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Improving Certain Properties of Wool Fibers by Applying Chitosan Nanoparticles and Atmospheric Plasma Treatment

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Abstract: The nanochitosan particles were prepared by ionic gelation method using sodium tripolyphosphate (TPP) as anionic chemical agent. Structural and morphological properties of the nanoparticles were characterized by dynamic light scattering (DLS), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FTIR) analyses. The results showed that nanoparticles were spherical with a diameter range of 17-105 nm. After nanochitosan synthesis, the effects of chitosan and nanochitosan concentrations on the dyeability, fastness properties, shrink-proofing, tensile strengths, and surface friction coefficients of untreated and plasma treated wool fabrics were investigated. The studies revealed that nanochitosan treated wool fabric possesses better dyeing and shrink-proofing properties in comparison with conventional chitosan treated fabrics.

Keywords: Chitosan, Nanoparticles, Ionic gelation, Wool, Atmospheric plasma

Introduction

Innovative technologies have focused on biomaterials. Biopolymers are the ideal materials for a wide range of uses such as ophthalmology, medicine, agriculture, textiles, and automotive because of their biodegradability, biocompatibility, sustainability, eco-efficiency, industrial ecology, and renewable nature. They are derived from naturally occurring substances such as crustacean shells, mushrooms, or wood [1]. Polysaccharide based polymers are the major class of biomaterials, including agarose, alginate, carageenan, dextran, and chitosan. Chitosan (poly(1,4)-2-amino-2-deoxy-β-D-glucan) is a cationic biopolymer produced by alkaline N-deacetylation of chitin. 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 [2]. Chitosan has been used in a variety of applications in the form of microparticles, nanoparticles, gels, or films due to its biocompatibility, biodegradability, low toxicity, and antimicrobial activity [3-6].

Chitosan can easily interact with the polyanions to form nanochitosan. The most widely used polyanion is TPP. The chitosan-TPP nanoparticles are formed upon the addition of TPP solution to chitosan solution under mild conditions [7]. Different methods such as emulsion cross-linking, coacervation/precipitation, ionic gelation, etc. have been used to prepare chitosan particulate systems. However, ionic gelation method has attracted much attention because the process is easier than the other synthesis methods [8]. Nanochitosan is an environmentally friendly and bioactive material with excellent physicochemical properties [9]. Since nanoparticles have large surface area to volume ratio and high surface energy, nanochitosan has many advantages for textile applications such as better affinity to fabrics and leading to an increase in durability of the given function. Although there are many studies on the use of chitosan based treatment of textiles where bulk chitosan has been used for coating or finishing, limited research has been carried out on the characterization and the applications of chitosan nanoparticles on wool fabrics [10-14]. The main problem for chitosan applications to wool is that it is weakly bound to the substrate. To enhance chitosan's adsorption on wool fibers and increase the uniformity of its distribution, it is convenient to increase the anionic character of the wool surface. For this aim, plasma treatment is used [15]. Plasma technology is a physical method used for surface modification of materials as it affects the surface without altering the bulk properties of the material. Plasma treatments can be classified according to their temperature and pressure intensities. Cold plasmas are some of the most implemented types in industrial applications. According to their pressure, plasmas can be categorized as low and atmospheric plasmas. Both plasma types can be used to induce surface modifications to achieve cleaning, surface activation, surface etching, crosslinking, chain scission, oxidation, grafting, and deposition effects on materials. These two types yield similar effects, but atmospheric plasma has many advantages over vacuum plasma. Atmospheric plasma can be generated under atmospheric conditions and requires no vacuum systems for continuous and open perimeter fabric flow [16]. Plasma treatments of wool only modify the cuticle surface of the fibers, generating new hydrophilic groups as a result of hydrocarbon chain oxidation, reducing the chain length of fatty acid, improving their surface wettability, dyeability, fiber cohesion, and shrink resistance. The oxidation process also promotes cysteine oxidation in the exocuticle, converting it into cysteic acid, and thus reducing

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the number of crosslinkages in the fiber surface [15].

This study aims to investigate the use of chitosan nanoparticles and plasma treatments for wool fabric applications in terms of dyeing, hydrophilicity, surface friction coefficient, color fastness, shrinkage, and tensile strength properties. Initially physical and chemical properties of chitosan nanoparticles treated and bulk chitosan treated fabrics have been investigated at the same concentration. Atmospheric plasma treatment in the presence of argon gas was also used to enhance the bonding of chitosan and nanochitosan to wool fabrics.

