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Antimicrobial Polypropylene Loaded by Silver Nano Particles

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Abstract: Nowadays antimicrobial polypropylene fabrics are increased due to incorporation of nano metals and metal oxides during their production. In situ, synthesis of silver nano particles onto non-woven polypropylene (PP) fabric bearing antimicrobial properties was investigated. Silver nanoparticles were prepared by chemical method using silver nitrate, concentrations 5-40 m mole/*l*, sodium hydroxide and glucose as a reducing agent at 90 °C for 2 hrs. Then, padding, drying and curing the PP treated fabric at 150 °C for 5 min was carried out. Silver nano particles dispersed onto PP was estimated before and after five washings. Characterization of silver nano particles was investigated by, XRD, SEM and EDX, which revealed the presence of silver nanoparticles in the size range 20-40 nm. PP color for untreated and silver treated samples was evaluated at λ_{max} 400 nm using colorimetric data L^*, a^*, b and colour strength (K/S). The antimicrobial activity of PP treated fabric against some microorganisms such as *S. aureus, E. coli* and *C. candida* was evaluated after 24 hrs contact time and proved to be highly effective with excellent results.

Keywords: Polypropylene (PP), Silver nitrate, Alkaline glucose, Silver nanoparticles, Antimicrobial activity

Introduction

Polypropylene fabric has excellent physical and mechanical properties [1]. It is a hydrophobic fabric and several surface modification techniques are adopted to improve wetting, adhesion to polymer surfaces by introduction of a variety of polar groups [2-4]. PP advantages include a great supply, good process, low energy demand, low cost and high chemical stability [5]. There is a great demand for antibacterial PP fabric to be used in different medical applications [6].

Nowadays, nanotechnology was highly improved with great important characteristic properties for textiles [7,8]. A new technique was used for deposition of silver nano particles onto polypropylene fabrics to inhibit the growth of pathogens microorganisms [9].

Nano particles are clusters of atoms in the size range 1-100 nm. Silver nano particles possess high antibacterial properties due to its large surface area. Various synthesis methods for silver nano particles are cited in the literature, such as chemical, photochemical, biochemical and electrochemical reductions. Chemical reduction by sodium borohydrate, hydrazine hydrate or L-ascorbic acid as a reducing agent are the most effective [10-13].

Incorporation of silver nano particles onto textiles has received a great attention due to their highly antibacterial activity. Silver is a relatively non-toxic disinfectant agent that can reduce many strains of bacteria, moulds and fungi. Recently, there is an increase in using silver or silver nano compounds in medicine due to the appearance of dangerous diseases and a great number of antibiotic resistant bacterial strains [14]. Silver is usually applied to textiles in different means such as a colloidal solution, a dispersion of nano-metallic form or non-soluble silver salt [15,16].

Silver is a safe and effective bactericidal metal because it is non-toxic to animal cells and highly toxic to bacteria such as *E. coli* and *S. aureas*. Colloidal silver, nano silver for coated fabric, silver nano metal oxide chips are used as antibacterial compounds. Nano silver in the form of powders as well as suspensions, due to its high surface to volume ratios, is applied in the above uses as they give loading of small silver quantity and thus provides low effective cost products [17].

Chemical reduction method of $AgNO_3$ by a reducing agent in the presence of a suitable stabilizer is important for protecting the growth and aggregation of silver nano particles. Silver nano particles synthesized by the chemical reduction method are affected by different parameters such as the particle size and agglomeration of silver nano particles including initial $AgNO_3$ concentration, reducing agent/ $AgNO_3$ molar ratios, and stabilizer concentration [18]. In one of the chemical reduction methods, highly dispersed silver nano particles with size of 20-80 nm were synthesized by reducing silver nitrate with glucose using protective agent as polyvinyl pyrrolidone (PVP), the addition of sodium hydroxide increased the reaction velocity and PVP has protected silver nano particles from aggregation. In another study, PVP was used as a dispersing agent in the reaction between silver ions and glucose [19]. An approach based on the polyol process for large-scale synthesis of silver nano wires with uniform diameters was shown. It has involved the reduction of silver nitrate by polyol in the presence of PVP as stabilizer. The production of silver nano wires 30-60 nm in diameter and 1-50 μ in length was well demonstrated in the above method [20].

