

EVALUATION OF ANTIBACTERIAL AND STRUCTURAL PROPERTIES OF COTTON FABRIC COATED BY CHITOSAN/TITANIA AND CHITOSAN/SILICA HYBRID SOL-GEL COATINGS

KİTOSAN/TİTANDİOKSİT VE KİTOSAN/SİLİSYUMDİOKSİT HİBRİT SOL-JEL KAPLAMALAR İLE KAPLANMIŞ PAMUKLU KUMAŞIN ANTİBAKTERİYEL VE YAPISAL ÖZELLİKLERİNİN DEĞERLENDİRİLMESİ

Buket ARIK
Ege University
Textile Engineering Department
e-mail: buket.arik@ege.edu.tr

Necdet SEVENTEKİN
Ege University
Textile Engineering Department

ABSTRACT

Coatings of chitosan with both of titania and/or silica at different ratios were prepared and applied to the cotton fabric. The antibacterial activity of the samples were evaluated quantitatively according to the modified procedure of the shake flask method (ASTM E2149-01). It was found that there was a corresponding relation between the media and the activity of titania coatings. To the experimental results, all the samples coated by titania have shown perfect activity after 5 hour irradiation under UV light. On the other hand, their activity values were found to be less than the other samples under dark media conditions. The combination of titania and chitosan solutions was found to be more favourable than only chitosan coating. In addition to this, it's seen that the combination of silica and chitosan sols was more effective than application of chitosan or silica sol alone. After washing process, the combined systems showed the best results. The structure of cotton fabric and its morphology were studied using SEM-EDX, X-ray diffraction and FT-IR analysis. From the SEM images, it's observed that there is a compatible bonding with cotton fiber and combined coatings and this fact ensures the washing durability. The EDX results has confirmed the presence of titania and silica in the coatings. To the X-ray analysis, no significant difference was observed among the processes showing the stability of the crystallinity of the samples.

Key Words: Sol-gel process, Chitosan, Titania, Silica, Antibacterial, Cotton.

ÖZET

Eriyikten çekme yöntemi ile 2500-4250 m/dak. arası sarma hızlarında üretimi yapılan izotaktik polipropilen liflerinin X-ışını Kitosanın, hem titandioksitle hem de silisyumdioksitle farklı oranlarda hazırlanmış kaplamaları, pamuklu kumaşa uygulanmıştır. Numunelerin antibakteriyel aktivitesi, çalkalamalı seyreltme yönteminin (ASTM E2149-01) modifiye edilmiş prosedürüne göre sayısal olarak değerlendirilmiştir. Titandioksit esaslı kaplamaların aktivitesi ile test edildikleri ortam arasında doğrusal bir ilişki olduğu bulunmuştur. Test sonuçlarına göre, titandioksit esaslı kaplamalarla kaplanmış numunelerin tümü, 5 saatlik bir UV ışık maruzundan sonra mükemmel aktivite göstermektedir. Ancak, aynı kumaşların, karanlık ortam koşullarında aktivitelerinin oldukça düştüğü görülmektedir. Titandioksit ile kitosan çözeltilerinin kombinasyonu ile hazırlanan kaplamaların ise yalnızca titandioksit veya yalnızca kitosan uygulanmış numunelerden daha iyi sonuçlar verdiği belirlenmiştir. Bununla birlikte, silisyumdioksitin de kitosanla kombinasyonunun aynı şekilde yalnızca kitosan veya yalnızca silisyumdioksit uygulanmasına göre daha etkili olduğu saptanmıştır. Yıkama işleminden sonra, kombine edilen kaplamalar en iyi sonuçları vermiştir. Pamuklu kumaşın yapısı ve morfolojisi SEM-EDX, X-ışını difraksiyonu ve FT-IR analizi kullanılarak incelenmiştir. SEM analizinden, kombine edilmiş kaplamaların, pamuk lifi ile uyumlu bir şekilde bağ oluşturduğu ve bu sayede yıkama dayanıklılığının sağlandığı belirlenmiştir. EDX sonuçları, kaplamalardaki titandioksit ve silisyumdioksitin varlığını kanıtlamıştır. X-ışını analizinde ise işlemler sonucunda numunelerin kristalinitesinde önemli sayılabilecek bir değişim olmadığı tespit edilmiştir.

Anahtar Kelimeler: Sol-jel yöntemi, Kitosan, Titandioksit, Silisyumdioksit, Antibakteriyel, Pamuk.

Received: 09.09.2010

Accepted: 13.01.2011

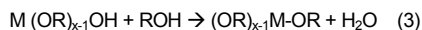
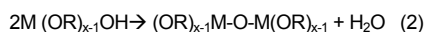
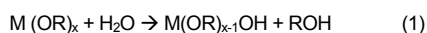
1. INTRODUCTION

The sol-gel process is an organic-inorganic material forming method (1, 2). By this method, a precursor sol that

has an ability to form network and organic compounds can be combined. Thus, optical, mechanical, thermal properties and chemical stability of the material have been enhanced (1).

The sol-gel processes have based on the hydrolysis and condensation of metal alkoxide compounds (3, 4). The kinetics of the hydrolysis and polycondensation reactions in the sol-

gel method can be described with the help of the equations shown below;



In the equations 1-3; M refers to metal species (Ti, Si, Al, Zr, etc.), and R refers to alkyl groups (methyl, butyl, ethyl, etc.). These reactions generate an oxide skeleton in the solution. When this solution is exposed to the air or heating, the solution gels and becomes rigid (3).

The sol-gel processes have been used in the textile industry for water-repellent, hydrophilic, hydrophobic, antistatic, antibacterial and UV-resistant applications. Among these, antibacterial applications have received much scientific attention at last few years.

