

## Research Article

# Photosynthesis of Carboxymethyl Starch-Stabilized Silver Nanoparticles and Utilization to Impart Antibacterial Finishing for Wool and Acrylic Fabrics

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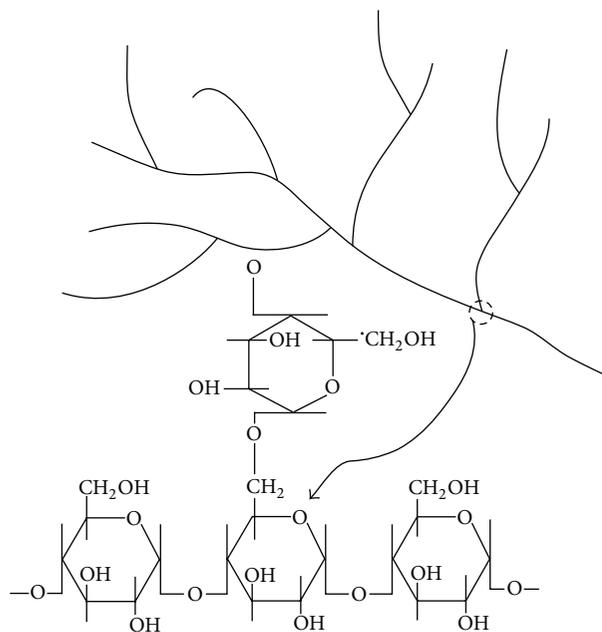
The water soluble photoinitiator (PI) 4-(trimethyl ammonium methyl) benzophenone chloride/UV system is used in the synthesis of silver nanoparticles (AgNPs). Green synthesis method involved using PI/UV system, carboxymethyl starch (CMS), silver nitrate, and water. AgNPs obtained had a spherical shape morphology and a size of 1–7 nm. To impart antibacterial properties, wool and acrylic fabrics were treated with AgNPs obtained. The PI/UV system was further utilized to fix AgNPs onto wool and acrylic fabrics by photocrosslinking to impart durable antibacterial properties. The effect of irradiation time on the antibacterial performance before and after repeated washing cycles was studied. *S. aureus* (as G +ve) and *E. coli* (as G –ve) were used to estimate the antibacterial performance of the finished fabrics. The antibacterial performance was directly proportional to the irradiation time but inversely proportional to the number of washing cycles. However, after the 15th washing cycle, samples still have bacteriostatic effect; that is, although they show zero inhibition zone, they cannot be attacked by the bacterial growth and do not inhibit the bacterial growth. AgNPs finished wool fabrics showed more antibacterial activity than those of AgNPs finished acrylic fabrics.

## 1. Introduction

It is well known that silver exhibits effective antibacterial properties with low toxicity for humans and animals compared with other heavy metals and some organic antibacterial agents. Silver and silver compounds are effective for both Gram –ve and Gram +ve bacteria, whereas the efficiency of conventional antibiotics varies with the species of bacteria [1]. Using AgNPs leads to increasing the number of particles per unit area, and, thus, antibacterial effects can be maximized [2]. Metal nanoparticles can be prepared and stabilized by physical and chemical methods; the chemical approach, such as chemical reduction, electrochemical techniques, and photochemical reduction, is most widely used [3, 4]. In the global efforts, to reduce generated hazardous waste, “green” synthesis of AgNPs is progressively integrating with modern developments in science and industry. This “green” synthesis is geared to guide in minimizing the use of unsafe reactants and maximizing the efficiency of synthesis process. AgNPs were green synthesized using different techniques [5–14].

Direct photoreduction and photosensitization are powerful approaches for the in situ synthesis in polymer matrixes [15–21]. The heart of the photochemical approach is the generation of  $M^0$  (metal NPs) in such conditions that their precipitation is thwarted.  $M^0$  can be formed through direct photoreduction of a silver source or reduction of silver ions using photochemically generated intermediates, such as radicals.

