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ELECTROCONDUCTIVE POLYAMIDE YARNS WITH GREEN SYNTHESIZED SILVER NANOPARTICLES

GÜMÜŞ NANOPARTİKÜLÜN GREEN SENTEZİ İLE ELETROİLETKEN POLİAMİD İPLİKLER

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ABSTRACT

The objective of this research is to study antibacterial and antistatic properties of polyamide (PA) yarn which coated with silver nanoparticles and carboxymethyl starch (CMS). Silver nanoparticles were synthesized by a green synthesis method and coated onto polyamide (PA) yarns. At the end of coating process, the composite PA yarns were removed and the absorbance of supernatant solutions was measured using Ultraviolet and visible light absorption (UV-Vis) techniques. The presence of nanosilver onto PA composite yarns was confirmed by plasma/optical emission spectroscopy (ICP/OES) and scanning electron microscope (SEM). Electrical conductivity of composite PA yarns was measured by four point probe electrical conductivity measurement technique and was changed from $1{,}452x10^{-5}$ to $2{,}853x10^{-3}$ S/cm. Also, the antibacterial activity of the composite PA yarns was measured by Kirby-Bauer method and all composite and PA yarns showed antibacterial activity against *E. coli* and *S. aureus.*

Keywords: Silver nanoparticle, polyamide multifilament yarn, green synthesis, antistatic and antibacterial property

ÖZET

Bu araştırmanın amacı, gümüş nanopartiküller ve karboksimetil nişasta (CMS) ile kaplanan poliamid ipliğin antibakteriyel ve antistatik özelliklerini incelemektir. Gümüş nanopartiküller poliamid (PA) lifleri üzerine yeşil sentez yöntemi ile kaplanmıştır. Kaplama işlemi sonunda, kompozit PA iplikler kaldırılarak kalan çözeltinin absorbans değerleri UV görünür spektrum tekniğinde ölçülmüştür. İpliklerde nano gümüş varlığı, ICP-OES spektroskopi ve taramalı elektron mikroskobu (SEM) ile doğrulanmıştır. Kompozit ipliklerin elektriksel iletkenliği dört nokta elektriksel iletkenlik ölçüm tekniği kullanarak $1{,}452x10^{-5}$ – $2{,}853x10^{-3}$ S/cm aralığında ölçümler kaydedilmiştir. Ayrıca, kompozit PA ipliklerinin antibakteriyel aktivitesi Kirby-Bauer yöntemi ile ölçülmüş ve tüm kompozit PA iplikler *E. coli* ve *S. aureus*'a karşı antibakteriyel aktivite göstermiştir.

Anahtar Kelimeler: Gümüş nanopartikül, poliamid multifilament iplik, yeşil sentez, antistatik ve antibakteriyel özellik

INTRODUCTION

The progress of new clothing products based on the connection of nanophased materials on textile fibers has recently been of increasing interest to both the academic and the industrial sectors Nowadays, a broad gap of nanoparticles with diverse structures can be connected on the fibers, bringing new properties to the latest textile product.

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Silver nanoparticles easily interact with other particles due to their physical, chemical, thermal, optical, high electrical conductivity and biological properties which lead to potential applications in industrial fields such as antimicrobial agents, conductive coating and sensors. Nanostructured silver deposited on textile surfaces can be used to make smart functional textiles, which have extensive potential for applications ranging from antibacterial materials to conductive textiles and electronic sensors (Perelshtein et al., 2008; Guzmán, Dille & Godet, 2009; Pollini et al., 2009; Xue et al., 2012; Dong, Zhang, & Cai, 2014; Zahran., 2014; Lee et al., 2015; Wei et al., 2015; Bhowmick, & Kaul., 2016).

There are various methods to obtain conductive textiles such as the use of conductive agent and particles, metallic fibers, coating with conductive polymers. Among the various chemical methods used for the preparation of silver nanoparticles, chemical reducing method by using a reducing agent such as sodium borohydrate citrate (or ascorbate in a silver salt solution is the most common. This chemical synthesis method endures complicated production steps and evacuates a lot of wastewater, which will attack the environment and human health (Puiso, Prosycevas, & Tamulevičius, 2009; Kardarian, 2014; Ashayer Soltani, Hunt, & Thomas, 2016; Montes-Hernandez et al., 2021; Yu et al., 2021).

Chemical reducing agents are commonly associated with environmental toxicity or biological hazards. Therefore, the development of silver nanoparticles based on natural extracts is observed as most appropriate method for environmental reasons. It can be provided a "green" approach to modify textile surfaces fiber without undesirable chemicals. The concept of green synthesis of nanoparticles was first contributed by Raveendran et al. (2003) in which glucose acted as a reducing agent and starch played the role of particles stabilizer. Silver nanoparticles were arranged in another study by means of using the carbohydrate polymer, sodium carboxymethyl cellulose for the nanoparticle preparation and in that case, sodium carboxymethyl cellulose was found to work effectively as both a reducing and stabilizing agent. The utilization of nontoxic chemicals, environmentally benign solvents and renewable materials are some of the key issues that merit important consideration in a green synthesis strategy. Also, green methods have also been adduced for the production of AgNPs with a narrow size distribution (Raveendran, Fu, & Wallen, 2003; Elzey, & Grassian, 2010; Osório et al., 2012; Hebeish et al., 2011).

