

Synergistic Combination of Reduction and Polymerization Reactions to Prepare Silver/Waterborne Polyurethane Nanocomposite for Coating Applications

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Abstract

Objectives: In this paper, a novel attempt has been made to develop anionic waterborne polyurethane with antibacterial properties. **Methods/Analysis:** To achieve this goal, a one-pot synthesis was used to incorporate silver nanoparticles into the Waterborne Polyurethane (WPU) via a combination of reduction of silver ions and polymerization reactions. This silver/waterborne nanocomposite was applied as a modifier for preparing antimicrobial viscose fabric with enhanced coloration and fastness properties. **Findings:** A bacterial reduction of 100% is observed during the antibacterial activity tests of the nanocomposites for both *Escherichia coli* and *Candida albicans*. Transmission Electron Microscopy (TEM) and X-ray Diffraction (XRD) was used to confirm the formation of Ag nanoparticles in WPU. Scanning Electron Microscopy (SEM-EDX) and Fourier Transform Infrared Spectroscopy (FTIR) were used to verify the presence of silver/waterborne composites layers. Exploration of the fastness properties and the color strength (K/S) of colored viscose fabrics were also performed. **Novelty/Improvement:** The obtained results can be considered as a measure of the degree of the interaction between dyes such as cationic and reactive classes and different modified surfaces.

Keywords: Antibacterial, Coating, Nanocomposites, Silver Nanoparticles, Water Borne Polyurethane

1. Introduction

Textile auxiliaries used in finishing, dyeing and printing wet processes must be compatible and not reduce the effects of each other. For this reason, serious attempts have been made to develop products with synergistic effects and do not interfere, neither in the finishing bath nor on the fabric. For example, O-acrylamido-methyl-N-[(2-hydroxy-3 trimethylammonium)propyl] chitosan chloride (NMA-HTCC) has been synthesized to improve dye-ability and anti-microbial properties of cotton¹. However, in this case, the antimicrobial effect of the treated cotton was almost lost after dyeing owing to the blocking of cationic groups of NMA-HTCC by anionic groups of the dye. In this regards, a modern colorant prepared to perform additional functions besides its specific coloristic and fastness properties, such as antibacterial action, increased UV or IR absorption, or water repellency².

Currently, nanocomposite materials and coatings are one of the most exciting and fastest growing areas of research³⁻⁶. Metal/polymer nanocomposites are considered one of the most attractive materials with synergistic properties to achieve better performance⁷. Those nanocomposites exhibit distinctive chemical and physical properties as a result of the stronger interfacial interactions between the polymer matrices and the nanofillers^{8,9}. Typically, these nanocomposites are synthesized by mixing a polymer with nanometer metal particles, such as hyperbranched polyethyleneimines¹⁰, polydimethylsiloxane¹¹, poly (vinyl alcohol)¹², polypyrrole¹³ and polyurethanes^{14,15}. The properties of metal/polymer nanocomposites are highly affected by the type and size of incorporated nanoparticles¹⁶, their concentration, and interaction with polymer matrix^{17,18}.

Among the metal nanoparticles, silver nanoparticles are considered to be the most widely used nanoparticles in

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industries as antibacterial^{19–26}. Their application increases in protective wear for medical and military personnel to reduce infection in wound dressings^{27–32}. One of the most known methods to synthesize colloidal silver nanoparticles is the chemical reduction method, as it is convenient and needs simple equipment³³. Most of the reported studies on the synthesis of silver nanoparticles are based on using reducing and stabilizing agents^{34–38}. Ag/polymer nanocomposites have gained much attention because of their potential applications in the fields of catalysis, bioengineering, photonics, and electronics³⁹. A suitable method to synthesize Ag/polymer is the in situ reduction of the silver ions into silver nanoparticles in the existence of the polymer. In this case, the reducing and/or stabilizing agents could be the polymer or the other chemicals existed in the system, and therefore, the Ag nanoparticles in the polymer matrix is obtained in good distribution and dispersion¹².

