(REFEREED RESEARCH)

ANALYSIS OF BIOPOLYMER APPLICATION ON COTTON FABRICS BY DIFFERENT METHODS

PAMUKLU KUMAŞLARA FARKLI YÖNTEMLERLE BİYOPOLİMER UYGULAMASININ ANALİZİ

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ABSTRACT

Increasing environmental awareness and the high demand for alternatives to non-renewable petroleum resources have led to extensive research focused on the concept of biomass-based bio-renewable materials. As well as constantly increasing environmental pollution, toxicological effects of industrial waste and the reflection of decreasing natural resources, environmental friendly production methods and the usage of biopolymers obtained from sustainable resources became an important issue in textile industry. Chitosan has several application areas in textile industry because of its biodegradability, biocompatibility and non-toxicological effects on living organisms. With the introduction of nanotechnology into our lives, chitosan nano particles were obtained in order to take the advantages of macro-sized chitosan more effectively. Therefore, better results could be obtained by using less amount of chitosan. Although there are several methods to reduce the size of chitosan, ionic gelation is the most commonly used method since it is easy to apply and it does not require the use of toxic chemicals In this study, the different forms of chitosan were applied onto the cotton fabrics by environmental friendly methods such as plasma and sol gel technology as an alternative to conventional finishing methods. The treated fabrics were compared in terms of their antibacterial activity, SEM, XPS and surface friction properties.

Keywords: Biopolymer, chitosan, nanochitosan, cotton, sol-gel, atmospheric plasma.

ÖZET

Artan çevre bilinci ve yenilenemeyen petrol kaynaklarına alternatiflerine olan yüksek talep, biyokütle esaslı biyolojik olarak yenilenebilir maddeler kavramına odaklanan kapsamlı araştırmalara yol açmaktadır. Bunun yanısıra artan çevre kirliliği, endüstriyel atıkların toksikolojik etkileri ve azalan doğal kaynakların yansıması, çevre dostu üretim yöntemleri ve sürdürülebilir kaynaklardan elde edilen biyopolimerlerin kullanımı tekstil endüstrisinde önemli bir konudur. Canlılara karşı toksik olmayan, biyobozunur ve biyouyumluluğa sahip olan kitosan tekstil endüstrisinde geniş kullanım alanı bulmuştur. Nanoteknolojinin hayatımıza girmesiyle birlikte kitosandan daha etkin bir şekilde yararlanmak için boyutu küçültülerek daha az miktarda kullanarak daha etkili sonuçlar veren nanokitosan elde edilmiştir. Kitosanın boyutunu küçültmek için birçok yöntem kullanılmasına rağmen iyonik jelleşme yöntemi kolay olması ve toksik kimyasal madde kullanımı gerektirmemesi nedeniyle en çok kullanılan yöntemdir. Bu çalışmada, geleneksel terbiye yöntemlerine alternatif olarak plazma ve sol jel teknolojisi gibi çevreye duyarlı yöntemlerle pamuklu kumaşlara farklı türde kitosan uygulanmıştır. İşlem gören kumaşların antibakteriyel aktivite, SEM, XPS ve yüzey sürtünme özellikleri açısından karşılaştırılmıştır.

Anahtar Kelimeler: Biyopolimer, kitosan, nanokitosan, pamuk, sol-jel, atmosferik plazma

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1. INTRODUCTION

Chitosan is a biopolymer derived from chitin which is found in a wide range of natural sources such as crustaceans, fungi, insects and some algae (1). It is composed of β (1→4)-linked 2-acetamido-2-deoxy-β-D-glucose (*N*-acetylglucosamine) (2) .Chitosan has primary and secondary hydroxyl groups and primary amino groups in its chemical structure. Due to the protonation of the amine groups, it is not soluble in water but it can dissolve in diluted aqueous acidic solvents. The charge density of chitosan depends on pH and the degree of acetylation.(3). As a natural biopolymer derived from the exoskeletons of crustaceans, it is used in biotechnology, wastewater treatment, pharmaceuticals, agriculture, food industry and textiles. The structure of chitosan is similar to that of cellulose except that the hydroxyl group in the C2 position of cellulose is substituted with an amino group in chitosan (4-7). Chitosan application can be seen as an alternative over traditional treatments due to its chemical and biological properties. It can be applied to cotton fabrics by different processes such as dyeing (8-11) sizing agent (12), antimicrobial treatment (12-15), wrinkle resistance (16), printing processes (17).