Silver is of great interest for bactericidal substrates. Its wide spectrum for bacteria and contrary to other heavy metals, its toxicological safety to the human organism, silver exhibits an alternative to antibiotics [21]. The incorporation of different silver compounds into melt spun fibres, e.g. polypropylene, polyester or polyamide, are the main features

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to produce bactericidal fibres. Application of silver nitrate on the surface of Lyocell fibre modified with an ion exchange resin is nowadays manufactured in a semi-technical scale smart fiber AG [22].

Silver nano particles were coated onto polypropylene film to study its antibacterial activity. Polypropylene surface film was treated by corona discharge and then the modified film was immersed in a uniform colloidal solution of silver nano particles which was synthesized by chemical reduction of silver salt using hydrazine hydrate. Characterization of silver nano particles and the coated surface were carried out using UV-vis spectroscopy, dynamic light scattering (DLS), X-ray diffraction (XRD) and scanning electron microscope (SEM) [23]. Effect of silver nano particles onto the fabric properties was demonstrated by in-situ technique [24].

Incorporation nano particles of noble metal into fabrics/ fibers has been applied to produce finished materials with different functional performance [25-27].

In the synthesis of nano silver to impart antibacterial properties onto wool, silver nitrate solutions with different concentration were used. XRD, EDX and SEM have proved the synthesis and loading of silver nano particles onto the wool fibers surface. Further, the antibacterial property of fine wool was confirmed using two different bacteria, including *Staphylococcus aureus* as a gram positive and *Escherichia coli* as a gram negative bacteria [28].

PP extruded composite fibers that contained 0.72 % silver and 0.60 % zinc nano particles had outstanding antibacterial efficacy as documented by the percentage count reduction growth of *Escherichia coli* and *Staphylococcus aureus*. Fibers containing silver nano particles had also improved PP antistatic properties [29].

In the following manuscript, silver nano particles were prepared by the reaction of $AgNO_3$ and NaOH using glucose as a reducing agent at 90 °C for two hours onto nonwoven PP. Padding, drying and thermal heating were effected at 150 °C for 5 min, drying, washing five times, then drying and weighed. Characterization of PP/silver nano fabric was performed by SEM, EDX analysis.

Experimental

Materials

Fabric: Nonwoven polypropylene (20 g/m^2, thickness 2.60 mm) was a gift from Egyptex Co., Cairo.

Chemicals

Chemicals used were silver nitrate (M.wt. 169.87), sodium hydroxide and D-glucose, were purchased from local market.

Methods

Scouring of Fabric

Nonwoven PP fabric was well extracted with acetone before treatment to remove antioxidants and lubricants.

Synthesis and Deposition of Nano Silver Particles onto PP

A known weight of silver nitrate (X gm., 5-30 mmole/*l*) was dissolved in 160 m*l* distilled water, sodium hydroxide (0.8 gm) in 40 m*l* distilled water was added dropwise to 2 gm. PP (10×10 cm) in a stoppered conical flask. The fabric was dipped in the silver nitrate solution and highly shacked in a water bath for 15 min at 60 °C, followed by addition one gm. glucose as a reducing agent. The temperature was raised from 60 to 90 °C and maintained for 2 hours at that temperature. Then, the fabric was padded on a padding machine (Roaches Co., England), dried at 105 °C for 30 min, cured at 150 °C for 5 min weighed, washed five times for 15 min each at 50 °C with distilled water and finally dried at 105 °C. The weight increase due deposition of nano silver onto PP was calculated.

Analysis Tests

Percent Add-on of Nano Silver

The percentage weight add-on of silver nano particles onto the treated fabric after drying, padding, heat treatment and washing was calculated as follows:

$$\% \text{ Weight add-on of nano silver} = [(W_2 - W_1)/W_1] \times 100 \quad (1)$$

where W_1: initial fabric weight, W_2: fabric weight after pad-cure treatment and washing.

Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX)

The fabric was well washed with distilled water to remove the unattached silver nano particles and then dried before SEM determination. The fabric was measured on SEM (Quanta FEG 250, FEI Co.) working at 20 kV. Then, the fabric was coated with carbon double face and fixed with stubs of Quanta holder and examined in low vacuum.

X-ray Diffraction (XRD)

X-ray diffraction pattern onto PP fabric was measured before and after treatment. Fabric was subjected to XRD with Emyrean Diffractometer operated at 45 kV (Cu-Ka radiation, 1.5406 Å) in 2θ angles ranging from 4.015 ° to 79.96 ° with a step size of 0.026 and scanning rate 18.87 seconds.

Color Measurements

The three coordinates (L^*, a^* and b^*) and color strength (K/S) of CIE LAB color system as a method for textile color measurement were done using Ultra Scan Pro Hunter Lab. L^* indicates the lightness and a^* and b^* show the redness-greenness and yellowness-blueness values, respectively. The color difference between two fabrics is determined by ΔE using equation (2) [30].

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5} \quad (2)$$

ΔE: the total difference between the untreated and treated

fabrics, L^*: represents white-black axis, a^*: the red-green axis, b^*: the yellow blue axis respectively.

Antimicrobial Activity

The antibacterial and antifungal studies of treated fabrics with Ag nano particles were accomplished in triplicates using standard method (AATCC TM100).

The treated fabric was introduced into 20 m*l* nutrient broth and inoculated with the respective bacterial strain followed by overnight (24 hrs) incubation at 37 °C. Growth of the bacterial strain was determined spectrophotometrically by measuring the optical density at 660 nm (OD 660) in presence of the treated fabric against a blank of un-inoculated sterile medium. Similarly, the fungal strain inoculated onto potato dextrose broth and incubated for 48 hours at 28 °C in a shaker incubator followed by measurement of optical density at 450 nm (OD 450) against a blank of un-inoculated sterile medium. Before recording the OD of the respective media after incubation, the culture tubes were shaken thoroughly in order to bring microorganisms into suspension. The optical density is directly proportional to the number of microorganisms (bacteria or fungi) in the medium. The percentage reduction of the microorganisms was expressed as follows.

$$\% R = [(B - A)/B] \times 100 \quad (3)$$

R is the percentage reduction of microbial population, B is the absorbance of the media inoculated with the microbes and A is the absorbance of the media inoculated with the microbes and the treated fabric [31].

Results and Discussion

Synthesis of Silver Nano Particles onto PP Fabric

Incorporation of 5-40 mmole/*l* concentration silver nano particles onto PP was carried out by reduction of $AgNO_3$ using NaOH and deposition AgOH which is reduced to nano silver by glucose at 90 °C for two hrs and dried. Then the treated fabric is cured at 150 °C for 5 min. During the thermal treatment AgOH was reduced to Ag by action of glucose as reducing agent, according to the following equations

$$AgNO_3 + NaOH \longrightarrow AgOH + NaNO_3 \quad (4)$$

$$2\,AgOH \longrightarrow Ag_2O + H_2O \quad (5)$$

$$Ag_2O + C_6H_{12}O_6 \xrightarrow{90^\circ C} 2Ag + C_6H_{12}O_7 \quad (6)$$

Silver D-Gluconic acid

From Table 1 and Figure 1, it is shown that Ag nano content onto PP increased from 0.44 to 2.60 % for 5-40 m mole/*l* $AgNO_3$ solution and it is low because PP is highly hydrophobic. After reaction completion, padding, thermal curing at 150 °C for 5 min washing and drying, PP fabric has acquired a slight tarnish brown color due to the reduction of Ag_2O by action of glucose to Ag at 90 °C.