Waterborne Polyurethane (WPU) is known for its various applications such as coatings, medical and adhesive applications^{40–42}, as a result of environmental regulations which purpose to decrease organic solvent consumption. Waterborne PU can be prepared by adding hydrophilic groups to the polymer chains. The WPU is classified into non-ionic one, anionic (i.e., sulfonate or carboxylate containing groups) and cationic (i.e., quaternary ammonium containing groups). As the anionic groups are able to form coordinate bonds with silver ions, as revealed in the work of⁴³ therefore the anionic WPU will be selected in the present work.

Different approaches are established for the preparation of silver/WPU nanocomposites, for instance, silver/WPU nanocomposites were prepared by combining silver colloid, which prepared by the reduction of silver nitrate using sodium borohydride, in WPU⁴⁴. So far, to the best of our knowledge, simultaneous reduction of silver ions in WPU matrix synthesized by in situ polymerization has not been reported. Therefore, the aim of the present work is the preparation of Ag/WPU nanocomposites without using any additional chemical (i.e., reducing agents and stabilizing agent).

In this current proposed approach, Polyethylene Glycol (PEG) is used as a reducing agent for silver nitrate, alongside its participation as a soft segment in the preparation of carboxylate-containing segmented polyurethane. The carboxylate-functional group in the prepared WPU is expected to offer an advantage for a chemical bonding with the silver ions. The prepared Ag/WPU nanocomposites will be characterized chemically

and morphologically. Furthermore, it will be utilized for coating of the viscose fabrics to impart antimicrobial properties. Also, the inherent coloration properties of the fabrics will be assessed.

2. Materials and Methods

2.1 Materials

Isophoronediiisocyanate (IPDI, Fluka), Dibutyltindilaurate (DBTDL, Sigma-Aldrich) and 2,2-bis(hydroxymethyl)propionic acid (DMPA, Sigma-Aldrich) were used as received. Polyethylene Glycol 600 (PEG 600; Mn = 600, Merck) dried at 80° C for 180 min before used. Polymerization medium was butanone of analytical grade.

Methylene blue dye, C.I. Reactive Blue 19, Ammonium sulfate solution, urea, Carboxymethylcellulose sodium salt (CMC sodium salt, Aldrich), citric acid. All other chemicals are of laboratory grades and were used without further purification.

100 % viscose fabric (110 g/m² (weight), 375/10 cm (warp) and 320/10 cm (weft) from Abou El-Ola for spinning and weaving, 10th of Ramadan, Egypt. The fabric was washed with 0.5 g/L non-ionic detergent and 1 g/L sodium carbonate solution at 70°C for 60 min. Then thoroughly rinsed and air dried at room temperature.

2.2 Preparation of in situ Ag/water Borne Polyurethane Nanocomposites

IPDI, PEG and DMPA in a molar ratio of (2:1:1), which equivalent to (12:15:3.35 g) respectively, 0.1% DBTDL as a catalyst plus AgNO₃ (0.001, 0.05, 0.1, 0.3% of the total polymer weight) and 20 g of butanone as polymerization media were charged in a three-necked flask equipped with mechanical stirrer, thermometer, reflux condenser and nitrogen inlet⁴⁵. The reaction was performed at 80°C for 4 h. The Ag/water borne polyurethane nanocomposite (Ag/WPU-NC) was left to cool to ambient temperature. Ag/WPU-NC contained different concentration of silver (0.001, 0.05, 0.1, and 0.3 %) were designed as Ag/WPU-NC_{0.001}, Ag/WPU-NC_{0.05}, Ag/WPU-NC_{0.1} and Ag/WPU-NC_{0.3} respectively.

2.3 Modification of Viscose Fabric

Ag/water borne polyurethane nanocomposite (Ag/WPU-NC) solution (60 % wt/wt) was initially diluted with water/butanone solution (30/70) until the concentration of solution become (1% wt/wt).

