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Improvement of Hygienic Characteristics of Material for Patients Clothing through Treatment with Chitosan/Nanosilver Mixed Solution

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키토산/은나노 혼합용액 처리에 의한 환자복 소재의 위생 성능 향상

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Abstract

In order to enhance the functionality of a cotton fabric actually used as the clothing material for patients, the fabrics are treated with chitosan/nanosilver mixed solution. The nanosilver has excellent biocompatibility, not causing an environmental pollution as a natural polymer, provides expectation of an additional performance, does not harm human beings, and shows a strong antibacterial activity even in a small amount, and supplements chitosan, which is disadvantaged if used alone for fabric treatment. This study evaluates functional improvement of the clothing material for patients and observes through hygienic characteristics which are the most important function. In antibacterial activity of the fabrics treated with chitosan/nanosilver mixed solution against *Staphylococcus aureus*, higher ratio of chitosan was observed to achieve better antibacterial activity. In antibacterial activity against *Klebsiella pneumoniae*, higher ratio of nanosilver was observed to achieve better activity. Regarding laundry durability of antibacterial activity after repeated laundering, activity against *Staphylococcus aureus* was little reduced, but was greatly lowered against *Klebsiella pneumoniae*. Deodorization activity was excellent as the mixed ratio of chitosan was increased, and air permeability, moisture permeability and moisture regain were reduced as the mixed ratio of nanosilver was increased.

Key words: Clothing material for patients, Chitosan, Nanosilver, Antibacterial activity, Moisture properties; 환자복 소재, 키토산, 은나노, 항균성, 수분특성

I. Introduction

Patient clothing should possess functionality for body temperature regulation, defense against germs, and relief of any undesirable influences on physical movement. It should be washed very often, and accordingly the fabrics should be durable against laundry and its chemicals, and the size should remain the same and be without wrinkles after laundry(Park et al., 2006). Especially in case of the disabled patients, excretion and contamination could reduce the physi-

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ological comfort of the clothes, and hygiene becomes a very serious issue resulting in smell and multiplying germs. However, existing cotton fabrics cannot satisfy the functionality associated with these issues. Therefore, the functional improvement of the clothing material for patients in terms of pleasure and the biological hygiene are very important problem.

The most important function of the patient clothing is the antibacterial activity, which reduce the direct harm of microorganisms by eliminating them and deterring their multiplication, and prevent foul smell being produced when organic substances are disintegrated by microorganisms(Chung & Kim, 2004). Antibacterial agents for such a purpose include amines, quarternary ammonium series, biguanides, alcohols, phenols, organic/inorganic series, oxidized materials, photocatalyst series, and natural compounds etc. (Lee, 1997). Some of organic antibacterial materials that have been used contain harmful halogen compounds, posing a serious problem, and have been avoided(Yeo et al., 2003). By the way, antibacterial agent to the fabrics should not be poisonous to the human body, should constrain the multiplication of microorganisms, should not cause environmental contamination and undesirable effects on the physical properties of the fabric(Menachem & Jack, 1991). Among substances satisfying such condition is chitosan(Lee et al., 1994).

Chitosan is superior in biological decomposition, does not cause environmental contamination, and have multiple functionalities such as antibacterial activity, deodorization activity and moisturizing effect (Ogura et al., 1980). It is a useful natural polymer and may be recycled as a resource, which is a meritorious aspect in this era when the environmental contaminations issues are seriously raised(Xu et al., 1996). However, the resin or the crosslinking agent should be used to enhance the adhesion efficiency, which affects the touch feeling negatively, and durability associated with washing and friction is also problematic(Kim et al., 1995). Therefore, multiple steps of processing the crosslinking agent, the softening agent, etc. are required to remedy the shortcomings, which is a tedious process. Such processes are complicated and drive up the cost, and for economic reason, in order to raise the processing effect, silver would be mixed to chitosan as a finishing agent. Moreover, silver is not poisonous(Simpson, 2003) and enhance the functionality when mixed as such.

