Functional Finishing of Cotton Fabrics by Treatment with Chitosan

Younsook Shin, Dong Il Yoo*, Kyung Wha Oh**, Kyunghye Min, Jeong In Jang

Dept. of Clothing & Textiles, Chonnam National Univ.
**Dept. of Textile Engineering, Chonnam National Univ.*
***Dept. of Home Economics Education, Chung-Ang Univ.*

키토산 처리에 의한 면직물의 기능화가공

신윤숙†, 유동일*, 오경화**, 민경혜, 장정인

전남대학교 의류학과
*전남대학교 섬유공학과
**중앙대학교 가정교육과

ABSTRACT

Cotton fabric was treated with chitosan by pad-dry(-cure) method to impart antimicrobial properties. Four chitosans of different degree of deacetylation (DAC: 65~95%) with similar molecular weight(MW: ca. 50,000) and one chitosan oligomer(MW 1,800, DAC 86%) were used. In order to improve the durability to laundering of antimicrobial activity for the fabrics treated with chitosan oligomer, crosslinker or binder was included in the finishing formulation. Antimicrobial activity against *Staphylococcus aureus* and *Proteus vulgaris* was evaluated by the Shake Flask Method. The treated fabrics were laundered up to 20 times according to AATCC Test Method 60-1986 or JIS 0217-104 and antimicrobial activity of the laundered fabrics was evaluated. The antimicrobial activity was increased with the increase of concentration and degree of deacetylation of chitosan. And the cured fabrics showed better durability to laundering than the not-cured fabrics according to AATCC Test Method 60-1986. Crosslinker and binder decreased antimicrobial activity of the fabrics treated with chitosan oligomer and were not effective to improve the durability to laundering according to JIS 0217-104. (*Korean J Human Ecology 1(1) : 103~112, 1998*)

KEY WORDS : chitosan, chitosan oligomer, antimicrobial activity, durability to laundering, crosslinker.

†Corresponding author : Dept. of Clothing and Textiles, Chonnam National Univ., 300 Yongbong-dong, Buk-gu, Kwangju, 500-757, Korea
Tel : 062-530-1343, Fax : 062-530-1349
E-mail : yshin@orion.chonnam.ac.kr

Ⅰ. INTRODUCTION

Recently, consumers' concern about sanitary property of textile products and their safety toward human and environment are getting increased. On this respect, biodegradable natural polymers such as chitin and chitosan draw much attention. Chitosan, the deacetylated derivative of chitin, has amine group on the No. 2 carbon atom instead of N-acetyl group. Because of the non-toxicity and biocompatibility of chitosan, chitosan fiber has been produced and applied as a suture or wound dressings in medical area (Biagini et al. 1992; Sanford 1989; Unitika 1985). Application of chitosan in the textile area has been studied for imparting antimicrobial properties to textile products (Park et al. 1996; Seo et al. 1992; Tokura et al. 1986). However, chitosan is used restrictively as an antimicrobial finishing agent by aftertreatment because of its low durability to laundering.

In this study, cotton fabric was treated with chitosan, and effect of treatment condition and DAC on the antimicrobial activity was investigated. And effect of curing and additives such as binder or crosslinker on the durability to laundering was also examined.

Ⅱ. EXPERIMENTAL

1. Materials

A desized, scoured and bleached 100% cotton fabric, four chitosan samples of similar molecular weight(ca. 50,000) with different degree of deacetylation(DAC: 65, 78, 84, 95, %, respectively) and one chitosan oligomer(MW 1,800, DAC 86%) obtained from Sehwa Co. were used. Polyurethan emulsion(TX-B-202F, Takamatsu Oils & Fats Co., Ltd., Japan) and DMDHEU (dimethyloldihydroxyethyleneurea, BASF Co., Ltd.) were used as a nonionic binder and a difunctional crosslinker, respectively. Other reagents used were of laboratory grade.

2. Treatment of fabrics

Cotton fabrics were padded with chitosan(MW 50,000) solution dissolved in 2% acetic acid. The padded samples were dried at 100℃ for 5 min and some of dried samples were further cured at 150℃ for 3 min. Cured fabrics were rinsed in distilled water to remove acidic solution before evaluation.