The viscose fabric was modified with Ag/WPU-NC solution, which contains a different concentration of nano-silver through padding technique (pickup 90%), followed by drying at 80 °C. Thermofixation of the modified fabrics was carried out at 110 °C for 10 min.

2.4 Coloration of Viscose Fabrics

The efficiency of different modifications of viscose fabrics with Ag/WPU-NCs has been studied regarding color strength (K/S), dye exhaustion (% E) and washing fastness test obtained from the printing and dyeing experiments by using a reactive and basic dyes.

2.4.1 Printing

The printing paste was prepared according to the recipe shown in Table 1. The thickener (CMC) was soaked in a small amount of water and kept overnight at room temperature. The dye is passed with the dye solvent, acetic acid and mixed with urea. Hot water (80–90 °C) is poured onto the paste to produce a solution, which is sieved and stirred into the thickener. Finally, the total mass of the whole paste was then adjusted to 1 kg by the addition of other auxiliaries and water.

Table 1. Printing paste composition

Constituents	Weight (g)
Thickener	100
citric acid	5
Urea	50
Ammonium sulphate solution (1:2)	60
methylene blue dye	20
Thickener	100
Water	765
Total	1000

The aforementioned printing pastes were applied to unmodified and modified viscose fabrics using the flat-screen printing technique. The printed samples were then air dried followed by steaming at 108 °C for 30 min. The printed samples were then washed with water containing (2 g/L nonionic detergent) at 60 °C for 30 min to remove the thickener and unfixed dye, then rinsed in water several times and finally air dried.

2.4.2 Dyeing

The effect of WPU and Ag/WPU nanocomposite on the dye-ability of modified viscose fabrics were studied by

using reactive and basic dyes through dye exhaustion method. Dyeing was carried out using C.I. Reactive Blue 19 and methylene blue dyes, 2% shade based on the weight of fabrics and a liquor ratio 1:40. In the case of a reactive dye, global salt 40 g/L was added to the dyeing solution at 40 °C initially for 30 min, then raised gradually to 60 °C. Then sodium carbonate (20 g/L) was added, and the dyeing process was continued for another 60 min. While in the case of methylene blue dye, the dyeing procedure was achieved at pH 7 and 80 °C for 60 min.

2.5 Characterization of Ag/WPU-NC and Modified Viscose Fabrics

2.5.1 Molecular Weight of WPU Composites

The molecular weight and molecular weight distributions of the polyurethane composites were obtained by Agilent Gel Permeation Chromatography (GPC), using a Waters peristaltic pump HPLC (flow rate of DMF 1 mL/min), and a Waters 410 refraction index detector.

2.5.2 Fourier Transform Infra-Red (FTIR)

The chemical structure of the polyurethane composites was investigated in a JASCO 6100 infrared spectrophotometer, provided with Fourier Transform Analysis (FTIR). The scanning range was 400–4000 cm^{-1} .

2.5.3 Transmission Electron Microscopy (TEM)

The morphology and particle size of Ag-doped PU matrix was investigated using TEM (JEOL, JEM- 2100, Japan, with an acceleration voltage of 120 kV). The Ag/WPU-NC samples for TEM analysis was obtained by placing a drop of the dispersion onto a carbon-coated copper grid. The samples were dried at room temperature, then examined using a TEM without further modification or coating.

2.5.4 Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Analysis (EDX)

The surface morphology of modified and unmodified viscose fibers was investigated using Scanning Electron Microscopy (SEM) HITACHI S-3000 (Hitachi, Japan) attached to energy dispersive X-ray spectrometer unit (EDX; Voyager III, NORAN Instruments, Inc., Middleton, WI). The fiber surface is tested without any pre-coating process. The EDX results were calibrated using tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) (Taihei Chem., Osaka, Japan) and

hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) (Taihei Chem.) as reference materials.

