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The Effect of Wool Protein as a Reducing Agent in the Making of Finer Antibacterial Wool Yarns by Nano Silver Synthesis.

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ABSTRACT

In the study at hand a new method for the synthesis of nano silver on wool (without the usual reducing agents) and slenderizing coarse wool fibers in one single bath was considered. Three parameters examined in order to reach the optimum conditions included the concentration of silver nitrate, temperature and processing time. Despite the fact the wool yarns became finer, the tensile strength notably enhanced. *XRD*, *EDX* and *SEM* techniques were used to analyze the wool fibers and the results confirmed synthesis of nano silver on the wool. Also, the antibacterial properties of the wool samples were checked with two different bacteria; *Staphylococcus aureus* and *Escherichia coli*. Overall, the diameter and tensile strength of the treated fibers depicted a significant improvement with partial yellowing.

Keywords: Nano silver, Fine wool, Slenderizing, Antibacterial.

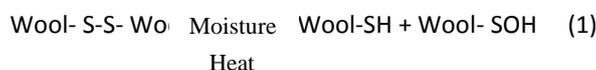
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INTRODUCTION

The remarkable properties of nano particles increasingly extend their applications in textile industry. Silver and its compounds are noted for their low toxicity and distinct properties for many years [1-4]. Various methods employed to synthesis nano silver include photocatalytic reduction [5], chemical reduction [6] radiation-chemical [7] photo-reduction [8], reverse micelle based methods [9] and even biological synthesis [10-11]. Likewise, diverse reducing agents (such as hydrazine and sodium borohydride [12]) have been used to synthesize nano silver. Recently, nano silver has been synthesized on wool fibers by applying a sulphur based reducing agent [13]. In addition, this method had been utilized to slenderize and give antibacterial properties to the fine wool fibers of pile carpet [14]. Furthermore, simultaneous acid dyeing with colloidal of nano silver on wool fiber has been experimented and the findings illustrated tenacity increase and antibacterial properties [15].

Wool is a natural fiber with a various proteins and a mixture of organic substances [16-17]. Autocatalytic degradation of cysteine in the wool proteins with moisture and heat (even below 100°C) is noted [18]. This is the cysteine–cysteine self-degradation and self-cross-linking mechanism [19-20].

Reaction 1 represents the schematic thiol groups creation with water and heat on wool structure [21].



It is noteworthy that making wool finer improved handle, luster, touch and other properties [22-23].

Sulfhydryl, amino, imidazole, phosphate and carboxyl protein groups could react with silver ions and stick to each other. Kumar et al proposed a bonding reaction between silver in oxide form and sulfhydryl (S-H) groups [24].

In the study at hand a novel method for the synthesis of nano silver on wool (without the usual reducing agents) was considered. The research was carried out using various silver nitrate concentrations and processing temperatures/times on wool yarn. Proteins and thiol groups of wool acted instead of reducing agents in this approach. Synthesizing nano silver using wool proteins instead of reducing agents can lead to new characteristics on the fine wool fiber.

EXPERIMENTAL

Materials and methods

Iranian scoured coarse wool yarn with the count of 2.38 Nm was used in this study. Silver nitrate and sodium carbonate were purchased from Merck Co. (Germany). The non-ionic detergent (Diadavin UN) used for scouring wool yarn was from Bayer Co. (Germany).

Table 1: Conditions of preparation of various samples

Sample code	Silver nitrate (%)	Temperature (°C)	Time (min)
A	0.03	70	10
B	0.05	60	10
C	0.03	50	10
D	0.03	60	5
E	-	60	10
F	0.03	60	15

The yarn was first scoured with 2 g/L non-ionic detergent, 1 g/L sodium carbonate at 70 °C, 30 min in L:G = 50:1 and then washed with tap water and dried at room temperature. The scoured wool was processed in the form of yarn on stretching equipment developed at Textile Department, School of Engineering Yadegar-e-Emam Khomeini (RAH), Shahr-e-Ray Branch of Islamic Azad University in Tehran.