Starch, symbolized as (R–OH or R–CH<sub>2</sub>OH), is a polymeric carbohydrate consisting of anhydroglucose units linked together primarily through  $\alpha$ -D-(1 → 4) glycoside bonds. It has been established that starch is a heterogeneous material consisting of two major types of polymers: amylose and amylopectin. Amylose is a linear polymer in which the anhydroglucose units are linked through  $\alpha$ -D-(1 → 4) glycoside bonds. Amylopectin, on the other hand, is a branched polymer containing, in addition to anhydroglucose units linked together as in amylose through  $\alpha$ -D-(1 → 4) glycosidic bond, periodic branches at carbon-6 position. These branches are linked to the 6 carbon by  $\alpha$ -D-(1 → 6) glycoside bonds.

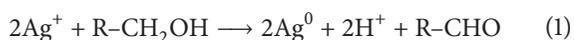


SCHEME 1: Starch structure (amylose and amylopectin).

One end of the polymeric molecule, the anhydroglucose unit, contains one primary and two secondary hydroxyls as well as an aldehydic reducing group in the form of an inner hemiacetal. This is called the reducing end of the molecule. The opposite end, or nonreducing end, contains an anhydroglucose unit containing one primary and three secondary hydroxyls. The other anhydroglucose units contain one primary and two secondary hydroxyls. The abundance of hydroxyl groups imparts hydrophilic properties to the polymer, giving it an affinity for moisture and dispersability in water [22] (Scheme 1).

Carboxymethyl starch (R-OCH<sub>2</sub>COONa) is one of the major starch derivatives. CMS is a water-soluble polysaccharide. It has wide applications in cosmetics, foods, textiles, petroleum, paper, pharmaceutical industries, and as a water retention agent and a dispersion stabilizer. It is produced by heterogeneous etherification of starch with monochloroacetic acid.

The so-called “alcohol reduction process” is a very general process for the production of metal nanoparticles, often stabilized by organic polymers. In general, the alcohols which were useful reducing agents contained  $\alpha$ -hydrogen and were oxidized to the corresponding carbonyl compounds. The oxidation of primary alcohols (R-CH<sub>2</sub>OH) by Ag<sup>+</sup> is also well established; the reaction is slow and requires heating to be accelerated as follows:



However, such a reaction is a very slow process and constitutes a minor route for Ag<sup>+</sup> reduction in comparison with the photoinduced generation of AgNPs [17, 23].

Antimicrobial property is generally important for textiles. These findings support a mechanism of the antibacterial action whereby high-molecular weight and hydrophobic

polycationic chains penetrate bacterial cell membranes/walls and fatally damage them. The bactericidal textiles prepared are lethal not only to pathogenic bacteria but also to fungi [24, 25]. The antibacterial agents are insoluble in water, detergent, and organic solvents and are thermally stable, so their activity is permanent. The agents are retained through normal fibers processes, for example, dyeing, washing, and so forth [26].

Methods and techniques of producing antimicrobial dry acrylic fibers were studied using nano-antimicrobial materials, production of nanoantimicrobial acrylic fibers, and antimicrobial Raschel blankets [27]. The antibacterial fibers were prepared by heat-treating acrylic fibers containing antibacterial metallic compounds at pH 1–6 [28, 29].

The fiber contained multifunctional groups, with nitrogen, oxygen, and heterocyclic compounds, had a better antibacterial activity, with good characteristics of broad spectrum and long-lasting and high efficiency [30]. Acrylic fibers containing alumina-zinc silicate were irradiated by electron beams and stimulated the antibacterial activity of the acrylic fibers, and their bacteriostatic and bactericidal activity values became higher than those of nonirradiated fibers [31]. The acrylic fibers containing silver-and/or zinc-exchanged titanium silicate particles act as slow-release antibacterial agents.

Medovic et al. [32] studied the possibility of obtaining biologically active acrylic fibers with bactericidal properties by chemisorptions of gentamicin sulphate, Ag<sup>+</sup>, and Cu<sup>2+</sup> on cation exchanging acrylic fibers. Quantity of sorbate (max gentamicin sulphate 138 mg/g, Ag<sup>+</sup> 1.3 mmol/g, and Cu<sup>2+</sup> 3 mmol/g fiber) depends on the sorption time, initial sorbent concentration in the solutions, static cation exchanging capacity of the fiber, type and form (H- and Na-), and porosity of the fibers.