There are two main types of sol-gel systems with antimicrobial activity; (5)

- photoactive titania coatings with anatase modification
- sol-gel coatings with embedded colloidal metal or metal compounds (especially silver)

However, these techniques have several disadvantages. First of all, high temperatures are required to produce highly photoactive thin films. In addition, strong acids used to keep aqueous sols in the peptized state have destructive effect on textiles at these high temperatures. Moreover, titania coatings need UV radiation to perform antimicrobial activity (6-8).

Recently, photocatalytic titania coatings have been obtained from alcohol-based sol at low temperatures to avoid the effects of the strong acids. The alcohol containing sols have various advantages such as high storage stability, good adherence on any textile samples and fast drying times at low temperatures (9). On the other hand, the use of alcohol instead of water as a medium brings several economical and ecological disadvantages (6, 8).

Another alternative to titania coatings are silica (SiO₂) based coatings. While, TiO₂ is an n-type semiconductor and active catalyst support, SiO₂ has high thermal stability and excellent mechanical strength (10). Moreover, both of them are non-toxic and can be used for antimicrobial finishing of textiles. When polycationic components

are embedded within the silica layer matrix, interaction occurs between positively charged biocidal additives and negatively charged microbial cell membranes. This reaction leads to leakage of proteinaceous and other intracellular constituents and damage to key cell functions so that microbes can neither grow, reproduce nor survive (9).

Chitosan, which is a copolymer of $\beta(1,4)$ -linked 2-acetamido-2-deoxy-D-glucopyranose and 2-amino-2-deoxy-D-glucopyranose, is a deacetylation product of chitin found in marine invertebrates. The chemistry of chitosan is similar to that of cellulose, but it reveals the fact that the 2-hydroxyl group of the cellulose has been replaced with a primary aliphatic amino group. This polysaccharide has several useful properties, such as non-toxicity, biocompatibility, biodegradability, antimicrobial activity, chemical reactivity and film forming ability, which makes it an important biopolymer for textile applications (11-13). The high content of nitrogen atoms in the chitosan provides bonding of several metal ions thanks to the mechanisms like chelation, electrostatic attraction or ion-exchange, depend on the metal ion and the pH of the solution (13, 14). The amine and two hydroxyl groups on each glucosamine in the repeating unit of chitosan can cause to a chemical modification. Chitosan shows cationic behavior in acidic conditions ($pK_a \sim 6.2$). The cationic behavior of chitosan make the biopolymer potential at catching anionic compounds, including metal anions or anionic dyes electrostatically (13). However, textiles coated with pure chitosan have insufficient stability during washing. Embedding it within silica enhances the washing durability and stabilises the optimum biocidal pH range of 5 (9). Incorporation of organic polymers, especially those with amino or amide groups, forms a molecular hybrid that has been stabilized by strong hydrogen bonding. By using this method, chitosan can form hybrids by silica gel. It is also known that the amino group of chitosan allows the chitosan to have polycationic character and to form intermolecular complexes with carboxylic and polycarboxylic acids (1).

The use of coatings based on the combination of chitosan, titania and silica brings an ecological benefit since all the components are completely harmless natural products (9-14).

In this study, chitosan solution, alcohol-based titania and silica sols and combination systems of these solutions prepared at low temperatures were applied to the cotton samples to form continuous and durable antibacterial coatings. After coating, they were washed. The antibacterial activity of the washed and unwashed samples under dark and UV light conditions were evaluated against both *S. Aureus* and *K. Pneumonia*. The structural properties of the coatings were characterized by SEM, X-ray and FTIR analysis.

2. MATERIAL AND METHOD

2.1 Material

Desized and bleached 100% cotton fabric (153g/m², 26 warp ends/cm, 24 weft ends/cm), titanium-IV-isopropoxide (Aldrich, 97%), tetraethylortosilicate (Aldrich, 98%), ethanol (Merck, 96%), 2-ethoxyethanol (Aldrich, 99%), acetic acid (Merck, 100%), hydrochloric acid (Carlo Erba 37%), nitric acid (Merck 65%) and medium molecular weight chitosan (Sigma-Aldrich) were used in the experiments.

2.2 Method

2.2.1 Titania and Chitosan Based Coatings

The preparation recipes of the coatings are given in Table 1. The titania nanosol (1%) was prepared in two ways at room temperature by mixing titantetraisopropoxide with ethanol or 2-ethoxyethanol and chitosan solution (1%) was prepared by dissolving chitosan in acidic solution (2% acetic acid). The 2-ethoxyethanol, which has a low evaporation ratio, was added to obtain the uniformity of film thickness by ensuring enough time for leveling of the coated solution during the solvent evaporation in the drying process. After stirring these mixtures vigorously they were mixed in the ratio of 1:1, 1:2 and 2:1. The titania solution prepared with ethanol was named as Sol A and the titania solution prepared with 2-ethoxyethanol was named as Sol B. The cotton fabrics according to their coating treatment and pH results of the solutions are shown in the Table 2.

10 cm x 20 cm cotton fabrics were dipped in the stated solution for 30 sec and then padded with a wet-pick-up of 90±1% at room temperature. The padded materials were then dried at 80°C for 10 min and cured at 150°C for

5 min. To evaluate the washing durability, the treated samples were washed with a liquor ratio of 50:1. Washing process was carried out at 60°C for 30 min. In order to prevent any effect of detergent, washings were carried out in a soap solution with a concentration of 5g/l. After washing, the samples were rinsed in cold pure

water, squeezed and dried at room temperature.

2.2.2 Silica and Chitosan Based Coatings

The silica nanosol was prepared as Sol A and Sol B in two ways and mixed for 24 h at room temperature.