In other procedure of treatment, chitosan oligomer was dissolved in distilled water and binder or DMDHEU with catalyst($MgCl_2$) was added in the padding bath to improve the durability to laundering. Cotton fabrics were padded, dried and cured at the same condition as described above.

3. Evaluation of the treated fabrics

Add-on was calculated from the difference in sample weight before and after chitosan treatment. Antimicrobial activity of treated fabrics was evaluated by Shake Flask Method(Min 1995) in terms of the reduction rates in the number of colonies of a gram-positive test bacterium, *Staphylococus aureus*(ATCC 6538). *Proteus vulgaris*(ATCC 881) was used as a gram-negative test bacterium for evaluating the effect of additives on antimicrobial activity and laundering durability of the fabrics treated with chitosan oligomer.

Treated fabrics with chitosan and chitosan oligomer were laundered 5, 10, 15, 20 times according to AATCC Test Method 60-1986 and JIS 0217-104 to investigate laundering durability of antimicrobial activity, respectively. After laundering, antimicrobial activity was evaluated as described earlier.

III. RESULTS AND DISCUSSION

1. Add-on of the treated fabrics

Table 1 gives the effect of treatment conditions and DAC on add-on of the treated fabrics. As shown in Table 1, add-on is increased with the treatment concentration. However, DAC and curing do not affect add-on of the fabrics treated with chitosan. On the other hand, compared with the add-on of fabrics treated with chitosan, add-on of the treated fabrics with chitosan oligomer is lower than that of fabrics treated with chitosan at corresponding concentration. Namely, the fixation efficiency of chitosan oligomer is lower compared with chitosan of MW 50,000. From the result, we can speculate that the molecular weight of chitosan affects fixation efficiency on the treated fabrics.

Table 1. Add-on(%) of the treated fabrics

	DAC(%)	Treatment concentration (%)			
		0.1	0.3	0.5	1.0
No cure	65	1.1	1.3	1.8	2.2
	78	1.1	1.3	1.8	2.2
	84	1.1	1.3	1.8	2.1
	95	1.1	1.4	1.8	2.2
Cure (150℃, 3min)	65	1.1	1.3	1.8	2.2
	78	1.1	1.3	1.9	2.2
	84	1.1	1.3	1.8	2.1
	95	1.1	1.3	1.8	2.1
	86[a]	0.9	1.0	1.0	1.2

a: molecular weight of this sample is 1,800 and others are 50,000

2. Effect of concentration on the antimicrobial activity

The effect of chitosan concentration on the antimicrobial activity is shown in Fig. 1. Antimicrobial activity is increased with chitosan concentration and approached to a maximum value at 0.5% and thereafter, it is not changed significantly. Whereas, antimicrobial activity of the fabrics treated with chitosan oligomer is increased continuously to 1.0% treatment concentration displaying ca. 88% of bacterial reduction rate. Chitosan of DAC 65% shows reduction rate below 40% even if chitosan concentration increases. Therefore, it is not effective against *S. aureus*. Chitosan of DAC 78% displays the maximum reduction rate of 93% at 0.5% chitosan concentration and it is not increased thereafter. Chitosan of DAC above 84% shows similar reduction rates and reaches to the reduction rate of 100% from 0.5% chitosan concentration. Generally, for the chitosan of MW 50,000, reduction rate is not increased anymore with chitosan concentration above 0.5% regardless of DAC.

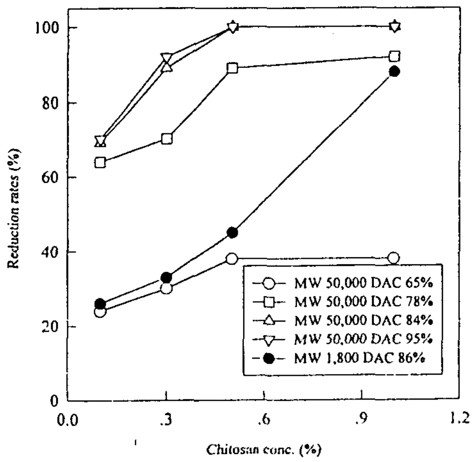

Fig. 1. Effect of chitosan concentration on the antimicrobial activity(*S. aureus*).