Hasan et al. (2019) reported a novel route for the coloration of polyester fabric with green synthesized silver nanoparticles (G-AgNPs@PET). They determined that the antibacterial properties of fabric were also found to be good as more than 80% bacterial reduction was determined even after 10 washing cycles. Pivec et al. (2017) studied new green in-situ process for introduction of silver nanoparticles on the cellulose fibres, using sodium hydroxide and silver nitrate. They investigate antibacterial properties against *S. aureus*, *Candida albicans* (*C. albicans)* and *Klebsiella pneumonia (K. pneumonia)* by using AATCC 100-1999 standard methods and determined good antimicrobial activity even after 20 washing cycles. El-Shishtawy et al. (2011) developed a practical procedure for the in-situ production of silver nanocoated cotton fabric and emphasized that green synthesis of silver nanoparticles, is an ecological and viable approach for the in situ forming silver nanoparticles. They investigated antibacterial and antifungal properties against. *E. coli* NRRL B-210, *Bacillus subtilis* (*B. subtilis)* NRRL B-543 and *S. aureus* NRRL B-313 and *C. albicans.* Ravindra et al. (2010) investigated that fabrication of antibacterial cotton fibres loaded with silver nanoparticles via 'green approach'. AgNP particle size was determined to have ~20 nm according to SEM images. Also, they found the AgNPs containing cotton fibres have exhibited > 1.5 mm inhibition zone in all the cases. Moreover, they emphasized that the inclusion of silver nanoparticles into cotton fibres enhanced their thermal stability and elongation properties. Fatma Nur et al. (2021) studied polyamide 6, polyamide 6/honey, and polyamide 6/honey/boric acid nanofibrous mats were fabricated by electrospinning and electrospraying technique to be used in wound healing applications. They demonstrated that antibacterial tests the polyamide 6/honey fiber was effective against *E. coli*, while the polyamide 6/honey fibers loaded with boric acid at 5 and 10 wt% concentration were effective against both *E.coli and S. aureus.*

Abdel-Halim et al. (2017) reported that hydroxypropyl cellulose molecules have certain molar substitution just enough for achieving complete water solubility using different reaction conditions, reaction duration and temperature. They determined that the molar substitution rises by increasing the concentration of sodium hydroxide during the alkalization step, up to 10% of the weight of cellulose and further increase above this limit is accompanied by gradual decrement in the molar substitution. El-Rafie et al. (2011) synthesized silver nitrate using in an alkaline aqueous solution of silver nitrate ($AgNO_3$)/hydroxypropyl starch (HPS). They studied the influence of the reaction parameters, such as the concentration of HPS and $AgNO_3$, pH, temperature, and duration of the reaction medium on the size and agglomeration of the formed AgNPs. Also, they emphasized that HPS is water soluble/ biocompatible starch derivative which proves a dual rule as reducing agent for silver ions and as stabilizing agent too for the formed

AgNPs. Tang et al. (2013) investigated that multifunctionalization of cotton through in situ green synthesis of silver nanoparticle. They studied using carboxymethyl cellulose (CMC), the effects of pH value, heating treatment, soaking time of silver ions and post-placement duration on the color durability of cotton were investigated.
Many recent studies focus on the green synthesis of AgNPs for textiles with improved applications. In this context, CMS may be an applicable green stabilizing agent for AgNPs with remarkable. CMS is a water-soluble polysaccharide which is widely employed as an additive; it is biodegradable and non-toxic products that are finding an increasing number of applications. CMS can be used as thicker, binder and emulsifying agent in various applications.
In order to obtain a multi-functional yarn with an extremely high advancement in adhesion of silver nanolayer, the polyamide multifilament yarn has been chosen as the surface. The polyamide yarns with multifunctional properties can be applied in various commercial usages due to good electrical conductivity, light weight, and corrosion resistance along with enhanced mechanical properties. Withal, Polyamide is an electron-rich and polar synthetic polymer (polyamide) usually made of adipoyl chloride and hexamethylene diamine monomers to form a linear molecular chain (Ravindra et al., 2010; Abdel-Halim, & Al-Deyab, 2011; El-Rafie et al., 2011; El-Shishtawy et al., 2011; Tang et al, 2013; Montazer, & Nia, 2015; Pivec et al, 2017; Hasan et al., 2019; CMS, 2022).

In this study, in-situ synthesis of nano-silver on PA yarns has been introduced through an environmentally method in order to create a thin layer of silver nanoparticles on PA yarns. This will produce an electro conductive PA composite yarns with considerable antibacterial properties. This process was performed by green synthesis approach in a two-step reaction process, a method that did not imply any toxic chemicals.