The main problem of chitosan application on cotton fabrics is the lack of bonding forces between cellulose and chitosan. Thus, chitosan can be removed partially from the fabric surface depending on the washing processes. To overcome this drawback, it is necessary to create additional binding sites and to activate the fiber surface. Moreover, the combination of appropriate treatment/chemical agents would be beneficial to provide the stability against multiple washings. Another way is to use nanotechnology in finishing processes. Nanotechnology presents high durability for textiles due to the better affinity of nano particles to the fabric and leading to an increase in durability of the function. Therefore recent studies have been focused on chitosan nano particles to take more advantage of chitosan in textile industry. Nanochitosan coating on fabrics will provide obvious improvement comparing to chitosan application due to the large ratio of surface to volume, high surface reactivity and surface-active multicentre. Also, it will not affect the breathability of fabric (18,19).

To improve chitosan nano particle coating on textiles, many methods have been applied. In this respect, plasma technology and sol-gel coating can be used as better alternative treatments. Plasma technology can be applied under atmospheric or reduced pressure to modify fiber surface depending on specific requirements. The species that participate in plasma reactions, such as excited atoms, free radicals and metastable particles, electrons and ions, can interact either physically or chemically with substrates. Plasma treatment is also an effective technique to modify the surface properties of fabrics without altering the interior part of the fibre. By this way, many functional properties can be given to the textile materials. Moreover, plasma treatment provides many advantages in comparison to conventional finishing processes by reducing the chemical, water and energy usage (7, 20, 21,27,28).

Recent researches have focused on modifying the cotton fabric surface using sol–gel method to improve the durability of the desired effects such as UV protection, antibacterial effect of the fabric during the laundering process (33,34).

There are several studies regarding plasma pretreatment prior to chitosan application on cotton fabrics (22, 23). However, very few studies can be found on the effect of atmospheric plasma pretreatment on nanochitosan coated cotton fabrics. The aim of the present study is to examine the effect of plasma pretreatment and sol gel application on chitosan and nano chitosan treated cotton fabrics. The chemical changes on the fiber surface were characterised by SEM (Scanning electron microscopy), FTIR-ATR (Attenuated total reflectance Fourier transform infrared spectroscopy), XPS (X-ray photoelectron spectroscopy) analysis. Also, the adhesion behavior on fiber surface was determined using surface friction coefficient test. The air permeability test was made to investigate the breathability of treated fabrics. The antibacterial activity of chitosan and nanochitosan treated fabrics was compared against multiple washings.

2. MATERIALS AND METHODS

2.1. Materials

The plain woven 100 % cotton fabric was used (150 g/m^2, yarn count of 20 Ne) in the experiments. Medium molecular weight chitosan (190-310 kDa, degree of deacetylation is 85%, Sigma-Aldrich), acetic acid (glacial, 98%, Merck), tetraethylortosilicate (Aldrich, 98%), ethanol (Merck, 96%), acetic acid (Merck, 100%), and hydrochloric acid (Merck 37%) were used in the experiments.

2.2. Preparation of nanochitosan

Various amounts of chitosan were dissolved in 1 % acetic acid. 0.02 % chitosan was dissolved in 1 % acetic acid. For nanochitosan preparation, TPP was dissolved in distilled water. The pH value of the chitosan solution were adjusted in the range of pH = 3-7. Chitosan-TPP nanoparticles were prepared based on ionic gelation method. A detailed preparation method is given in a paper of Demir and Gökce (24).

