



Development of Softener Containing Metal Nano-Particle for Multipurpose Textile Finishing

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Abstract: Treatment of cotton-based fabrics with softeners is very important to enhance its agreeable soft hand, antistatic and sewability properties as well as to improve wear-ability of cotton fabrics. Functional finishing of cotton fabrics with nanoparticles impart the fabrics one or more functional properties. These functions include, for example, self-cleaning, antimicrobial, UV-protective as well as antimicrobial activity. This research work aimed to develop a new type of softeners formulation having one or more nanoparticles for application as multi-functional softener. The effect of softener type and kind of nanoparticles used on the ultimate softener and nano-particles properties were investigated. The stability of softener nanoparticles hybrid formulation as function of softener and nanoparticles type were as determined. The treated fabrics were monitored for tensile strength, softness, wrinkle recovery angle and antibacterial activity particle size and shape by mean of UV-vis-spectrophotometer, X-ray diffraction, SEM and TEM analysis.

Keywords: Cotton, Functional Finishing, Softener, Nanoparticles, Antimicrobial.

Introduction

At the point when a fabric or garment is purchased, the consumer dependably tries to choose it on the basis of his own assessment method for a particular end use. This assessment is called 'subjective evaluation of fabric'; the result of this kind of assessment varies from a fresh fabric and the same fabric after a certain use, i.e. the fabric becomes inferior due to a certain number of wash cycles in which it goes.

Needing for a fabric softener was recognized to the market after introducing synthetic detergents to it. Fabric softeners may be known as chemical compositions applied to textile fabrics which claim to give a better comfort feeling. Fabric softeners may be roughly classified into two groups: Non-permanent softeners, which can be removed fairly easily by its washing, and permanent softeners, which still exhibit a distinctly soft handle even after several washing cycles¹.

Application of such softening treatment technique on textiles fabric provide it with desired handle, making further processing easier and improving the wear properties of the treated fabrics². The main ingredients in fabric softeners are anionic, cationic, non-ionic and amphoteric surfactants³. Dissolving softener and water produce colloidal solution. Due to water-soluble property between softener molecules and solvent (water) not only free ions but ion and solvent molecular compounds are composed⁴. Cationic softener is the most widespread between all fabric softeners. There are two distinct parts on which surfactant of softeners consist: hydrophobic part and hydrophilic part^{3,4}. The hydrophobic (or fatty) part is water repellent, and does not blend with water. The hydrophilic part is water loving part, resulting in compounds dispersing and blends in water. During softening treatment process softener's positively charged surfactant ions are directed and attracted to the negatively charged fibers and stick to them

strongly. The surfactant particles adhere to textile fabric with their long hydrophobic chains pointing outward. These surfactant particles decorate every fiber in every thread of the textile fabric material, producing an oily coating on them. As a result of lubrication of the fabric by hydrocarbon chains, so each fiber slides easily within a thread and each thread slides easily within the fabric. This lubrication treatment enhances the fabric flexibility and makes it feel softer and more flexible⁵.

Nanotechnology is a branch of a scientific technology in which structures that have excellent properties creates by controlling atoms and molecules, functional materials, devices and systems on the nanometer scale by involving precise placement of individual atoms of the size around 0.1- 100 nm. The unique and new properties of materials nano-particles have attracted scientists and researchers of the textile industry also and hence the research interest in using nanotechnology in the textile industry has rapidly increased. This is mainly due to the fact that textile is one of the best areas for developing nanotechnology. Fibres provide optimal substrates where a large surface area is present for a given weight or volume of fabric⁶.

Application of Nanotechnology and utilization of nanoparticles to textile materials has been the object of several studies, producing finished fabrics with different functional performances was the main target. For example, nano-Ag has been used for imparting antimicrobial properties⁷⁻⁹, nano-TiO₂ for UV-blocking and self-cleaning properties¹⁰⁻¹² and ZnO nanoparticles for antibacterial and UV-blocking properties¹³⁻¹⁵.

Conventional textile finishing methods used for imparting different properties, such as water repellence and stain repellence, to the textile fabrics often do not lead to permanent effects, and may lose their functions after use or laundering for several times. Nanoparticles can provide the treated fabrics with high durability as they possess large surface area and high surface energy that ensure better affinity for fabrics and lead to an increase in durability of the desired textile functions¹⁶. Thus, decreasing the size of particles to nano-scale dimensions fundamentally changes the properties of the material. By virtue of its small size and high surface energy, nanoparticles are bound to the fabric surface by Van der Waals forces which give a reasonable wash fastness. Generally, as wash fastness is one of the particular requirements for fabrics, it is strongly correlated with the specific nanoparticles adhesion to the fibers. For increasing the wash fastness, application of such nanoparticles can be carried out by dipping the fabrics in a solution containing a specific binder^{13,17}. Improvement of wash fastness may be done by the formation of covalent bonding between the fabrics surface and nanoparticles. In these cases, the excellent functional properties are still maintained after about 55 home launderings¹⁸.