Chitosan solution was prepared by aforementioned way. After stirring these mixtures vigorously they were mixed in the ratio of 1:1, 1:2 and 2:1. The treatment recipes are shown in Table 3 and Table 4.

Table 1. The preparation of chitosan and titania nanosols

	Chitosan	Sol A	Sol B
Chitosan	5 g		
Acetic Acid	10 ml		
Distilled Water	490 ml		
TTIP (Titanetraaisopropoxide)		5 ml	5 ml
Ethanol		495 ml	-
2-Ethoxy Ethanol		-	495 ml

Table 2. The cotton fabrics according to their coating treatment and pH results of the solutions

Sample	Chitosan Solution	Sol A	Sol B	pH
0	-	-	-	-
1	150 ml	-	-	3
2	-	150 ml	-	5
3	-	-	150 ml	5
4	100 ml	50 ml	-	4
5	75 ml	75 ml	-	4.5
6	50 ml	100 ml	-	4.5
7	100 ml	-	50 ml	4
8	75 ml	-	75 ml	4.5
9	50 ml	-	100 ml	4.5

Table 3. The preparation of silica nanosol

	Sol A	Sol B
TEOS (Tetraethylortosilicate)	190 ml	190 ml
Ethanol	250 ml	-
2-Ethoxy Ethanol	-	250 ml
0.01 N HCl	60 ml	60 ml

Table 4. The cotton fabrics according to their coating treatment and pH results of the solutions

Sample	Chitosan Solution	Sol A	Sol B	pH
0	-	-	-	-
1	150 ml	-	-	3
2	-	150 ml	-	5
3	-	-	150 ml	5
4	100 ml	50 ml	-	3.5
5	75 ml	75 ml	-	4
6	50 ml	100 ml	-	4.5
7	100 ml	-	50 ml	3.5
8	75 ml	-	75 ml	4
9	50 ml	-	100 ml	4.5

10 cm x 20 cm cotton fabrics were dipped in the stated solutions for 30 sec and then padded with a wet-pick-up of 90±1% at room temperature. The padded materials were then dried at room temperature for at least 2 h and cured at 120°C for 1 h to obtain uniform silica film layer. Washing

process was carried out in the aforementioned way.

2.2.3 Antibacterial Assessment

The antimicrobial assessment against Gram-positive bacteria (*Staphylococcus Aureus*) and Gram-negative bacteria (*Klebsiella Pneumoniae*) was carried

out quantitatively according to a modified procedure of the shake flask method (ASTM E2149-01). All glassware and test solutions were sterilized in an autoclave at 120°C for 20 min before experiments. Two pieces of each test specimen were cut in spherical shape with a weight of

±0,1 g. After bacterial injection they were transferred into 250 ml capped Erlenmeyer flasks containing buffer solution at the predetermined time. The flasks were capped and placed on a wrist-action shaker. Each flask were shaken at maximum speed for 1 min ± 5 sec. 1 ml of solution from each flask was transferred to a test tube containing 9 ml of ddH₂O, diluted and placed into agar plates. After incubation of the plates at 37°C for 24 h, the number of viable cells (colonies) was counted manually and the results after multiplication with the dilution factor were expressed as mean colony forming units (CFU) per ml after averaging the duplicate counts. The UV irradiation was performed using a UV lamp with a maximum intensity wavelength (λ_m) at 365 nm.

2.2.4 Characterization

The structure of the coatings were studied by scanning electron microscopy (SEM-EDX) using Phillips XL-30S FEG device. The characteristic properties were analyzed using a Fourier Transform Infrared Spectrophotometer (FT-IR), Perkin Elmer, in the region from 4000 to 800 cm⁻¹. The X-ray diffraction patterns of untreated cotton, chitosan treated cotton and blend films of chitosan with titanium and silica were determined on a Philips PW 3040/60 diffractometer, using Nickel-filtered Cu K α radiation at 60 kV and 55 mA in the 2 θ range of 10-40.

3. RESULTS AND DISCUSSION

3.1 Antibacterial Activity Assessment

3.1.1 The activity results of the samples coated by titania and chitosan based coatings

The antibacterial activity of the samples coated by titania based coatings were assessed both under dark media and UV light. It was found that there was a corresponding relation between the media and the activity of titania coatings. To the experimental results, all the samples coated by titania showed perfect activity after 5 hour irradiation under UV light. However, the effect of the alcohol type used in the sol was found to be negligible in terms of the activity.

The combination of titania and chitosan solutions was found to be more favourable than only chitosan coating since this coating formed more stable, effective and washing durable film and showed better activity than chitosan coating. With regard to mixing ratio of titania and chitosan sols, it was found when chitosan amount increases, the activity increases too. But the difference between the activities was quite little.

The activity values of the samples that coated by only titania sol were found to be less than the other samples under dark media conditions. This fact has proved that titania coatings need UV radiation to perform antimicrobial activity and confirmed the results of the involved studies (3, 5, 6, 8).

The activity of the samples were also evaluated under ambient fluorescent white light after 24 hours. The bacterial

reduction % values were found to be between the values of the dark and UV light conditions. This fact verifies the previous study of Daoud et al (6).

After washing process, the combined systems showed the best results. On the other hand, the activity of the other samples decreased considerably. So, it's concluded that application of chitosan and titania together has provided strong adsorption between the cotton fiber and the antibacterial coating and this interaction can stand to washing process.

The activity results of the samples are shown in the Tables 5 and 6.

3.1.2 The activity results of the samples coated by silica and chitosan based coatings

The activity results of the samples coated by silica and chitosan based coatings are given in Table 7. Since silica and chitosan sols weren't affected from the media very much unlike titania sols, the antibacterial tests were made under ambient fluorescent white light for 24 hours. As a result of the antibacterial tests, it's seen that the combination of silica and chitosan sols was more effective than application of chitosan or silica sol alone. With respect to mixing ratio of silica and chitosan sols, it was found that 1:1 was favourable in case of Sol A whereas 1:2 silica:chitosan was favourable in case of Sol B. In addition, it was observed that the coatings prepared by Sol A gave generally better results than the coatings prepared by Sol B in terms of both *S.aureus* and *K.pneumonia*.