MATERIAL AND METHOD

Material

Polyamide multifilament yarns (technical properties; 70 denier, two ply,10 fılament (70/2/10)) were supplied from Karacasu Textile, Turkey. $AgNO_3$ (>99 %) were purchased from Tekkim Chemicals. Carboxy methyl starch (CMS) was synthesized from potato starch waste in ÜSKİM laboratory by Dolaz et al (Dolaz, and Akarsu, 2018). Ethanol acetone and sodium hydroxide (NaOH) were supplied from Sigma Aldrich and were used as received.

Method

Preparation of Silver Coated Polyamide Yarns

PA multifilament yarns were pretreated with acetone and ethanol, respectively. After the PA multifilament yarns were mixed with NaOH solution for 30 minutes, CMS solution prepared at 50 °C. After dissolution of CMS powders, the solution including CMS cooled to 25 °C. PA multifilament yarns were treated with prepared CMS solution at 25 °C for selected concentration. Then, the wetted PA yarns were taken out. $AgNO_3$ solution was added dropwise to CMS solution and PA yarn was treated with that solution at 25 °C for 2 h to obtain a thin silver nanolayer formation on the fiber surface. Selected concentrations of $AgNO_3$ (i.e.; 0,25 g/100 mL, 0,5 g/100 mL, 1 g/100mL, 2 g/100mL and 5 g/100mL) were dissolved in distilled water at 25 °C.

After 5 minutes addition of silver nanoparticle solution, the CMS solution acquired light yellow color indicating the reduction of silver nitrate to nano metallic silver. The color of reducing solution turned light brown depending on amount of silver ions. Finally, the composite PA multifilament yarns were washed with distilled water and dried in an oven at 60 °C.

Table 1.The Amount of $AgNO_3$ and CMS in Coating Process

Sample	$AgNO_3$ (g)	CMS (g)
S025	0.25	0.05
S05	0.5	0.1
S1	1	0.2
S2	2	0.4

The effect of process parameters such as $AgNO_3$ and CMS concentration were investigated and optimum conditions have been determined for the coating process (Table 1). In order to investigate the effect of NaOH on the yarns, NaOH and without NaOH coating were made on multifilament PA yarns.

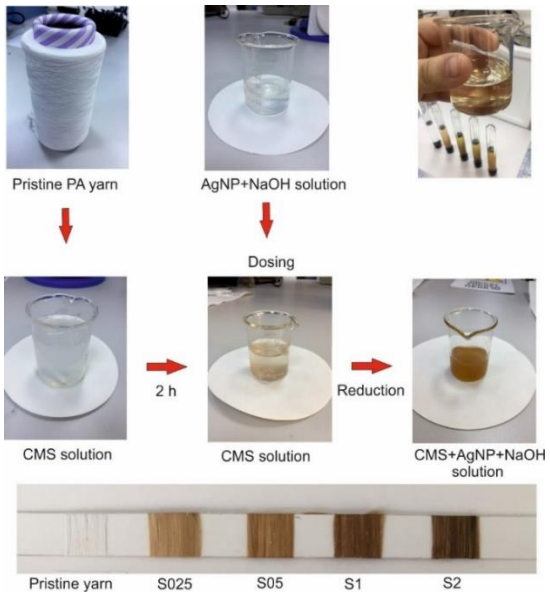

Figure 1. Preparation of AgNPs Coated Composite PA Yarn

Preparation of CMS Powder

Initially, the reactions were performed in a glass batch reactor equipped with mechanical stirrer and thermocouple. The first process was the purification of the starches. waste potato starch (WPS) (50 g) and 3 g of NaOH in 15 mL water were suspended in a certain volume of isopropanol (IPA) and heated to 45 °C. Then, hydrogen peroxide (5 mL, 30% w/w) was added and the mixture was stirred for 90 min. After cooling down to room temperature, the sample was neutralized with glacial acetic acid, washed with distilled water three times, and dried at 40 °C in vacuum. In the second step, the carboxymethylation of WPS was realized and the sodium salt solution of monochloroacetic acid was dissolved in IPA in the glass reactor and an aqueous solution of sodium hydroxide was added. After 15 min, 10 g of starch (ca.15 wt% moisture) and NaOH microgranules were slowly introduced (Dolaz, & Akarsu, 2018).

Characterization of Silver Nanoparticle Solution

Firstly, the solution was characterized by Ultraviolet and visible light absorption (UV-Vis) Spectroscopy. A Perkin-Elmer Lambda 750 spectrometer was used to investigate the mono dispersity of the nanosilver particles in the solution. It is well known that silver nanoparticles exhibit ruby red color in water, having an intense absorbance band around 400–450nm arising due to surface plasmon excitation vibrations in the metal nanoparticle (Montazer, Babaahmadi, 2015).

ICP/OES Spectroscopy

The concentration of silver deposited on the composite PA yarns was measured by ICP/OES spectroscopy.