Table 1. Percentage of Ag deposit onto PP fabric using 5-40 m·mole/*l* $AgNO_3$

Wt. $AgNO_3$/200 m*l* gm.	Concentration $AgNO_3$ mmole/*l*	% Ag deposit onto PP fabric after final washing
0.17	5	0.44
0.34	10	0.53
0.68	20	1.20
0.85	25	1.46
1.02	30	1.60
1.36	40	2.6

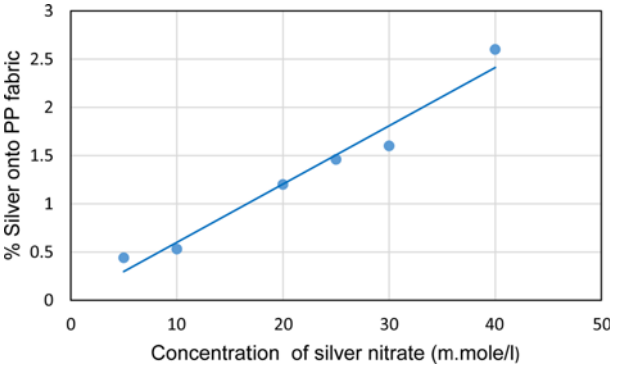

Figure 1. Percentage Ag deposit onto PP fabric from alkaline $AgNO_3$.

Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX)

Figures 2, 3 illustrate SEM images and EDX patterns of the untreated and treated PP fabric coated with nano Ag particles respectively.

SEM has shown homogeneous deposition of silver nano particles onto the treated PP fabrics and that silver nano particles are well dispersed onto the fibers. Also, EDX spectrum of the treated PP fabric has indicated the elements present onto PP based on weight and atomic percentages. It also has confirmed the presence of Ag nano particles onto the treated PP fabric.

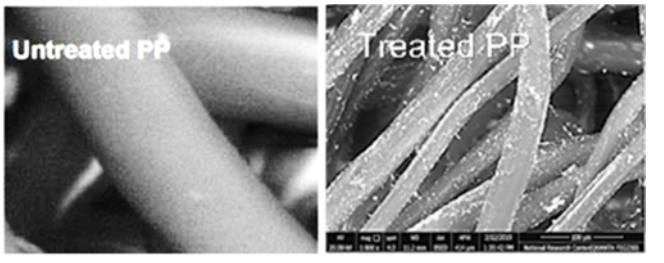

Figure 2. SEM for untreated PP & treated PP/nano Ag composite fabric.

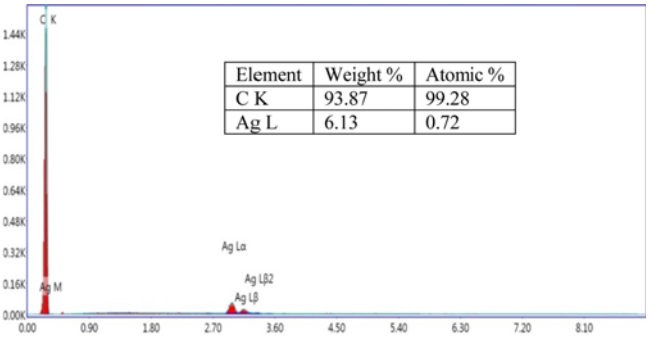

Figure 3. EDX for PP/nanoAg composite fabric.

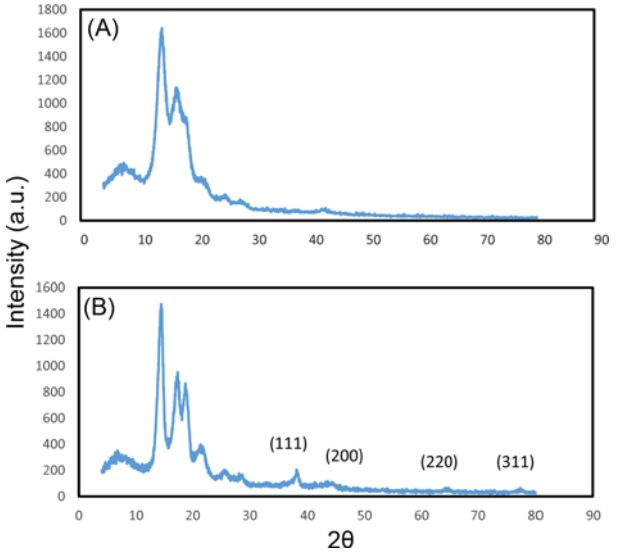

Figure 4. XRD for (A) untreated PP and (B) PP/Ag nanoparticles.