2.5.5 Color Strength (K/S) of Printed Fabrics Measurement

The efficiency of different surface modifications has been compared regarding K/S absorption spectra. The color strength of the printed viscose fabrics was measured using a recording filter Spectrophotometer Hunter Lab (The Colour Management Company, USA). The color value expressed as K/S of the printed samples was determined by applying the Kubelka-Munk⁴⁶ Equation (1).

$$K/S = \frac{(1-R)^2}{2R} - \frac{(1-R_0)^2}{2R_0} \quad (1)$$

Where, R: is the decimal fraction of the reflectance of the dyed substrate.

R_0 : is the decimal fraction of the reflectance of the undyed substrate.

S: is the scattering coefficient.

K: is the absorption coefficient.

2.5.6 Dye Exhaustion (%)

For all dyeing's, the dye exhaustion was measured by sampling the dye-bath before and after dyeing. The dye concentration (g/L) of the dye-bath was measured on Shimadzu UV-2401PC UV/vis spectrophotometer at a maximum wavelength of each dye. The percentage of dye-bath exhaustion (E) was calculated using Equation (2):

$$E(\%) = \left(1 - \frac{C_2}{C_1}\right) \times 100 \quad (2)$$

Where C_1 , C_2 are the concentrations of the dye-bath before and after dyeing, respectively.

2.5.7 Antimicrobial Properties of Modified Viscose Fabrics

E. coli serotype O157: H7 was isolated from lambs. C. Albicans strain was isolated from bovine milk samples.

Implementing standard plate count technique, all antimicrobial tests were conducted. All viscose fabrics were prepared with a diameter of 4.8 ± 0.1 cm in plastic bags and sterilized. The antibacterial and antifungal properties of untreated viscose fabric, viscose fabric coated with polyurethane nanosilver composite were quantitatively evaluated by using plate count agar method

according to the AATCC test method 100–2004. The antimicrobial activity is expressed in % reduction in the organisms after making contact with the test specimen compared to the number of the organism cells surviving after making contact with the control. All results were calculated according to Equation (3):

$$\text{Reduction (\%)} = \frac{A-B}{A} \times 100 \quad (3)$$

Where, A is the number of microorganisms present on untreated viscose fabrics.

B the number of microorganisms present on treated viscose fabrics.

2.5.8 Washing Durability of Modified Viscose Fabric

Washing durability test method for the treated antibacterial fabrics was assessed according to the AATCC test method 61–1989. One gram sample was soaked in 40 mL solution containing 2 g/L Egyptol PLM (nonionic detergent). Washing was conducted for 20 min at 40°C ²³.

3. Results and Discussions

3.1 Characterization of Ag/WPU Nanocomposites

The formation of silver nanoparticles could be understood based on the high reduction ability of Polyethylene Glycol (PEG) toward silver ions^{47–49}. PEG ($\text{HO}-\text{CH}_2(\text{CH}_2\text{OCH}_2)_n-\text{CH}_2\text{OH}$) is nonelectrolyte, having many polar groups such as C–O, C–H, H–O. After addition silver nitrate, Ag^+ was bonded to the polar side groups such as C–O, C–H, H–O in Polyethylene glycol. The in-situ reduction of silver ions during the polymerization of WPU in the presence of PEG solution can occur as the hydroxyl groups in PEG is oxidized to aldehyde groups ($\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{CHO}$) and Ag^+ is reduced to Ag^0 .

3.1.1 Molecular Weights of Ag/WPU Nanocomposites

The number average molecular M_n and weight average molecular weights M_w , also the molecular weight distribution ($D = M_w/M_n$) for each polymer sample examined, are indicated in Table 2. Both M_n and M_w of the prepared polymers decreased gradually with the increase in the concentration of silver nitrate added

during the polymerization while the molecular weight distribution value raised from 1.4 to 2.7. These show that the molecular weight of the polymers became more disorder as the amount of the added silver increased, which could be attributed to the preoccupation of the polyethylene glycol in the reduction of silver ions besides its participation in the polymerization reaction. It's worth noting that similar results were obtained by adding nanotitanium during polyurethane RAFT polymerization⁵¹.