Experimental

Materials

100 % wool woven fabric (31 ends/ cm, yarn count 40 tex in warp; 26 ends/cm, yarn count 40 tex in weft; and 190 g/m^2 fabric density) was used in the experiments. The samples were treated with atmospheric plasma in the pretreatment processes. Medium molecular weight chitosan (190,000-310,000 Da, degree of deacetylation is 85 %) and TPP were provided from Sigma-Aldrich while acetic acid (glacial) was supplied from Merck.

Treatment Methods

Preparation of Nanochitosan

Chitosan-TPP nanoparticles were prepared by ionic gelation method [7] using the preparation conditions determined in previous study [17]. Briefly, chitosan was (3 mg/m*l*) dissolved in 10 m*l* of 1 % (v/v) acetic acid solution and pH of the solution was adjusted to 4.6 with 10 M NaOH. Chitosan nanoparticles were spontaneously cross-linked by the addition of 12 m*l* (0.5 mg/m*l*, w/v) of TPP aqueous solutions to chitosan solution. After stirring for 60 min at room temperature, the suspension centrifuged at 16,000 rpm and 4 °C for 30 min. The isolated nanochitosan was rinsed with distilled water and freeze-dried at -50 °C for 12 h in the presence of 5 % (w/v) trehalose as a cryoprotectant. Trehalose was used to maintain the particle stability against the freezing and dehydration stress during freeze-drying process.

Plasma Treatments

A dielectric barrier discharge (DBD) atmospheric plasma device was used for plasma treatments. The distance between the electrodes was 0.2 cm. The samples were placed between the electrodes and passed continuously with the speed of 0.45 m/min. Argon gas was used under a constant power of 130 W in all treatments. The samples were treated for 20 s in the plasma device.

Chitosan Treatments

Chitosan solutions (0.05 %, 0.1 %, and 0.2 % w/v) were freshly prepared by dissolving the biopolymer in distilled water containing acetic acid (1 % v/v). Wool fabrics were dipped into the chitosan solution, wet-pick-up of 90±1 % at 20 °C, pre-dried 5 min under 80 °C and then cured for 3 min at 100 °C.

Nanochitosan Treatments

Nanochitosan solutions were freshly prepared by stirring in distilled water using ultrasonic probe. Wool fabrics were dipped into the nanochitosan solution, wet-pick-up of 90±1 % at 20 °C, pre-dried for 5 min under 80 °C, and then cured for 3 min at 100 °C.

Characterization

Analysis of Nanochitosan Particles

The particle size distribution of the chitosan nanoparticles was determined using Dynamic light scattering (DLS) (Malvern Zetasizer Nano Series Nano-S). FTIR analyses of the chitosan and chitosan nanoparticles were recorded on a Shimadzu FTIR-8040. The measurements were performed at 20 °C and a relative humidity of 65 %. TEM analysis of prepared particles was made by an FEI Tecnai G2 Spirit Bio (TWIN) device.

Hydrophilicity

The hydrophilicity values of fabrics were measured according to AATCC 79-1995 standard test method. A drop of water was allowed to fall from a fixed height to a taut surface of test specimen. The time required for the specular reflection of the water drop to disappear was measured and recorded as wetting time(s). The smaller dropping time indicates better hydrophility.

Dyeing

The dye used in this study was Realan Rot G (wool reactive dye, pH=4.5-5). Fabrics were dyed at 50 °C for 15 min and the temperature was raised to 98 °C with 1 °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.

The *K/S* values of the dyed fabrics were measured using a HunterLab ColorQuest II spectrophotometer instrument over a wavelength range of 390-700 nm. In a typical test, reflectance values (R) were measured and relative color strength (K/S) values were then established according to the following Kubelka-Munk equation:

$$K/S = [(1-R)^2/2R]$$

where K and S are the absorption and scattering coefficients, respectively.

Color Fastness

The color fastness to washing, rubing and light were determined according to BS EN ISO 106 C06 at 40 °C, BS EN 105 X12 and BS EN ISO 105 B02 standard test methods respectively.

Determination of Shrinkage

Shrinkage tests were carried out in a Wascator using the ISO 6330 5A programme, as described in IWS Test Method 31.

Tensile Strength

The samples were conditioned at standart atmosphere conditions (20 °C, relative humidity 65 %) for 24 h before measurement. The tensile strength of the wool fabrics was determined by ISO 13934-1 with LLOYDX LR5K machine. An average result was obtained from the values of 10 samples.