Characterization of Silver Coated Polyamide Yarns

The quantity of silver in composite PA yarns was determined by Perkin- Elmer Optima 2100 DV ICP/OES. In this process, composite PA yarns of 0.2 g were added to 8 ml nitric acid and a microwave digestion was executed the conditions were 800 W, 190 ^{o}C for 15 min. For measuring, the resulting material was diluted with two distilled water to a volume of 25 mL (Textor et al., 2010).

In order to investigate the formation of silver nanoparticles on the PA yarns, a Carl Zeiss Evo LS10 scanning electron microscope (SEM) is used with an accelerating voltage of 3 kV. The samples were gold coated and placed on the aluminum stub and observed under vacuum. The thickness of the AgNPs coated PA yarns was measured by Mitutoyo MDC-25SB Digimatic Outside Micrometer. The direct current (DC) electrical conductivity measurements were carried out by a Entek FPP 510 DC conductivity meter using four point probe method. The antimicrobial activity of AgNPs coated PA yarns was determined by evaluating of inhibition zones after 24 h of incubation at 37 ^{o}C by ISO 20645:2004.

Antibacterial Efficacy

Firstly, a mixture of nutrient broth and nutrient agar in 1 L distilled water at Ph 7.2 as well as the empty Petri plates were autoclaved. The agar medium was then cast into the Petri plates and cooled in laminar airflow. Approximately 10^5 colony-forming units of each bacterium were inoculated on plates, and then each yarn samples was planted onto the agar plates.

The assessment of antibacterial activity was based on the observation of the presence of bacterial growth in the contact zone between agar and specimen (inhibition zone), on the appearance and size of the inhibition zone formed around the specimens and on the evaluation of bacterial growth under the sample. Zones of inhibition were measured in terms of millimeter after 24 hr of incubation at 37 ^{O}C (Guzmán, Dille & Godet, 2009; Khalil-Abad & Yazdanshenas, 2010; Wu et al., 2014; Raghavendra et al., 2016; Holubnycha, Pogorielov, & Korniienko, 2017).

RESULTS AND DISCUSSION

Characterization of Silver Nanoparticle Solution

The characterization of the solutions containing silver nano-particles was carried out using UV–Vis spectrophotometer. Figure 3 shows the UV–Vis spectra of the AgNPs colloid solutions which were obtained in the wavelength range 300–800 nm.

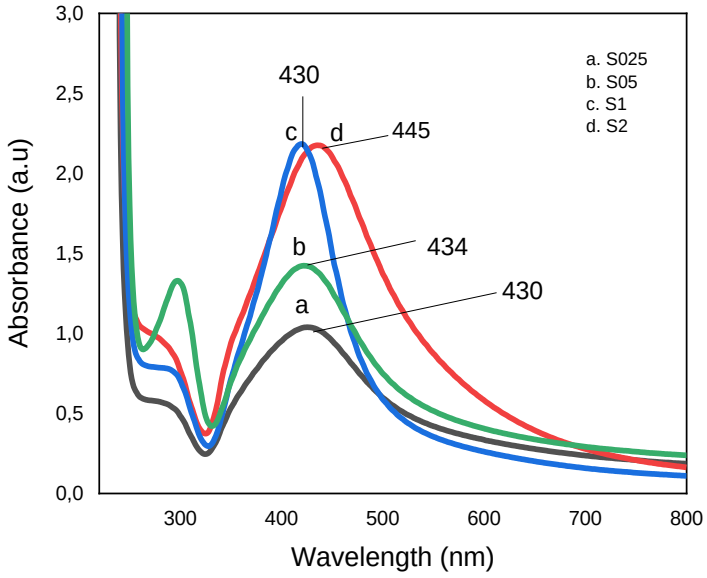

Figure 2. UV-Vis Spectra of AgNP Solutions at Different $AgNO_3$/CMS Concentrations (a.S025, b.S05, c. S1, d. S2)

It was determined that the absorbance value of this peak increased due to the increase in the amount of silver in the solution which reflects the formation of silver Nanoparticles (Figure 2). The UV–Vis spectra showed a sharp peak in the visible region around 430-450 nm due to surface plasmon excitation and it confirmed the formation of AgNPs. The absorbance peak of Ag ions normally appears in range of 400 nm and this peak was not recorded here, indicating that, full reduction of Ag^+ was carried out by the CMS in our study. This conclusion has been arrived basing on the relevant literature on silver nanoparticles.

Comparing with Figure 2 a-d for the Ag Nanoparticles, Silver colloidal obtained at lowest AgNP concentration appeared yellow, showing a surface plasmon resonance (SPR) peak at 430 nm. As the AgNP concentration increased, the color of the solution gradually changed to yellow-orange, showing a blue shift of the SPR peak from 430 nm to 445 nm with increase in its intensity but decrease in its broadness. This study shows that the absorption intensity increases as the concentration of AgNP increases, which reflects in the formation of more Ag nanoparticles. For all that, It was observed that there was no significant difference in S1 and S2 coded composite solutions in terms of absorbance values.

