

A GREEN APPLICATION OF NANO SIZED CHITOSAN IN TEXTILE FINISHING

TEKSTİL TERBİYESİNDE NANO BOYUTTA KİTOSANIN YEŞİL UYGULAMASI

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Received: 03.05.2016

Accepted: 10.08. 2016

ABSTRACT

Wool fabrics are subjected to different surface modification methods in order to improve their hydrophilicity, dyeability, antimicrobial, shrinkproofing properties. Especially environmental friendly methods and application of biopolymers are gaining importance instead of conventional processes and textile chemicals. In this study, nanochitosan particles were synthesized, applied on wool fabrics and compared with bulk chitosan in terms of various properties. Ag-loaded chitosan nanoparticles was also synthesized and examined in terms of its antibacterial activity by different application methods. It has more than 95 % antibacterial effect against gram positive and negative bacteria. The influences on hydrophilicity, antibacterial activity, dyeing, air permeability, surface morphology and tensile strength were studied. Enzyme and atmospheric plasma treatments were used both alone and combined treatments before application of chitosan/nanochitosan to increase their effects. It was noticed that enzyme and plasma treatments showed significant contributions on chitosan and nanochitosan in all investigated properties. From surface observations, it was seen that especially combined treatments caused a smoother surface on wool fabrics. Therefore improved hydrophilicity and dyeability properties could be obtained by ecological methods. As a result of dyeing process, the synergetic effect of enzyme, plasma and nanochitosan treatments led to 2.5 times higher K/S values than that of untreated fabric. Moreover, all treatments had no detrimental effects on bulk properties of fabrics.

Keywords: Chitosan, Nanochitosan, wool, enzyme, plasma.

ÖZET

Yünlü kumaşlar hidrofilit, boyanabilirlik, antimikrobiyal ve çekmezlik özelliklerinin geliştirilmesi için farklı yüzey modifikasyonu yöntemlerine tabi tutulmaktadır. Klasik işlemler ve tekstil kimyasalları yerine özellikle çevre dostu işlemler ve biyopolimerlerin uygulaması giderek önem kazanmaktadır. Bu çalışmada nanokitosan partikülleri sentezlenmiş yünlü kumaşlara aplikasyon yapılmış ve normal kitosan ile farklı özellikler açısından karşılaştırılmıştır. Ayrıca, gümüş yüklü nanokitosan partikülleri de sentezlenmiş ve farklı yöntemlerle uygulanarak antibakteriyel q aktiviteleri açısından incelenmiştir. Hidrofilit, antimikrobiyal, boyama, hava geçirgenliği, yüzey morfolojisi ve mukavemet üzerine etkileri incelenmiştir. Kitosan/nanokitosan uygulaması öncesi etkileri artırmak için enzim ve atmosferik plazma işlemlerinin tek başına ve kombinasyon halinde uygulanmıştır. Kitosan ve nanokitosan üzerine enzim ve plazma uygulamalarının incelenen tüm özelliklere önemli katkılar sağladığı gösterilmiştir. Yüzey incelemelerinden, özellikle kombine işlemlerin yünlü kumaşlarda daha pürüzsüz yüzey oluşturduğu görülmüştür. Böylece, ekolojik yöntemlerle geliştirilmiş hidrofilit ve boyanabilirlik özellikleri elde edilebilmiştir. Enzim, plazma ve nanokitosan işlemlerinin sinerjetik etkisi ile boyama işlemi sonucunda, işlemsiz kumaşa gözegöre 2.5 kat daha fazla K/S değerlerine ulaşılmıştır. Buna ilaveten, tüm işlemler kumaşların temel özelliklerine zarar verici etki meydana getirmemiştir.

Anahtar Kelimeler: Kitosan, Nanokitosan, yün, enzim, plazma.