Silver is safe enough to be used as an additive even for foods, and is known to have an ability of killing germs even at a concentration as low as 1ppm or even lower(Hong et al., 1998). Especially, if silver is processed in nano unit, its antibacterial activity increases because of the increased total surface area along with the increased antibiotic efficiency(Rong et al., 2001). When nanosilver colloid solution is treated on the fabrics with the developed nano technology, the nanosilver particles are transferred to the fabric surface to prevent the growth of microbes. The nanosilver is greater in its total surface area when compared with the silver of the same volume, and is more skin-friendly, without causing the skin trouble(Choi et al., 2006).

This research practically tried to improve the function of cotton fabric used for patient clothing while considering the process effect and the economic aspect. As a eco-friendly finishing agent, chitosan was chosen because it is a natural polymer excellently appropriate to the human body. Along with it, the nanosilver solution was mixed to treat the fabric because it can complement the defect of chitosan and provide an additional effect to enhance the functionality. At this stage, the mixed ratios of chitosan/nanosilver solution were examined according to their performance in comparison with the chitosan-only treatment. Especially, through hygienic characteristics of the treated fabric such as antibacterial activity, deodorization activity and moisture properties, it was inferred that it is appropriate as treatment material of patient clothing.

II. Experimental

1. Materials

For the cotton fabric, specimen provided by Silverday Co. was used. The characteristics of the specimen is shown in <Table 1>. The reagent used for the mixed solution of chitosan/nanosilver was provided

Table 1. Characteristics of fabric

Fabric	Weave	Fabric count (threads/inch)		Weight ($g/100cm^2$)	Thickness (mm)
		Warp	Weft		
Cotton 100%	twill	102	58	1.98	0.40

Table 2. Characteristics of chitosan

Particle condition	powder
Viscosity	11 cps
Degree of deacetylation	95.33%
Average molecular weight	1.5×10^5
Moisture content	6.84%
Residue on ignition	0.18%
Concentration	40,000ppm

Table 3. Characteristics of nanosilver

Particle size	below 10nm
Concentration	30,000ppm

from Texan Med. Tech. Co. Ltd. and the supplied solution was diluted before use. The characteristics of chitosan and nanosilver that have been used for the mixed solution were shown in <Table 2-3>.

2. Methods

1) Processing of the Fabrics

The solution of chitosan(CH) and nanosilver(NS) were mixed in the ratios of 3:1(CH3/NS1), 1:1(CH1/NS1), and 1:3(CH1/NS3), and the fabrics treated with them were compared with that treated only with chitosan(CH4). At this time, the carboxyl acid was added as a crosslinking agent for the mixed solution of chitosan/nanosilver and the solution of chitosan only. The treatment was performed with the one bath processing. The fabric was immersed in the solution at the liquor ratio of 40:1 for 1 hr and padded for its weight pick up to be 100±2%. The specimen was dried naturally and then heated for 3 min. at 160°C. Then, to determine the add-on ratio after applying treatment with chitosan/nanosilver solution, the sample was dried completely at 105°C, and weighed before and after the drying.

$$Add\text{-}on(\%)=\frac{(W_1-W_0)}{W_0}\times 100$$

W_0 : *dry weight of sample before processing*
W_1 : *dry weight of sample after processing*

2) Antibacterial Activity

To examine the antibacterial activity of the fabric treated with chitosan/nanosilver mixed solution, a quantitative test by the shake flask method(KS K 0693-2001) was carried out. *Staphylococcus aureus*(ATCC 6538), a gram-positive bacterium and *Klebsiella pneumoniae*(ATCC 4352), a gram-negative bacterium were used as the testing bacteria. The reduction rate in the number of colonies was calculated using the following equation. And also, to find out the antibacterial activity after the laundry, the specimens were washed 2 times, 5 times, and 10 times and were compared with pre-laundry specimen through Launder-O-Meter(ATLAS, Model LEF) according to KS K 0430-2001(A-1).

Bacterial reduction rate (%) = $(A\text{-}B)/B\times 100$
A : *number of bacteria recovered from the control specimen incubated for 18hrs*
B : *number of bacteria recovered from the test specimen incubated for 18hrs*

3) Deodorization Activity

Deodorization activity by ammonia gas was measured using a gas detective conduit method. The weight of the specimen in a measuring flask was set to about 2g, the amount of injected ammonia solution to 2μm and the deodorization test was performed in the container of 1000ml. The change in the density of ammonia was quantitatively measured with the gas detector tube and the deodorization rate was measured using the following formula.