The aim of this work was to develop a new softeners formulation based on silicon microemulsion and silver nanoparticles. The stability of these nanoparticles in its nano-form in the formulation was investigated and the efficacy of SiME-Ag hybrid as softener for cotton fabrics was evaluated.

1. Materials and Methods

1.1. Cotton fabric

Mill desized, scoured and bleached cotton fabric, plain weave, supplied by El-Nasr Company for spinning weaving and Dyeing El-Mahallah El-Kubra, Egypt. The fabric was further purified in the laboratory by washing at 100 °C for 60 min using a solution containing 20 g/L, Na₂CO₃ and 1 g/L, non-ionic surfactant. The fabric was then washed several times with boiling water then with cold water and finally dried at ambient conditions.

2.2. Chemicals

3-Chloro-2-hydroxypropyl trimethyl ammonium chloride (69%) of technical grade chemicals was kindly supplied under the commercial name Quatt-188 by Aldrich, Sodium hydroxide, acetic acid, hydrochloric acid, monochloroacetic acid, sodium carbonate, silver nitrate, carboxymethyl cellulose were of laboratory grade chemicals. amino functional silicon softener, micro emulsion (SiME) and nonionic softener was kindly supplied form by Texchem Egypt Co., Ltd.

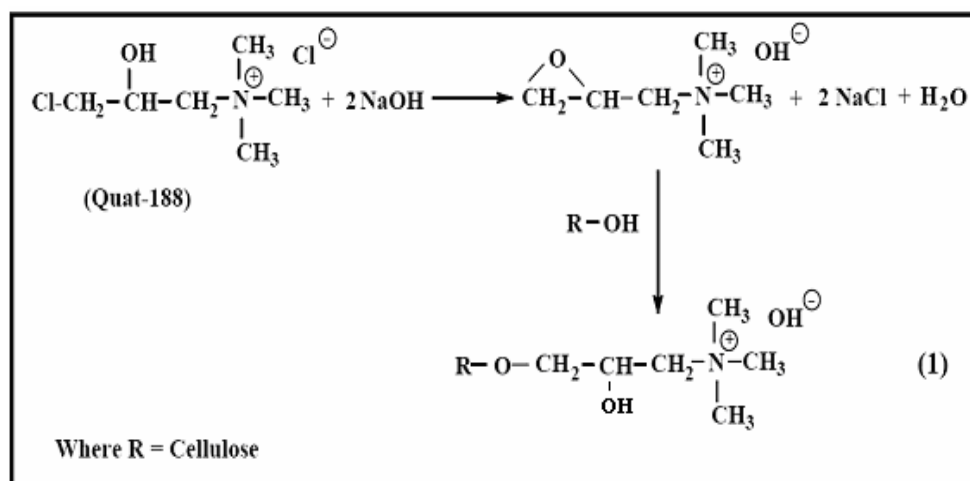
2.3. Methods

Carboxymethylation of cotton fabric (CMC)

Cotton fabric was partially carboxymethylated (CMC) by a method similar to those previously reported¹⁹⁻²². Carboxymethyl cellulose (CMC) is produced commercially in a two-stage process consisting of a mercerization in which, bleached cotton fabric were impregnated with 15 wt. % aqueous NaOH for 5 min at room temperature squeezing to a wet pick up of 100% then dried at 60 °C for 5 min. Etherification is the second stage in which the alkali treated samples were steeped in aqueous solution of ammonium salt of monochloroacetic acid (0–3 mol) for 5 min at room temperature. These samples were then squeezed to 100% wet pick up, sealed in plastic bags and heated at 80°C for 1 h then washed and dried at room temperature.

Cationization of cotton fabric

Cationic modification of the cotton fabric was applied by using the pad-dry-cure method²². The experimental procedures were carried out as follows: Quat-188 was mixed with sodium hydroxide solution at a NaOH/Quat-188 molar ratio of 2:1. The fabrics were padded in this mixture in two dips and nips, and then squeezed to a wet pick-up of about 100%. The cotton fabric was dried at 80°C for 10 min and then cured at 120°C for 3 min. The fabric was washed with cold water and 1% acetic acid, followed by several washing cycles and finally dried under the normal laboratory conditions.



Preparation of silver nanoparticles (AgNPs):

AgNPs were prepared as per the devised method as follows. A known weight of carboxymethyl cellulose CMC was dissolved in 95ml distilled water and the pH of the solution was adjusted at certain pH within 10 using dilute solution of sodium hydroxide. The solution was completed to 100 ml by distilled water then brought to heating at 80°C temperatures for some minutes. At this end the already prepared AgNO₃ solution were added drop-wise under the action of magnetic stirrer. Factors affecting the reduction efficiency and stability as well as shape and size of the formed nanoparticles were studied as given later²³.

Application of silicon micro emulsion (SiME) and nonionic Softener loaded with silver nanoparticles (AgNPs) on cotton and modified cotton fabric.

Two different concentrations [25,50ppm] of pre-prepared silver nano particle were drop-wise added to different concentration of both silicon micro emulsion and nonionic softener [1-5%]. The stability of the nano particles in the softener solution was evaluated using UV-vis spectra. The blank cotton, carboxymethyl cotton and cationized cotton fabric was treated with these different concentrations of softener loaded with silver nanoparticles solution for about 5min followed by padding at 100% pickup then the treated fabrics were dried at 100 °C for 5 min then cured at (140 °C) for (5 min).