These approximate absorbance values related that the fact that the amounts of $AgNO_3$ used are very close to each other. The primary study shows that the absorption intensity increases as the concentration of $AgNO_3$ increases, which reflects in the formation of more Ag nanoparticles. These possible changes in the SPR band depend on particle size, shape, state of aggregation, and dielectric medium. At a low concentration of $AgNO_3$, the maximum absorption wavelength gives rise to a blue shift, meaning a decrease in the particles size. This conclusion has been arrived basing on the available literature on silver nanoparticles.

According to these results, the low wavelength and narrow peak width reflect a small particle size distribution. The narrower widths of the SPR bands confirm the smaller size and more uniform size distribution of the silver nano-particles by increasing concentration (Ravindra et al., 2010; Montazer et al., 2012; Hebeish et al., 2013; Kanmani, & Lim, 2013; Abdel-Halima, Alanazia, & Al-Deyab, 2015 ; Paszkiewicz et al., 2016; Saad et al., 2016).

Characterization of Polyamide Yarns

The quantity of silver adsorbed on the composite PA yarns was measured quantitatively by ICP/OES method (Table 2).

Table 2. The Quantity of Silver Adsorbed on The Composite PA Yarns

Parameter	Sample	The quantity of silver (mg/cm^2)
$AgNO_3$	S025	0.017
	S05	0.006
	S1	0.081
	S2	0.089

It was determined that the quantity of silver adsorbed on the composite PA yarns increased when the $AgNO_3$ concentration increase. The Ag contents in S025, S05, S1 and S2 were found to be 0.13, 0.45, 0.61 and 0,67 mg/L. It was determined that there was no significant difference in S1 and S2 coded composite PA yarns in terms of adsorbed silver quantity.

Surface Morphology of Composite Polyamide Yarns

In the section, surface morphology was investigated in the absence of NaOH. In figure 3, the smooth surface of synthetic PA multifilament yarns was observed before the coating process.

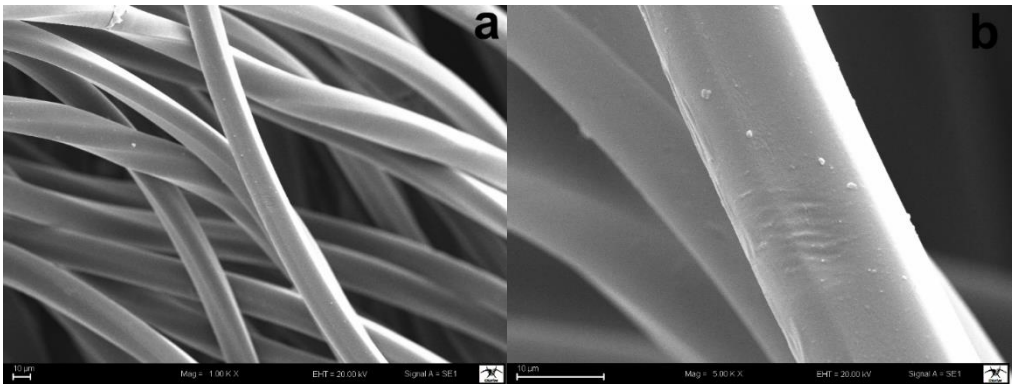

Figure 3. SEM Images of Uncoated PA Yarn (Mag a:1.00 KX , b:5.00 KX)

Figure 4 shows the SEM images of AgNPs coated composite PA yarns which were processed in the absence of NaOH at different concentrations.