Deodorization rate (%) = $(A\text{-}B)/A \times 100$
A : *gas concentration of blank*
B : *gas concentration with specimen*

4) Air Permeability

An air permeability tester(FX 3300, Textest, Swit-

zerland) was used to measure the same specimen at 5 times under 100Pa using the Frazier method(KS K 0570-2001) at the area of $20cm^2$ and then its average value was obtained.

5) Moisture Permeability

Moisture permeability through water vapour transmission rate(WVTR) was measured according to the evaporation method(KS K 0594). The cup for the WVTR was covered with the specimen and its weight was measured. Then, it was left in the fixed temperature and humidity chamber of 40±2°C, 50±5% RH for 24 hours and its weight was measured again. It was compared with that of cup left in the same chamber without covering to obtain the water vapour transmission rate for three samples.

$$WVTR\ (g/m^2 \cdot 24h) = \frac{(W_1 - W_0)}{S}$$

W_0 : *weight of sample before vapourization*
W_1 : *weight of sample after vapourization*
S : *transfer area of water vapour*

6) Moisture Regain

Moisture regain was measured according to the oven method(KS K 0220). First, the specimen was left for more than 24 hours at 20±2°C, 65±2% RH, and then was dried for 2 hours at 105°C. The weights before and after drying were measured for three samples and the moisture regain was calculated with the following formula.

$$Moisture\ regain\ (\%) = \frac{(W_w - W_d)}{W_d} \times 100$$

W_w : *weight of sample before drying*
W_d : *weight of sample after drying*

III. Results and Discussion

1. Antibacterial Activity

Microbe sometimes benefits the human and harms other times in our daily life. It inhabits the textile products that are deeply related to our life or human body, causing bad smell, damage to textile, or harm to our health. In this regard, antibacterial finishes restrain the inhabitation or propagation of bacteria or mold in textiles while it retains the physical or chemical property of textile products, contributing to the protection of human body or hygienic living environment. Since sanitary nonwoven fabrics directly contact human skin, it is important to select the antibacterial agent that doesn't badly affect to human body even though it has lower sterilization than organic bacterial agents with excellent sterilization. In the previous study, the chitosan(Lee et al., 1994) and the silver(Kwon et al., 2003; Lee & Jeong, 2001) were found to have excellent antibacterial activity. To examine it more concretely, the antibiotic feature was measured through the *Staphylococcus aureous*(ATCC 6538), a kind of pyogenic bacteria that usually live on the skin or fabric, and the *Klebsiella pneumoniae*(ATCC 4352), a typical gram-negative bacteria.

First of all, the actual attached amount affects the hygienic characteristics of nonwoven fabric treated with chitosan/nanosilver mixed solution. <Table 4> shows that the add-on ratio of the fabrics treated with 200ppm chitosan/nanosilver solution was higher than that of the fabric treated only with chitosan. Also, as the mixing ratio of nanosilver became greater, the add-on ratio increased. It was assumed that the fine particles of nanosilver are attached more to the gaps between textiles, fibrils and the pores of cotton fabric.

To examine the influence by the mixing ratio of chitosan and nanosilver, the antibacterial activity of treated fabric was measured for diverse concentrations of mixed solution. <Fig. 1> shows the antibacterial activity of the fabric treated with the chitosan/nanosilver mixed solution against the *Staphylococcus aureous*. According to it, when the treating concentration of mixed solution was low, the antibacterial activity was rather low at the higher mixing ratio of

Table 4. Add-on ratio of the fabrics treated with 200 ppm chitosan/nanosilver sol'n

Samples	Add-on ratio
CH4	0.21%
CH3/NS1	0.29%
CH1/NS1	0.44%
CH1/NS3	0.54%

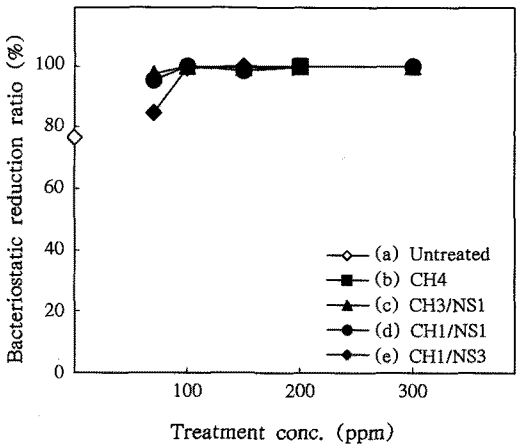

Fig. 1. Effect of treatment concentration on the antibacterial activity of Staphylococcus aureus of the fabrics.