Table 5. The antimicrobial activity results of the untreated, chitosan coated, titania coated and chitosan/titania coated cotton fabrics under UV light and in the dark conditions after 5 hours (reduction %).

Sample	UV Light (before washing)		UV Light (after washing)		Dark Media (before washing)		Dark Media (after washing)	
	S.a	K.p	S.a	K.p	S.a	K.p	S.a	K.p
0	58.77	29.82	55.45	27.77	-	-	-	-
1	95.63	72.04	83.61	64.85	55.71	21.75	25.22	-
2	99.42	95.85	97.44	94.99	-	-	-	-
3	98.91	94.53	96.99	94.51	-	-	-	-
4	99.69	94.98	98.56	94.60	53.33	18.87	45.53	-
5	99.23	94.29	98.66	94.23	45.68	-	37.91	-
6	98.34	94.00	96.41	93.54	32.56	-	27.40	-
7	99.73	96.97	97.55	95.73	54.41	16.66	48.11	-
8	99.47	96.92	97.02	95.69	50.18	-	38.88	-
9	98.94	96.84	95.63	94.22	38.46	-	29.60	-

-: Since the bacterial reduction is less than 10% it is accepted as no activity
 S.a: *Staphylococcus Aureus* K.p: *Klebsiella Pneumoniae*

Table 6. The antimicrobial activity results of the untreated, chitosan coated, titania coated and chitosan/titania coated cotton fabrics under ambient fluorescent white light after 24 hours (reduction %).

Sample	Ambient Fluorescent Light			
	Before Washing		After Washing	
	S.a	K.p	S.a	K.p
0	-	-	-	-
1	92.31	59.36	78.67	42.76
2	45.85	25.45	22.13	-
3	42.99	22.88	21.23	-
4	88.26	41.09	85.66	37.64
5	77.08	27.07	76.99	24.42
6	65.62	19.98	61.74	16.50
7	82.61	37.87	79.86	35.51
8	71.25	24.44	67.54	23.88
9	53.85	16.21	50.05	-

-: Since the bacterial reduction is less than 10% it is accepted as no activity
S.a: *Staphylococcus Aureus* K.p: *Klebsiella Pneumoniae*

Table 7. The antimicrobial activity results of the untreated, chitosan coated, silica coated and chitosan/silica coated cotton fabrics under ambient fluorescent white light after 24 hours (reduction %).

Sample	Ambient Fluorescent Light			
	Before Washing		After Washing	
	S.a	K.p	S.a	K.p
0	-	-	-	-
1	92.81	59.40	81.75	44.02
2	74.08	43.35	67.56	34.60
3	58.12	37.52	51.34	30.51
4	94.29	87.65	92.99	86.88
5	95.53	88.31	94.77	88.11
6	91.84	77.24	86.21	73.00
7	91.17	64.64	90.99	64.22
8	83.55	51.43	79.64	47.88
9	82.36	42.58	77.33	37.61

-: Since the bacterial reduction is less than 10% it is accepted as no activity
S.a: *Staphylococcus Aureus* K.p: *Klebsiella Pneumoniae*

After washing process, the antibacterial activity of the samples were tested again. To the results, it was observed that sample 5 (1:1 chitosan:Sol A coating) was the most effective and washing durable one. Except for the pure chitosan coated sample, all coatings were found to be washing durable since there was little change in the activity. On the other hand, the activity of the sample 1 (pure chitosan coating) was considerably decreased after washing process.

Considering the results generally, it's concluded that the silica and chitosan based sols seemed to have more available and practical application than titania and chitosan based solutions. In addition to this, silica and chitosan based solutions have intensive and washing durable activity independent from the media too.

3.2 SEM-EDX Analysis

In Figure 1, the SEM images of the untreated and chitosan treated cotton are shown. As seen from the images, chitosan treated sample has smoother and cleaner surface than untreated sample. On the other hand, there are some grooves and fibrils on the surface of the untreated sample.

Figure 2 shows the SEM images of the titania treated samples and silica treated samples. To the SEM images, it is observed that silica coatings have dense and low porous character. When the alcohol type used in the solutions is considered it is seen that ethoxy ethanol provides more uniform coating film and gelation between the fibers.

To evaluate the presence of titania and silica on the fibres after washing process, EDX analysis was made to

the washed samples. The EDX results (Figure 3) has confirmed the durability of the coatings.

It is observed that there is a compatible bonding with cotton fiber and combined coatings and this fact ensures the washing durability. If the titania and silica are compared in terms of compatibility, it is found that silica and chitosan based coatings are more compatible and more uniform. In terms of alcohol type used in the silica and chitosan coating solutions, it is observed that ethoxy ethanol based solution (Sol B) forms more uniform layer, since there are less cracks on the coating. On the other hand, while the surface of the pure chitosan is smooth, the combined coatings exhibit a bit rougher surface morphology with titania and silica particles distributed in the chitosan matrix.