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1. INTRODUCTION

Wool fibers are one of the most outstanding natural fibers employed considerably in textile industry. It is composed of keratinous protein as a basic constituent and the minor component cell membrane complex (CMC). CMC forms a continuous phase in the fiber, links cortical and cuticular

cells. The cuticular cells are located on the outermost part of the fiber surrounding the cortical cells. The surface of these cells is hydrophobic nature due to the presence of a fatty acid monolayer covalently bounded to the epicuticle layer (1-3). External layer of the fiber is a bundle of cells which have a structure of scales (2). The scales having relatively hard and sharp edges act as a barrier for the diffusion,

which adversely affects the sorption behavior of wool fibers. Scaly structure determines performance and quality of the finished wool fabric such as handle, luster, pilling dyeability, felting, and shrinkage. To overcome shrinkage and hydrophilicity disadvantages of wool, various surface modification methods on fiber surface are necessary. Chemical methods were the major treatment for eliminating these problems in the past. However, the increasing environmental pressure has motivated textile industry to use ecological processes, such as enzyme, plasma and biopolymers instead of chemical treatments. In addition to escape potential chemical pollutants and their effluents as a result of chemical processes, bulk properties of fabric can be protected.

A renewable polysaccharide-based cationic biopolymer, chitosan, is derived from the chitin component of the shells of crustaceans. It can be seen as a suitable candidate for replacing some synthetic polymers with advantageous properties including nontoxicity, biocompatibility, biodegradability, antimicrobial activity and chemical reactivity. It can be used mainly for the purpose of shrink-resistance, dyeability, antimicrobial effect in wool finishing treatments (3). In order to reduce wool damage, chitosan application before enzyme treatment is used in many studies (1, 4-7). Because of its polycationic character, it has an interaction with oppositely charged molecule or surfaces of enzymes and wool fibers (4). On the other hand, it can be removed partially from the fabric surface depending on washing conditions. The combination of appropriate treatment/chemical agents would be beneficial to provide the stability against multiple washings. To obtain more advantages of chitosan, new studies have been focused on nano sized chitosan particles. In textile industry, nanochitosan usage is relatively new subject. Nano-particles possess unique properties, such as large ratio of surface to volume, surface-active multicentres and high surface reactivity. The advantages of chitosan and nano-materials have emerged as nanochitosan with excellent physicochemical properties. It is bioactive and frequently used in many industrial areas including textiles (10-15).

Enzyme treatments offer the prospect of environmentally acceptable processes for treating protein fibers. To modify the surface of wool by enzymatic treatments, proteases have been widely used due to their ability to catalyze the hydrolysis of peptide bonds in wool scales. Protease treatment of wool can remove the lipid layer and also cause some oxidation of peptide links to a certain degree (8,9).

Plasma treatment is offering an attractive alternative to add new functionalities such as water repellence, hydrophilicity, mechanical, antibacterial properties, etc. due to the nano-scaled modification on textile fibers. At the same time, the natural aspect of fiber properties as well as the handle of the material remains unaffected (4). For wool fabrics, plasma treatments are replacing chemical textile treatments to achieve shrink-resistance and improved dyeability substantially. Also, additional effects can be achieved such as modification of the cuticle layer, generation of new hydrophilic groups as a result of hydrocarbon chain oxidation, reduction of the chain length of fatty acids, improving of surface wettability, dyeability, fiber cohesion,

and shrink resistance (5). Atmospheric plasma treatments have significant advantages in large-scale textile applications in terms of the expense, time and space in comparison to the vacuum plasma applications (6).

In present study, bulk chitosan and nanochitosan particles were used. All treated fabrics were evaluated in terms of their antimicrobial effect, dyeing by acid dyes, air permeability, and tensile strength and surface morphologies. For antibacterial treatments, Ag-loaded chitosan particles were synthesized as well. Different treatments (enzyme, plasma and enzyme + plasma combinations) were applied to modify the wool surface to enhance biopolymer particles effect and to obtain desired properties.

2. MATERIALS AND METHODS

2.1. Materials

100% woven wool fabric was used in the experiments. Acetic acid (98%) and sodium tripolyphosphate (TPP) were all reagent grades and purchased from Merck. Protease enzyme (Perizym AFW) was supplied by Dr. Petry, Germany. Medium molecular weight chitosan (190.000-310.000 Da, degree of deacetylation is 85%) was provided from Sigma-Aldrich.

2.2. METHODS

2.2.1. Synthesis of chitosan and chitosan-silver nanoparticles

Chitosan nanoparticles were prepared by ionic gelation method as described in Ref 16. The average size of synthesized nanoparticles is 75 nm (16).

