PEG molecular weight. When chitosan was blended with the PU prepolymer, the small effect on the T_g indicates that chitosan may be interacting with PEG by hydrogen bonding.

Effect of temperature in the curing process on properties of the treated fabric

The shrinkage of the untreated fabrics in both warp and weft direction was larger than that of the treated fabric, as shown in Figure 3. This result is because the yarn of the untreated fabrics is stretched taut during weaving, whereas the treated fabrics have reactive polymers completely covering the fiber scales or an even layer of protective thin membrane formed over the surface. In addition, there were many sporadic linkages or bridges established between individual fibers that afforded the fibers fixed in the set shape complex much less freedom to move around than the fibers in the untreated fabric. In turn, the latter would make the tightness of the yarn, structure of the fabric, and weaving density more restrictive to the movement of individual fibers. Under such circumstances, the fibers in the treated fabric would of course become much more resistant to outside forces and not glide against each other; that is, the fabric would become more shrink-proof.²³ These changes in the treated fabric explain why it is more shrink-resistant than the untreated fabric. It was also noticed that the shrinkage

TABLE II
 T_g^a of Waterborne PU Prepolymer

| Prepolymer | T_g (°C) |
|-------------|------------|
| PU(400) | -7.03 |
| PU(400) + C | -6.27 |
| PU(600) | -11.14 |
| PU(600) + C | -10.23 |

^a Glass transition temperature.

along the warp direction was always greater than that in the weft direction. This difference is because the warp yarn is stretched more tightly than the weft yarn during weaving, which is also the main reason why it is very easy for woolen fabrics to shrink when heated and why the shrinking in the warp direction is larger. Another point illustrated in Figure 3 is that the higher the curing temperature, the lower are the warp and weft shrinkages. This result might be because when the curing temperature increases, the membrane over the fibers becomes more fixed by the heat, and the fibers lose the freedom of relative mobility. Moreover, at a higher temperature, the reaction between the PU membrane and the fiber would be facilitated, resulting in better shrinking resistance. When the curing was conducted at 160°C, the treated fabric had better shrink resistance with than without the addition of chitosan. This result was presumably because chitosan would link with the fiber to form a two-dimensional (2D) framework, and the strengthened fabric structures, weaving density, etc. enhanced the bondage and restriction, which afforded the fabric higher elasticity. It is also evident that the size of the PEG molecule has some influence on the shrink resistance in the treated fabric; that is, higher the molecular weight of PEG, the less the shrinkage. The reason for this effect is that when the molecular weight of PECS increases, the molecular chain becomes longer and the structure more stable, so there is less gliding mobility between fibers. Therefore, the PU(600) + C blended polymer gave the fabric the best shrink resistance.

The strength of the treated fabric was greater than that of the untreated fabrics, as shown in Figure 4. This

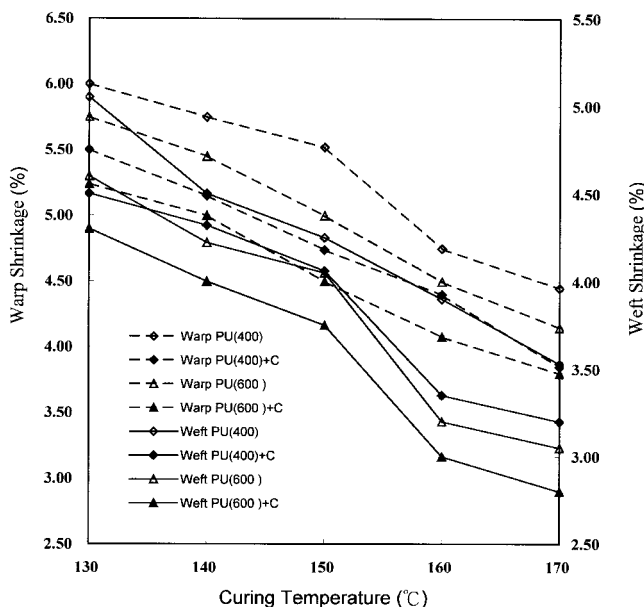


Figure 3 The effect of different curing temperature conditions on wool fabric shrinkage (finishing agent concentration, 6%; curing time, 60s; shrinkage of raw fabric, 11.67% (warp) and 8.61% (weft)).