There are two proposed mechanisms of antimicrobial activity by chitosan. In one mechanism, the polycationic nature of chitosan interferes bacterial metabolism by stacking at the cell surface (Uchida 1988). The other mechanism is the binding of chitosan with DNA to inhibit mRNA synthesis(Kendra, Hadwiger 1984). However, the mechanism of antimicrobial activity is not clearly defined yet.

3. Effect of degree of deacetylation on the antimicrobial activity

As shown in Fig. 2, bacterial reduction rate is increased with the increase of DAC regardless of treatment concentration. The increase of DAC plays a positive role onto antimicrobial activity because the number of amine group, which is known to impart antimicrobial activity, is increased. Chitosan of DAC 65% does not show significant antimicrobial activity. And chitosan of DAC 78% shows significant antimicrobial activity at the concentration above 0.5%. Although antimicrobial activity is increased sharply up to 84% of DAC, it is not increased significantly above 84%. Effect of DAC on the antimicrobial activity is more evident at lower chitosan concentration. Chitosan of higher DAC is desirable if it is necessary to use low chitosan concentration, considering end uses. From the results, it is thought that DAC is a major factor affecting antimicrobial activity of chitosan and it should be above 75% at least for imparting antimicrobial activity.

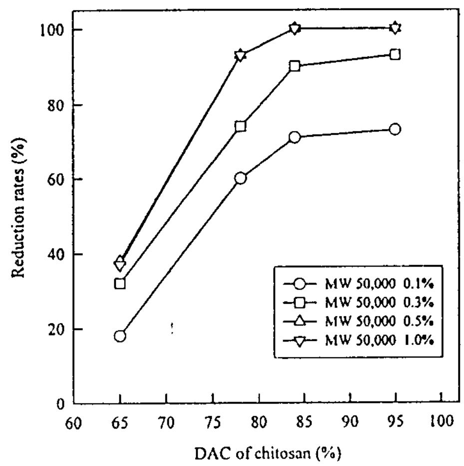

Fig. 2. Effect of DAC on the antimicrobial activity(*S. aureus*).

Chitosan oligomer shows lower reduction rate at the same concentration compared with chitosan of MW 50,000 with similar DAC(84%). Molecular weight is thought to be another factor affecting antimicrobial activity of chitosan. Uchida et al.(1992) studied the effect of molecular weight of chitosan oligomer on the antimicrobial activity and found that chitosan oligomer consisted of 4~7 unit inhibited the growth of *E. coli*, while oligomer mainly consisted of 3~4 unit did not retard the growth of *E. coli*. On the other hand, Tokura et al.(1997) reported that although chitosan oligomer of MW 9,300 showed the growth inhibitor of *E. coli*, chitosan oligomer of MW 2,200 is not growth inhibitor but growth accelerator. Until now, the effect of molecular weight on the antimicrobial activity of chitosan is controversal.

4. Effect of curing on the antimicrobial activity

Figs. 3 and 4 show the effect of curing on the antimicrobial activity at 0.1 and 0.5% chitosan concentration, respectively. Bacterial reduction rate of the cured fabrics is slightly lower than that of not-cured fabrics at 0.1% chitosan concentration, but there is no difference in bacterial reduction rate between cured and not-cured fabrics at 0.5% chitosan concentration. Therefore, it can be concluded that curing does not affect significantly on antimicrobial activity of the treated fabrics. This is advantageous when chitosan treatment is applied together with other finishes, such as durable press finish for which curing is required.

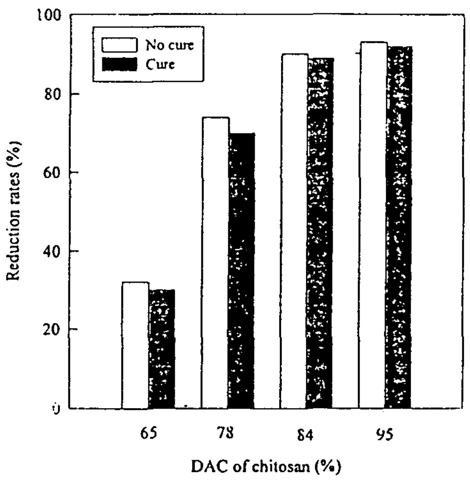

Fig. 3. Effect of curing on the antimicrobial activity(0.3% chitosan concentration).