The wool yarns were treated with various concentrations of silver nitrate at different temperatures for various time periods with 30% under tension. Experimental conditions are presented in Table 1. The yarns were stretched and post oxidized by 0.5 g/L H₂O₂ at room temperature for 5 minutes under tension to set the wool yarns chemically. Then the yarns were dried at room temperature and cured at 130 °C for 10 min through steaming.

Instrumentals

The samples were analyzed with FTIR Bruker Tensor 27(Germany), X-RAY diffraction Inel Equinox 3000 (France) and SEM Philips XL30. The diameter of the fibers were measured by light microscope from Nikon ELWD 03/0075, Japan. The tensile properties of the yarns were measured with Testometric M500-25CT, UK. The color of samples were decided by spectrophotometer Color-Eye 7000, USA and antibacterial test was carried out based on AATCC100.

RESULTS AND DISCUSSION

Synthesis of nano silver on wool yarn

Wool protein fibers contain free carboxylic acid and amino groups. Cationic compounds can interact with the free carboxylic acid groups to form ionic bonds. Silver ions can attach to sulfhydryl, amino, imidazole, phosphate and carboxyl protein groups. The reaction between silver oxide and sulfhydryl (-S-H) groups of wool has been indicated [24]. Many reducing agents have ability to convert Ag⁺ to Ag⁰. Furthermore, the silver ions are absorbed to the thiol groups within wool fibers through ionic attraction. Ag⁺ was substituted with H⁺ because of the higher positive chemical potential of Ag⁺ (+0.7991). Reactions 1 and 2 point to the reducing ability of silver nitrate, wool fiber and the creation of -S-Ag. Additionally, nano silver can be connected to the imine groups of wool through electrovalence attraction as indicated in Fig 1.