The chitosan-silver nanoparticles were synthesized according to the precipitation method using a green synthesis approach. Chitosan was used as stabilizing and reducing agent. Chitosan stabilized nanoparticles were produced at different chitosan/AgNO₃ weight ratios of (1:1), (1:2), (1:3), (1:5) and (1:10) in order to investigate the nanoparticle formation. An appropriate amount of AgNO₃ was added to the chitosan solution to adjust the required weight ratio. All the resulting colorless suspensions were heated to 95 °C and kept at constant temperature for 12 h. The color of the suspensions obtained progressively changed from light yellow to yellowish brown. The chitosan-silver nanoparticles were collected by centrifugated and resuspended two times with deionized water to remove impurities. The nanoparticles were dried at 105 °C for 12 h.

2.2.2. Enzymatic treatment

Protease enzyme was used in the experiments. Enzymatic treatment was made by using 1 g/l protease 0,5 g/l non-ionic wetting agent at 70 °C, pH 8 for 60 min. Following enzyme treatment, fabrics were rinsed with water at 60 °C pH= 4 for 10 minutes to denature enzyme on the substrate. The fabrics were rinsed several times with deionized water to remove any remaining enzyme from the treatment.

2.2.3. Atmospheric plasma treatment

In the experiments, a dielectric barrier discharge atmospheric plasma device was used (17). The samples were passed

continuously with the speed of 0.45 m/min between the electrodes. The treatments were carried out at 130 W for 60 sec with using argon as process gas in the plasma chamber.

2.2.4. Chitosan Treatments

Chitosan solutions (0.2%) were freshly prepared by dissolving the biopolymer (MMW chitosan) in distilled water containing acetic acid (1% v/v). Wool fabrics impregnated with the chitosan solution at wet-pick-up of 90%. Then, fabrics were dried at 80°C for 5 min and cured at 100°C for 3 min.

2.2.5. Nanochitosan and Chitosan-Silver Nanoparticle Treatments

Nanochitosan solutions were freshly prepared by stirring in distilled water using ultrasonic probe. Wool fabrics were impregnated with nanochitosan solution (0.2%) at 90 % WPU, pre-dried for 5 min at 80°C, and cured for 3 min at 100°C.

2.2.6. Dyeing

Dyeing of fabrics was carried out using milling type acid dye (pH = 5.5-6, CI Acid Blue 203). Fabrics were dyed at 50 °C for 15 min and the temperature was raised to 98 °C with 2 °C/min heating rate and kept at this temperature for 60 min. After dyeing, the fabrics were rinsed with water and then dried at room temperature. K/S values of dyed fabrics were measured using HunterLab ColorQuest II spectrophotometer within the wavelength range of 390 -700 nm according to the Kubelka–Munk equation:

$K/S = [(1-R)^2 / 2R]$, where K and S are the absorption and scattering coefficients, respectively.

3. CHARACTERIZATION OF MODIFICATIONS

The antimicrobial activity assessment against Gram-positive (*Staphylococcus Aureus*, ATCC 6538) and Gram-negative bacteria (*Escherichia Coli* (ATCC 8437), *Klebsiella pneumoniae* (ATCC 4352) was determined quantitatively according to AATCC 100 test method.

To determine the hydrophilicity of fabrics, capillarity (vertical wicking) test method was applied according to DIN 53924 using distilled water.

The tensile strength was measured according to ISO 13934-1 standard by using Lloyd LLOYDX-LR5K device.

The air permeability test of the samples was carried out according to standard method of EN ISO 9237 with FX 3300 (Switzerland) air permeability tester.

Surface observation analysis were made by scanning electron microscopy with Phillips XL-30S FEG scanning electron microscope.

Washing, rubbing and light fastness properties were evaluated using ISO 106 C06 at 40°C, ISO 105 X12 and ISO 105 B02 standard methods respectively.

4. RESULTS AND DISCUSSION

Antibacterial Activity

There are several mechanisms regarding antimicrobial activity of chitosan. Due to the polycationic structure at weak acidic conditions, it can easily interact with the bacteria cell wall. By this way, the growth of microorganisms is hindered. Especially, the mode of antimicrobial action of chitosan on gram-negative bacteria involves binding of the cationic chitosan to the anionic cell surface resulting in changes in permeability. Therefore, it can be said that the effect of chitosan against gram negative bacteria is more dominant than gram positive bacteria (14,29).