3. Testing and analysis

3.1. Ultraviolet-visible (UV-vis) Spectra:

UV-vis spectra have been proved to be quite sensitive to the formation of silver colloids because AgNPs exhibit an intense absorption peak at 314-318 nm due to the surface Plasmon excitation which describes the collective excitation of conductive electrons in a metal.

3.2 Transmission Electron Microscopy (TEM):

Shape and size of AgNPs were practically obtained using TEM; JEOL-JEM-1200. Specimens for TEM measurements were prepared by placing a drop of colloidal solution on 400 mesh copper grid coated by an amorphous carbon film and evaporating the solvent in air at room temperature. The average diameter of the prepared AgNPs was determined from the diameter of 100 nanoparticles found in several arbitrarily chosen areas in enlarged microphotographs.

3.3. Scanning electron microscopy measurements

Microscopic investigations on fabric samples were carried out using a Philips XL30 scanning electron microscope (SEM) equipped with a LaB6 electron gun and a Philips-EDAX/DX4 energy-dispersive spectroscope (EDS). Images were taken at different magnifications, using secondary electrons (SE) in accordance with the clarity of the images. Fabric samples were fixed with carbon glue and metalized by gold vapor deposition to record images.

3.4. X-ray diffractometry

X-ray diffraction patterns of samples were recorded on a STOE STADI P transmission X-ray powder diffractometer system by monitoring the diffraction angle from 10 to 80 (2 θ) using monochromatized Cu K α ($k = 1.54051 \text{ \AA}^\circ$) radiation.

3.5. Antibacterial tests

All antibacterial activity tests were done in triplicate to ensure reproducibility. The antibacterial activity of fabric samples was evaluated against Escherichia Coli and staphylococcus aureus, (ATCC 1533) bacteria using disk diffusion method. 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 105 colony-forming units of E. coli bacteria were inoculated on plates, and then 292 cm² of each fabric samples was planted onto the agar plates. All the plates were incubated at 37°C for 24 h and examined if a zone of inhibition was produced around samples.

3.6 Wrinkle recovery angles measurement.

Dry crease recovery angles (DRA) of the treated samples were determined in warp and weft direction; (w+f) according to the AATCC standard method [66-1998].

3.7. Roughness Measurement:

Roughness was measured according to AATCC standard test method using a Surfacer (1700a).

4. Results and Discussion

4.1 Stability of silicon micro emulsion and non ionic softener loaded with silver nano particles.

Figure1 shows the UV-vis spectra of the silicon micro emulsion and nonionic softener loaded with different concentrations (25ppm, 50ppm) of silver nano particle colloid. Obviously by using nonionic softener (d) at 50ppm silver nano particle the electronic absorption spectra is broadened with small absorption intensity of the Plasmon peak around 405 nm. The implication of this is that the silver ions could not be stable under this concentration. In contrast carrying out at 25 ppm of AgNPs (c) verifies the stability of Ag⁰ as evidenced by the Plasmon peak appearance at 415nm which, in turn, signifies enhancement in the absorption intensity and slitting the band toward longer wavelength. Similar absorption bands but with greater intensity are observed when using silicon micro emulsion SiME the silver nanoparticles was more stable at different concentrations (a,b). It may be, therefore, concluded that the stability of AgNPs in the SiME is more than that of nonionic softener at the same concentrations of AgNPs.