2.3. Chitosan and Nanochitosan Application

Chitosan solutions were freshly prepared by dissolving the biopolymer in distilled water containing acetic acid. Cotton fabrics were dipped into the chitosan solution, wet-pick-up of 90±1 % at 20 ^oC, pre-dry 5 min under 80 ^oC, and then curing for 3 min under 130 ^oC.

2.4. Plasma Pretreatment of Cotton Fabrics

Uniform glow discharge plasma system operating under atmospheric conditions were used in the experiments. In the plasma environment, the samples were placed between the electrodes and passed continuously. Each electrode pair was placed 4 cm apart from each other with the 0.2 cm distance between the electrodes. In all treatments, Argon (purity of > 99.99) was used as process gases under the power of 150 Watt for 60 seconds.

2.5. Nano sol preparation and fabric treatment

The recipe of the nanosol was given in Table 1. Chitosan solution (1%) was prepared by dissolving chitosan in acidic solution (2% acetic acid). Chitosan and silica nanosol was mixtured (the ratio of 1:1) and stirred vigorously. The cotton fabrics were dipped into the solution for 30 min and then passed through laboratory padder with a wet-pick-up of 80 % at room temperature. Then the padded fabrics were dried at 80^0C for 5 min and cured at 130^oC for 3 min.

Table 1. The recipe of silica nanosol

Chemical	Amount of Chemical (ml)
TEOS (Tetraethylortosilicate)	15
Ethanol	50
0,01 N HCl	10
Distilled water	32
pH	5.5

3. CHARACTERIZATION METHODS

Analysis of chitosan nano particles

The particle size distribution of the chitosan nano particles were determined using Dynamic light scattering (DLS) (Malvern Zetasizer Nano Series Nano-S) technique. The

UV-Vis analysis of particles were measured by Scinc4.7o-S-3100 UV-Vis spectrophotometer.

Scanning Electron Microscopy (SEM)

The surface morphologies of the treated and untreated cotton samples were investigated using Carl Zeiss 300VP scanning electron microscope operating at a typical accelerating voltage of 15 kV. Prior to the observation, the samples were mounted and sputter-coated with gold using Emitech K550X device for 5 min.

X- ray photoelectron spectroscopy (XPS) Analyses

X- ray photoelectron spectroscopy (XPS) measurements were performed in a K-Alpha (Thermo Scientific) with monochromatic AlKα (1486.68 eV) X- ray source with a spot size of 300 µm and 26.04 W (12.4 kV x 2.1 mA) power. All measurements were conducted inside an UHV chamber with pressure at 10-6 Pa (10-8 mbar).The XPS spectra were background subtracted using the Shirley method and deconvoluted using a mixed Gaussian/Lorentzian peak shape with XPS Peak Avantage software (version 5.952).

Antibacterial activity

The antibacterial properties of all samples were quantitatively evaluated against *Staphylococcus aureus (S. aureus)*, ATCC 6538, a Gram-positive bacterium and *Klebsiella pneumoniae (K. pneumoniae),* ATCC 4352, a Gram-negative bacterium, according to AATCC 100 standard test method. The antibacterial effect of fabrics was evaluated after certain contact time and calculated percent reduction of bacteria.

Surface Friction Coefficient

To measure the kinetic friction coefficient of the fabric surface, a Frictorq instrument was used as described by Lima et al. (25).

4. RESULTS and DISCUSSION

4.1. Characterization of Nano Chitosan Particles

From the results obtained from DLS measurements, the diameter of chitosan nano particles prepared in pH:4.6 and ratio of chitosan/TPP 5:1 conditions. The average diameter of the particles was 52 nm.

"Nanoparticle size should be under 100 nm for better penetration onto the cotton fabrics. Also, the homogenity of particle size is in the range of nearly 90 %."