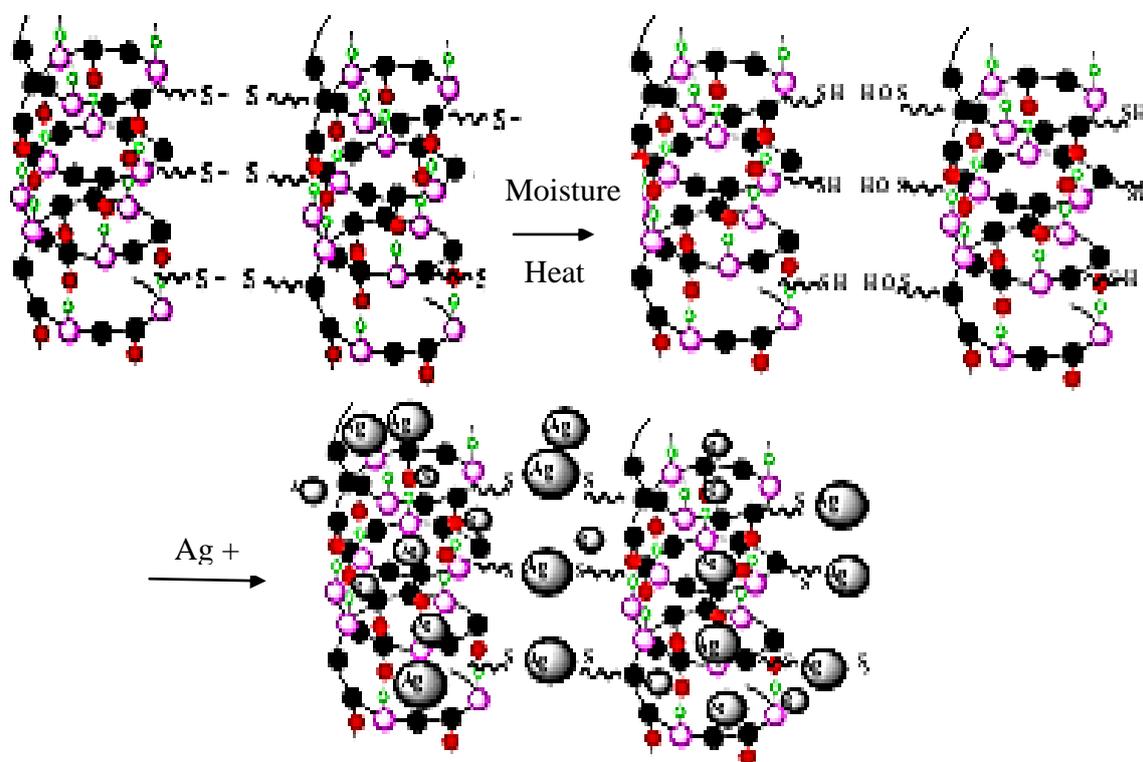


Figure 1: Synthesis of nano silver with side groups and thiol created on wool fiber

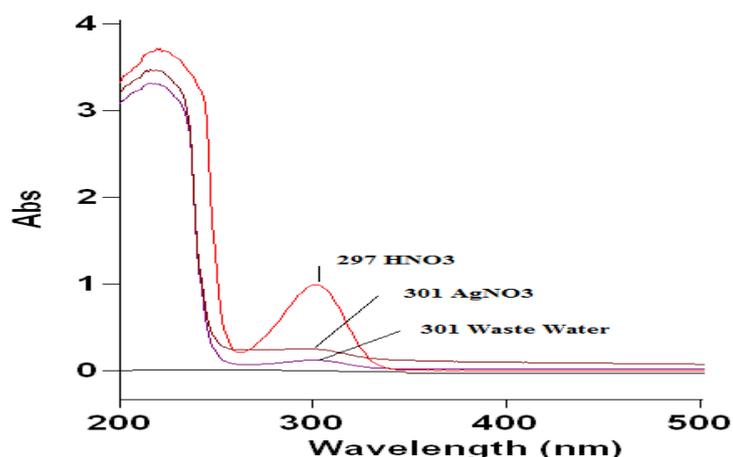
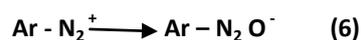


Figure 2: UV-vis absorption spectra of different solution (a: nitric acid, b: silver nitrate, c: remaining solution of sample A)

The thiol groups created on wool fibres due to the presence of moisture and heat reduced silver nitrate to silver metal and shifted the absorption peak from 289 nm to 301 nm in UV-vis absorption of the silver nitrate solution. And this will happen only if silver nitrate is exposed to wool fibers for a minimum of 20 minutes. Reaction 2 shows the dissociation of silver nitrate and reaction 3 indicates the interaction of thiol groups of wool with silver ion. Peak intensity and peak shift are represented in Fig. 2. These values show different concentrations of nitrate ion. A number of processes may account for the change nitrate ion to nitrite ion in the presence of nitric acid (Reaction 4). Besides, nitrite ions produced diazotization reaction with amine groups of wool (5) which resulted in cross-linking on wool chains (reaction 6-7) [25]. The produced crosslinked wool benefits from enhanced tenacity. The diazotization reaction may create azo chromophor on wool leading to wool yellowing.



After the initial synthesis, the continuation of the process causes nano silver to start growing inside the protein chains. The growth rate will depend on processing conditions. For the same reason the tenacity of the treated fibers increased as more cross-linkage occurred within the protein chains of wool fibers.

Tenacity

Tensile properties of the yarn samples were tested with ASTM D2256-97 test method. The percentage of changes in yarn tenacity is reported in Table 2. The results varied (within the range of -11% to 21.3%) for different wool samples obtained through various processing conditions.

The findings illustrate a reasonable tenacity for the sample treated with high concentration silver nitrate (0.05%), 60°C, 10 min due to the synthesis of nano silver and formation of ionic linkages between the protein chains of wool (thiol groups and imine, amide and carbonyl). Therefore, silver nitrate concentration and processing conditions appear to be very important factors. Temperature affects the rate and size of synthesis nano silver that may lead to breakage of some cross-linking between proteins of wool macronucleus. Therefore, temperature must be controlled in the experiment.