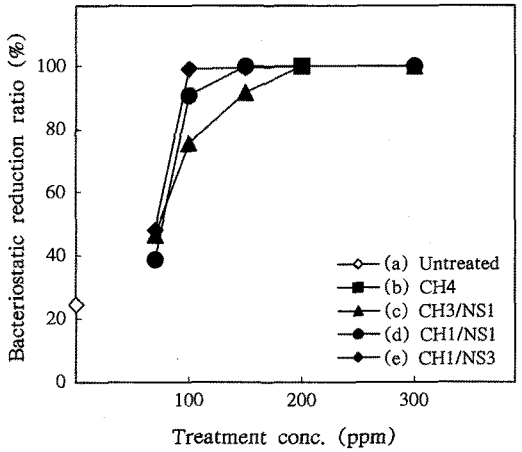

Fig. 2. Effect of treatment concentration on the antibacterial activity of Klebsiella pneumoniae of the fabrics.

nanosilver solution. But, when the concentration of mixed solution was 200ppm or higher, the antibacterial activity was as excellent at 99.9% regardless of the mixing ratio. When the concentration of mixed solution was low, the higher ratio of chitosan in the mixed solution was observed to achieve more excellent antibacterial activity. So, it seems that the chitosan has better antibiotic function against the *Staphylococcus aureous.*

The generally accepted mechanism of antibacterial activity of chitosan is that amine group is positively ionized(Katsumasa & Takao, 1994), in which $-NH_2$ in the C-2 location of glucosamine becomes positively ionized as $-NH_3^+$, and the charged amine group imposes a pulling force on the negative ions of the sialic acid or the phospholipid that forms the walls of microorganisms, reducing the freedom of the microorganisms, which results in antibacterial activity.

<Fig. 2> shows the antibacterial activity of the fabric treated with the chitosan/nanosilver mixed solution against the *Klebsiella pneumoniae.* When the treating concentration of mixed solution was low, the antibacterial activity was as low as 50% or less. But, when the concentration of mixed solution was 200ppm or higher, the antibacterial activity was excellent regardless of the mixing ratio. While the antibacterial activity of low concentrated solution against the *Staphylococcus aureous* was higher at the higher ratio of chitosan as shown in <Fig. 1>, the antibacterial activity against the *Klebsiella pneumoniae* was higher at the higher ratio of nanosilver. At any rate, the antibioses against *Klebsiella pneumoniae* and *Staphylococcus aureous* were excellent regardless of the mixing ratio when the concentration of mixed solution was 200ppm or higher. Therefore, all futher tests for the performance of chitosan/nanosilver treated solution were made for the fabrics treated with 200 ppm mixed solution.

It is important how long the antibacterial activity of the fabric is maintained in the process of use or laundry. Especially, the laundry durability of antibacterial activity is very important for patient clothing that have to be laundered frequently. In general, the processing of fabrics after treatment is easy and economic but becomes less durable. In this study, to examine how much the antibiotic effect of chitosan/nanosilver mixed solution on the fabric remains after the laundry, the antibacterial activity was measured after the 10 laundries.

<Fig. 3> shows the antibacterial activity of chitosan/nanosilver treated fabrics against the *Staphylococcus aureous* after 2, 5 and 10 laundries, and <Fig. 4> shows the laundry durability of antibacterial activity against the *Klebsiella pneumoniae.* According to them, the antibacterial activity against the *Staphylococcus aureous* did not diminish even after 10 laun-

dries, and also showed a good laundry durability regardless of the mixing ratio of chitosan/nanosilver in the solution.