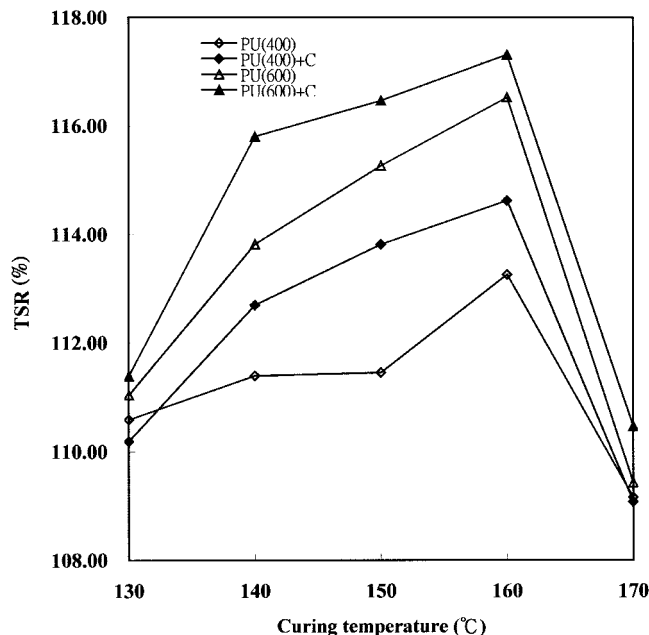


Figure 4 The effect of different curing temperature conditions on the tensile strength retention (TSR) of wool fabric (finishing agent concentration, 6%; curing time, 60 s; TSR of raw fabric, 100%).

result was due to the combination of PU membrane and fiber that tightened up the fiber structure so that the membrane filled the gaps and holes in the fabric, the density of fabric was heightened, and eventually the fabric became stronger and more rigid. The fabric strength increased with higher curing temperature because of the accelerated fix reaction between the blended polymer and fiber. However, when the temperature reached 170°C, the strength decreased. Perhaps the higher temperature also speeded up the degradation of the fiber structure and the bonds between blended polymer and fiber were broken down, so the fabric strength withered at too high a temperature. At 160°C, the fabric treated by the blended polymer with chitosan was stronger than that without chitosan. Again, this result is due to the 2D framework formed by chitosan and fiber, which gives the fiber greater strength. It is also evident that the size of the PEG molecule has some influence on the strength of the treated fabric; that is, the bigger the molecular weight of PEG, the stronger the fabric. The reason for this effect is that when the molecular weight of PEG increases, the molecular chain becomes longer and there is more chance for it to link with the fiber, which forms a more solid structure and gives a shrink-proof rigidity to the fiber. Therefore, the blended polymers made of PEG 600 afford the fabric higher strength.

As seen in Figure 5, the softness of the untreated fabrics was better than that of the treated fabric. This difference is because the union of the PU and fiber forms a layer of tough membrane on the surface of the fabric