Surface Friction Coefficient

The samples were conditioned at 20 °C and 65 % relative humidity for 24 h before measurement. To measure the kinetic friction coefficient of the fabric surface, the Frictorq instrument was used as described by Lima *et al*. [18]. An average result was obtained from 10 samples.

Results and Discussion

Synthesis and Characterization of Nanochitosan Particles

It is well known that the pH of the chitosan solution and the weight ratio of chitosan:TPP have significant effects on nanochitosan preparation [17,19]. These parameters were selected according to the results of previous study [17] as pH of 4.6 and the weight ratio of 5:1. The particle sizes of the prepared nanochitosan particles were determined by using dynamic light scattering (DLS) and TEM measurements. Figure 1 shows DLS measurements of nanochitosan particles. The curve clearly shows that the mean diameter of nanochitosan particles is in the range of 44 nm to 106 nm. Indistinct peak of chitosan nanoparticles ranged from 300 to 800 nm is negligible because percent of the number of nanoparticles is less than 1 %. The polydispersity index of the sample is 0.446.

The TEM image of the prepared nanochitosan particles is shown in Figure 2. Before TEM analysis, nanochitosan particles were suspended in distilled water by ultrasonication in order to prevent particle agglomeration. The nanochitosan particles are spherical in shape with a smooth morphology and are between the range of 17 nm and 105 nm. The difference between the results of DLS and TEM is attributed to adhesive nature of chitosan in aqueous medium. While DLS measurements give the hydrodynamic diameter of the nanoparticles, TEM images show the actual diameter.

FTIR spectra of commercial chitosan and cross-linked chitosan nanoparticles were presented to compare the changes in the structure of chitosan after the ionically cross-linking with TPP (Figure 3). The characteristic peaks of chitosan can be clearly seen in Figure 3(a). The peaks at 1100-960 cm^{-1}, 1383 cm^{-1}, 1657 cm^{-1} and 3400-3200 cm^{-1} correspond to C-O-C symetrical streching, acetyl groups ($-COCH_3$), amide groups ($-CONH_2$) and combined peak of O-H stretching, intramolecular hydrogen bonding and primary amines, respectively. $-CONH_2$ (at 1657 cm^{-1}) and NH_2 (low intensity peak at 1597 cm^{-1}) bending vibrations disappeared and two new sharp peaks observed at 1643 cm^{-1} and 1543 cm^{-1} in the spectrum of nanochitosan particles (Figure 3(b)). The dense peak in the range of 1300-800 cm^{-1} observed after treatment with TPP corresponds to phosphate peaks of TPP in the structure of nanoparticles. This is attributed to interaction between the phosphoric groups of TPP and the ammonium groups of chitosan [17,19,20]. FTIR spectrum of chitosan nanoparticles indicated that cross-linking was succesfully carried out.

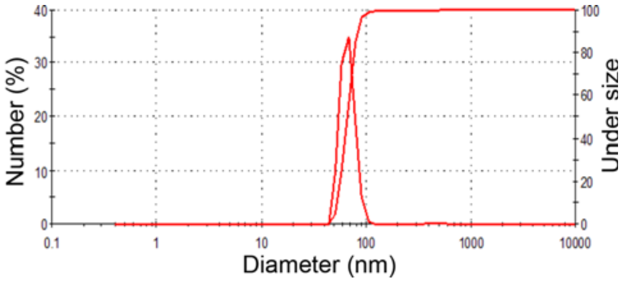

Figure 1. Particle size distribution of chitosan nanoparticles.

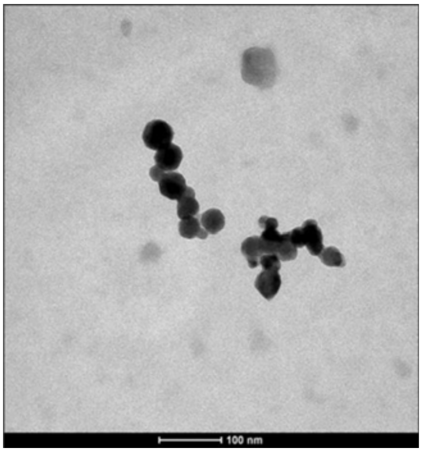

Figure 2. TEM image of chitosan nanoparticles.