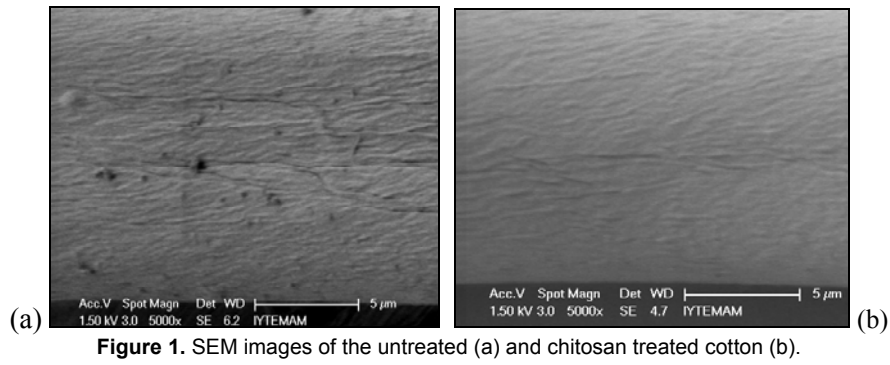


Figure 1. SEM images of the untreated (a) and chitosan treated cotton (b).

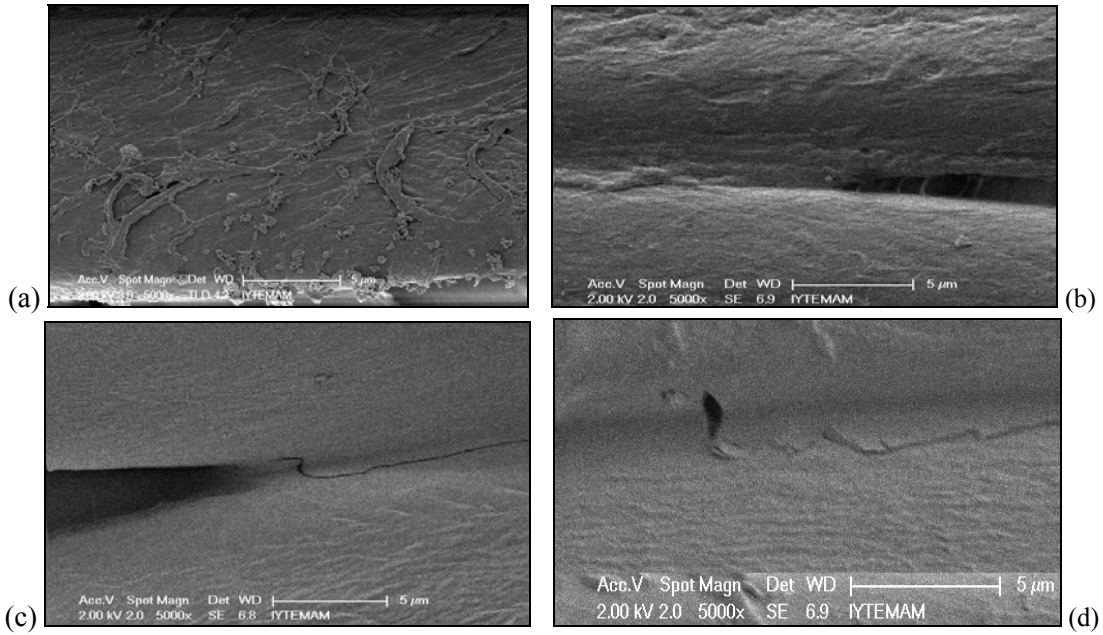


Figure 2. SEM images of the titania treated samples and silica treated samples; (a) Titania coating (Sol A), (b) Titania coating (Sol B), (c) Silica coating (Sol A) (d) Silica coating (Sol B).

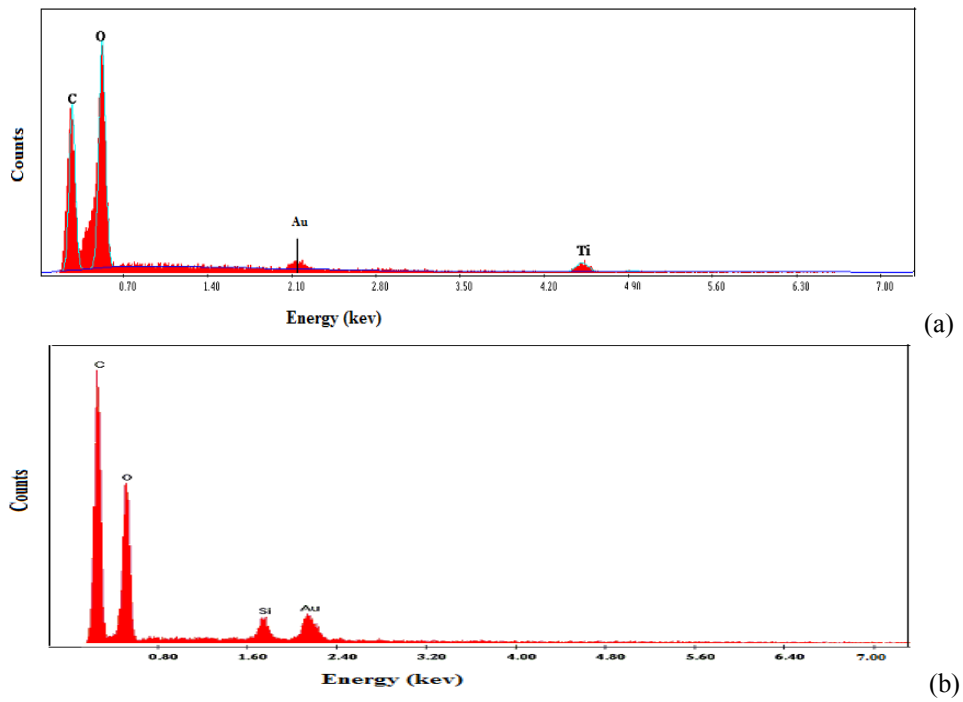


Figure 3. EDX analysis of the titania coating (a), silica coating (b).

Figure 4 shows the SEM images of the combined coatings.