Table 2. The number, weight average molecular weights and molecular weight distribution for WPU and its nanocomposites

Sample	Mn	Mw	D
WPU	7.7×10^4	10.78×10^4	1.4
Ag/WPU-NC _{0.001}	6×10^4	8.4×10^4	1.4
Ag/WPU-NC _{0.05}	5.3×10^4	8.48×10^4	1.6
Ag/WPU-NC _{0.1}	4.8×10^4	10.08×10^4	2.1
Ag/WPU-NC _{0.3}	3.2×10^4	8.64×10^4	2.7

3.1.2 FTIR of Nanocomposites

FTIR is extensively applied to analyze the micro domain structures of the WPU coating. Figure 1 shows the (FTIR) spectra of WPU and Ag/WPU-NC_{0.3} composites between 400 and 4000 cm^{-1} . These shows the following characteristics polyurethane bands (N-H stretching of urethane at 3319 cm^{-1} , CH₂ symmetric and asymmetric at 2909 cm^{-1} , CO ester, and urethane at 1710-1665 cm^{-1} , C-N-H urethane at 1540 cm^{-1} , C-O-C of polyethylene glycol at 1246 cm^{-1} , C-O urethane and ether groups at 1104 cm^{-1})⁴².

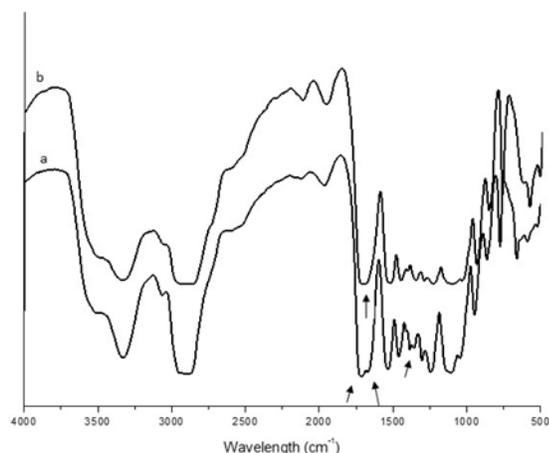


Figure 1. Fourier Transform Infra-red (FTIR) spectra of WPU and its composite. (a) Pure WPU. (b) Ag/WPU-NC_{0.3}.

The effects of silver on the FTIR spectral structure of the WPU shows the following: Absorption bands at 1703 and 1731 cm^{-1} that characteristic for a carbonyl group stretch. The band at 1703 corresponds to hydrogen bonded carbonyl with the -NH groups occurred in the hard segment while the band at 1731 cm^{-1} is attributed to the non-hydrogen bonded carbonyls occurred in the soft segment. The similar peak ratio for WPU is changed to varying degrees for the silver polyurethane nanocomposite. The peak at 1310 is attributed to the NH-stretches and that at 1537 cm^{-1} is regarded to C-N stretches, are improved in the silver-loaded WPU. The aliphatic ether stretching (C-O-C) peak at 1090 cm^{-1} has a shoulder, and the (-NH stretching) peak at 3326 cm^{-1} is increased and becomes broader. The spectral disturbances in the WPU spectra indicate that silver interacts with the high electronegative atoms (O and N) existed in the polymer macromolecule, and that was found to be inconsistent with previous work interested in mixing silver nano-particles with polyurethane⁵².

3.1.3 TEM

The effectiveness with which the addition nanoparticles improve the properties of the composite is mostly dependent on the degree of nanoparticle distribution in the polymer matrix as well as the nanomaterial particle size and that is well recognized. Another important and significant factor in the improvement in the coatings properties of the nanocomposite is the nanoparticles adhesion with the polymer matrix is. Also, one of the most critical parameters for obtaining the desired properties of nanocomposites coatings is the interface morphology of polymer nanocomposites. The transmission electron microscopy was used to detected the physical shape and size of Ag/WPU nanocomposites, and the recorded images are presented in Figure 2. Most of the particles are spherical in shape. The smallest average particles size was 24 nm at Ag/WPU-NC_{0.001}. As the silver load increases, the silver particle sizes was enlarged to 34 nm at Ag/WPU-NC_{0.3}. Also, lower silver loads exhibit narrow particle size distribution and high dispersion.