Color differences

Silver diffusion into the wool samples and reduction of wool chain protein caused changes in the color of wool samples. The color differences in various wool samples were measured and the results (ΔE) are presented in Table 2. Color variations ranged from 3.4 to 11.9. Thus, the processing conditions influenced the color changes of the samples which were measured with equation 1 and CIE Lab mode of color measuring.

$$\Delta E = ((\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2)^{1/2} \quad (1)$$

Reduction of yarn count

Yarn drawing caused relocation of fibers in the yarn structure; therefore, the count of yarn could be reduced to the results shown in Table 2.

Utilizing a higher concentration of silver nitrate led to the reduction of nano silver and the increase of nano silver synthesis on wool. Here, applying a higher concentration of silver nitrate may be helpful.

FTIR Spectroscopy

Fig 3 depicts the FTIR spectra in wave number range of 1300 cm^{-1} to 2000 cm^{-1} for the raw and other wool samples. The various amides in peptide groups have different absorbency peaks; amide I, 1600-1700 cm^{-1} , amide II, 1500-1600 cm^{-1} and amide III, 1200-1300 cm^{-1} . In the presence of amide groups, the carbonyl groups ($-\text{CO}-$) show their absorbency/stretching peak in the range of 1640-1700 cm^{-1} . The absorbency peak in 1510~1530 cm^{-1} is related to the bending deformation peak of ($-\text{C}-\text{N}-\text{H}$) and represents ($\text{C}-\text{N}$) strongly coupled with ($\text{N}-\text{H}$) bending. The peak positions of the bonds shifted in the stretched wool yarns compared to raw wool yarn.

Table 2: Tenacity, change of colour (ΔE) reduction of yarn count and antibacterial properties for different samples

Sample Code	Tenacity change (%)	ΔE	Count yarn change (%)	Fineness reduction (%)	<i>Escherichia coli</i> (%R)	<i>Staphylococcus aureus</i> (%R)
A	-7.6	11.8	10.6	34.4	48	58
B	21.3	9.0	9.0	40.4	39	56
C	10.7	11.9	13.6	27.9	47	72
D	1.9	6.0	12.7	19.3	45	67
E	-11.0	3.4	15.1	26.5	62	93
F	-4.9	4.1	9.2	28.2	43	62

Raw wool were had for *Escherichia coli* (%R= 56) and *Staphylococcus aureus*(%R=87) antibacterial properties.

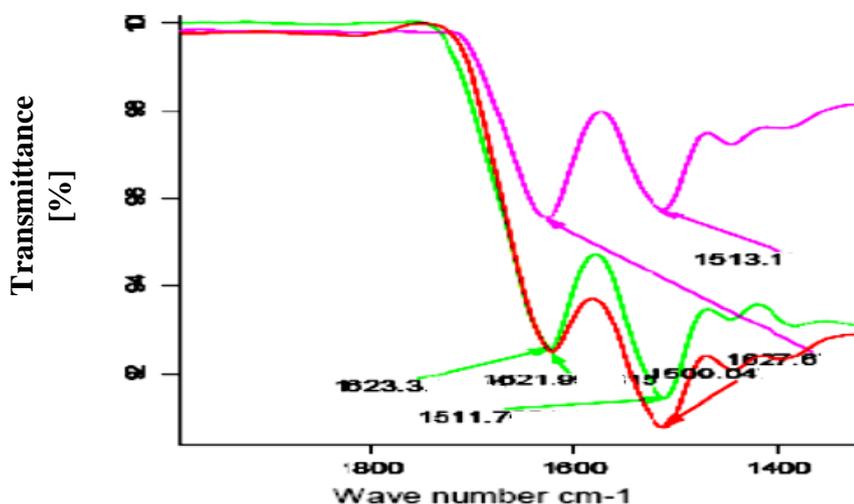


Figure 3: FTIR spectra of some wool samples from top raw wool, B and C samples

Moreover, the synthesis of nano silver on wool caused changes in some peaks. The peak of Carbonyl group samples shifted between 2-10 cm^{-1} and the peak of some imine groups shifted depending on the experiment conditions. The changes can be related to processing conditions. Therefore, the shift in peaks indicated nano silver synthesis and protein conformation changes due to the extension of wool.