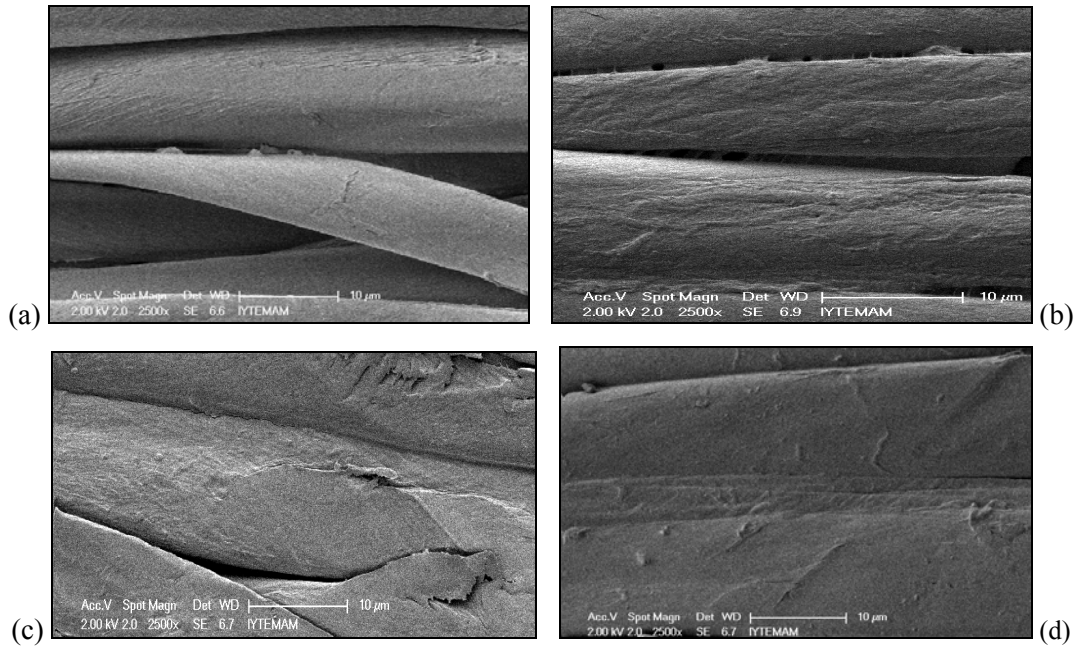


Figure 4. SEM images of the combined coatings; (a) Chitosan and titania coating (Sol A), (b) Chitosan and titania coating (Sol B), (c) Chitosan and silica coating (Sol A), (d) Chitosan and silica coating (Sol B).

3.3 XRD Analysis

In Figure 5, the XRD spectra of the samples is shown. No significant difference was observed among the processes showing the stability of the crystallinity of the samples. Three intense diffraction peaks located at 14.8, 16.7 and 22.5° have been found. However, one different small peak was appeared at 20.2° for the chitosan treated sample. This was attributed to the pure chitosan structure and this fact confirmed the previous studies (15, 16).

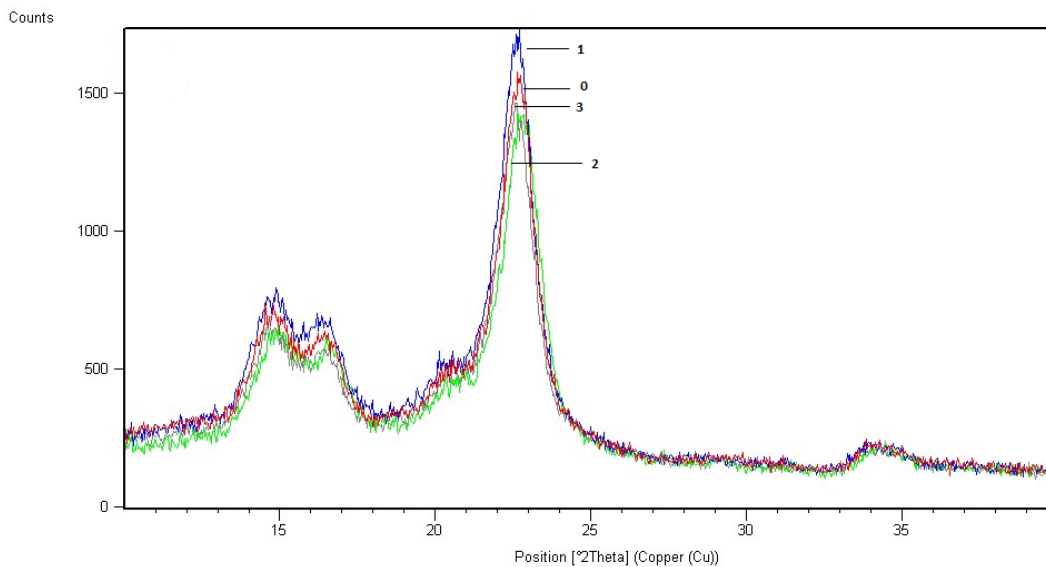


Figure 5. XRD spectra of the samples, 0 untreated 1 chitosan treated 2 titania and chitosan treated 3 silica and chitosan treated

3.4 FTIR Analysis

Figure 6 shows the FTIR spectra of the untreated cotton and chitosan treated cotton. As shown in the spectra, for chitosan treated cotton, a decrease of absorbance in the bands at 894, 1025, 1158, 1200 (cellulosic bonds) and 1640 cm^{-1} (-CO-NH-bonding) was observed. It was also seen that the band at 3331 cm^{-1} (stretching vibration of the OH group) shifted to 3330 cm^{-1} and the band at 2895 cm^{-1} (symmetric stretching of CH_2) shifted to 2889 cm^{-1} after chitosan treatment.