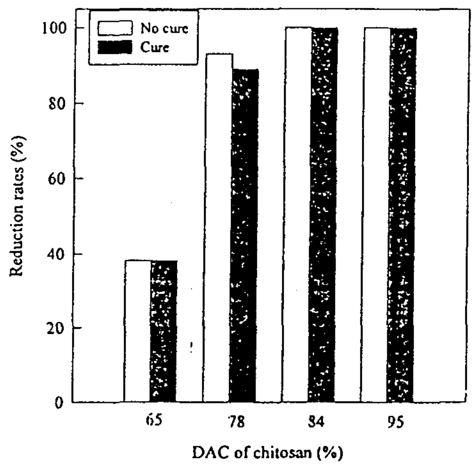

Fig. 4. Effect of curing on the antimicrobial activity(0.5% chitosan concentration).

5. Effect of curing on the durability to laundering

The effect of curing on the durability to laundering of antimicrobial activity is shown in Figs. 5 and 6. Chitosan of DAC 65% was excluded in laundering test because it does not show significant antimicrobial activity as discussed earlier. At any treatment condition and DAC, bacterial reduction rate is decreased with the increase in laundering cycle. Bacterial reduction rate is decreased sharply up to 5 laundering cycles and reached to an equilibrium state at 20 laundering cycles. Cured fabrics show superior laundering durability to not-cured fabrics. Curing effect is more remarkable at higher DAC and higher chitosan concentration. There is a report that application of chitosan on the fibers having hydroxy and/or carboxyl acid groups, such as cellulosic fibers, cellulose acetate, protein fibers, etc., permits coatings tightly by ionic interactions

(Allan et al. 1989). Nevertheless, better laundering durability of the fabrics treated with chitosan should be produced for practical uses.

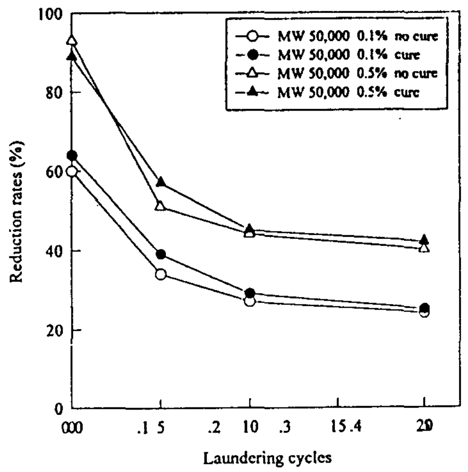

Fig. 5. Effect of curing on the durability to laundering(DAC 78%).

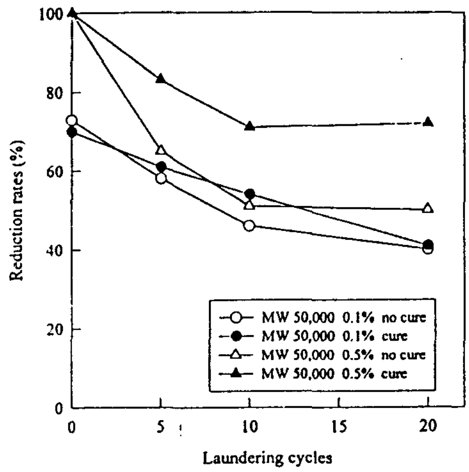

Fig. 6. Effect of curing on the durability to laundering(DAC 78%).

6. Effect of additives on add-on of the fabrics treated with chitosan oligomer

In order to improve durability to laundering of the fabrics treated with chitosan oligomer, binder or DMDHEU was included in the finishing formulation. Table 2 shows the effect of additives on add-on of the fabrics treated with chitosan oligomer. The addition of binder or DMDHEU increases add-on of the treated fabrics slightly. But the concentration of additives does not affect significantly add-on of the treated fabrics.