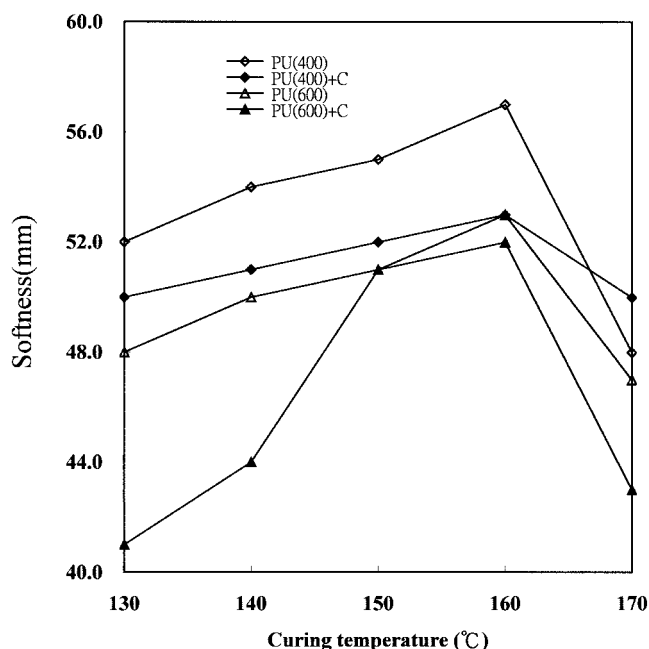


Figure 5 The effect of different curing temperature conditions on the softness of wool fabric (finishing agent concentration, 6%; curing time, 60 s; softness of raw fabric, 31 mm).

that gives the fiber surface rigidity and renders it less soft. The higher temperature of the curing lowered the softness of the fabric. However, when the temperature reached 170°C, the softness improved, presumably due to overheating. The overheating damaged the structure of the fiber itself, breaking apart the bond between blended polymer and fiber and thus weakening the strength of the fiber. If the temperature was 160°C, the fabric treated with blended polymer plus chitosan was less soft than that without chitosan. Again, this result is due to the 2D framework formed by chitosan and fiber, which results in higher rigidity of the fiber and thus greater strength and lower softness. It is also obvious that the higher the molecular weight of PEG, the higher the strength of the treated fabric. The reason for this effect is that when the molecular weight of PEG increases, the molecular chain would be longer and there is more chance for this chain to link with the fiber, forming a more closely knit structure that gives increased rigidity to the fiber. This process is the reason why the blended polymer made from PEG 600 rendered the fabric less soft.

The effect of curing temperature on the antimicrobial property of the treated fabric is shown in Figure 6. The antimicrobial properties of untreated fabrics were much worse than those of the fabric treated with the PU-chitosan blended polymers. This difference is presumably because the amine group in the chitosan molecule is apt to form positively charged quaternary ammonium ions in an acidic medium that would in turn, reduce bacterial metabolism by the adsorption and stacking of chitosan polymer chains on the bacte-

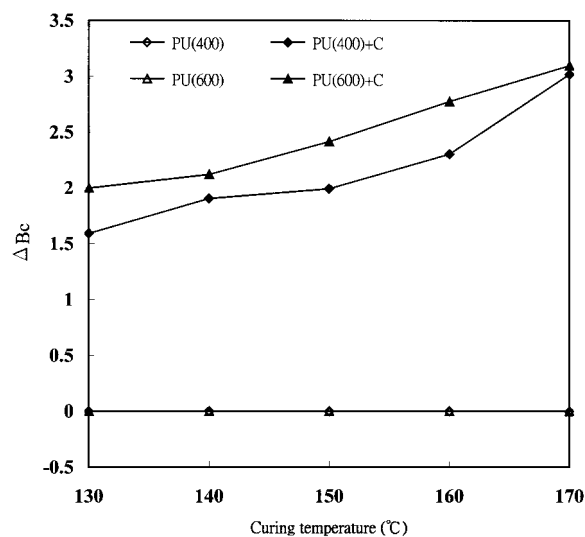


Figure 6 The effect of different curing temperature conditions on the antibacterial properties of wool fabric (finishing agent concentration, 6%; curing time, 6 s; ΔBC value of raw fabric, 0).

rial cell wall and by blocking DNA transcription by chitosan. This process would thereby enhance the antimicrobial property of the treated fabric.²⁴ At 160°C, almost no bacteria grew in the fabric treated with chitosan and the finishing process using the PU-chitosan blended polymer was more effective than the one using PU alone. The size of the PEG molecule had little influence on the antimicrobial properties of the treated fabrics.