From Table 1, it is clear that the both chitosan and nanochitosan particles have greater impact on the antibacterial activity in comparison to the effect of each individual agents. On the other hand, nanochitosan shows greater antibacterial activity than bulk chitosan treated fabric because of its larger surface area and higher number of positively amino groups to interact with the negatively charged bacterial cell surface. In addition, the molecular weight of nanochitosan is very low so the osmosis to the bacterial cell membrane is strong, its antibacterial effect is greater (14,18).

Table 1. The results of antibacterial activity (%)

Treatment	Bacterial Reduction (%)		
	Types of Bacteria		
	<i>S.aureus</i>	<i>E.coli</i>	<i>K. Pneumanea</i>
Untreated	-	-	-
Chitosan	73,15	81,83	33,73
Plasma+Chitosan	77,02	83,16	40,42
Enzyme+Plasma+Chitosan	80,64	89,21	48,54
Nanochitosan	84,86	89,56	51,16
Plasma+Nanochitosan	86,99	91,55	60,66
Enzyme+Plasma +Nanochitosan	90,35	93,98	68,62
Chitosan-silver nanoparticles (Ag-NCHT)	96,38	97,66	66,62
Enzyme+Plasma+ Ag-NCHT	99,27	99,99	84,24

As known, silver is a strong antimicrobial agent against a wide spectrum of bacteria. Since its low charge density, the addition of silver nanoparticles onto the textile materials is difficult. Therefore, several application methods were investigated but these kinds of methods can reduce the antimicrobial efficacy of the silver particle. In the experiments, chitosan acts as a stabilizing and reducing agent. By this way, it prevents the oxidation of silver which forms black color on the textile substrates by converting silver to silver oxides (10). Moreover, silver loaded in chitosan nanoparticle could be integrated into the textile material readily. As an evidence, Ag loaded nanochitosan particles have excellent activity against both gram positive and gram negative bacteria. Only Ag-loaded nanochitosan particles showed the highest antibacterial affect on wool fabrics up to 97,66 % alone. This value is increased up to 99.99 % by the combination of enzyme and plasma treatments.

Hydrophilicity Properties

As known, protease enzymes specifically act on the peptide bonds of proteins and hydrolyze them. The removal of the proteinaceous matter also causes covalently bounded fatty acids to be removed, which consequently enhances the hydrophilicity of the wool surface (19). Oxidation and etching reactions occurred by plasma modification enhance capillarity of fibers surface. There was seen *significant improvement in capillarity values of plasma treated fabrics*.

Table 2. Capillarity values (cm)

Treatment	Capillarity value (cm)
Untreated	0
Chitosan	1,8
Enzyme	3,2
Enzyme+Chitosan	3,9
Plasma	8
Nanochitosan	3,2
Enzyme+Nanochitosan	4,6
Enzyme+Plasma	10,2
Plasma+Chitosan	8,8
Plasma+Nanochitosan	10,7
Enzyme+Plasma+ Chitosan	11,4
Enzyme+Plasma+ Nanochitosan	12,6

Increment in capillarity values of treated fabrics is due to the hydroxyl and amine functional groups of chitosan on the

fiber surface. When chitosan particle sizes were taken into consideration, it was found that nanochitosan had greater capillarity on account of its large surface area and smaller size when compared with bulk chitosan.

Since enzymatic treatment can remove the hydrophobic layer of wool, plasma pretreatment modifies the fiber surface more efficiently, which makes hydrophilicity value higher before the application of chitosan. The synergetic effects of enzyme+plasma+chitosan treatment can be seen from the capillarity results.

Dyeing Properties

Cuticle provides hydrophobic barrier at the fiber surface and limits the rate of dye uptake. Hydrophobic structure of wool can be removed to a certain extent by different methods for increasing dye uptake. Protease enzyme hydrolyses surface layer of wool by improving moisture diffusion from the surface into the fiber interior. Preferably, the enzymes attack the surface of the fiber, break down the epicuticle and thus enable improved absorption of the dye (20). The increased hydrophilicity of wool by protease treatment was also helpful to improve the dye affinity for wool fiber. This can be proved by significant differences between K/S values of protease treated and untreated fabrics (Figure 1).