Wool is a suitable medium for growing bacteria and fungi under favorable temperature and humidity conditions resulting in wool degradation and skin irritation or infections. Incorporation of acidic groups into wool macromolecules by pretreatment with phosphoric acid enhanced its reactivity towards metal ions of silver nitrate, cadmium chloride, copper sulphate pentahydrate and AgNPs by nanolayer condensation. Treatments of wool fabrics with metal ions and silver nanoparticles were found to be effective in antimicrobial activity. The activity of antimicrobial finish of wool fabrics as a function of type and chelated ions follows the ascending order: samples with silver nanoparticles 100 nm > Silver ions > Cadmium ions > Copper ions > untreated wool fabrics. The treatments were durable after five washing cycles. UV-protection properties were also improved. These treatments did not involve hazardous chemicals, and they are, thus, environmentally friendly [33].

The sulfur nanosilver colloidal solution had perfect antibacterial efficiency with very small amount of the nano-sized silver against *S. aureus* and *K. pneumoniae*. Antibacterial efficiency on wool fibers was easily achieved by the conventional pad-dry-cure method using the nanosized silver colloid including sulfur compound. The manufactured wool textiles using the treated fibers with the silver particle showed excellent antibacterial products [34].

The modified wool fabrics with anisotropic silver nanoparticles exhibited brilliant colors due to the localized surface plasmon resonance properties of AgNPs. The colors of wool fabrics altered with the morphologies of AgNPs. The results indicated that anisotropic AgNPs were effectively assembled on the surface of wool fibers when the solution pH and temperature were about 4 and 40°C, respectively. The fabrics treated with anisotropic AgNPs showed high antibacterial activity against the bacteria of *E. coli*. Anisotropic AgNPs were used to color wool fabrics at a temperature much lower than the typical wool dyeing temperature (close to boil). The color was tunable by changing between metal NPs and wool fibers. The combination of plasmon materials and different fibers has the potential in functionalizing a range of conventional textile materials [35].

The silver loaded nano-TiO<sub>2</sub>, as a nanocomposite, was prepared through UV irradiation in an ultrasonic bath. The nanocomposite was stabilized on the wool fabric surface by using citric acid as a friendly cross-linking agent. The treated wool fabrics indicated an antimicrobial activity against both *Staphylococcus aureus* and *Escherichia coli* bacteria [36].

Maleknia et al. [37] carried out study with the nano-scaled silver particles on the wool fabric to evaluate the antibacterial effect and its durability. The antibacterial efficiency was over 96% after 20 washing times. SEM images showed that the AgNPs were well dispersed on samples. The results obtained for the surface of samples showed that the percent of nanosized silver particles increased on the surface of samples with increased concentration of colloid solutions nanosilver.

Normally, there is no attraction between inorganic particles and polymeric materials such as textiles [38]. The difference between surface energy of the two aforementioned organic and inorganic materials causes a kind of repellency in their interfaces [39]. This problem is intensified by using NPs because of their high specific surfaces. Consequently, surface modification of textiles with NPs is not permanent, especially against washing. Photocuring of AgNPs on textile fabrics using PI/UV system could serve as an alternative solution for the fixation problem [40].

Bottom et al. [41, 42] developed and assessed the efficiency of a novel, water-soluble photosensitizer, 4-(trimethyl ammonium methyl) benzophenone chloride, and used it for the photoinitiated graft copolymerization of 2-hydroxyethyl acrylate onto cellulose. El-Sheikh and coworkers [43–46] further utilized this efficient photoinitiator in the graft copolymerization of acrylic acid and acrylamide onto carboxymethyl starch and in the photooxidation of starch. The above cited references are the only ones found in the literature about the using of 4-(trimethyl ammonium methyl) benzophenone chloride. To the knowledge of the authors, the latter has never been used in the photosynthesis of AgNPs.

Benzophenone compounds are powders. They can absorb and dissipate UV radiation. Benzophenone compounds are used in bath products, makeup products, hair products, sunscreens, and skin care products. They protect the skin from the harmful effects of the sun.