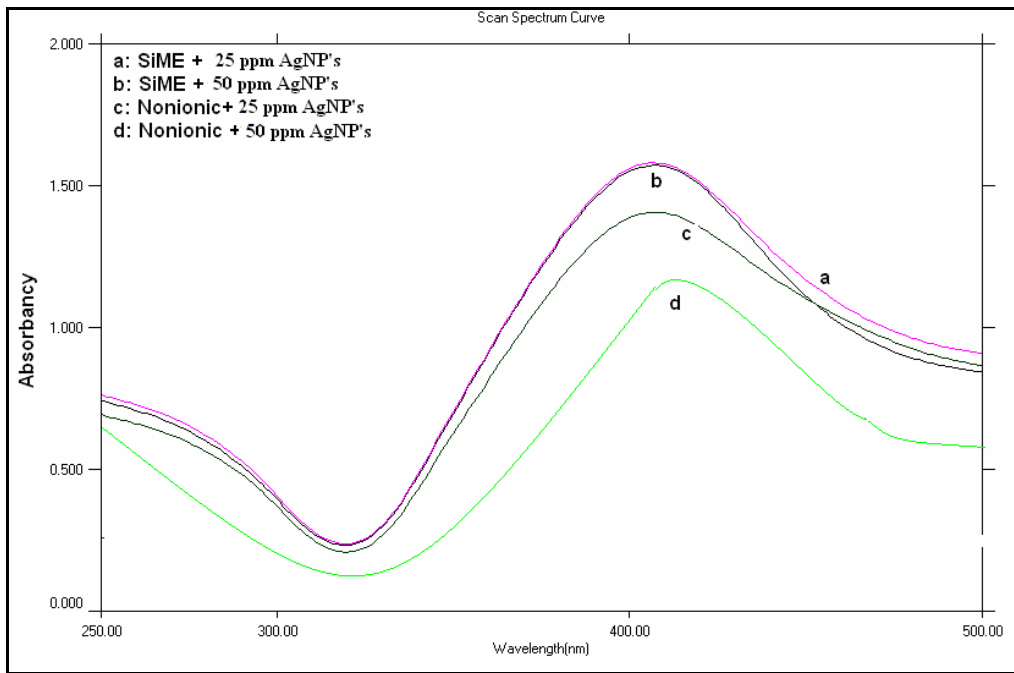


Figure 1 UV-vis spectra of the SiME and nonionic softener loaded with different concentrations of silver nano particles

4.2 Characterization of silicon micro emulsion loaded with silver nano particles using TEM.

Figure 2A illustrates the TEM image and the particle size distribution histograms of nonionic softener loaded Ag-NPs formed using 25ppm silver nanoparticles. The TEM image shows small size spherical particles. The corresponding size distribution histogram clearly illustrates the size of the formed particles. The majority particle size distribution was attained 10nm.

Figure 2B shows the TEM image and particles size distribution histograms of SiME loaded Ag-NPs formed using 25ppm silver nanoparticles. The size of the majority of the formed particles ranges between 14-15 nm.

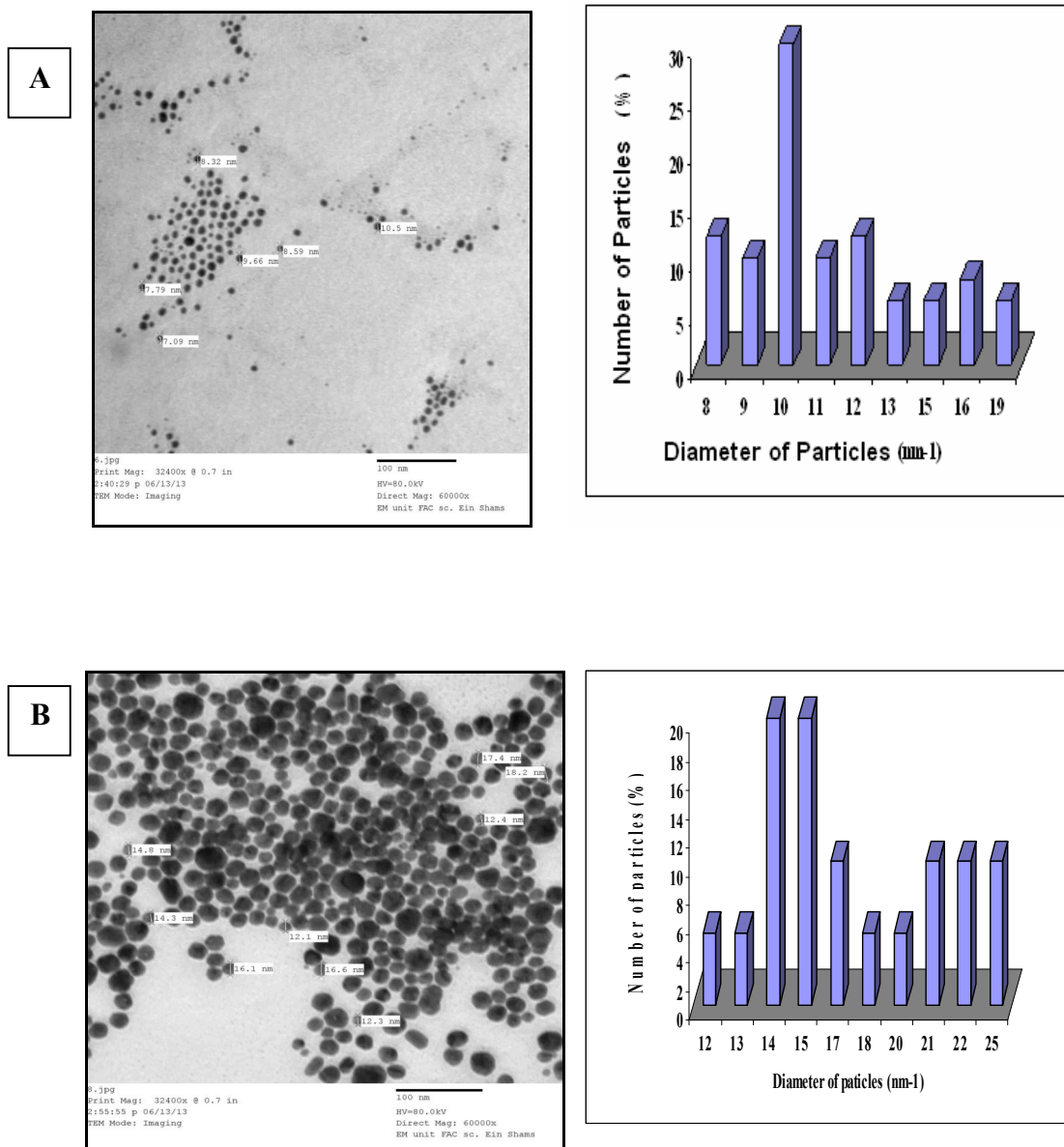


Figure 2. TEM images and Histograms of Particles Size Distribution of (A) nonionic softener loaded Ag-NPs and (B) SiME loaded Ag-NPs