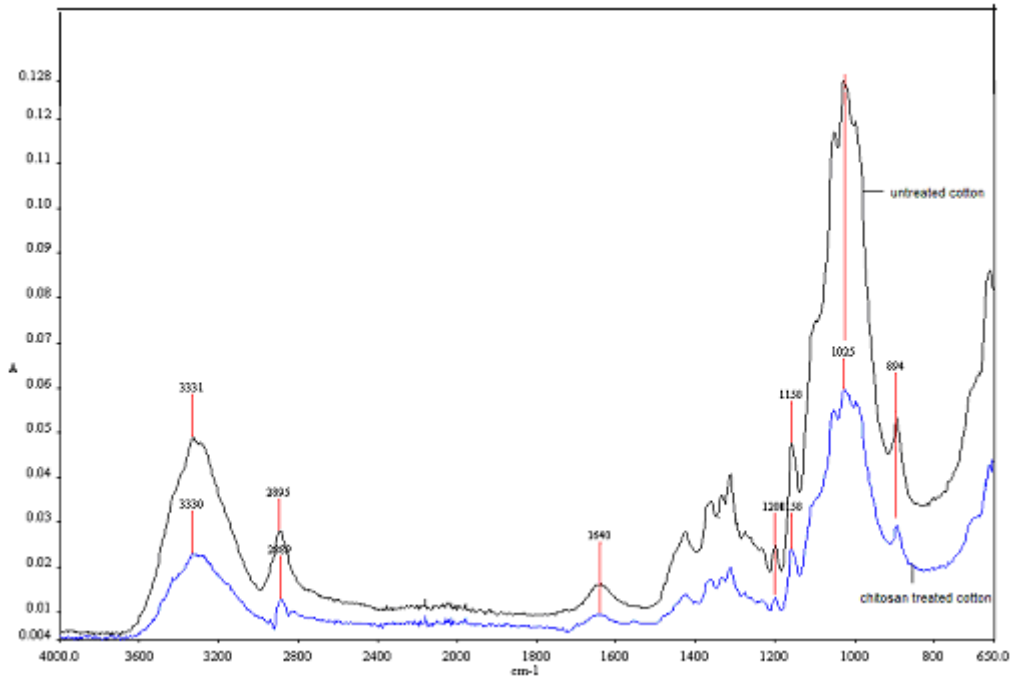


Figure 6. FTIR spectra of the untreated cotton and chitosan treated cotton

Figure 7 shows the FTIR spectra of the untreated, chitosan/titania coated and chitosan/silica coated cotton. To the spectra, a decrease of absorbance in the bands at 1640, 1314, 1200 and 894 cm^{-1} was observed after combination of chitosan with titania and silica. In addition to these, it was seen that the band at 3331 cm^{-1} (-OH bond) shifted to 3329 cm^{-1} for chitosan/silica coated cotton and to 3320 cm^{-1} for chitosan/titania coated cotton. The bands at 2895 cm^{-1} (-CH₂ stretching) and 1158 cm^{-1} (cellulosic structural bond) were appeared at 2890 cm^{-1} and 1157 cm^{-1} respectively for both chitosan/titania coated cotton and chitosan/silica coated cotton. On the other hand, the band at 1025 cm^{-1} shifted to 1026 cm^{-1} for chitosan/titania coated cotton and to 1027 cm^{-1} for chitosan/silica coated cotton and a considerable decrease in the absorbance of this band was observed after coatings.

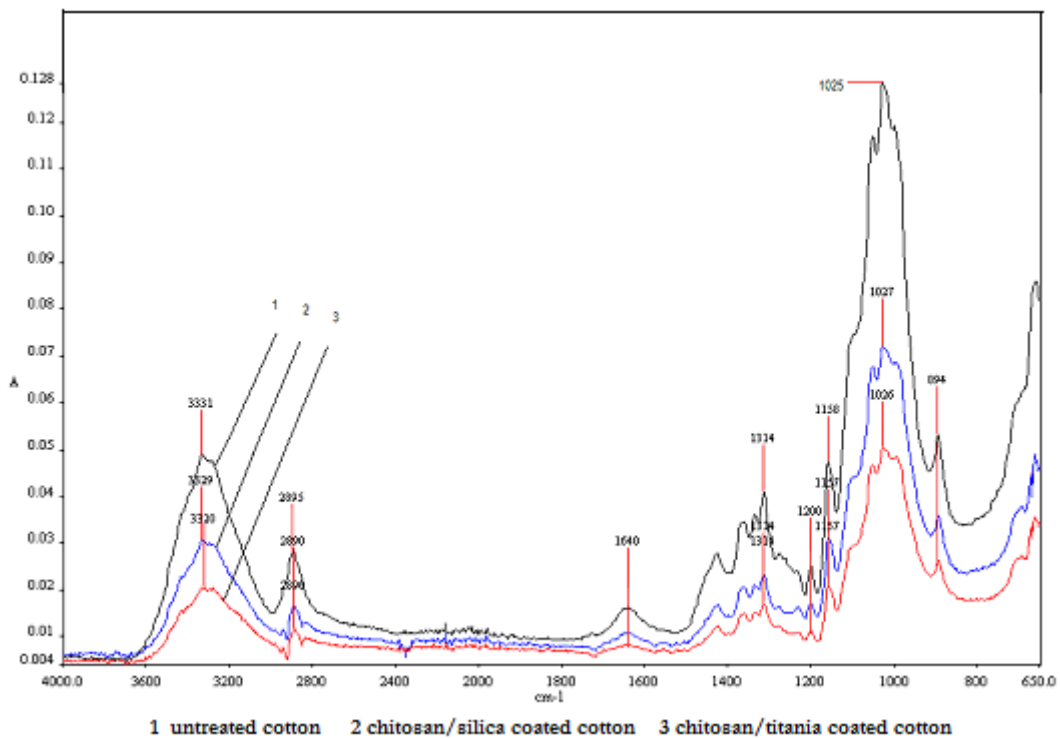


Figure 7. FTIR spectra of the untreated, chitosan/titania coated and chitosan/silica coated cotton