4.2. Antibacterial Activity and Washing Durability

The antibacterial activities of untreated, chitosan and nano chitosan treated cotton fabrics by different methods were given in Table 2. As can be seen from the results, both chitosan and nanochitosan treatments showed good or excellent antibacterial activities due to the cationic structure of the chitosan coated cotton surface in the acidic pH range. This confirms the concept that bulk chitosan particle could not tightly bound to the fiber surface because of their high surface energy and viscosity. On the other hand, chitosan nano particles possess high surface area and can not get released after washing cycles as compared to bulk chitosan. Also, the osmosis to the bacterial cell membrane of the nanochitosan is strong and it shows greater antibacterial effect on the fabric surface (26).

When application methods are concerned, the best results were obtained with plasma-nanochitosan-sol-gel combination. Plasma pretreatment activates the fiber surface for post chitosan or nanochitosan application and makes easier to bond tightly onto the fiber surface. Also, it enhances the adhesion of the sol-gel treatment. When the fabric is treated with nanosol containing bulk chitosan and nano chitosan particles, the adhesion is improved by the formation of smooth and uniform layer on the fiber surface as can be seen clearly from SEM micrographs. The formation of these coating on the fabric surface imparts efficient antibacterial effect to the treated fabrics against washing cycles.

4.3. SEM analysis

SEM images show the morphological changes of treated and untreated fabric surfaces. As can be seen clearly from Fig 3. the chitosan nano particles are well and finely dispersed on the cotton fiber surfaces. While the control sample showed a smooth and even surface, cracks and grooves as results of etching by the plasma treatments were observed on the surfaces of both plasma treated fabric samples. Since cracks on the surface makes the coating of materials easier, it is suggested that plasma pre-treatment enhanced the distribution of both bulk and nano chitosan coatings. Therefore, it provides a good surface for the two polysaccharides to physically bonds together (4).