In this work, a novel green method was adopted to synthesize AgNPs using the water-soluble 4-(trimethyl ammonium methyl) benzophenone chloride/UV system and silver nitrate as a precursor in the presence of a water-soluble polymer (CMS). While PI photogenerated AgNPs, CMS acted as both reducing and stabilizing agent. All components were water soluble; the process was simple and easy, and the synthesis conditions used were mild. The synthesized AgNPs are assessed by measuring the absorbance of the colloidal solution and the size and the shape of the synthesized AgNPs. The antibacterial properties and the durability of the finished wool and acrylic fabrics are characterized by measuring the growth of *S. aureus* (as G +ve) and *E. coli* (as G –ve) on the surface of the fabrics.

The same PI/UV system was further utilized to fix the synthesized AgNPs on wool and acrylic fabrics surface by photocrosslinking of AgNPs-CMS composite on wool or acrylic fabrics to impart durable antibacterial properties. The effect of irradiation time on antibacterial performance before and after repeated washing cycles was studied. The durability of the wool and acrylic fabrics finished against bacterial activity was tested by performing the antibacterial activity of the AgNPs treated fabrics towards Gram +ve and Gram –ve bacteria before and after repeated washing cycles (1, 3, 5, 7, 10, and 15).

## 2. Experimental

**2.1. Materials.** Wool fabrics were supplied by Misr for Spinning and Weaving Co., El Mehalla El Kobra, Egypt, and Plan weaved (25 yarns/cm in both weft and warp directions). Wool fabrics were scoured for 30 min at 30°C in a 2% nonionic detergent (based on weight of fabric), fabric:liquor ratio 1:50. The scoured fabrics were then rinsed with warm water and air dried.

Acrylic fabrics were supplied by Misr El Mahalla Co., Egypt. The fabrics were soaped with (2 g/L) nonionic detergent solution (Hostapal CV from Clariant, Egypt) with a liquor ratio 1:50, at 45°C, for 30 min. The scoured fabrics were then rinsed with warm water and air-dried.

Native maize starch (St.) was supplied by the Egyptian Company for Starch and Glucose Manufacture, Cairo, Egypt.

4-(Trimethyl ammonium methyl) benzophenone chloride was supplied by the associated Octel Ltd., Widnes, UK, and used without further purification.

Egyptol, a nonionic detergent of technical grade chemical, was provided by The Egyptian Company for Starch, Yeast, and Detergents, Alexandria, Egypt.

Monochloroacetic acid, sodium hydroxide, sodium carbonate, silver nitrate, hydrochloric acid, acetic acid, ethanol, and isopropanol were laboratory grade chemicals.

**2.2. Instrumentation.** The irradiation reaction vessel consisted of a quick fit water-cooled 125 W medium-pressure Hg lamp assembly as a UV-irradiation source immersed in a quick fit 150 mL cylindrical tube. The total dose of the UV irradiation was controlled by controlling the time of

exposure, that is, the reaction time. The reaction temperature was controlled using a thermostatic water bath.

### 2.3. Method

**2.3.1. Carboxymethylation.** Water-soluble carboxymethyl starch with DS = 0.2 was prepared according to a reported method [47].

**2.3.2. Preparation of Silver Nanoparticles.** AgNPs were prepared by photoreduction of silver nitrate using 4-(trimethyl ammonium methyl) benzophenone chloride/UV system [48]. AgNPs were prepared using a known weight of CMS (10 g/L) stirred in a known volume of distilled water (material : liquor ratio 1 : 20) in a beaker using a mechanical stirrer. After complete dissolution of CMS, an aqueous solution of PI (1 g/L) was added to the CMS solution followed by adding silver nitrate solution (1 g/L) under continuous stirring until complete mixing. The pH was finally adjusted to 7. Doing so, the beaker contents were poured in the irradiation tube and transferred to a thermostatic water bath with a magnetic stirrer. The UV lamp is now immersed in the solution to just above the bottom of the tube to allow the magnet to move and to let the whole solution be exposed to the UV irradiation. The temperature was then allowed to rise gradually until the required temperature (40°C) is reached. Finally, the UV lamp is switched on, and the whole contents were kept at this temperature for 60 min under continuous stirring. At the end of the reaction, the yellowish-brown colloidal solution is kept in a stoppered bottle at room temperature (25°C) [48].