On the other hand, the antibacterial activity against the *Klebsiella pneumoniae* diminished a lot when the number of laundry increased, and the antibacterial activity in case of chitosan only treatment dropped a lot. When the mixing ratio of nanosilver solution increased, the reduction of antibacterial activity after laundry became relatively small. But, after 10 laundries the antibacterial activity against the *Klebsiella pneumoniae* could hardly be expected.

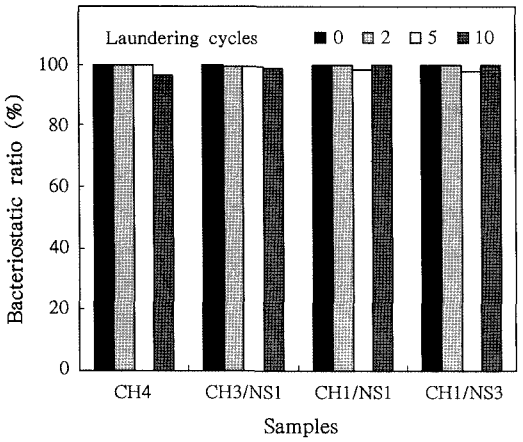

Fig. 3. Antibacterial activity of Staphylococcus aureus of the chitosan/nanosilver treated fabrics after various number of laundering cycles.

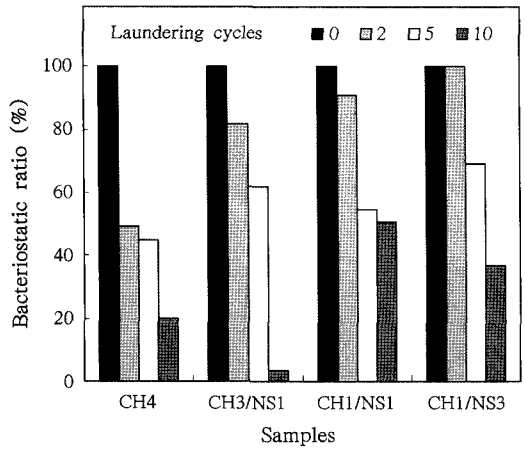

Fig. 4. Antibacterial activity of Klebsiella pneumoniae of the chitosan/nanosilver treated fabrics after various number of laundering cycles.

2. Deodorization Activity

Deodorization that removes the stinking smells generated in a confined space is a necessary element in pursuing the pleasant and healthy life. For elderly and especially handicapped patients who cannot move their body as they wish, it is very hard to change the clothes frequently. So the microbes such as bacteria and molds in the clothes can cause bad smells. This kind of smell has an influence on the health of others around them, let alone the health of patients themselves. Therefore, the measurement of deodorization activity is very important. In this study, it was presupposed that the vanishing speed of ammonia gas would be similar to that of gas from the human body and thus the deodorization activity was measured with ammonia on the basis of odor evaluation standard. <Fig. 5> shows the deodorization rate of the fabric treated with chitosan/nanosilver mixed solution. The deodorization activity of treated fabric was higher than that of untreated fabrics, and the higher the ratio of chitosan was observed to achieve better deodorization. Therefore, if the main purpose of the treatment is deodorization activity, increasing the ratio of chitosan in the mixed solution seems to perform better.

3. Air Permeability

Air permeability of textiles is affected by the inter-

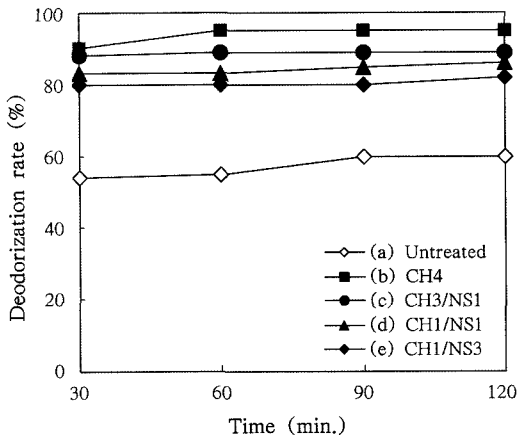

Fig. 5. Deodorization rate of the chitosan/nanosilver treated fabrics.