4.3 Studying application of SiME loaded with silver nano particles on the cotton fabric and CMC cotton and cationized cotton

4.3.1. Physical properties of the treated CMC cotton

Proposed reactions pathway and development of semi-interpenetrate network during the application process and the subsequent curing step, amino-silicones undergo two types of reactions. The first is ionic interaction between protonated amino groups of the amino silicon softener molecule and the negatively charged cotton or CMC fabric, which brings about which brings about an improvement in wet wrinkle recovery angle of the treated cotton fabric. The second reaction is between the silicone molecules themselves through their respective reactive groups, prompting a self-polymerized, cross-linked elastomeric network. The second reaction occurred during the curing step, (i. e. collapsed fabric state) which mean improvement the dry wrinkle recovery of the fabric. Both these reactions ensures durable higher wet and dry wrinkle recovery as well as permanent softness and hence the permanency to the overall treatment. We proposed that incorporation of ammonium based silicon softener in the structure of ionically crosslinked cotton fabric induces besides strong

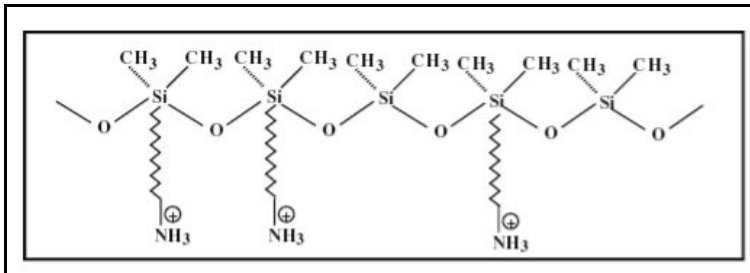
coulombic forces, weaker forces such as dipole–dipole, hydrogen bonds, van der Waals interactions in addition to ether crosslinking with cotton cellulose²⁴⁻²⁷.

These interactions can be clarified as takes after. Cotton cellulose reacts with monochloroacetic acid in presence of sodium hydroxide to bring about carboxymethylated cotton (CMC) as recommended by structure I.

Cell O CH₂ COO⁻ Na⁺

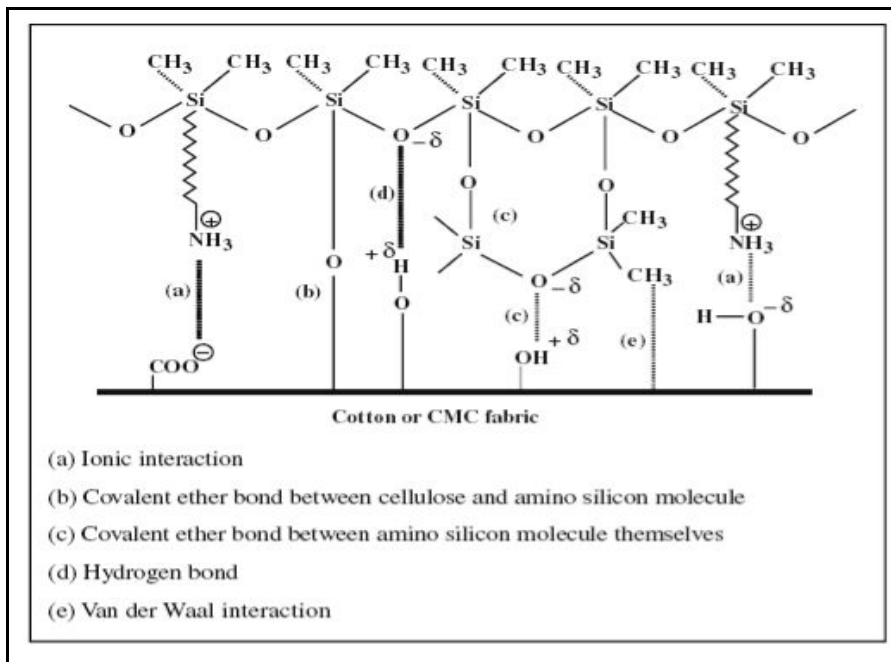
(Structure I, CMC).

In acidic medium the nitrogen atom in amino functional SiME/ AgNPs is protonated and converted to cationic as represented by structure II



(Structure II, protonated amino silicon softener molecule). CMC bearing the negatively charged carboxymethyl groups and the positively charged protonated amino group in SiME/ AgNPs molecule- which loaded with silver nano particles -may allow crosslinking when these groups are localized at two adjacent cellulose chains as suggested by structure III. The latter shows also the final proposed semi-interpenetrate network (semi-IPN) formed inside the cotton fibers. Once, structure III is achieved, the wet and dry wrinkle resistance properties as well as durable softness of cotton fabric may be realized.