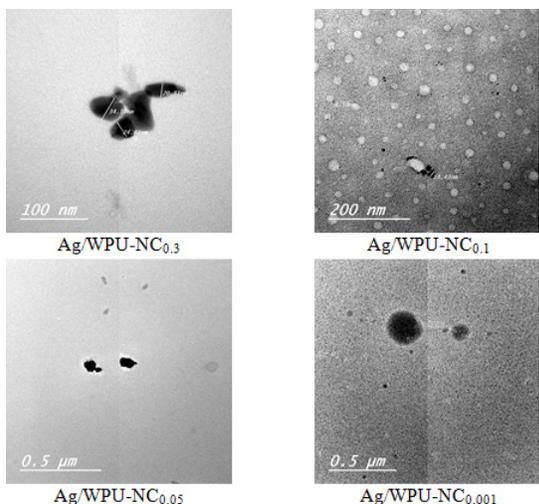


Figure 2 TEM images of Ag/WPU-NCs.

3.2 Application of the Prepared Ag/WPU-NC onto Viscose Fabrics

3.2.1 Scanning Electron Microscopy (SEM)

SEM images of the virgin viscose, viscose/WPU and viscose/Ag/WPU-NC_{0.3} are shown in Figure 3(a-c) respectively. The micrographs confirm the formation of a uniform homogeneous polymer layer on the fabric

surface. Also, no noticeable change in the morphological structure of the formed layer was observed, as a result of the silver nanoparticles existence.

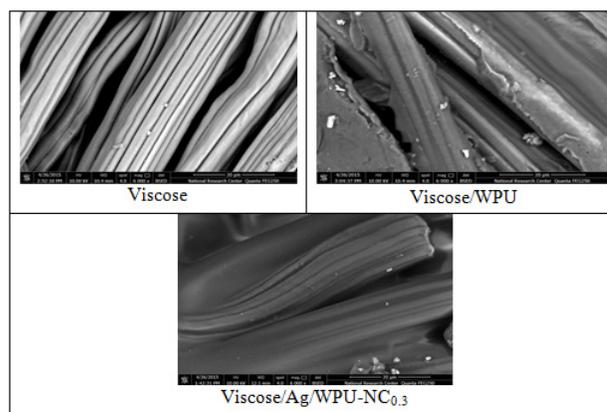


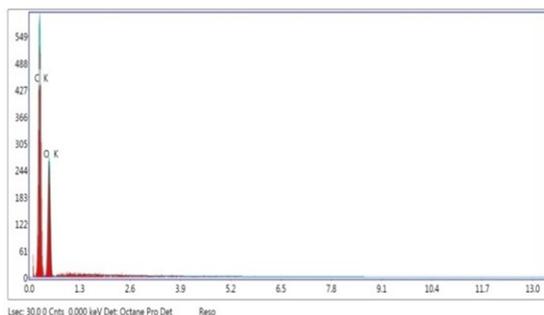
Figure 3 SEM micrographs of virgin viscose and modified viscose.

3.2.2 Energy Dispersive X-ray Analysis (EDX)

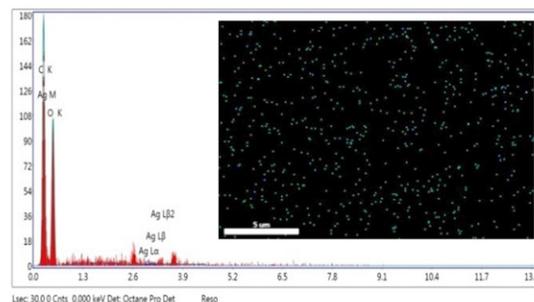
To further elucidate the nature of the nanocomposite coating layer on the viscose fabric surface, the elemental composition of fabric surface was determined by EDX (Figure 4 and Tables 3). The EDX graphs (Figure 4) confirm the existence of silver in case of fabrics treated