**2.3.3. Antibacterial Finishing.** Finishing procedure was applied to acrylic and wool fabrics as follows. The fabrics were immersed in the AgNPs colloidal solution at room temperature for 1 h then padded to pick up 100%, dried at 60°C for 20 min, and finally washed thoroughly with water and air dried.

**2.3.4. Photocuring of AgNPs Finished Acrylic and Wool Fabrics.** AgNPs finished acrylic and wool fabrics were photocured at room temperature (25°C) using the water-cooled 125 W medium-pressure Hg lamp assembly as a UV-irradiation source for different irradiation durations (15, 30, and 60 min). The finished acrylic and wool fabrics were then washed by immersing the fabrics in an aqueous solution containing 5 g/L nonionic detergent and 2 g/L sodium carbonate using a fabric : liquor ratio of 1 : 50 at 45°C for 15 min. The fabrics were then picked up, rinsed twice with 100 mL water with stirring, hand squeezed, and air dried.

**2.4. Characterizations and Analyses.** The DS of the carboxymethylated starch sample was determined via determination of the carboxyl content according to a reported method [49].

The UV-Vis spectra of silver nanoparticles and 4-(trimethyl ammoniummethyl) benzophenone chloride were recorded using UV-2401, UV-Vis Spectrophotometer, Shimadzu, Japan, for the wavelength range from 190 to

550 nm. The wavelength ( $\lambda_{\max}$ ) at 256 nm is characteristic of 4-(trimethyl ammonium methyl) benzophenone chloride whereas  $\lambda_{\max}$  at 390–420 nm is characteristic of AgNPs. Synthesis of silver nanoparticles is expressed by absorbance of the colloidal solution of the samples under test. The absorbance, the broadening, and the wavelength of the band measure the intensity of the colloidal solution, that is, the conversion of silver ions to AgNPs. Very concentrated AgNPs samples did not show one smooth band (neither sharp nor broad) but showed a number of crowded sharp bands. This behavior leads to false readings. So, concentrated samples which showed this behavior were diluted “x” times, and the obtained absorbance value was then multiplied by “x” to obtain the actual absorbance value. The accuracy of this dilution technique was tested by comparing the absorbance readings of certain samples with moderate concentration before and after dilution. The readings were found approximately the same after multiplying by “x” times of dilutions.

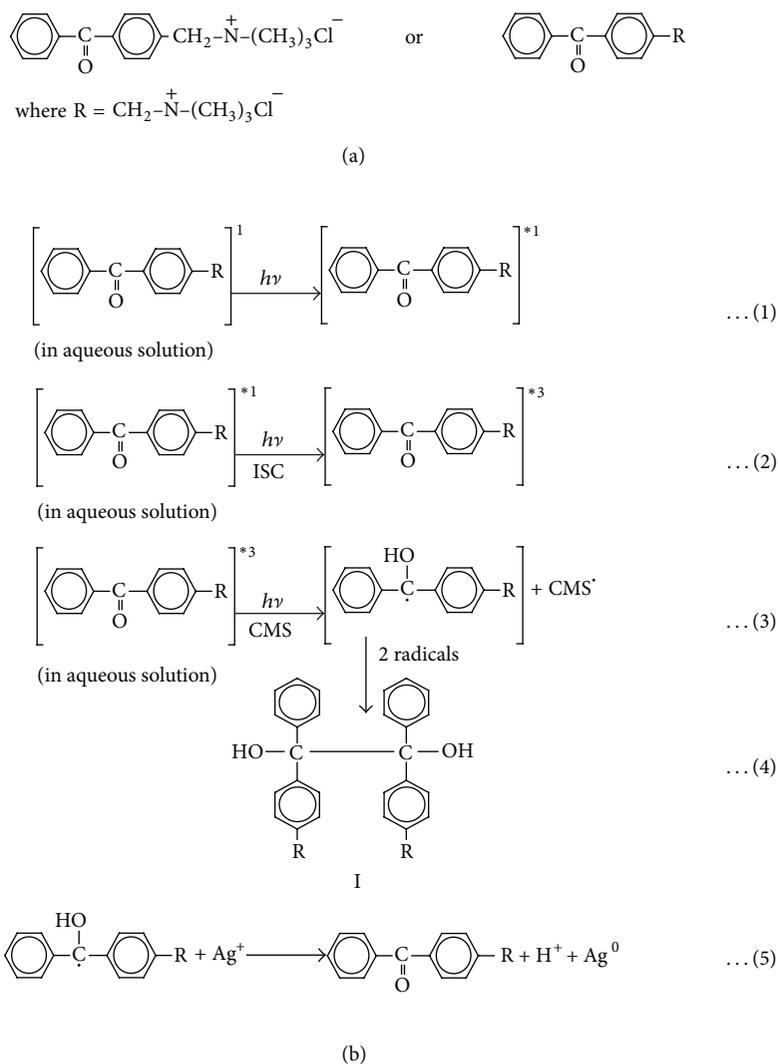
Transmission electron microscope was used to characterize AgNPs. Thus, the shape and size of the synthesized AgNPs were characterized by means of a JEOL-JEM-1200 transmission electron microscope. The samples were prepared by placing a drop of the colloidal solution on a 400 mesh copper grid coated by an amorphous carbon film and evaporating the solvent in air at room temperature.