As shown in Figure 7, the treated fabric yellowed

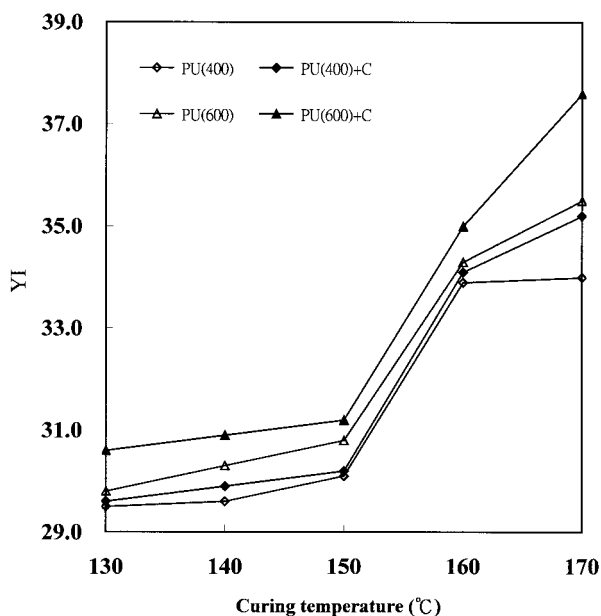


Figure 7 The effect of different curing temperature conditions on the yellowing index (YI) of wool fabric (finishing agent concentration, 6%; curing time, 60 s; YI of raw fabric, 25.3).

TABLE III
Physical Properties of Various Treated Fabrics Finished^a with Different Curing Times

| Molecule weight of PEG (g/mol) | Finish agent | Curing time (s) | Shrinkage (%) | | TSR ^b (%) | Softness (mm) | ΔB_c^c | YI |
|--------------------------------|----------------------------|-----------------|---------------|------|----------------------|---------------|----------------|------|
| | | | Warp | Weft | | | | |
| 400 | Raw Fabric PU ^d | 15 | 11.67 | 8.61 | 100.00 | 31 | 0.00 | 25.3 |
| | | 30 | 6.14 | 5.25 | 108.47 | 48 | 0.00 | 27.9 |
| | | 45 | 6.01 | 5.03 | 109.19 | 50 | 0.00 | 28.7 |
| | | 60 | 5.75 | 4.40 | 110.36 | 50 | 0.00 | 29.0 |
| | | 90 | 5.52 | 4.25 | 111.46 | 55 | 0.00 | 30.1 |
| 400 | PU + C ^e | 15 | 5.00 | 3.85 | 115.70 | 55 | 0.00 | 31.0 |
| | | 30 | 5.50 | 5.05 | 109.08 | 48 | 1.17 | 28.0 |
| | | 45 | 5.15 | 4.56 | 110.28 | 49 | 1.34 | 28.9 |
| | | 60 | 5.05 | 4.25 | 112.70 | 50 | 1.47 | 29.6 |
| | | 90 | 4.74 | 4.06 | 113.82 | 52 | 2.00 | 30.2 |
| 600 | PU | 15 | 4.20 | 3.50 | 115.20 | 54 | 3.02 | 31.6 |
| | | 30 | 5.75 | 4.95 | 106.89 | 42 | 0.00 | 28.6 |
| | | 45 | 5.43 | 4.50 | 108.93 | 43 | 0.00 | 29.0 |
| | | 60 | 5.20 | 4.30 | 111.12 | 47 | 0.00 | 29.9 |
| | | 90 | 5.00 | 4.05 | 115.27 | 51 | 0.00 | 30.8 |
| 600 | PU + C | 15 | 4.12 | 3.00 | 118.47 | 51 | 0.00 | 32.0 |
| | | 30 | 5.35 | 4.50 | 102.81 | 46 | 1.35 | 30.0 |
| | | 45 | 5.14 | 4.21 | 104.58 | 47 | 1.61 | 30.3 |
| | | 60 | 4.86 | 3.90 | 114.90 | 50 | 1.36 | 30.7 |
| | | 90 | 4.50 | 3.75 | 116.47 | 51 | 2.21 | 31.2 |
| | | 90 | 3.05 | 2.85 | 120.66 | 53 | 3.40 | 33.3 |

^a Finishing agent conc., 6%; curing temperature, 150°C.