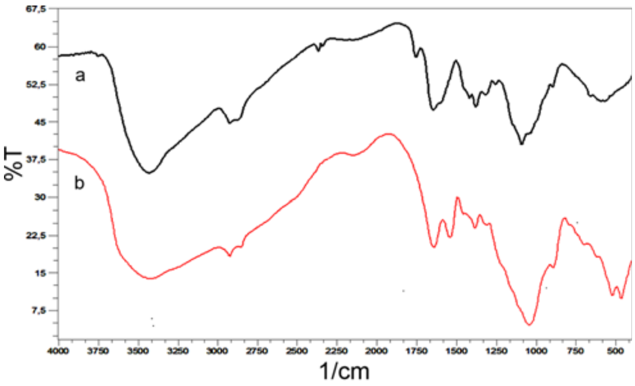

Figure 3. FTIR spectra of (a) chitosan and (b) chitosan nanoparticles.

Hydrophilicity and Dyeing Properties

The hydrophilicity of treated fabrics is reported in Table 1. It is clear that plasma, chitosan, and nanochitosan treatments improved the hydrophilic nature of the fabrics. Etching by

Table 1. Hydrophilicity and *K/S* values of the fabrics

Sample	Hydrophilicity value	*K/S* value
Untreated	Hydrophobic (> 1800 s)	6.22
Chitosan (0.05 %)	922.80	6.72
Nanochitosan (0.05 %)	507.40	7.43
Chitosan (0.1 %)	795.90	7.42
Nanochitosan (0.1 %)	322.70	8.65
Chitosan (0.2 %)	613.10	8.42
Nanochitosan (0.2 %)	193.20	9.99
Plasma	20.79	14.79
Plasma+Chitosan (0.05 %)	17.72	16.44
Plasma+Nanochitosan (0.05 %)	7.20	18.08
Plasma+Chitosan (0.1 %)	15.40	18.31
Plasma+Nanochitosan (0.1 %)	4.50	20.25
Plasma+Chitosan (0.2 %)	8.90	21.23
Plasma+Nanochitosan (0.2 %)	1.70	23.80

Table 2. The rubbing and light fastness values and area shrinkage (%) of the treated fabrics

Sample	Rubbing fastness		Light fastness	Area shrinkage (%)
	Dry	Wet		
Untreated	3-4	3	6	89.60
Chitosan (0.05 %)	3-4	3	6	85.70
Nanochitosan (0.05 %)	3-4	3	6	73.30
Chitosan (0.1 %)	5	4-5	6	82.70
Nanochitosan (0.1 %)	5	4-5	6	70.10
Chitosan (0.2 %)	5	4-5	6	78.80
Nanochitosan (0.2 %)	5	4-5	6	63.50
Plasma	5	4-5	6	62.70
Plasma+Chitosan (0.05 %)	5	4-5	6	55.90
Plasma+Nanochitosan (0.05 %)	5	4-5	6	47.80
Plasma+Chitosan (0.1 %)	5	4-5	6	53.20
Plasma+Nanochitosan (0.1 %)	5	4-5	6	45.10
Plasma+Chitosan (0.2 %)	5	4-5	6-7	50.80
Plasma+Nanochitosan (0.2 %)	5	4-5	6-7	41.20

plasma treatment destroyed the hydrophobic layer partially and hydrophilicity was significantly improved. This effect depends on the plasma treatment time and plasma power [21]. It should also be noted that the size of chitosan particles treated and the concentration of the chitosan/nanochitosan solution have significant effects on hydrophilicity.

The *K/S* values of treated fabrics are given in Table 1. The plasma, chitosan, and nanochitosan treatments enhance the color strength of the wool fabrics, whether applied together or separately. The highest dyeing efficiency is observed for the combined treatment of plasma and nanochitosan.

Plasma treatment enhances the binding of chitosan and nanochitosan by promoting/introducing new anionic groups on the fiber [21]. The increment in hydrophilicity of wool fiber caused by plasma treatment leads to increased dye uptake and chitosan adhesion during finishing. The results also show that the color yield is significantly improved by nanochitosan treatment when compared to bulk chitosan treated wool fabric. The chitosan nanoparticles possess high specific surface area and surface energy which enhance the adsorption possibility between dye molecules and nanoparticles [22].