Table 3. Surface elements composition of virgin viscose, Viscose/WPU and Viscose/Ag/WPU-NC_{0.3}

Sample	Element	Weight %	Atomic %	Net Int. Error
Untreated viscose	C K	54.04	61.03	0
	O K	45.96	38.97	0.01
	Ag L	0	0	1
Viscose/WPU	C K	58.9	63.38	1.78
	O K	41.1	36.62	1.51
	Ag L	0	0	1
Viscose/Ag/WPU-NC _{0.3}	C K	52.15	59.44	8.09
	O K	47.80	40.49	13
	Ag L	0.05	0.07	70



(a)



(b)

Figure 4 EDX graphs of viscose and viscose/Ag/WPU-NC_{0.3}. (a) Viscose. (b) Viscose/Ag/WPU-NC_{0.3}.

with nanocomposites. Figure 4(b) (Viscose/Ag/WPU-NC_{0.3}) confirms that there is 0.05% of Ag on the surface of the viscose fabric and homogeneously distributed on the surface.

3.2.2 Antimicrobial Activity of Modified Viscose Fabrics

Both untreated and treated viscose fabrics were subjected to a challenge for killing a Gram-negative bacteria (*Escherichia Coli*) and the famous fungus (*Candida albicans*). Data of Table 4 reveal the incapability of the untreated viscose fabrics to resist the growth of the microorganism on its surface. On the other hand, a unique ability to stop the growth of these microorganisms on the viscose fabric treated polyurethane nanosilver composite was observed. It is also obvious that the resistance to the microorganism's growth is increased with the increase in the silver concentration. The small microorganism resistance that observed at lower concentrations of silver (Viscose/Ag/WPU-NC_{0.05}, Viscose/Ag/WPU-NC_{0.001}) could be attributed to the complete impedance of the silver in the polymer matrix, and hence, its effect on the microorganism resistance is diminished.

Table 4. Antimicrobial property of untreated and treated viscose fabric

Sample	Reduction %	
	<i>Escherichia Coli</i>	<i>Candida albicans</i>
Untreated viscose	Nil	Nil
Viscose + WPU	Nil	Nil
Viscose/Ag/WPU-NC _{0.001}	24	13
Viscose/Ag/WPU-NC _{0.05}	44	37
Viscose/Ag/WPU-NC _{0.1}	84	72
Viscose/Ag/WPU-NC _{0.3}	100	100

3.2.3. Coloration of Viscose Fabrics

3.2.3.1 Printing

Textile printing is an important method of beautifying textile fabric. Viscose fibers are classified as regenerated cellulose fibers, and reactive dyes are the most usually use dyes in the field of textile printing. The printer's choice of dyestuffs for any particular pattern is determined by the availability of the desired shade in any dyestuff range. On the other hand, cationic dyes have very low substantivity for cellulosic fibers unless excessive oxidation has

generated anionic carboxylate groups. They usually have brilliant colors and high tectorial strength, but their wet fastness properties are poor. These restrictions in coloration properties of viscose fabrics have inhibited their further application in garments and other industries. As a result, it is important for viscose fabric to undergo surface treatment to overcome the adhesion problem with cationic dyes.