^b TSR, tensile strength retention.

^c ΔB_c , antibacterial property.

^d Polyurethane.

^e Chitosan.

more than the untreated fabrics because chitosan in the blended polymer can cause the fabric to excessively yellow through high-temperature curing. In addition, yellowing occurs because wool is a protein fiber, which tends to yellow naturally. At 160°C and with the addition of chitosan, the treated fabric yellowed to a greater extent than the treated fabric without chitosan added, which is expected because it is known that chitosan yellows easily under high temperature conditions.

Effect of the duration of curing on the properties of the treated fabric

The results in Table III reveal that the longer the curing time, the better the shrink resistance of the fabric. This effect is presumably a result of the completion of the reaction between the finishing agent and fiber, which makes the structure of the fibers tighter and thus promotes the resistance to shrinkage. In addition, the fabric strength and antimicrobial property were also improved, but its softness and the tendency of yellowing apparently suffered due to the long duration of high-temperature treatment.

Effect of concentration of processing agent on the properties of the treated fabric

The results in Table IV show that if the concentration of the blended polymer used in the process is high, the

chances for it to react with fiber obviously increases, so the dimensional stability of the fabric is practically higher and, theoretically, there are more bonding chains. The end result is that the treated fabric does not easily shrink because the agent filled in the gaps between the fibers, the binding between fibers was more complete, and the individual fibers became more rigid and strong. However, the softness deteriorated with higher concentrations of processing agent. Similarly, higher processing agent concentration promoted the antimicrobial property by providing more opportunities for the fiber to react with the agent, but also worsened the yellowing problem.

CONCLUSIONS

1. Shrink-proof and antimicrobial properties of the treated fabric improve as the temperature, the duration of curing, and the concentration of processing agent increase, but the yellowing tendency and softness of the fabric suffer along with these increases.
2. The blended polymer made from chitosan and PU synthesized from PEG of MW 600 gives the best shrink-proofing and antimicrobial properties to the treated fabric.
3. Treatment of fabric with blended polymer with chitosan results in better shrink-proofing and an-

TABLE IV
Physical Properties of Various Treated Fabrics that were Finished^a with Different Concentrations of Finishing Agent

| Molecular weight of PEG (g/mol) | Finishing agent | Finishing agent concentration (%) | Shrinkage (%) | | TSR ^b (%) | Softness (mm) | ΔB_c^c | YI |
|---------------------------------|----------------------------|-----------------------------------|---------------|------|----------------------|---------------|----------------|------|
| | | | Warp | Weft | | | | |
| 400 | Raw fabric PU ^d | | 11.67 | 8.61 | 100.00 | 31 | 0.00 | 25.3 |
| | | 2 | 6.45 | 5.94 | 101.08 | 43 | 0.00 | 28.0 |
| | | 4 | 6.23 | 5.25 | 103.31 | 45 | 0.00 | 29.8 |
| | | 6 | 5.52 | 4.25 | 111.46 | 55 | 0.00 | 30.1 |
| | | 8 | 4.50 | 3.75 | 112.01 | 57 | 0.00 | 31.0 |
| 400 | PU + C ^e | 10 | 4.05 | 3.00 | 112.73 | 57 | 0.00 | 31.9 |
| | | 2 | 6.00 | 5.22 | 109.08 | 47 | 1.36 | 28.2 |
| | | 4 | 5.50 | 4.97 | 109.08 | 49 | 1.46 | 29.9 |
| | | 6 | 4.74 | 4.06 | 113.82 | 52 | 2.00 | 30.2 |
| | | 8 | 4.00 | 3.21 | 115.19 | 52 | 2.29 | 31.3 |
| 600 | PU | 10 | 3.25 | 2.25 | 116.59 | 54 | 3.25 | 32.0 |
| | | 2 | 6.22 | 5.25 | 103.77 | 41 | 0.00 | 30.0 |
| | | 4 | 6.00 | 4.75 | 109.43 | 43 | 0.00 | 30.7 |
| | | 6 | 5.00 | 4.05 | 115.27 | 51 | 0.00 | 30.8 |
| | | 8 | 4.00 | 3.80 | 117.93 | 51 | 0.00 | 31.8 |
| 600 | PU + C | 10 | 3.05 | 2.13 | 119.70 | 52 | 0.00 | 32.3 |
| | | 2 | 5.47 | 4.75 | 105.66 | 39 | 1.43 | 30.1 |
| | | 4 | 5.05 | 4.22 | 111.39 | 44 | 1.73 | 30.7 |
| | | 6 | 4.50 | 3.75 | 116.47 | 51 | 2.21 | 31.2 |
| | | 8 | 3.51 | 3.05 | 119.12 | 54 | 3.06 | 31.9 |
| | | 10 | 2.75 | 2.00 | 120.70 | 55 | 3.80 | 32.5 |