Fastness and Shrinkage Properties

The color fastnesses to washing, dry and wet rubbing, and wet rubbing were studied in dyed samples. In the case of color fastness to washing, all samples showed staining and color change values between four and five. When the color fastnesses to dry and wet rubbing were studied, similar values of staining in dry and in wet (ranging between three and five) were observed for the treated fabrics. 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 by half a degree. The values of fastness to light of the treated and untreated samples did not differ from each other within the range of 6.5-7. The results of light fastness show that plasma, bulk chitosan, nanochitosan, and the combined treatments have no detrimental effects on light fastness values. The rubbing and light fastness values of the treated fabrics were presented in Table 2.

As well known, the etching effect of plasma reduces the differential friction coefficients of fibers and thus decreases the natural shrinkage tendency [15]. It is reported that chitosan provides felting shrinkage to wool by covering its cuticle surface. Therefore, when the diffusion of chitosan in fabric is better, the area covered by chitosan on the surface of the fiber becomes larger and the absorption of dye molecules into the fabric can be improved [12]. The shrinkage properties of the fabrics were listed in Table 2. It is clear that the nanochitosan treated fabrics have better shrink-proofing properties. The shrink-proofing of treated fabrics is improved with the increase in concentration of nanochitosan and bulk chitosan. After combined plasma and nanochitosan treatment, the area shrinkage of treated wool shows a significant reduction in contrast to untreated samples.

Tensile Strength Properties and Surface Friction Coefficients

The wool fabrics were treated by atmospheric plasma to increase the bonding efficiency of chitosan to the wool and to increase the uniformity of its distribution on surfaces. The tensile strength values of the fabrics were given in Table 3.

Table 3. The tensile strengths and surface friction coefficients of the treated fabrics

Sample	Tensile strength (N)		Surface friction coefficient
	Weft	Warp	
Untreated	457.60	572.13	0.3875
Chitosan (0.05 %)	460.81	577.30	0.3802
Nanochitosan (0.05 %)	464.34	583.44	0.3804
Chitosan (0.1 %)	468.12	581.67	0.3769
Nanochitosan (0.1 %)	479.97	599.11	0.3792
Chitosan (0.2 %)	482.25	593.76	0.3715
Nanochitosan (0.2 %)	504.58	621.42	0.3752
Plasma	444.12	569.67	0.4989
Plasma+Chitosan (0.05 %)	446.20	571.31	04834
Plasma+Nanochitosan (0.05 %)	449.23	574.33	0.4823
Plasma+Chitosan (0.1 %)	450.98	573.65	0.4802
Plasma+Nanochitosan (0.1 %)	457.89	578.14	0.4795
Plasma+Chitosan (0.2 %)	453.80	576.20	0.4782
Plasma+Nanochitosan (0.2 %)	461.22	587.77	0.4765

Nanochitosan and bulk chitosan treatments have a coating effect on the fiber surface of the wool. Moreover, the loss of tensile strength after plasma treatment is recovered, to a certain degree, by nanochitosan and bulk chitosan treatment. The improvement of tensile strength by plasma+nanochitosan in comparison to plasma+bulk chitosan treatment can ce attributed to better bonding of nanochitosan particles with the fiber structure. It is concluded that the physical properties of the wool fabrics were not deteriorated after finished with plasma, chitosan and nanochitosan particles.

Fabric friction is one of the important properties that characterize the surface behavior of fabrics. Chitosan and nanochitosan treated fabrics exhibit different surface characteristics when compared with the untreated fabrics. The surface of wool fibers was strongly oxidized as a result of plasma treatment, so that the surface lipid layer was removed and the surface of scales was etched. Surface friction coefficients of untreated and treated wool fabrics were given in Table 3. As can be seen, the values increased due to the etching effect of atmospheric plasma treatment. After chitosan application, because of the coating, surface friction coefficient decreased. The results also showed the effect of coating on the surface of the fabric. Since etching effect of the plasma treatment, chitosan could properly be applied on the surface of the fiber.

SEM Analysis

The surface appearances of the treated and untreated wool samples were seen from Figure 4. As can be seen from the images, micro cracks and very small grooves were formed after atmospheric pressure plasma treatment caused by the etching of the fiber surface [21]. The SEM images also confirmed the results of area shrinkage results.