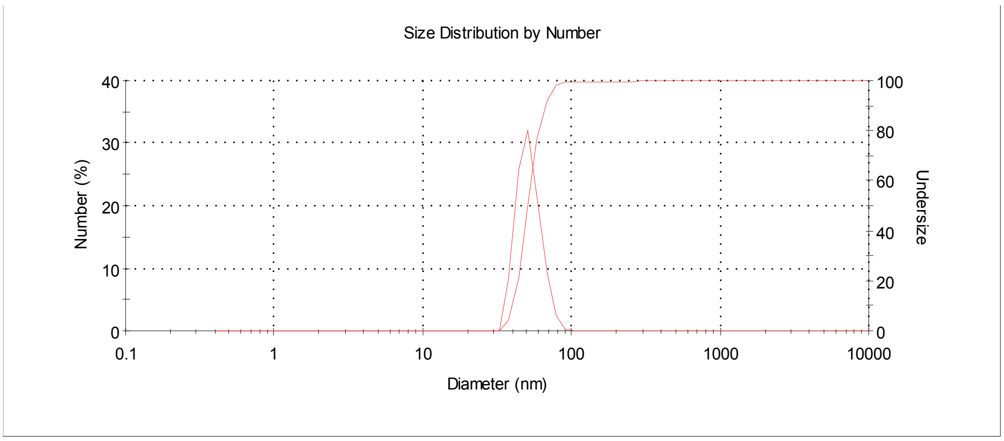


Figure 1. DLS measurements of chitosan nano particles

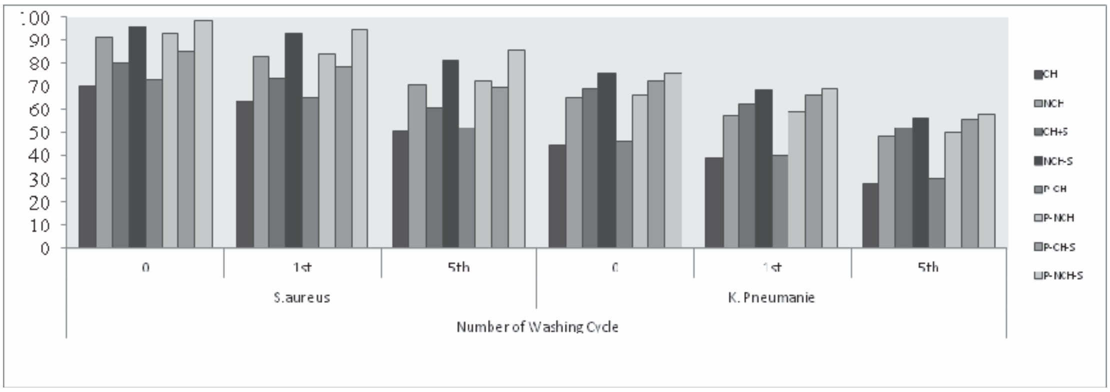


Figure 2. Antibacterial activity results of treated fabrics

4.4. Friction Coefficient (Roughness)

Surface friction measurements were made to indicate the roughness characteristic of the fabric surface. Friction coefficient values of untreated and treated cotton fabrics were given in Table 2. The results showed that plasma treated fabrics increased the fabric surface friction coefficient values in comparison to untreated fabric. Also, it can be seen clearly from SEM images that surface roughness of plasma treated fiber surface has more cracks and tiny groves due to the etching effect of the atmospheric plasma treatment (27). These effects caused by ablation process improve the coating of chitosan/nanochitosan adhesion to the fiber surface. By this way, the enhanced durability of desired effects, such as antibacterial activity against washing cycles can be achieved which can be seen from Figure 4.

The decrease in the friction coefficient values is associated with the uniform coating with chitosan, nanochitosan and sol-gel applications. This outcome confirms the SEM images (Figure 3).

Table 2. Surface friction coefficient of cotton fabrics treated by different methods

Application Method	Surface Friction Coefficient
Untreated cotton	0,244
CH	0,227
NCH	0,216
S	0,221
P(A)	0,271
P(A)-S	0,247
P(A)-CH	0,239
P(A)-NCH	0,228
P(A)-NCH-S	0,230
P(A)-CH-S	0,236