yarn pore size of a fabric structure(Backer, 1948). As the material for patient's clothes is in contact with the skin directly, its feeling character is very important. Especially, the air permeability is related with the feeling that directly influences the comfort. In general, when fabrics are treated with the chitosan of a strong coating function, the reduction of air permeability is expected as in the cases of polyurethane resin or silicon water repellent processing. It is because the chitosan solution coats the fabric surface to create a thin film on it. Moreover, in case of silver particles with the size of nanometer, they can deposit between the textile structures. Therefore, it is expected that the air permeability will change after the treatment with chitosan/nanosilver solution. <Fig. 6> shows that the air permeability of treated fabric decreased even in comparison with that of fabric treated only with chitosan. When the mixing ratio of nanosilver in the solution was high, the reduction of air permeability dropped much. It seems because the nanosilver particles were penetrated into the inter-yarn pore and gaps in the fabric and thus reduced the air pores.

4. Moisture Properties

While human wears clothes, human body transpires moisture in the form of sweat or insensible perspiration even if it is not felt. Accordingly, the moisture transfer is directly related to the comfort of clothing in order to keep the comfortable clothing climate. In particular, the touch and moisture properties of fabrics are important since the material for patient's clothing contact the skin for a long period of time. However, the moisture properties of the material for patient's clothes are considered to change after applying chitosan treatments since chitosan has water-binding capacity as cationic polysaccharide.

<Fig. 7> shows the moisture permeability of fabrics treated with the chitosan/nanosilver mixed solution. When the fabric was treated only with the chitosan, the moisture permeability increased a little bit. But when it was treated with the chitosan/nanosilver mixed solution, the moisture permeability decreased similarly to air permeability. In general, if the fabric is treated with the chitosan with the water-binding capacity, its moisture-related features such as moisture absorbance and moisture regain become better. Therefore, it seems that the moisture permeability of the fabric treated only with chitosan increased a little. Meanwhile, if the fabric is treated with the chitosan/nanosilver mixed solution, the fine particles of nanosilver are attached to the gaps between textiles or fibrils and the pores of cotton, interrupting the transmission of moistures.

One of the important moisture features along with the moisture permeability is the moisture regain. As the amine and hydroxyl groups in the chitosan are

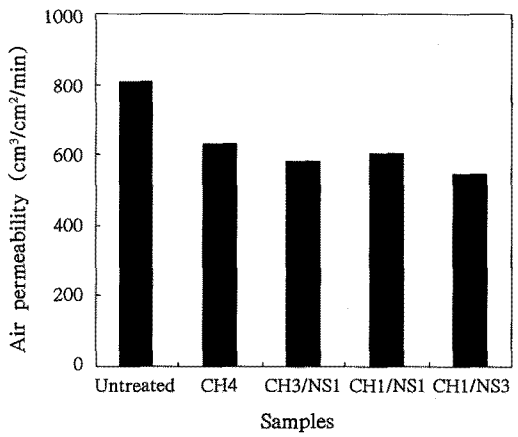

Fig. 6. Air permeability of the chitosan/nanosilver treated fabrics.

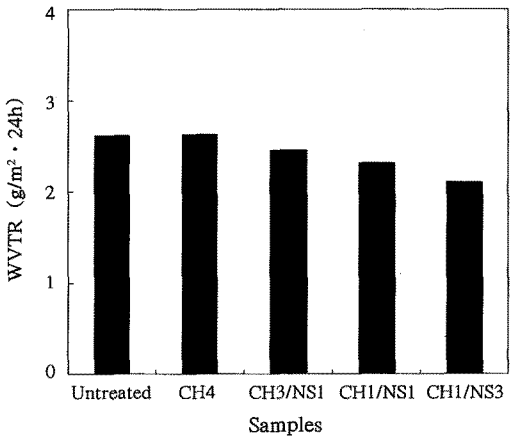

Fig. 7. Water vapour transmission rate of the chitosan/nanosilver treated fabrics.