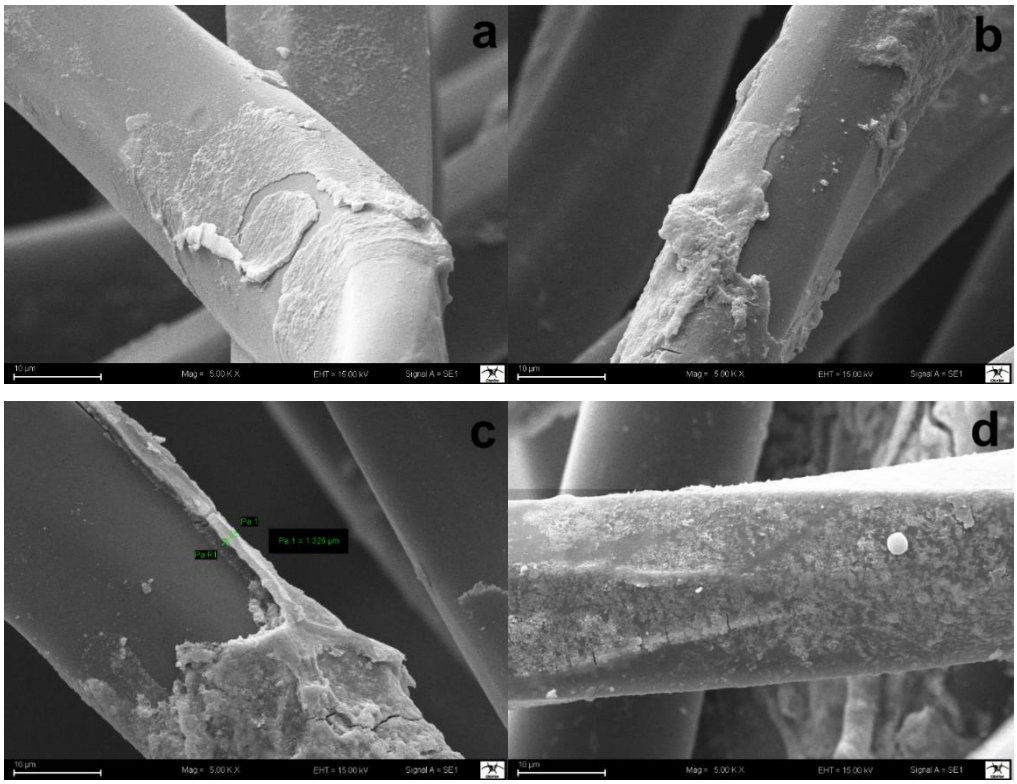

Figure 4. SEM Images of AgNPs Coated PA Yarns Without NaOH (a. S025 b. S05, c. S1, d. S2, Mag: 5.00 KX, Scale: 10 µm)

Figure 4 shows the SEM images of coated PA yarns in the absence of NaOH. It was observed that the coating thickness of the composite PA yarns increased and the coating homogeneity decreased when the silver concentration increased. In addition, the presence of agglomerated silver nanoparticles on the surface of the PA fibers was observed. The agglomerated particles may be attributed to process mixing speed of the silver nanoparticles during dosage. At high concentrations of silver nitrate, most of the carboxyl sites in polyamide chains were occupied which caused the formation of a continuous silver nanoparticle network producing a nanolayer on the fiber surface (Montazer & Nia, 2015; Babaahmadi, & Montazer, 2015; Sadanand et al., 2017).

Figure 5 shows the comparison of surface morphology of S1 coded composite PA yarns in the absence and in the presence of NaOH.

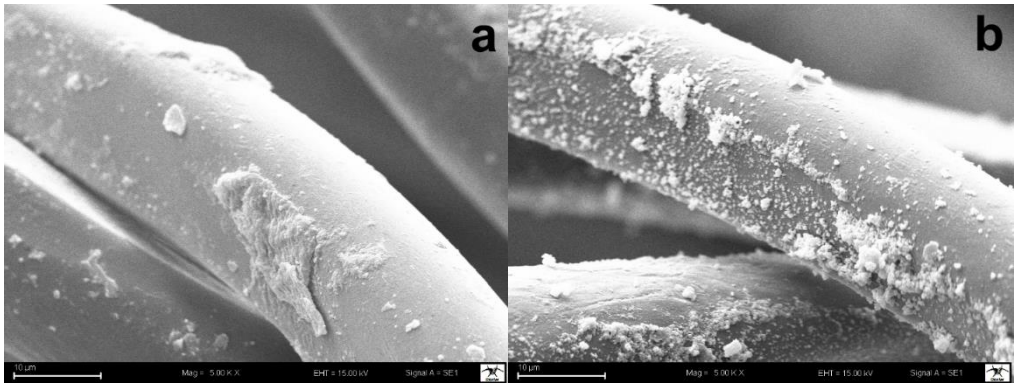

Figure 5. SEM Images of S1 Coded Composite PA yarns (a. In the absence of NaOH, b. In the presence of NaOH, Mag: 5.00 KX, Scale: 10 µm)

The presence of NaOH had a remarkable effect in the formation of AgNPs coated PA yarn surface. In the presence of NaOH, relatively more homogeneously dispersed and less agglomerated AgNP was observed in our study (Figure 5).

SEM observations confirmed the presence of NaOH of silver coating more homogeneous onto yarns surface. It can be explained that the surfaces of yarn seen the less agglomeration with more silver bonding. NaOH is found to play an important role in creating specific intermediates in the reduction of Ag^+ to Ag^0 and in increasing the rate of formation of the AgNPs in Nishimura et al study. In that study, possible reasons why NaOH significantly accelerated the formation process of AgNPs; solid-liquid interface reaction and higher reduction rate constant of Ag(OH). In another study in the literature, when hydroxylamine hydrochloride (HH)/NaOH was used as a reductant in the $AgNO_3$ reduction process, it was determined that the order of addition of chemicals to the reaction mixture significantly affected the grain size and agglomeration degree of nanoparticles. The quasi-spherical nanoparticles with smaller average sizes and less agglomeration degree were obtained when HH/NaOH solution was added to $AgNO_3$. In our study, results consistent with the literature (Nishimura et al., 2011; Kurt & Çelik, 2020).