The magnitude of wrinkle resistance whether wet or dry, fabric softness and other fabric properties would depend on the degree of crosslinking, eventual location of the crosslinks, proportion of intra/inter-chain crosslinks, concentration of amino silicon softener, pH and state of cotton during crosslinking.



(Structure III, schematic representation show the final proposed

Semi-interpenetrate network (semi-IPN) obtained inside the cotton fibers. Ionic crosslinked, ether crosslinking, hydrogen bonding and van der Waal interaction are formed between cotton or carboxymethylated cotton fabric and amino silicon softener).

Figure.3 show the effect of SiME/ AgNPs concentration on dry and wet wrinkle recovery angle of the treated fabric respectively. It's seen that increasing SiME/ AgNPs concentration from zero to 30 g/L was accompanied by an increment in both DRA and WRA. Further increased in SiME concentration up to 40 g/L, has for all intents and purposes no impact on the DRA and WRA of the treated cotton fabrics.

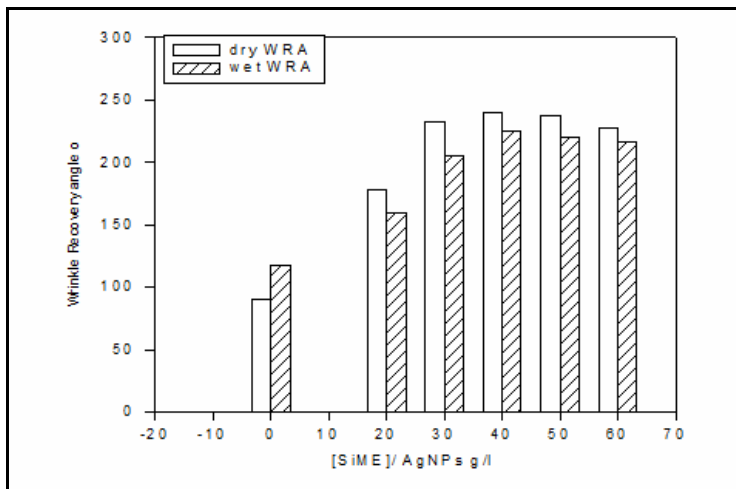


Figure.3 Effect of SiME concentration loaded with silver nanoparticles on Wrinkle recovery angle (wet and dry) of the treated CMC fabric

The tensile strength of a fabric is a standout amongst the most imperative properties of a fabric and most of the finishes affect the tensile strength to the largest extent than any other property. The change in the values of tensile strength of various concentrations of SiME/ AgNPs nanoparticle treated fabrics compared with untreated are given in Figure 4. There is a decrease in the tensile strength but not very significant. The tensile strength of the fabric diminishing as increasing the concentration of the SiME/ AgNPs concentration loaded with AgNPs on the fabric.

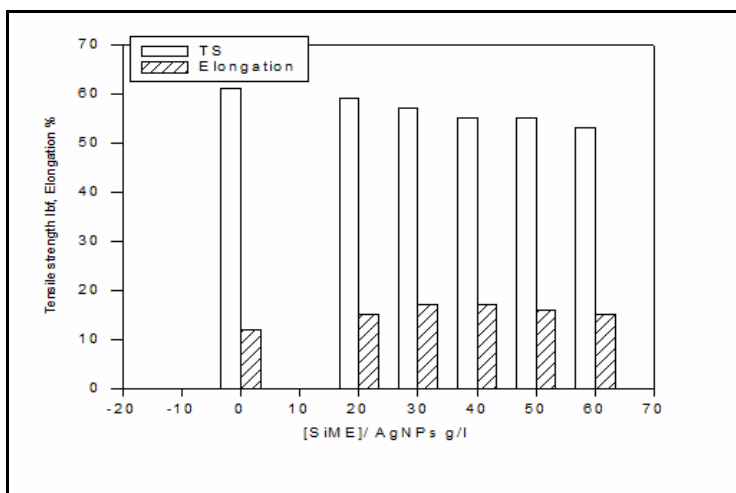


Figure. 4 Effect of SiME concentration loaded with silver nanoparticles on tensile and elongation properties of the treated CMC fabric

4.3.1.1 Effect of Ag nanoparticles concentration on roughness properties of softener treated fabric.

Table 1: Effect of Ag nanoparticles concentration on roughness properties of softener treated fabric

Sample / silver nanoparticles	Roughness ((μm)		
	Blank cotton	Carboxymethyl cotton	Cationized cotton
Zero	17.63	20.03	17.04
25ppm	19.41	18.44	15.25
50 ppm	18.01	16.82	16.82

Table 1. disclosed that roughness properties of cotton fabric treated with non ionic softener along with silver nanoparticles, increase by increase amount of silver nanoparticles up to 25ppm in case of cotton treated fabric while decrease in case of Carboxymethylcotton as well as Cationized cotton further increase in silver nanoparticles leads to decrease in roughness properties in case of blank cotton and carboxymethyl cotton .This effect is oppositely observed in case in cationized cotton.