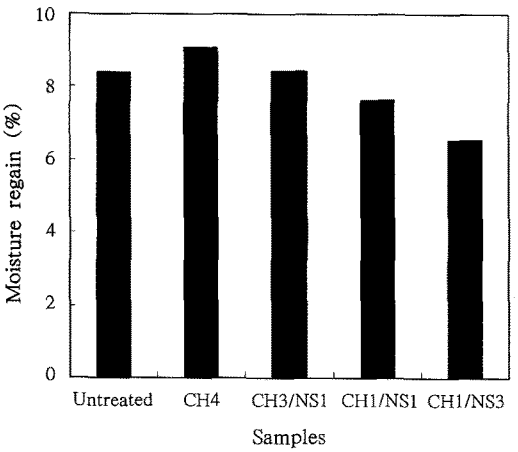

Fig. 8. Moisture regain of the chitosan/nanosilver treated fabrics.

hydrophillic because of high polarity, they make a hydrogen bond with the water molecule. Moreover, the existence of amino group raises the moisture absorption more than the cellulose(Hong et al., 1998). So, it is expected that the moisture regain will increase. <Fig. 8> shows the change of moisture regain by the chitosan/nanosilver treatment. As the ratio of nanosilver became greater, the moisture regain dropped rapidly, and became worse than that of untreated fabric. It coincides with the result of previous study(Oh et al., 1997).

IV. Conclusions

This research evaluated and observed functional improvement of the clothing material for patients through hygienic characteristics. The fabric was treated with chitosan/nanosilver mixed solution. Even though Chitosan is a natural polymer with an excellent bioavailability, to complement the defect of treatment by only chitosan and to manifest the additional functions, the nanosilver, being nontoxic to human body with strong antibiotic effect even with a small amount, was added and mixed together. The results of the examination are as follows:

1. Antibacterial activity of chitosan/nanosilver treated fabric against the *Staphylococcus aureous* and the *Klebsiella pneumoniae* was as excellent as 99.9% when the treatment concentration of mixed solution was 200ppm or more.

For *Staphylococcus aureus*, antibacterial activity of the treated fabric, higher ratio of chitosan showed better antibacterial activity. Thus, the chitosan achieved better antibacterial activity against the *Staphylococcus aureous*. For *Klebsiella pneumoniae*, higher ratio of nanosilver achieved better antibacterial activity. After 10 laundries, the antibacterial activity against the *Staphylococcus aureous* was little reduced, but the antibacterial activity against the *Klebsiella pneumoniae* was reduced a lot.

2. Deodorization rate of chitosan/nanosilver treated fabric improved a lot, and even better as the mixed ratio of chitosan was increased. The air permeability of chitosan/nanosilver treated fabric reduced a little when compared with that of chitosan only treatment. The reason seems be the adhesion of nanosilver particles.

3. As the ratio of nanosilver became greater in mixed solution, the fine particles of nanosilver are attached more to the gaps between textiles or fibrils and the pores of cotton, interrupting the passage of moistures. Thus, the moisture permeability decreased. Meanwhile, the reduction of hydrophilic chitosan caused the reduction of moisture regain.

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요 약

환자복은 생리적 쾌적성이 저하되고, 위생 문제가 심각하게 대두되지만 기존의 소재로는 쾌적성, 위생성 등 환자복으로서의 요구 성능을 충족하기 어려우므로 실제 환자복 소재로 사용되는 면직물의 성능을 개선하고, 가공 효과와 경제적인 측면을 고려한 기능성 가공을 함으로써 위생적 특성의 변화를 도모하였다. 가공제로는 천연고분자이며 생체적합성이 우수한 키토산과 아울러 키토산의 단점을 보완하면서 부가적인 성능을 기대할 수 있는 은나노 용액을 혼합비율에 따라 처리하여 항균성, 소취성, 수분 특성 등의 위생적 특성의 변화를 검토하였다. 가공처리 직물의 항균성은 키토산/은나노 혼합용액의 처리농도가 200ppm 이상에서 아주 우수한 항균성을 보였으며, 황색포도상구균은 10회 세탁 후에도 항균성이 감소되지 않았으나 폐렴간균에 대한 세탁내구성은 크게 저하되었다. 또한 키토산의 비율이 높을수록 아주 우수한 소취성을 보였으며 공기투과도, 투습도, 수분율은 은나노의 혼합비가 커질수록 다소 감소하였는데 이는 은나노 입자의 부착 때문으로 생각되었다.