Electrical Conductivity of Polyamide Yarns

The DC electrical conductivity measurements were repeated five times with different parts of the composite yarns and the arithmetic average of the results was used. The electrical conductivity of composite PA yarns without NaOH depending on $AgNO_3$/CMS concentration was given in Table 3.

Table 3. DC Conductivity of Composite PA Yarns without NaOH Depending on $AgNO_3$/CMS wt%

Yarn Code	Thickness (µm)	Coating (%)	Conductivity (S/cm)
Uncoated	590	-	-
S025	593	0.50	$1.452x10^{-5}$
S05	600	1.69	$3.528x10^{-4}$
S1	601	1.86	$2.566x10^{-3}$
S2	603	2.20	$2.853x10^{-3}$

In the silver coating process of composite PA yarns; it was determined that the electrical conductivity increased from $1.452x10^{-5}$ S/cm to $2.853x10^{-3}$ S/cm depending on the increase in $AgNO_3$/CMS concentration. It has been determined that silver coated PA composite yarns can be evaluated in the conductive region in agreement with the literature. The Ag and CMS amount in the coating solution are the key factors in controlling its electrical conductivity. The best electrical conductivity was measured for S1 and S2 coded composite yarns. As the silver nanoparticle content is higher in S1 and S2 yarns, so the conductivity of the solution increased, corresponding to the hypothesis of controlled releases of Ag ions in aqueous solution (Pıca, Fcal and Guran, 2012). According to the electrical conductivity and surface morphology analysis, optimum coating was determined as for S1-coded yarn. According to these measurements, when the coating thickness increased on yarn surfaces, the electrical resistance was decreased and electrical conductivity increased.

NaOH is found to play an important role in creating specific intermediates in the reduction of Ag^+ to Ag^0 and in increasing the rate of formation of the AgNPs in Nishimura et al study. In that study, possible reasons why NaOH significantly accelerated the formation process of AgNPs; solid-liquid interface reaction and higher reduction rate constant of Ag(OH) In another study in the literature, when hydroxylamine hydrochloride(HH)/NaOH was used as a reductant in the $AgNO_3$ reduction process, it was determined that the order of addition of chemicals to the reaction mixture significantly affected the grain size and agglomeration degree of nanoparticles. The quasi-spherical nanoparticles with smaller average sizes and less agglomeration degree were obtained when HH/NaOH solution was added to $AgNO_3$. In our study, results consistent with the literature. However, it was determined that composite PA yarns with more homogeneous AgNPs distribution and less agglomerated silver nanoparticles had higher electrical conductivity values. For example, in the S1 coded yarn, the electrical conductivity was measured as $2.566x10^{-3}$ S/cm in the absence of NaOH, while the electrical conductivity was measured as $2.114x10^{-2}$ S/cm in the presence of NaOH. This increase was evaluated as a result of improved coating homogeneity in the presence of NaOH (Nishimura et al., 2011; İlkan, 2020; Kurt & Çelik, 2020).

Antibacterial Activity of Polyamide Yarns

The antibacterial activity of composite PA yarns was evaluated against *E. coli* (ATCC 25923) and *S. aureus* (ATCC 25922) using ISO 20645:2004 standard. Figure 6 and Table 4 present antibacterial activity of AgNPs coated composite PA yarns for different $AgNO_3$/CMS concentrations.