4.3.2. Scanning electron micrograph (SEM)

In this study, we investigated the effects of SiME/ AgNPs treatments on cotton fabrics by comparing the micrographs of cotton, CMC before and after treatment with the same concentration of SiME in presence and absence of AgNPs. Fig 5 shows scanning electron micrograph of CMC. It is evident for micrograph that the fibers are swelled and show flat ridges, concave grooves, and harsh fibre surface. From CMC micrograph Fig 5, we can see that the change in the structure of fibers surface is comparatively notable. After carboxymethylation treatment the surface of cellulose fibers become rough, loose and striated^{28,29}. Fig. 6 shows SEM of CMC fabric after treatment with SiME. It is evident that, the surfaces of CMC fibers treated with SiME/ AgNPs had swelled and circulated fibres ridges, very smooth fibre surface, no concave grooves or protruding fibrils are observed. Although carboxymethylation reaction reduces the fibre smoothness and increase the surface ditches (as seen in Fig. 5), subsequent treatment of CMC fabric with SiME/ AgNPs highly improved the surface roughness and homogenously covered all ditches and grooves (Fig. 7). This may be attributed to the increased surface negativity after carboxymethylation reaction which results in an increase adhesion of SiME/ AgNPs to the fibres. It could be concluded that, post-treatment with SiME/ AgNPs results in a remarkable changes in surface properties regardless of the used substrate i.e., cotton, CMC as confirmed by SEM. The extent of surface modification, expressed as smoothness, coating of loose fibers, as well as disappearing of ditches and grooves, was determined by the type of post-treated substrate and, location, extent of distribution as well as degree of fixation of SiME onto and/or within this substrate.

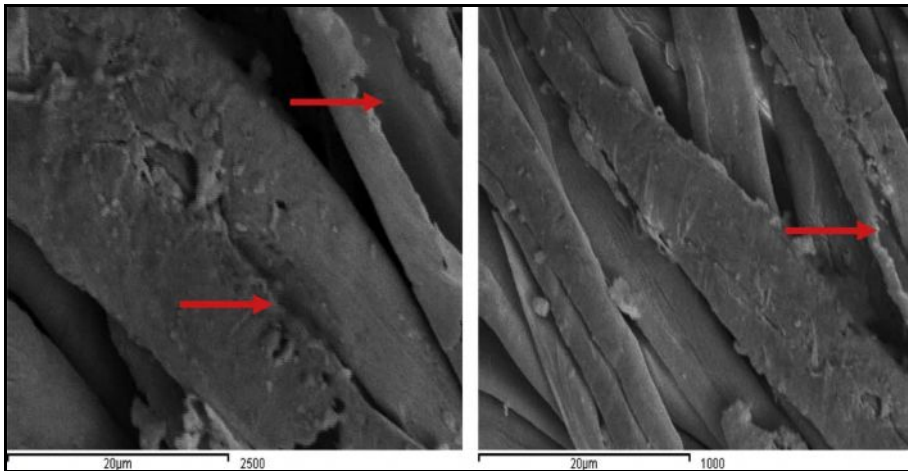


Figure. 5. SEM of CMC fabric

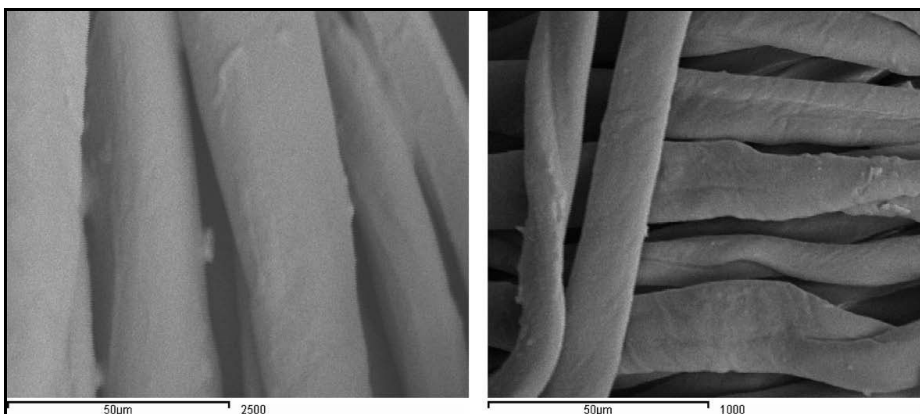


Figure 6 SEM of CMC Cotton treated with SiME.