Durability of the treated acrylic and wool fabrics against bacterial activity was obtained by performing the antibacterial activity of the AgNPs untreated and AgNPs treated acrylic and wool fabrics before and after repeated washing cycles (1, 5, 10, and 15 cycles). Each washing cycle was performed by washing the finished fabrics in an aqueous solution containing 5 g/L nonionic detergent and 2 g/L sodium carbonate using a fabric : liquor ratio of 1 : 50 at 45°C for 15 min. The fabrics were then picked up, rinsed twice with 100 mL water with stirring, hand squeezed, and air dried.

**2.5. Evaluation of Antibacterial Activity In Vitro.** The two bacterial strains used as well as the antibacterial spectrum of the samples were determined against the test bacteria by disk diffusion method on an agar plate [50].

## 3. Results and Discussions

**3.1. Mechanism of Photosynthesis of AgNPs.** 4-(Trimethyl ammonium methyl) benzophenone chloride structure is represented in Scheme 2(a). Under UV light excitation, 4-(trimethyl ammonium methyl) benzophenone chloride (in an aqueous medium) is first promoted to its excited singlet state (1); then, via fast intersystem crossing (ISC), it converts into triplet state (2). In the presence of CMS, which acts as an H-donor, the triplet transient state can undergo hydrogen abstraction with CMS to yield reactive radical species (3). Inactive species formation could take place by combination of two radicals of PI (4) forming the pinnacle derivative (I) (Scheme 2(b)). The greater the extent formation of compound I, the more pronounced the inactivation of the photosynthesis process [43–45]. The formation of CMS<sup>•</sup> radical (Equation (3)) initiates a photooxidation reaction which leads to the generation of new aldehydic end groups in



SCHEME 2: (a) Chemical structure of PI. (b) Mechanism of photosynthesis of AgNPs.

the CMS chain. The hydroxyl and carboxyl groups originally present in the CMS molecules in addition to the newly generated aldehydic end groups, due to the photooxidation reaction, all can act as reducing groups of the  $\text{Ag}^+$  to  $\text{Ag}^0$ . In addition, the radical of the PI formed according to Equation (3) can further reduce the silver ions to AgNPs as shown in Equation (5). Accordingly, one can expect a very efficient reducing system to arise from (1) reducing groups of CMS molecules, (2) radicals of CMS, and (3) radicals of PI. At the same time while the reduction is keeping on and AgNPs grow gradually, CMS will further form a stable protection layer on the AgNPs surface.

**3.2. Photosynthesis of AgNPs.** Figures 1(a) and 1(b) show the UV-Vis spectrum and TEM micrograph of the photosynthesized AgNPs, respectively. Figure 1(a) shows an intensive band with ideal bell shapes and high absorbance values at 406 nm. This indicates the formation of AgNPs [5, 8, 12, 51] and reflects how efficient is the current system in synthesizing

AgNPs under conditions used. The sharp band at 256 nm represents the PI. The appearance of this band means that PI is not totally consumed in the photoinitiation process or that it is regenerated from its radical according to its "life cycle" (Equations (1)–(5)). The reduction of  $\text{Ag}^+$  to  $\text{Ag}^0$  was successfully achieved via the generation of active PI $^*$  and CMS $^*$  free radicals [48]. Figure 1(b) shows the TEM micrograph. As clear from the figure, silver nanoparticles have spherical shape morphology and fine dispersion with mean particle sizes between 1 and 7 nm.