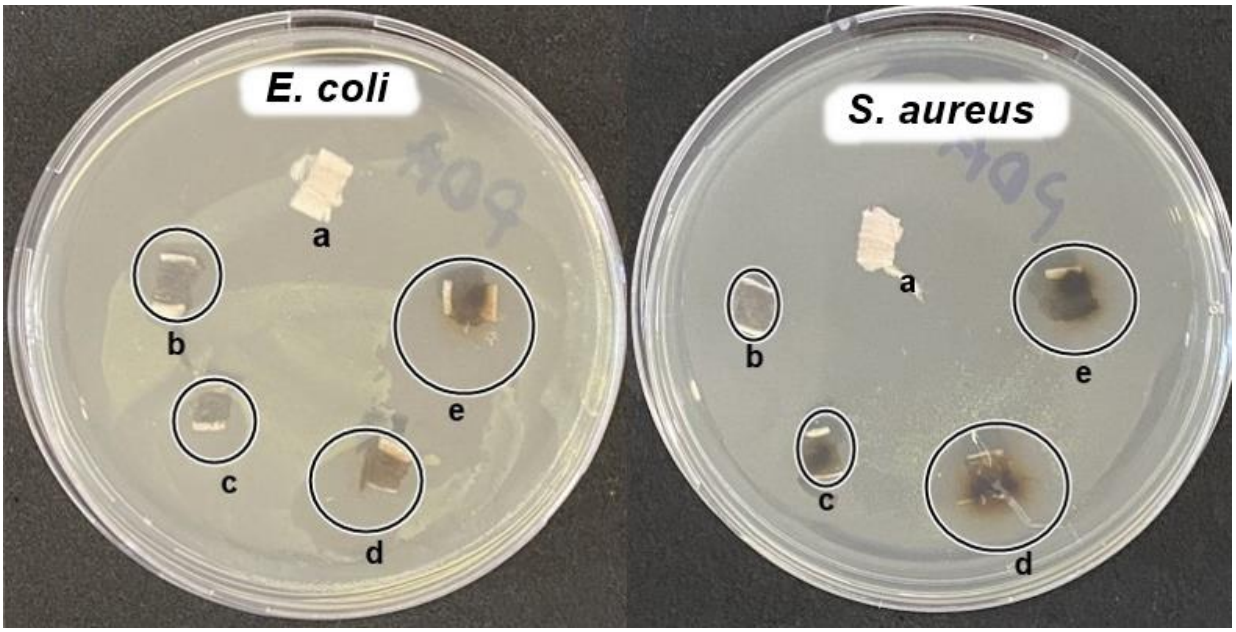

Figure 6. The Antibacterial Activity of AgNPs Coated Composite PA Yarns Against to *E. coli* and *S. aureus* (a:Uncoated yarn, b:S025, c:S05, d:S1, e:S2)

Figure 6 shows that the uncoated PA yarns, which were used as control, did not show any antibacterial activity. The AgNP-coated yarns placed on the bacteria-inoculated surfaces killed all the bacteria under and around them. According to the results, antibacterial activity against *E. coli* and *S. aureus* was good for all AgNPs coated composite PA yarns. However, inhibition zone measurement showed variation. The inhibition zone for *E. coli* was measured between 7.29 mm and 12.27 mm; it was measured between 5.63mm and 12.6mm for *S. aureus.*

Table 4. Inhibition Zone of Composite PA Yarns for *E.coli* and *S. aureus*

Yarn Code	***E. coli***	***S. aureus***
	Inhibition Zone (mm)	
Uncoated	-	-
S025	7.29	5.63
S05	7.11	6.21
S1	10.13	12.6
S2	12.27	11.32

According to inhibition zone measurements, antibacterial activity increased with increasing $AgNO_3$/CMS concentration against *E. coli* and *S. aureus.* The interactions between Ag ions with bacteria, the metabolic activity of bacteria can change and finally cause their death. Silver nanoparticles show good antibacterial properties due to their large surface area to volume ratio, which provides a better contact with microorganisms. AgNPs also have the potential, through oxidation–solvation, to cross cell membranes at an increased rate into the cytosol to disrupt intracellular protein thiol groups. The antibacterial properties of silver are caused by the loss of biochemical competence via the binding of AgNPs to bacterial cell walls and cell membranes and from interactions with the thiol groups of bacterial proteins. The higher diameter of inhibition zone around the sample shows that the AgNPs-coated yarn has a better antibacterial effect. The antibacterial property of composite PA yarns can be attributed to the combination of chemical and physical interactions of bacteria with silver particles (Guzmán, Dille & Godet, 2009; Khalil-Abad & Yazdanshenas, 2010; Wu et al., 2014; Holubnycha, Pogorielov, & Korniienko, 2017; Moazzenchi, & Montazer, 2019).

CONCLUSIONS

This research presents a novel and easy method of green synthesis of silver NPs on PA yarns. The synthesized Ag NPs were coated on polyamide yarn so as to enhance the multifunctional properties of the yarn. Owing to physical and chemical interaction, the nanoparticles were bound uniformly on the yarn surface. The advantages of this process

are its ease to carry out and its efficiency. This green method is reliable, non-toxic and cost effective in nature. UV measurements indicated that the higher $AgNO_3$ concentration, the higher yields and smaller size of silver nanoparticles were produced. ICP/OES measurement results were determined that the increase in the reduction efficiency of silver depending on the concentration. SEM images clearly depicted the formation of a nanolayer around fibers and approved the importance of AgNPs concentration on the electrical conductivity of the yarns. At the same time, it was observed that Ag was formed dominantly and local-uniformly distributed on yarn surface. Relatively more homogeneously dispersed and less agglomerated AgNP was observed in the presence of NaOH. Furthermore, it was determined that composite PA yarns with more homogeneous AgNPs distribution and less agglomerated silver nanoparticles had higher electrical conductivity values. According to inhibition zone measurements, antibacterial activity increased with increasing $AgNO_3$/CMS concentration against *E. coli* and *S. aureus*. In summary, the green synthesis of silver nanoparticles, using carboxy methyl starch as reducing agents, is an environmentally friendly, simple and efficient route for synthesis of metallic nanoparticles. This method is an effective way for the preparation of antistatic and antibacterial composite yarns. These modified polyamide yarns are potentially useful; as antistatic in a wide variety of textile and protective textile applications. The AgNPs coated composite PA yarns developed in our study, can be preferred in product development studies for technical textiles such as heating textiles, medical textiles etc.

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