Also, SEM images are in consistent with the surface

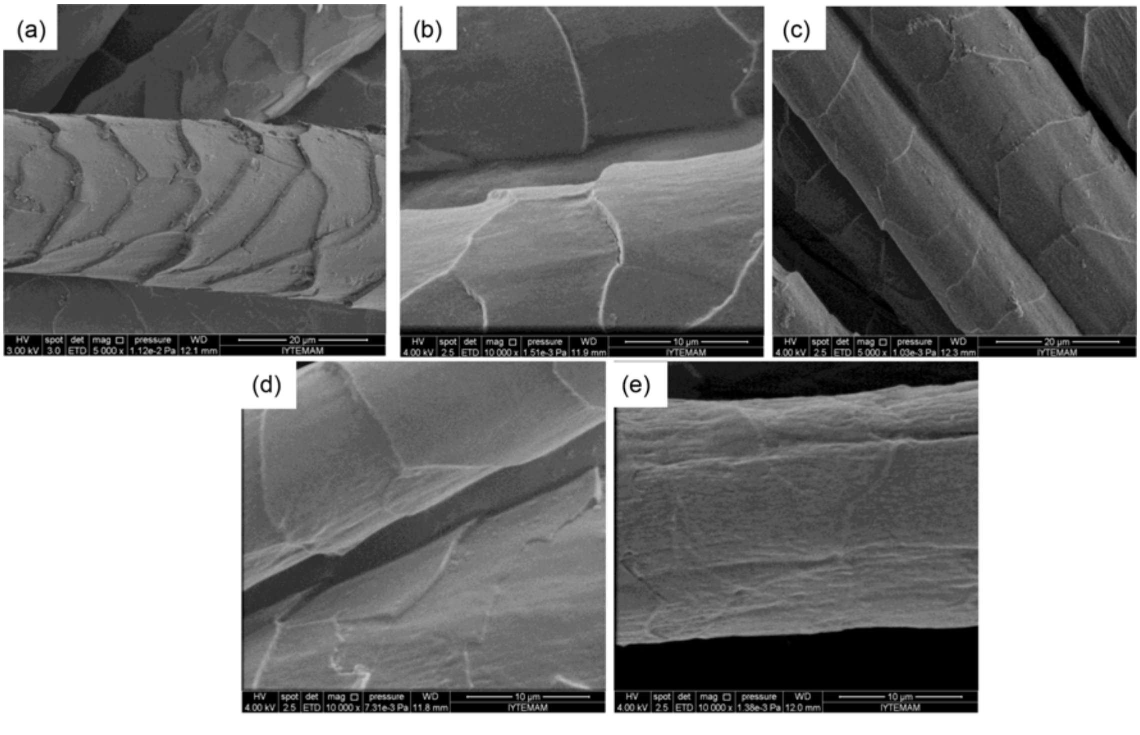

Figure 4. SEM images of (a) untreated, (b) chitosan, (c) nanochitosan, (d) Plasma+chitosan, and (e) plasma+nanochitosan tretaed wool samples.

friction coefficient properties. Figure 4(d) and (e) showed that the surface of atmospheric plasma+chitosan and atmospheric plasma+nanochitosan treated fabrics became smoother than that of untreated wool. The majority of the wool fiber scales have apparently been modified and even removed after plasma+chitosan, plasma+nanochitosan treatment respectively.

Conclusion

This study focuses on the preparation of novel chitosan nanoparticles and their applications to enhance the properties of wool fabrics such as dyeability, fastness, shrinkage, and tensile strength properties at a very low concentration. The nanoparticles are spherical in shape and ranged from 17 nm to 105 nm. The enhanced surface area of nanochitosan particles with higher amount of available active amino groups is also confirmed by higher dye uptake of negatively charged reactive wool dye than bulk chitosan. The combined plasma, bulk chitosan, and nanochitosan treatments improve the hydrophilicity, dyeability, and fastness properties of the wool fabrics.

Surface roughening resulted from ablation process of plasma treatment made positive contribution to the improvement of fiber-chitosan/nanochitosan adhesion, owing to more surface contact. Therefore, the effect of biopolymer on properties of wool fabrics can be improved by plasma surface modification. This outcome is in consistent with area shrinkage values of treated fabrics. These results revealed that chitosan provides shrink-resistant properties to wool, being more evident when wool has been previously treated with atmospheric plasma. After combined plasma+nanochitosan treatment, the area shrinkage of treated wool fabric showed a significant reduction in contrast to untreated one as can be confirmed by SEM images. Fabric tensile strength was also improved with this treatment by better bonding of nanochitosan particles to the fiber surface.

To summarize, this study can be considered as an eco friendly, biocompatible wool process by applying chitosan and nanochitosan to wool previously subjected to atmospheric plasma treatment without deteriorating the bulk properties of wool fabrics.

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