**3.3. Effect of Irradiation Time on the Durability of the Antibacterial Finishing.** Tables 1 and 2 show the effect of subjecting the AgNPs finished acrylic and wool fabrics to UV irradiation for different irradiation durations (15, 30, and 60 min) before and after repeated washing cycles (1, 5, 10, and 15 cycles) on the durability of the antibacterial finished acrylic and wool fabric, respectively.

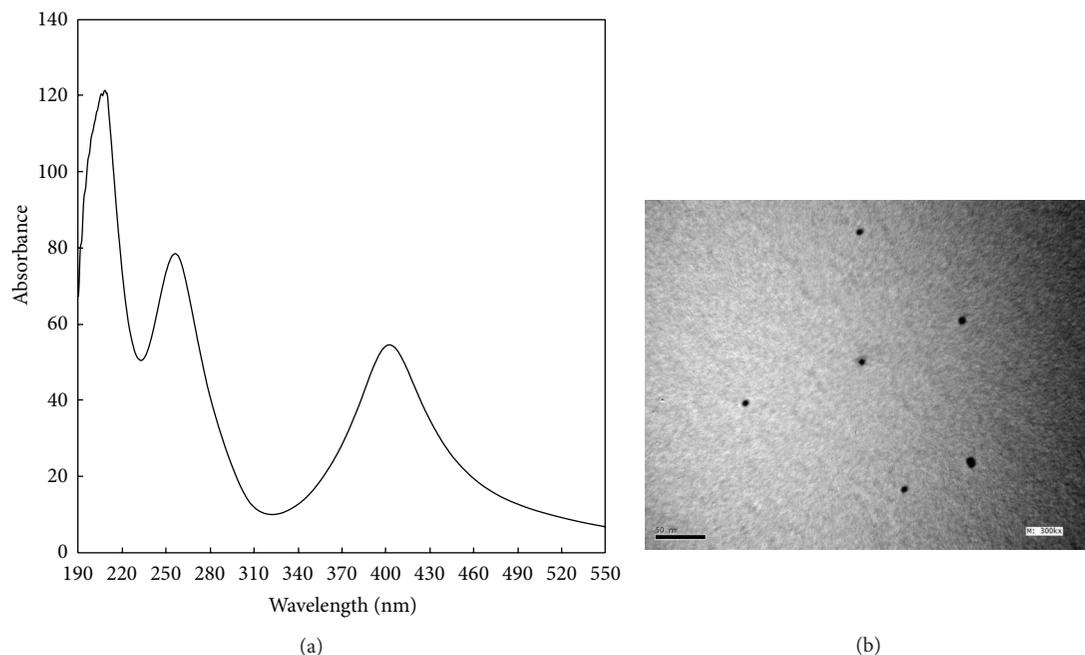


FIGURE 1: UV-Vis spectrum (a) and TEM micrograph (b) of the photosynthesized AgNPs. Synthesis conditions: CMS, 10 g/L; PI, 1 g/L; AgNO<sub>3</sub>, 1 g/L; 40°C; 60 min; pH 7.

TABLE 1: Effect of irradiation time on the durability of the antibacterial finished acrylic fabric. Finishing conditions: padding for 1 h, drying at 60°C for 15 min. Curing conditions: UV curing for 15, 30, and 60 min. Washing conditions: 5 g/L nonionic detergent and 2 g/L sodium carbonate using a fabric: liquor ratio of 1:50 at 45°C for 15 min., rinsing twice in 100 mL water.

Irradiation time (min)	Number of washing cycles	Inhibition Zone (mm)	
		<i>S. aureus</i>	<i>E. coli</i>
0	0	7	6
30	0	14	9
60	0	20	15
0	1	5	4
30	1	11	9
60	1	17	18
0	5	3	2
30	5	7	7
60	5	10	7
0	10	1	0
30	10	2	0
60	10	7.5	1
0	15	0	0
30	15	0	0
60	15	1	0.5

Tables 1 and 2 also show the effect of the different treatments of acrylic and wool fabrics with AgNPs and irradiation with UV on its antibacterial activity against two strains of bacteria *S. aureus* as G (+ve) bacteria and *E. coli* as

TABLE 2: Effect of irradiation time on the durability of the antibacterial finished wool fabric. Finishing, curing, and washing conditions: as Table 1.