SEM and EDX Analysis

SEM proved synthesis and loading of silver nano-particles on the wool yarns as indicated in Fig 4. EDX results presented in Fig 4 confirmed the presence of nano silver on the wool fibers and also proved the effects of the processing conditions on the silver content of the wool surface. Amount of nano silver in the samples depended on experimental conditions, silver nitrate concentrations, temperatures and time. Considering these parameters, B sample had 0.32 (% Wt, Ag), and C sample 0.19 (% Wt, Ag).

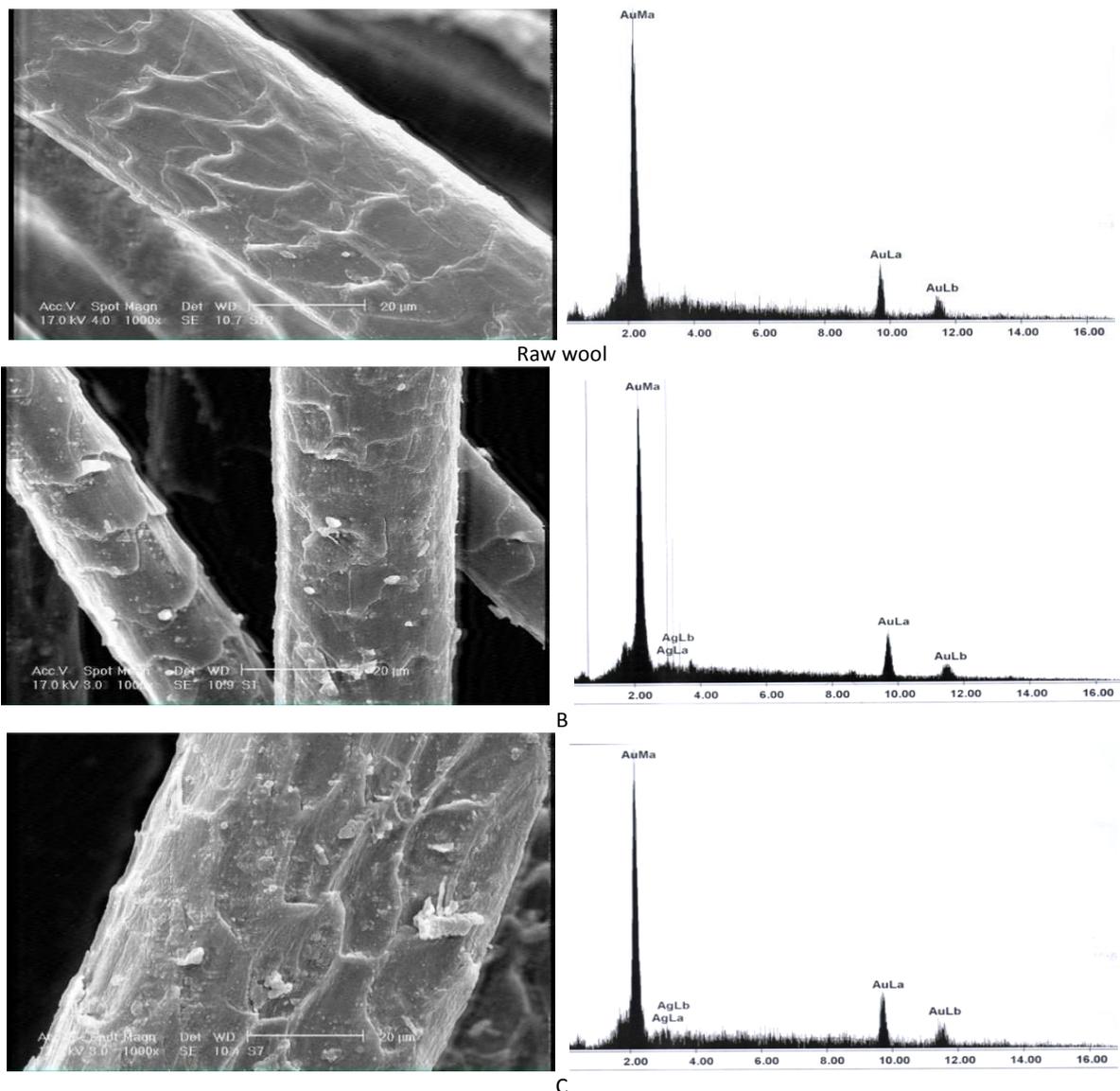


Figure 4: SEM and EDX images of samples (Raw, B and C samples)