*P(A):Plasma argon, CH: Chitosan, NCH: Nanochitosan S:Sol-gel

4.5. XPS analysis

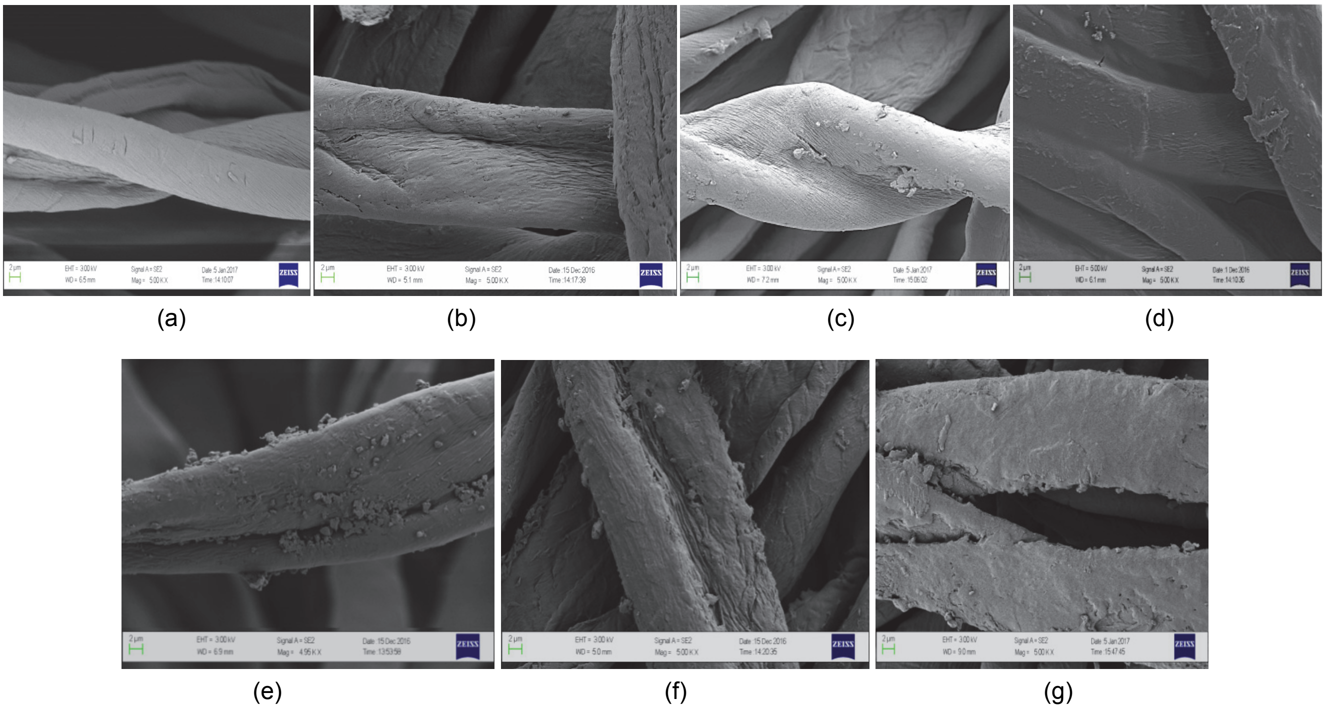
XPS has been extensively used for analyzing the compositions of outermost surface layer of the cotton fabric. The relative atomic concentrations of carbon, oxygen and nitrogen on the surface of the untreated and treated cotton fabrics can be seen from Table 3. The detailed characterization of the changes in surface chemistry caused by chitosan particles and treatment methods are observed from C 1s region spectra (Figure 4).

The C1s peak showed that the peaks around 284-285 eV was attributed to C-C, C-H bond. The peak around 285-286 eV was assigned to C-C-H bond. The peaks occurring around 286-287 eV and 288-289 eV were due to C-O bond; C=O or O-C-O bonds relatively. When chitosan and nanochitosan treated samples were considered, the new peak around 288-289 eV was because of O-C-O, N–C=O, a typical acetal and amide bond (29-32). It clearly indicates that there is incorporation of oxygen-containing moieties on the surface, as evidenced by the enhanced intensity of the peaks and the formation of new peaks around 286-288 eV. The intensity of the oxygen peaks of atmospheric plasma treated surfaces was significantly much stronger than the peaks of the untreated surfaces. The O/C ratio increased from 0,37 to 0,44 with plasma treatment. These changes could be attributed to radical formations by bond breakage between C1 and ring oxygen; C1 and glycoside bond oxygen, dehydrogeneration and dehydroxylation between C2 and C3 after the ring opening of anhydroglucose of cellulose chains (27). The sol gel treatment also made contribution to oxygen containing bonds (Fig. 5) because of used chemicals in nanosol solution. The elemental composition of Si emerged together with the application of sol gel treatment which can also be seen from survey spectra (Fig 4). XPS spectra show that the existence of nitrogen by the application of chitosan applications. Nanochitosan treated fabrics had more nitrogen than chitosan treated fabrics due to the more interaction with fiber surface.