Chitosan has high affinity for many classes of dyes such as disperse, direct, acid and reactive dyes. In acidic medium, the cationized amino groups can adsorb anionic dye molecules by the electrostatic attraction. It is also known that the binding of chitosan to wool fiber is occurred by ionic interactions (21, 22). From Figure 1, it can be seen that the K/S values of chitosan treated fabrics are higher than that of untreated fabrics. This improvement in color strength (K/S) values of chitosan treated wool fabrics is associated with the introduction of primary amino groups to the fiber structure.

The dyeing rate of wool fabric and color depth can be significantly increased after treated by nanochitosan in comparison to the bulk chitosan treated wool. It was mainly caused by the enhancement of the adsorption rate of dye molecules by chitosan nanoparticles.”The combined treatment of enzyme and chitosan particles showed higher K/S values in comparison to enzyme and chitosan treatments alone.

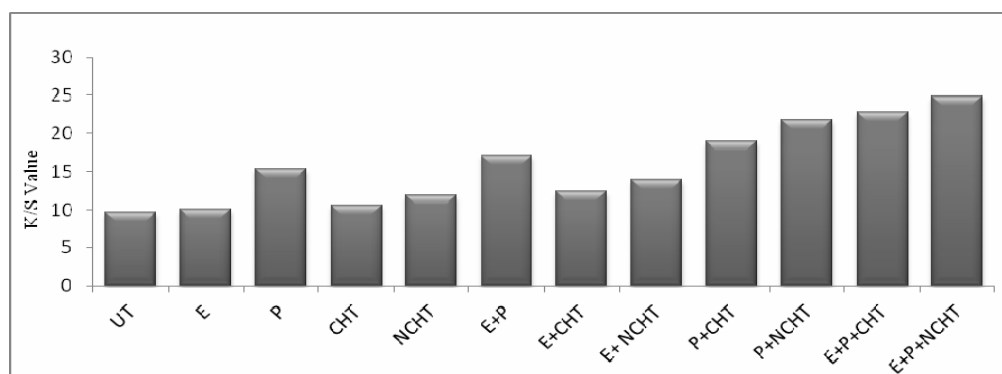


Figure1. K/S Values of chitosan and nanochitosan treated fabrics (*)

(*) Abbreviations :Untreated (UT), Enzyme (E), Plasma (P), Chitosan (CHT), Nanochitosan (NCHT), Enzyme+Plasma (E+P), Enzyme+Chitosan (E+CHT), Enzyme+Nanochitosan (E+NCHT), Plasma+Chitosan (P+CHT), Plasma+Nanochitosan (P+NCHT), Enzyme+Plasma+ Chitosan (E+P+CHT), Enzyme+Plasma+ Nanochitosan (E+P+NCHT)

By means of plasma treatment, new functional groups are created on the surface and some changes occur in the surface composition (23,24). In addition, plasma etching effect contributes positively to the K/S values for both enzyme and chitosan treated fabrics. As can be seen from the results, enzyme + plasma + chitosan treated wool fabric gave K/S values by more than 2.5 times in comparison to untreated one.

Fastness Properties

The colour fastness to light, washing and rubbing was studied in dyed samples. All samples showed staining onto multifiber and colour change values of between four and five. When the colour fastness to dry and wet rubbing was examined, similar values (ranging between 3-4 and 4) were observed among the treated fabrics for both dry and in wet states. Since dye molecules were adsorbed on the surface and could not penetrate into the fiber as easily as treated samples, all treated fabrics show better values than untreated fabric to half a degree. The values of fastness to light of the treated samples gave values changing between 6 and 6-7. Since colour strength values are higher for dual or triple combinations, these samples had better light fastness values. The results of all fastness tests showed that plasma, enzyme, chitosan and the combined treatments have no detrimental effect on fastness values.

Surface Observation

The surfaces of untreated and treated the fabrics were morphologically observed by scanning electron microscope

(SEM). After partial degradation of cuticle layer by enzyme treatments, flattened scales on the fiber surface can be obtained. Atmospheric pressure plasma treatments created rounding scales, forming micro cracks, tiny grooves by etching of the material (24).