X-ray

X-ray diffraction patterns appear in Fig 6. Wool exhibited a broad peak corresponding to amorphous structure. Interestingly, a sharp peak was observed at $2\theta=38^\circ$ for the raw wool with the intensity of 550 cps. The same can be noted for wool–Ag with the intensity of 550–750 cps as indicated in Fig 5. The variation of peaks intensity depended on the processing conditions such as silver nitrate concentration, time and

temperature. It turns out that the processing conditions were very important in both of nano silver synthesis and wool damage.

Full width at half maximum (FWHM) of X-ray diffraction represents changes in the range of 1.009 to 1.0252 which indicates that the structure and morphology of the samples changed. Changes in structure depend on condition of synthesis nano silver and extension of wool yarn samples.

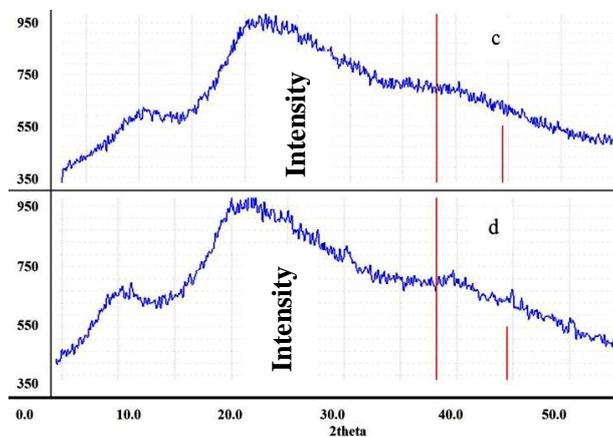


Figure 5: X-ray diffraction patterns of some wool samples.

Wool fiber fineness

The fibers diameter averages of different samples were measured and percentages of fineness reduction were reported in Table 2. The fiber diameter of various samples reduced from 19.3% to 40.4%. The results illustrate that changes in the diameter of wool fibers depended on silver nitrate, time and temperature of the process.

Antibacterial properties

The antibacterial properties of the treated wool samples were evaluated by colony count method according to AATCC 100. *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive) bacteria were used as a testing organisms. The microbial reduction was determined by counting the colony forming units (CFU) and calculating the bacteria reducing percentage (R) after incubation, using Eq. 2 and the results are presented in Table 3.

$$R(\%) = \frac{A - B}{A} \times 100 \quad (2)$$

The antibacterial properties of various wool samples confirmed the effect of various processing conditions and types of the bacteria. However, the processing conditions and reducing agent led to wool damages and consequently decreased the antibacterial properties of wool as noticed in sample E.

Therefore, increasing silver nitrate concentration, time and temperature led to the reduction of silver nitrate and damage to wool. Thus the antibacterial properties of the samples were reduced as indicated in Table 2.

CONCLUSIONS

This paper explored a new method of the in situ synthesis of nano silver within wool fibers protein chains (without using any reducing agent, benefiting from wool yarn extension) to obtain fine wool fibers. The synthesis of nano silver was confirmed by SEM, EDX and XRD patterns on wool fibers. Interestingly, the higher tensile strength observed was related to the ionic cross-linking of synthesized nano silver within protein chains of wool fibers. Overall, the fine wool treated with 0.05% AgNO₃ at 60°C for 10 minutes was selected as optimum fine wool with 40.4% higher fineness, 21.3% higher tensile strength and 11.9 color change.

Antibacterial results showed the relation between increase of silver nitrate/temperature and synthesis of nano silver.

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