Table 2. Add-on(%) of the fabrics treated with chitosan oligomer

Additive conc. (%)		Treatment concentration(%)	
		1.0	1.5
None		1.2	1.8
Binder	0.1	1.4	1.6
	0.3	1.3	1.8
	0.5	1.3	1.7
DMDHEU[a]	0.1	1.4	1.9
	0.3	1.3	1.9
	0.5	1.4	2.0

a: with 6% $MgCl_2$ on the weight of DMDHEU

7. Effect of additives on antimicrobial activity of the chitosan oligomer

Fig. 7 shows the effect of additives on antimicrobial activity of the fabrics treated with chitosan oligomer. Antimicrobial activity is decreased with the concentration of binder or crosslinker (DMDHEU). DMDHEU is less detrimental to antimicrobial activity than polyurethane binder. DMDHEU decreases bacterial reduction rate by 10~30% depending on concentration of the chitosan oligomer. Since DMDHEU reacts with amine groups in chitosan as well as hydroxyl groups in cellulose, antimicrobial activity of the treated fabrics is decreased due to the decrease of amine groups. Polyurethan binder decreases bacterial reduction rate by 40%. Polyurethan binder seems to mask amine groups in some way, resulting in the decrease of antimicrobial activity of the treated fabrics.

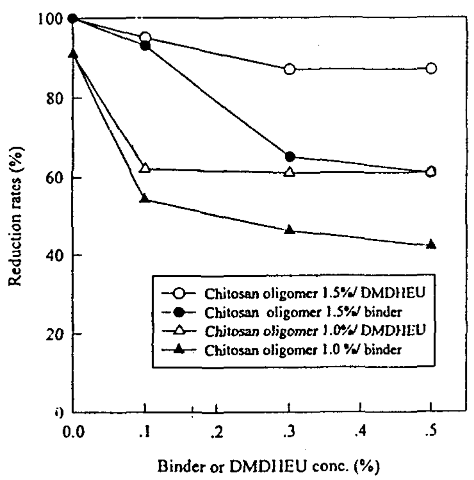

Fig. 7. Effect of binder or DMDHEU concentration on the antimicrobial activity (*P. vulgaris*).

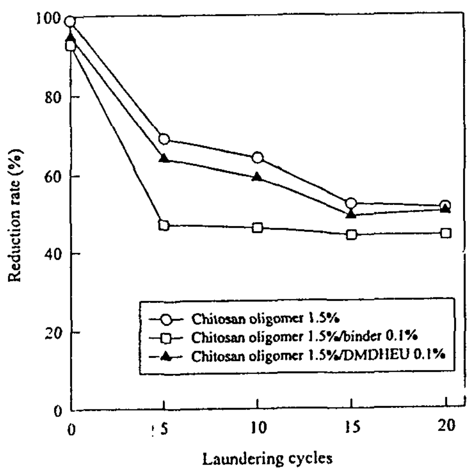

Fig. 8. Effect of binder or DMDHEU on the durability to washing (*P. vulgaris*).

Durability to laundering of the chitosan/binder or DMDHEU treated fabrics is shown in Fig. 8. According to the results followed by JIS 0217-104, both of binder and crosslinker are not effective to improve the durability to laundering of the fabrics treated with chitosan oligomer. On the other hand, Lee et al.(1997) reported that they improved laundering durability of the fabrics treated with chitosan oligomer by addition of DMDHEU in finishing formulation. However, different experimental results of durability to laundering could be obtained depending on laundering method. On this matter, more comprehensive studies are necessary.

Ⅳ. CONCLUSIONS

We have investigated four chitosans and one oligomer for their effect of treatment condition, DAC, and additives such as binder and crosslinker on the antimicrobial activity and durability to laundering of cotton fabrics. Add-on of the treated fabrics is increased with treatment concentration, but it is not dependent on curing and DAC. Antimicrobial activity of the fabrics treated with chitosan is increased with treatment concentration and reached to the maximum at 0.3~0.5% depending on DAC. Antimicrobial activity is increased sharply with the increase of DAC and it is not changed significantly above DAC 84%. Curing improves durability to laundering up to 20 % for the fabrics treated with chitosan. Chitosan oligomer shows bacterial reduction rate of 88% at 1.0% treatment concentration. Addition of binder or crosslinker increases add-on, but decreases antimicrobial activity of the treated fabrics. Both of binder and crosslinker are not effective to improve durability to laundering of the treated fabrics.