Enzyme+plasma treated wool fiber surface showed these combined effects apparently (b). As can be seen from the images, chitosan and nanochitosan treatments covers wool surface. The combined effects of enzyme, plasma and chitosan created a smooth surface which is a significant improvement for wool fabrics in terms of their hydrophilicity, dyeability properties.

Air Permeability

Figure 3 shows the effect of different treatments on air permeability of the wool fabrics. Air permeability is defined as the air velocity in millimeters per second, which is passing through the fabric at a given pressure difference. The air permeability is mainly dependent on thickness and porosity. The effect of air permeability on enzyme treated fabrics is nearly negligible (Fig 3). The values of untreated and enzyme treated fabrics are very similar to each other. Plasma treated fabrics showed lower air permeability than untreated fabrics since etched fibres by plasma effect limits the the air flow through the fabric. By this way, air could not escape easily within the plasma treated fabric (15, 25).

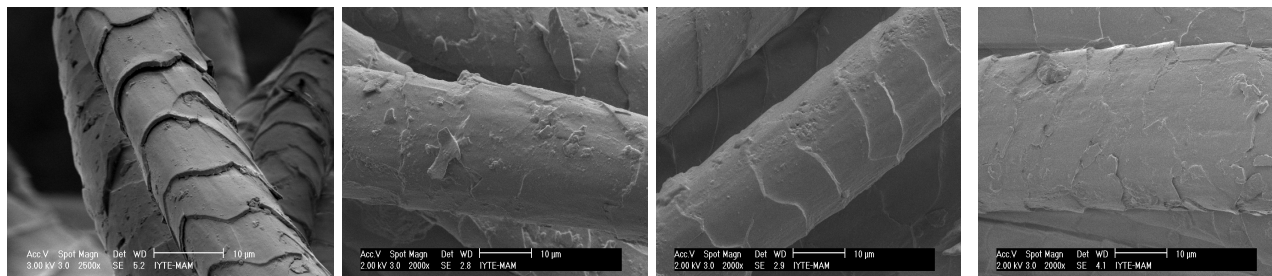


Figure 2. SEM images of (a) untreated (b) enzyme +plasma (c) enzyme+plasma+chitosan (d) enzyme+plasma+nanochitosan treated fabrics

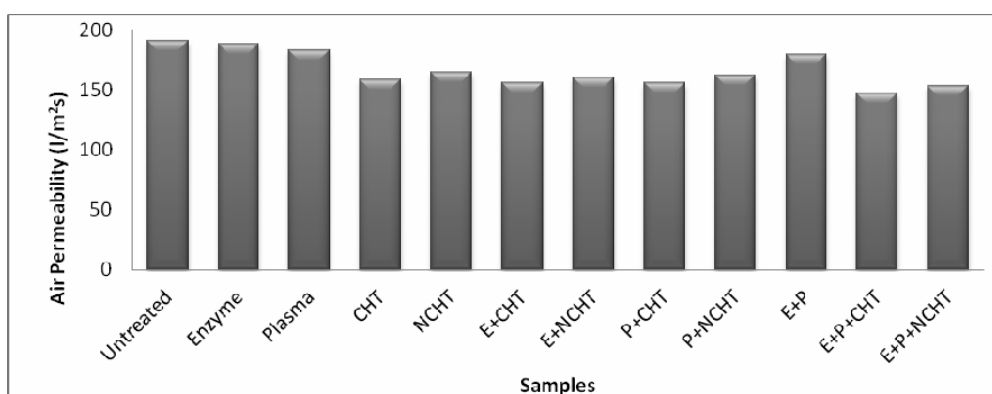


Figure 3. Air Permeability of Fabrics (**)

(**) Abbreviations :Untreated (UT), Enzyme (E), Plasma (P), Chitosan (CHT), Nanochitosan (NCHT), Enzyme+Chitosan (E+CHT), Enzyme+Nanochitosan (E+NCHT), Plasma+Chitosan (P+CHT), Plasma+Nanochitosan (P+NCHT), Enzyme+Plasma (E+P), Enzyme+Plasma+ Chitosan (E+P+CHT), Enzyme+Plasma+ Nanochitosan (E+P+NCHT)

Air permeability of the treated samples decreases by nanochitosan and chitosan applications. This is because chitosan or nanochitosan molecules deposit on the fiber surface to block pores through which air could pass rather than penetrate into the fiber. The effect of nanochitosan is dominant as against chitosan (26-28)

Tensile Strength

The effect of enzyme, plasma, chitosan and their combined treatments were evaluated in terms of tensile strength changes of the fabric. Effect of applied treatments on tensile strength values (% average loss) of the wool fabrics were given in Table 3.