X-ray Diffraction (XRD)

XRD for PP/Ag nano composite fabric is presented in Figure 4 which has proved that PP exhibits intense peak at 2θ equal 14, 16, 18 and 20. In addition four 2θ weak peaks for Ag are at 37.895 °, 44.04 °, 64.043 ° and 76.889 ° were detected, which were respectively attributed to the following Muller indices (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of silver.

Color Measurements

The color strength (K/S) of the treated samples is slightly increased from 2.7 to 3.78 with increasing the concentration of $AgNO_3$ from (10-25 m mole/*l*), Data of Table 2 was measured at λ_{max} 400 nm and shows that L^* value of untreated sample is the highest one among all samples, meaning that it is the most lighter shade in all samples, while the value L^* for the sample treated with 25 m mole/*l* $AgNO_3$ is the lowest one, as it is the darkest shade among all samples. For a^* and b^* values, the color of the untreated sample is located in the area of greenish yellow zone, while the other samples are located in the area of reddish yellow zone. For ΔE values, in the change of color difference between untreated and treated samples increased with increasing $AgNO_3$ concentration.

Antimicrobial Activity

The modified fabric obtained by treatment PP with Ag nano particles is important for medical and hygiene applications. Also, there is an increase demand for anti-microbial PP fabrics especially those used in hospitals to prevent infection or transmission of disease for protecting and heath care workers.

Silver nanoparticles have high antimicrobial efficacy against a wide range of bacteria, fungi, moulds, algae, etc [32]. The effect of the antimicrobial PP/Ag nano fabric is in wound healing dressings, for incisional wound healing rats was investigated at experimental level [33]. In addition, PP/Ag nano fabric produced by melt-extrusion of fibers are applied for hospital uses.

In the present work, PP/2.6 % silver nano treated fabric was tested against *S. aureus* (gram-positive), *E. coli* (gram negative) bacteria and *C. candida* (fungi). An excellent antimicrobial effect was achieved for the treated fabric due to the presence of silver nano particles and was studied after 24 hrs contact time by OD method (Table 3).

PP/Ag nano particles fabric showed maximum percentage reduction growth for *C. candida* (99 %) followed by *S. aureus* (97 %) and finally *E. coli* (93 %). These highly excellent antimicrobial growth results were evaluated for the above bacteria and fungi.

Ag action mechanism is due to its cell wall binding and cell membrane, deactivating enzymes with the inhibition of

Table 3. Antimicrobial activity of PP fabrics loaded with 2.6 % nano silver particles

Sample	Percentage microbial reduction		
	S. aureus	*E. coli*	*C. candida*
2.6 % Silver deposit onto PP fabric	97	93	99

Table 2. Color difference for the untreated and nano Ag treated PP at [λ_{max} = 400 nm]

Fabric	*K/S*	L^*	a^*	b^*	Δ*E*
Untreated	0.30	75.42	-0.01	1.13	0
PP treated with $AgNO_3$ (10 mmole/*l*)	2.70	49.45	1.95	6.45	26.51
PP treated with $AgNO_3$ (20 mmole/*l*)	3.67	47.19	2.04	9.36	29.44
PP treated with $AgNO_3$ (25 mmole/*l*)	3.78	46.9	2.44	9.43	29.7

the respiratory system of bacteria [14].

Similar research work was done by Gawish *et al.* onto PP using micro Cu_2O as antibacterial agent against the same previous microorganism and they gave very good results [34].

Conclusion

In situ, synthesis of silver nano particles onto polypropylene (PP) fabrics was carried out by reduction of silver nitrate into silver nano particles using glucose as a reducing agent at 90 ^oC for two hours. The treated PP fabric was padded, dried and thermal cured at 150 ^oC for 5 min, then washed five times, dried and weighed. Characterization and confirmation of the presence of nano silver onto the treated fabrics were performed by Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) pattern. SEM images indicated the well distribution of silver nano particles onto PP fabric surface. The treated PP fabric exhibited excellent antibacterial and antifungal activities against *S. aureus, E. coli* and *C. candida*. Also, color characterization was measured for the untreated and treated fabric after 24 hrs contact time.

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