Irradiation time (min)	Number of washing cycles	Inhibition zone (mm)	
		<i>S. aureus</i>	<i>E. coli</i>
0	0	0	0
15	0	16	13
30	0	19	19
60	0	24	22
0	1	0	0
15	1	14	12
30	1	16	15
60	1	19	18
0	5	0	0
15	5	7	3
30	5	10	7
60	5	14	10
0	10	0	0
15	10	1	0
30	10	5.5	2.5
60	10	10	5.5
0	15	0	0
15	15	0	0
30	15	1.5	0
60	15	3	1

G (-ve) bacteria. The irradiated treated samples to UV for up to 60 min show remarkable enhancement in the antibacterial



FIGURE 2: Inhibition zone of AgNPs finished wool fabric.

activity, in comparison with the nonirradiated acrylic and wool samples. In general, the antibacterial activity was found to increase with the increasing in irradiation time. Also, Tables 1 and 2 show that the antibacterial activity decreased by increasing the number of washing cycles from 1, 5, and 10 to 15 times, but these samples still have bacteriostatic effects; that is, although they show zero inhibition zone, they cannot be attacked by the bacterial growth and do not inhibit the bacterial growth. The antimicrobial activity of the treated acrylic and wool fabrics (Tables 1 and 2) is due to the effect of AgNPs on the fabrics, which interact with bacterial cells. The poor antibacterial function of Ag-treated acrylic and wool fabrics is due to the lack of strong binding between Ag ions (II) and acrylic fabrics as shown in nonirradiated samples with UV and washed samples over 15 times. The powerful antibacterial function of Ag-treated acrylic and wool fabrics is due to the strong binding between Ag ions (II) and fabrics as a result of irradiation with UV.

The PI/UV system cross-linked AgNPs-CMS film onto the surface of acrylic or wool sheet (acrylic or wool fabric) by photocrosslinking of AgNPs-CMS composite with both fabrics, consequently increased the durability of the AgNPs finished acrylic or wool fabrics.

AgNPs finished wool fabrics show more antibacterial activity than that for AgNPs finished acrylic fabrics as shown in Tables 1 and 2 due to more functional groups in wool that are more affected by irradiation time and less affected by washing cycles.

Figure 2 shows the disc diffusion test for AgNPs finished wool fabric sample. The sample (disc of 17 mm in diameter) is seen at the center of the figure; the clear ring around the sample is the area where the microorganisms are dead; the remaining area is the zone where the microorganisms are growing (bactericidal effect). From the figure, zero inhibition zone indicates killing of the microorganisms that existed on the sample but did not affect those outside the sample (bacteriostatic effect).

#### 4. Conclusions

PI, an ecofriendly photoinitiator/UV system, carboxymethyl starch and an ecofriendly polymer, and water (a solvent) were

used to synthesize AgNPs using silver nitrate as a precursor. Thus, the chemicals and the process are totally green. The reduction of  $\text{Ag}^+$  to  $\text{Ag}^0$  was successfully achieved via the generation of active  $\text{PI}^*$  and  $\text{CMS}^*$  free radicals using CMS, PI, and  $\text{AgNO}_3$  concentrations of 10 g/L, 1 g/L, and 1 g/L, respectively, at 40°C for 60 min at pH 7 using a M:L ratio of 1:20. AgNPs so obtained have spherical shape morphology. The sizes of synthesized AgNPs were in the range of 1–7 nm. The antibacterial performance is directly proportional to the irradiation time but inversely proportional to the number of washing cycles. However, after the 15th washing cycle, samples still have bacteriostatic effect; that is, although they show zero inhibition zone, they cannot be attacked by the bacterial growth and do not inhibit the bacterial growth. AgNPs finished wool fabrics show more antibacterial activity than that for AgNPs finished acrylic fabrics.

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