Protease treatment caused damage to the wool fiber and the fabric tensile strength because of hydrolytic reaction of protease. The hydrolytic attack of protease cannot be restricted only to the fibre surface in general. Enzymes can diffuse inside the fibre, causing strength loss (2). Plasma treatment following after enzymatic treatment increases strength slightly. On the other hand, plasma modification has no detrimental effect on mechanical properties since the plasma species can penetrate only to a depth of about 1000 Å (24).

Table 3. The effect of different treatments on tensile strength values

Treatment	Change in Tensile Strength (%)
UT	-
CHT	+8,5
E	-3,3
P	-0,5
E+CHT	+2,1
E+P	-3,6
NCHT	+8,7
E+NCT	+1,4
P+CHT	+6,8
P+NCHT	+7,2
E+P+ CHT	+4,7
E+P+ NCHT	+5,9

The covering of the surface by bulk chitosan or nanochitosan particles leads to the recovery in tensile strength of wool fabrics. The protective effect on tensile strength loss by biopolymer treatment is more dominant by nanochitosan treatment due to its larger surface area.

5. CONCLUSION

The applications of chitosan in textiles have received great attention in numerous studies due to its several unique properties. The huge molecular size and high viscosity of chitosan polymer limit its penetration into the fiber. Therefore, only surface deposition takes place and it causes deterioration in handle and appeal of the fabric. Reducing the particle size of chitosan to nano level increases the extent of penetration into fiber structure and maintains inherent properties of cotton fiber (32).

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There are limited studies on the application of nano formed chitosan in textile industry (11-14, 30, 31). In this study, chitosan nanoparticles and chitosan-silver nanoparticles were synthesized. Enzyme and plasma treatment contributions of nanochitosan treatments on wool fabrics were investigated in terms of various properties. Comparison of chitosan and nanochitosan in dyeing, antimicrobial effect, tensile strength, and surface morphology and air permeability properties was also investigated.

Chitosan addition on the wool surface generates additive functional groups which cause increase in hydrophilicity. Protease enzyme has hydrolytic effect on wool fibers and the diffusion barrier to water and dye molecules can be overcome. Plasma treatment enhances capillarity by means of oxidation and etching reactions. Considering all these aspects; dual effects of enzyme, plasma and chitosan showed significant improvements while triple effects gave the best results.

When dyeing results were evaluated, it was seen that chitosan, enzyme and plasma treatments alone increase dye uptake of wool by different mechanisms to a great extent compared to the control sample. Enzyme and plasma treatments facilitate dye diffusion prior to chitosan treatment. This effect is more pronounced for enzyme+plasma+chitosan combined treatments by 2.5 times higher K/S values in comparison to untreated one with good fastness properties.

Nanochitosan showed better properties due to its large surface area and smaller size when compared with bulk chitosan. When antibacterial effects are concerned, chitosan showed 93,98% effect against gram negative bacteria with combined treatments of enzyme and plasma. Chitosan-silver nanoparticles showed the highest antibacterial affect on fabrics up to 97, 66%. Nearly 100% antibacterial effect was achieved by means of enzyme and plasma pre-treatments prior to chitosan-silver nanoparticle application.

Enzyme treatment caused the loss of tensile strength in acceptable limits. However, post application of chitosan or nanochitosan showed protective effect and improved tensile strength. When air permeability test is concerned, enzyme, plasma and chitosan decreased permeability to a certain degree. Especially chitosan and nanochitosan have lower values than that of untreated one.

Chitosan and nanochitosan particles are substitutes for chemical agents used in conventional textile finishing processes. As can be seen from the results, ecological processes such as enzyme and plasma enhance their effect substantially without deteriorating bulk properties of wool fabrics. In wool finishing processes, nano-sized chitosan and its application with ecological processes seems to be more applicable and promising for a sustainable textile industry.

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