Table 3. Atomic concentration (%) of the elemental surface composition of cotton fabrics

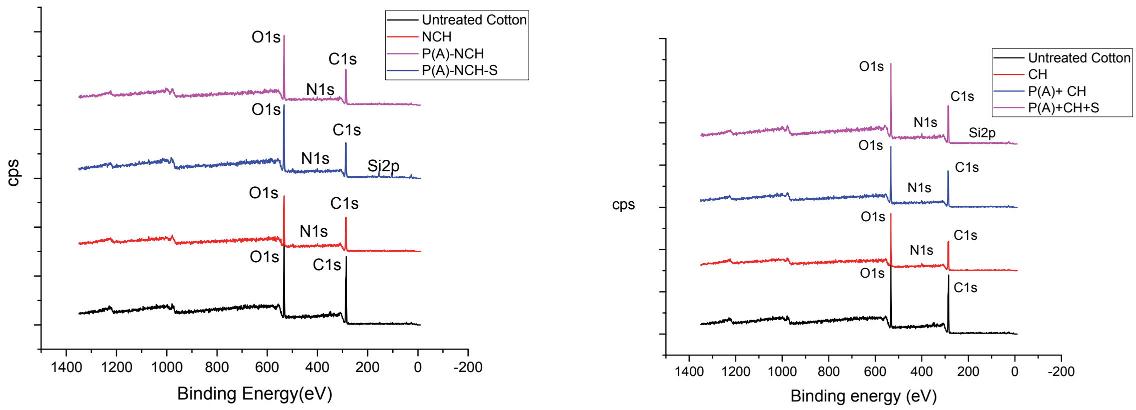
Sample	**C**	**O**	**N**	**Si**	**O/C**
Untreated	72,71	27,29	-	-	0.37
CH	67,20	27,91	4,44	-	0.41
NCH	66,79	28,75	4,90	-	0.43
S	63,16	35,85	-	0,99	0.57
P(A)	69,48	30,52	-	-	0,44
P(A)-CH-S	62,46	31,84	3,42	2,29	0,51
P(A)-NCH-S	62,71	32,05	3,66	1,58	0,51

*P(A):Plasma argon ,CH:Chitosan, NCH:Nanochitosan S:Sol-gel



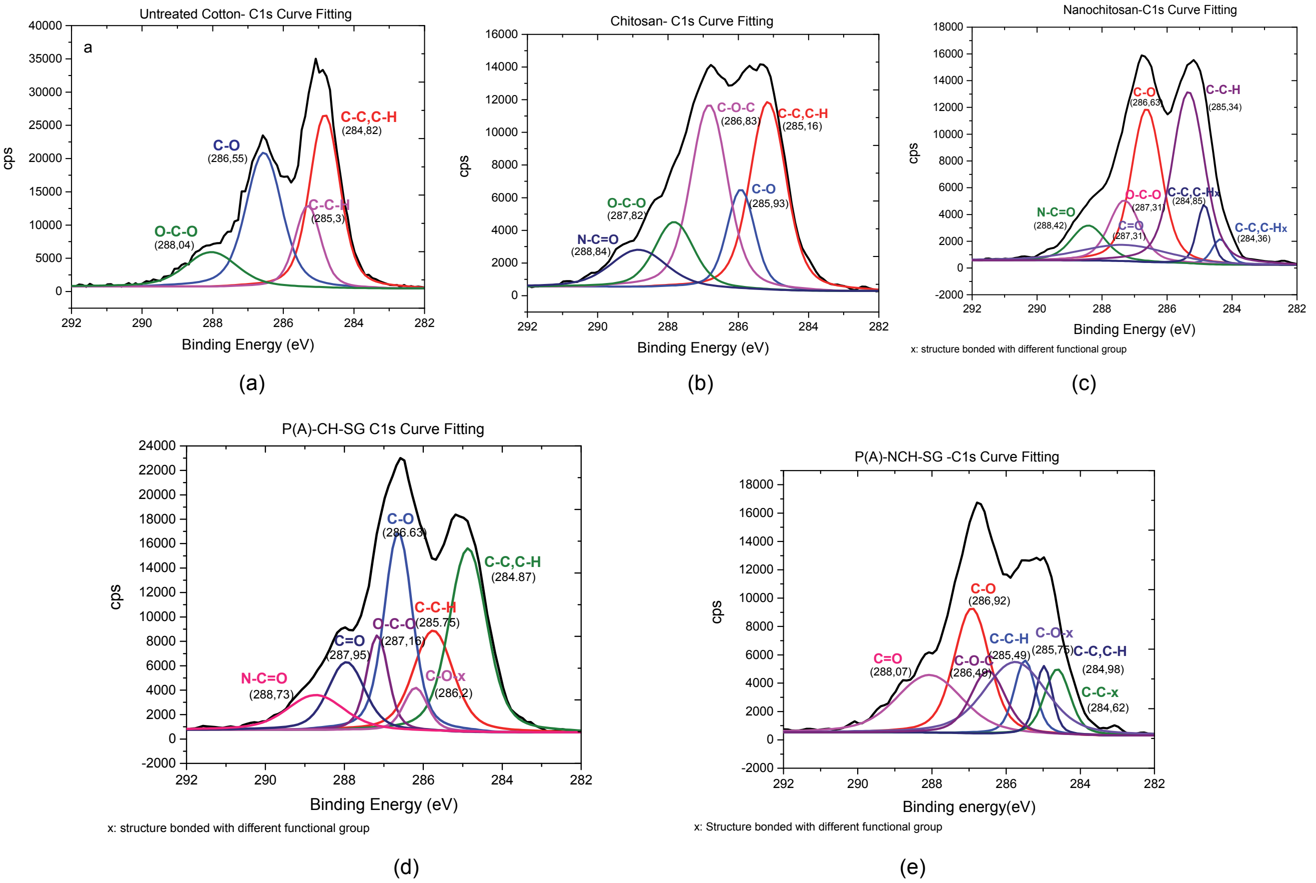
*P(A):Plasma Argon ,CH:Chitosan, NCH:Nanochitosan S:Sol-gel