4. CONCLUSION

In this study, chitosan solution, alcohol-based titania and silica sols and combination systems of these solutions prepared at low temperatures were applied to the cotton samples to form continuous and durable antibacterial coatings. It's found that the combined systems showed the best antibacterial activity. Considering the results generally, it's concluded that the silica and chitosan based sols seemed to have more available and practical application than titania and chitosan based solutions. In addition to this, silica and chitosan based

solutions have intensive and washing durable activity independent from the media too. From the SEM images, it's observed that there is a compatible bonding with cotton fiber and combined coatings. When the alcohol type used in the solutions was considered it's seen that ethoxy ethanol provided more uniform coating film and gelation between the fibers. The EDX analysis confirmed the presence of titania and silica on the washed fibres and washing durability of the coatings. FTIR analysis showed the structural bond changes in the cotton fibre after the treatments. To the X-ray analysis,

no significant difference was observed among the processes.

ACKNOWLEDGEMENT

We would like to thank to the Izmir Institute of Technology for SEM-EDX and XRD analysis, Assoc. Prof. Dr. Mustafa ATES for his support in antibacterial assessments and Prof. Dr. Mithat YUKSEL for his precious contribution. This study was supported by Pamukkale University through project 2005 DPT 003.

REFERENCES

1. Martinez, Y., Retuert, J., Yazdani-Pedram, M., and Colfen, H., 2004, "Hybrid ternary organic-inorganic films based on interpolymer complexes and silica", *Polymer*, 45, 3257-3265.
2. Tao, Y., Pan, J., Yan, S., Tang, B., and Zhu, L., 2007, "Tensile strength optimization and characterization of chitosan/TiO₂ hybrid film", *Materials Science and Engineering B*, 138, 84-89.
3. Xu, P., Liu, X., Wang, W., and Chen, S., 2006, "Improving the Antibacterial and UV-Resistant Properties of Cotton by the Titanium Hydrosol Treatment", *Journal of Applied Polymer Science*, 102, 1478-1482.
4. Xie, K., Yu, Y., and Shi, Y., 2009, "Synthesis and characterization of cellulose/silica hybrid materials with chemical crosslinking", *Carbohydrate Polymers*, 78, 799-805.
5. Mahltig, B., Gutmann, E., Meyer, D.C., Reibold, M., Dresler, B., Gunther, K., Fabler, D., and Böttcher, H., 2007, "Solvothermal preparation of metallized titania sols for photocatalytic and antimicrobial coatings", *J. Mater. Chem.*, 17, 2367-2374.
6. Daoud, W.A., Xin, J.H., and Zhang, Y-H, 2005, "Surface functionalization of cellulose fibers with titanium dioxide nanoparticles and their combined bactericidal activities", *Surface Science*, 599, 69-75.
7. Wei, S-w., Peng, B., Chai, L-y, Liu, Y-c., and Li, Z-y., 2008, "Preparation of doping titania antibacterial powder by ultrasonic spray pyrolysis", *Trans. Nonferrous Met. Soc. China*, 18, 1145-1150.
8. Daoud, W.A., and Xin, J.H., 2004, "Low Temperature Sol-Gel Processed Photocatalytic Titania Coating", *Journal of Sol-Gel Science and Technology*, 29, 25-29.
9. Mahltig, B., Haufe, H., and Böttcher, H., 2005, "Functionalisation of textiles by inorganic sol-gel coatings", *J. Mater. Chem.*, 15, 4385-4398.
10. Pabon, E., Retuert, J., Quijada, R., and Zarate, A., 2004, "TiO₂-SiO₂ mixed oxides prepared by a combined sol-gel and polymer inclusion method", *Microporous and Mesoporous Materials*, 67, 195-203.
11. Demir, A., Karahan, H.A., Ozdogan, E., Oktem, T., and Seventekin, N., 2008, "The Synergetic Effects of Alternative Methods in Wool Finishing", *Fibres & Textiles in Eastern Europe*, 16, 89-94.
12. Vilchez, S., Manich, A.M., Jovancic, P., and Erra, P., 2008, "Chitosan contribution on wool treatments with enzyme", *Carbohydrate Polymers*, 71, 515-523.
13. Gouda, M., and Keshk, S.M.A.S., 2010, "Evaluation of multifunctional properties of cotton fabric based on metal/chitosan film", *Carbohydrate Polymers*, 80, 504-512.
14. Guibal, E., 2004, "Interactions of metal ions with chitosan-based sorbents: A review", *Separation and Purification Technology*, 38, 43-74.
15. Xu, X., Dong, P., Feng, Y., Li, F., and Yu, H., 2010, "A simple strategy for preparation of spherical silica-supported porous chitosan matrix based on sol-gel reaction and simple treatment with ammonia solution", *Anal. Methods*, 2, 546-551.
16. Lai, S.-M., Yang, A.J.-M., Chen, W.-C., and Hsiao, J.-F., 2006, "The properties and preparation of chitosan/silica hybrids using sol-gel process", *Polymer-Plastics Technology and Engineering*, 45, 997-1003.

Bu araştırma, Bilim Kurulumuz tarafından incelendikten sonra, oylama ile saptanan iki hakemin görüşüne sunulmuştur. Her iki hakem yaptıkları incelemeler sonucunda araştırmanın bilimselliği ve sunumu olarak "Hakem Onaylı Araştırma" vasfıyla yayımlanabileceğine karar vermişlerdir.