^a Curing temperature, 150°C, time, 60 s.

^b tensile strength retention.

^c ΔB_c , antibacterial property.

^d Polyurethane.

^e Chitosan.

timicrobial properties than treatment with PU alone, but the tendency to yellow and softness are less ideal.

References

- Dyeing & Finishing of Woolen Fabrics: Theoretical & Practical; Kung, F. C. Ed.; Textile Ind. Publication; Beijing, China, 1989; pp 402–405.
- Chang, K. P.; Shang, C. C.; Chuan, M. L. Multi-functional Finishing of Woolen Fabrics; Woolens Tech; Beijing, China, 1997; Vol. 4, pp 61–62.
- Mark, H.; Wooding, N. S.; Atlas, S. M. Chemical after Treatment of Textiles; Wiley Interscience: New York, 1971; pp 520–537.
- Dyeing & Finishing Work Process, Tao, L. C., Ed.; China Textile Publication: Beijing, China, 1989; pp. 229–236.
- Wang, W. H. Application of Chitin & Chitosan to Antimicrobial & Deodorization; *Textile Comm* 2000, 8(14), 5–25.
- U.S. Pat. 3,236,685.
- U.S. Pat. 4,063,887.
- U.S. Pat. 4,617,340.
- U.S. Pat. 4,831,098.
- U.S. Pat. 4,980,108.
- Mathur, N. K.; Narang, C. K. *J Chem Educ* 1990, 67, 938.
- Muzzarelli, R. A. A. Chitin; Pergamon Press: Oxford, 1977.
- Masri, M. S.; Randall, V. G.; Pittman, A. G. Proceedings of the 1st International Conference on Chitin and Chitosan; MIT Press: Cambridge, MA, 1978; pp 306–314.
- U.S. Pat. 2,047, 218, 1936.
- Davidson, R. S.; Xue, Y. J. *J Soc Dyers Colour* 1994, 110, 24.
- Jocic, D.; Julia, M.R.; Erra, P. *J Soc Dyers Colour* 1997, 113, 25.
- Takeshi, K.; Tsugio, M. M. *Japan Silk Study Magazine* 1996, 6, 507.
- Erra, P.; Molina, R.; Jocic, D.; Julia, M.R.; Cuesta, A.; Tascon, J.M.D. *Textile Res J* 1999, 69(11), 811.
- Kan, C. H.; Hu, P. H. Chemistry of Natural Polymers; High Education Publication: Beijing, China, 1993; pp 207–208.
- Li, J. S. *J Textile Center* 1997, 17(4), 270.
- Chau, C.H. Medical Functional Fiber; China Petroleum Publishing; Beijing, China, 1996; pp 38–39.
- Color/Color Difference Measuring Unit —User's anual (Model: ND-300A), Nippon Denshoku Industries Company Ltd., Japan, Feb 1991.
- Liu, C. T. Woolens Technology; Institute of Beijing Wool Spinning Science: Beijing, China, 1997; 5, pp 47–50.
- Ueno, K.; Nishi, N.; Tokura, S. *Kitosan Kenkyu* 1996, 2, 112.