Figure 3. SEM images of untreated cotton (a), CH,P(A)-CH,P(A)-CH-S coated (b,c,d) and NCH,P(A)-NCH, P(A)-NCH-S (e,f,g) coated fabrics.



*P(A):Plasma Argon ,CH:Chitosan, NCH:Nanochitosan S:Sol-gel

Figure 4. XPS survey spectra for untreated, NCH (a) and CH (b) applications by different methods.



*P(A):Plasma Argon ,CH:Chitosan, NCH:Nanochitosan S:Sol-gel

Figure 5. C 1s peak core level spectra for (a) Untreated (b) Bulk chitosan (c) Nanochitosan (d) P(A)+CH+S and (e)P(A)+NCH+S treated cotton fabrics

5. CONCLUSION

In this paper, the effects of plasma and sol gel application methods of chitosan and nanochitosan on cotton fabrics were discussed in terms of their antibacterial effect, surface friction properties, SEM and XPS analysis. Also, the comparison of bulk and nano-sized chitosan particles were made.

The antibacterial test results revealed that the most washing durable effects was obtained by combined plasma and sol-gel treatments. Chitosan nano particles can be bound tightly onto the fiber surface due to high surface energy and low viscosity, as can be seen by washing durability test of antibacterial effects. confirmed the presence of chitosan and nanochitosan on the surface of treated cotton fabrics The survey scan and atomic concentration (%) of the elemental surface compositions showed the effect of plasma pretreatment on post application of chitosan/nanochitosan particles by sol gel method.

Since atmospheric plasma treatment causes ablation and cross- linking, the fiber surface is activated and probably enhances the adhesion of the sol-gel coating. Moreover, SEM observations proved the uniform coating of biopolymers. The changes on surface friction properties of plasma and sol-gel treated fabrics confirmed the presence of rougher and smoother surfaces of treated cotton fabrics respectively.

The present study proved that atmospheric plasma-sol combined treatments enhanced the antibacterial effects of chitosan/nanochitosan treatments against multiple washing. To that end, it is thought that further investigations are needed to ensure the sol-gel and plasma combined coatings to withstand more washing cycles.

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