REFERANCES

1. Allan, G.G., Carroll, J.P., Hirabayashi, Y., Muvundamina, M., Winterowd, J.G.(1989). Chitosan-coated fibers. In: Skjak-Braek, G., Anthonsen, T., Sandford, P.A., eds. Chitin and Chitosan, pp. 765-776, Elsevier Applied Science, London and New York.
2. Biagini, G., Muzzarelli, R.A.A., Giardino, R., Castaldini, C.(1992). Biological materials for wound healing. In: Brine, C.J., Sandford, P.A., Zikakis, J.P., eds. Advances in Chitin and Chitosan, pp. 16-24, Elsevier Applied Science, London and New York.
3. Kendra, D.F., Hadwiger, L.A.(1984). Characterization of the smallest oligomer that is maximally antifungal to Fusarium solani and elicites Pisantin formation in pisum sativum. Exp. Mycology. 8:276-281.
4. Lee, J.W., Nam, C.W., Ko, S.W.(1997). Antimicrobial finish of cotton fabric with chitosan oligomer in the proceedings of 4th Asian Textile Conference, 2:845-848.
5. Min, K.(1995). Antimicrobial finishing of cotton fabrics with chitosan. M.H.E. thesis, Chonnam National University.
6. Park, W.H., Lee, K.Y., Choi, J.H., Ha, W.S., Chang, B.H.(1996). Characterization of chitosan-treated wool fabric(I). *J. Korean Fiber Soc.* 33:855-860.
7. Sanford, P.A.(1989). Chitosan: Commercial uses and potential applications. In: Skjak-Braek, G., Anthonsen, T., Sandford, P.A., eds. Chitin and Chitosan, pp. 51-69, Elsevier Applied Science, London and New York.

8. Seo. H., Mitsuhashi. K., Tanibe. H.(1992). Advances in Chitin and Chitosan: Antibacterial and antifungal fiber blended by chitosan. pp. 34-40. Elsevier Applied Science. London and New York.
9. Tokura. S., Nishimura. S., Nishi. N., Nakamura. K., Hasegawa. O., Sashiwa. H., Seo. H.(1987). Preparation and some properties of variously deacetylated chitin fibers. Sen-I Gakakaishi. 43: 288-2938.
10. Tokura. S., Ueno. K., Miyazaki. S. Nishi. N.(1997). Molecular weight dependent antimicrobial activity by chitosan. Macromol. Sym., 120:1-9.
11. Uchida. Y.(1988). Antimicrobial activity by chitin and chitosan. Food Chemical. 2:22-29.
12. Uchida. Y., Izume. M., Ohtakara. A.(1989). Preparation of chitosan oligomers with purified chitosanase and its application. In: Skjak-Braek. G., Anthonsen. T.Sandford. P.A., eds. Chitin and Chitosan. pp. 373-382. Elsevier Applied Science. London and New York.
13. Unitika Ltd(1985). Shaped chitin body. European Patent No. 0171254.

초 록

면직물에 항균성을 부여하기 위하여 패드-건조(-열처리법)에 의해 키토산처리를 하였다. 분자량이 약 50,000으로 비슷하고 탈아세틸화도가 65~95%인 4종의 키토산과 분자량이 약 1,800이고 탈아세틸화도가 약 86%인 1종의 키토산올리고머를 사용하였다. 키토산올리고머로 처리한 경우에는 세탁내구력을 증진시키기 위하여 가교제 또는 바인더를 가공처리액에 첨가하였다. 항균성은 쉐이크플라스크법에 의해 공시균 *Staphylococcus aureus* 와 *Proteus vulgaris*를 사용하여 측정하였다. 세탁내구력은 AATCC Test Method 60-1986 또는 JIS 0217-104에 따라 20회까지 세탁한 후 항균성을 측정하였다. 실험결과, 항균성은 키토산의 농도와 탈아세틸화도가 증가함에 따라 증가하였으며 열처리 유무는 항균성에 큰 영향을 미치지 않았다. AATCC Test Method 60-1986에 따르면 열처리한 시료의 세탁내구력이 열처리하지 않은 시료보다 우수하였다. 가교제나 바인더의 첨가는 키토산올리고머를 처리한 시료의 항균성을 감소시켰으며, JIS 0217-104에따라 실험한 결과 세탁내구력 향상에 효과가 없었다.

주요 단어 : 키토산, 키토산올리고머, 항균성, 세탁내구력, 가교제.