The K/S values of the virgin and treated viscose fabrics with different Ag/WPU-NC are summarized in Table 5. For the unmodified viscose fabric, the K/S value is about 6.54. This can be explained by viscose fibers may carry negative charge due to carboxylate functional groups at aldehydic end groups or oxidized hydroxyl groups, which induced by some pretreatment processes. Comparing the K/S value of the unmodified viscose fabrics to those modified with Ag/WPU-NC_{0.001}, Ag/WPU-NC_{0.05}, Ag/WPU-NC_{0.1}, and Ag/WPU-NC_{0.3}. The high (K/S) values indicate the great attraction of the dyes to the modified fabrics. The improvement in the printability could be attributed to the presence of the carboxylic groups in the polymer chains, which attract and fix the positively charged dye molecule to the viscose fabric surface. Bearing in mind, the methylene blue dye is bonded to the carboxylic groups of fibers by the principle of ion exchange⁵³

Table 5. Washing fastness properties of the printed untreated viscose and different treated viscose fabrics with Ag/WPU-NC using methylene blue dye

Sample	K/S	Washing fastness	
		Alt.	St.
wool			
Untreated Viscose fabric	6.54	2-3	2
Viscose/WPU	10.35	3-4	4
Viscose/Ag/WPU-NC _{0.001}	10.56	3-4	4
Viscose/Ag/WPU-NC _{0.05}	10.89	3-4	4
Viscose/Ag/WPU-NC _{0.1}	10.02	3-4	4
Viscose/Ag/WPU-NC _{0.3}	9.79	3-4	4

Alt. = Alteration, St. = Staining

Also, the prepared polyurethane molecular weights are an important parameter in the fixation of the polymer layer on the fabric surface, and therefore, good printability as well as enhance fastness properties from moderate to very good (Table 5).

3.2.3.2 Dyeing

The practical modification of viscose fabrics by WPU or Ag/WPU-NC has prompted us to explore the dye-ability of the modified fabrics with conventional reactive and basic dyes, respectively. The exhaustion percentages of the modified fabrics are shown in Table 6. The coating of viscose fabrics with Ag/WPU-NC doesn't alter the inherent dye-ability of viscose fabrics with reactive or basic dyes.

Table 6. Exhaustion percentage of untreated and treated viscose fabric with reactive and basic dye

Sample	Exhaustion (%)	
	Reactive dye	Basic dye
Untreated Viscose	67.49	71.47
PU/Viscose	62.55	78.00
Viscose/Ag/WPU-NC _{0.001}	70.55	77.66
Viscose/Ag/WPU-NC _{0.05}	74.38	71.36
Viscose/Ag/WPU-NC _{0.1}	74.77	64.57
Viscose/Ag/WPU-NC _{0.3}	75.91	61.22

Regarding the reactive dye, data of Table 6 draw the attention to the increases in the exhaustion percentage with the increases in the amount of silver in the composite. That slight increase in the exhaustion percentage could be attributed to the ability of the silver atoms to coordinately bonding to the sulphonic groups in the dye molecule. The Ag nanoparticles act as a mordant; the dye gets attached toward the fabric probably due to the polarity developed in the metal particles by induction, which results in a better bonding between the dye and fabrics. On the contrary, the minor decrease in the exhaustion percentage of the basic dye with the increase in the amount of silver added. This could be understood on the basis of the occupation of the favored attractive groups for the dye molecules (COO-) with the silver atoms and/or the effect of the silver on the polymer chains characteristics structure of the prepared WPU.

4. Conclusion

Gel Permeation Chromatography (GPC) analysis of the Ag/WPU-NC polymers was pointed out that the molecular weight became more disorder as the amount of the added silver increased. The FTIR spectral disturbances in the WPU spectra indicate that silver interacts with the high electronegative atoms (O and N)

existed in the polymer macromolecule. The TEM images show spherical shaped particles in the polymer matrix (24-34 nm), and upon the modification of the viscose fabrics with Ag/WPU-NC the EDX graphs confirm the existence of silver on the viscose fabric surface (0.05% of Ag) and homogeneously distributed on the surface. The viscose fabrics treated polyurethane nanosilver composite showed exceptional ability to stop the growth of the investigated microorganisms. Also, the coating of viscose fabrics with Ag/WPU-NC doesn't alter the inherent dye-ability of viscose fabrics with reactive or basic dyes, whereas the printability of the modified viscose fabrics with methylene blue dye was improved.

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