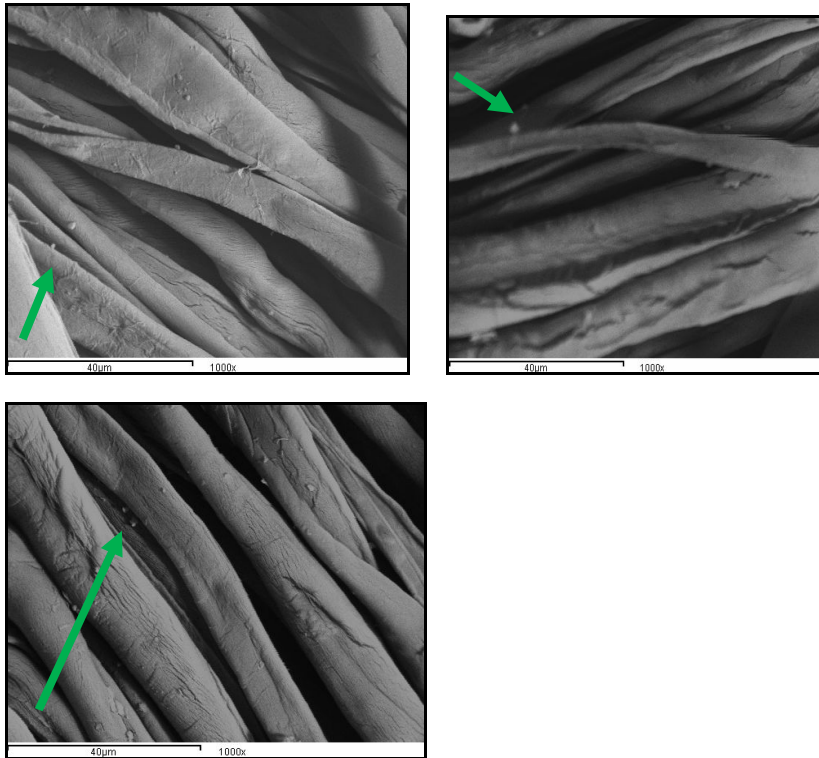


Figure 7 SEM of CMC Cotton treated with SiME/AgNPs.

4.3.4. XRD of CMC Cotton treated with SiME/AgNPs

Treated fabric was analyzed through X-ray diffraction Analysis for confirming the crystalline nature of the silver nanoparticles. Numbers of Bragg reflections was shown through The XRD pattern that may be indexed on the basis of the face-centered cubic structure of silver. A comparison between standard and our XRD spectrum confirm the formation of silver nanoparticles in our experiments were in the form of nanocrystals, as evidenced by the peaks at 2θ values of 40.28° , 44.04° , 64.34° , and 77.28° corresponding to (111), (200), (220), and (311) Bragg reflections, respectively [30], which may be indexed based on the face-centered cubic structure of silver. X-ray diffraction results clearly show that the silver nanoparticles formed by the reduction of Ag^+ ions by the carob leaf extract are crystalline in nature. The unassigned peaks at $2\theta = 27.96^\circ$, 32.28° , and 46.18° in Figure 8 are thought to be related to crystalline and amorphous of the cotton fabric.

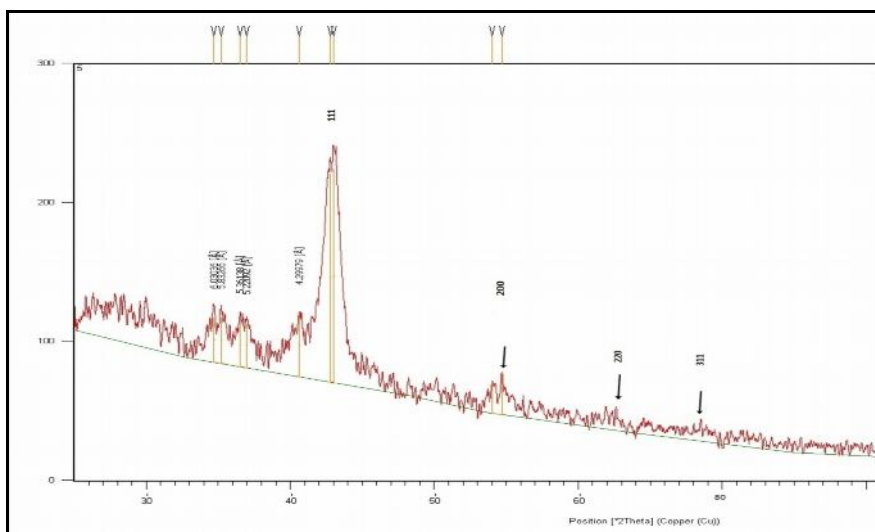


Figure 8 XRD of CMC Cotton treated with SiME/AgNPs

4.3.5 Antibacterial Activity of CMC Cotton Fabrics Treated With SiME/ AgNPs:

Figure 9 shows the inhibition zone diameter, as a measure of the antibacterial activity of nanosilver-loaded fabric chemically modified CMC in presence of the Silicon micro-emulsion SiME/AgNPs. The antibacterial action of the cotton fabrics in question is unequivocally due to the release of Ag^+ from the Ag nanoparticles present in the fabric. These Ag^+ ions come in contact with bacterial cells and kill them. The bactericidal action of Ag-loaded fabric is manifestation of the nature of the cotton substrates and ability of the latter to absorb the silver nanoparticles. Presence of SiME molecules would certainly open up the structure of cotton thereby helps establish better adsorption of nanosilver particles. Hydrophilicity of these molecules by virtue of their carboxylic groups enhances the swell-ability of cotton fabric and, therefore, diffusion and adsorption of nanosilver particles.


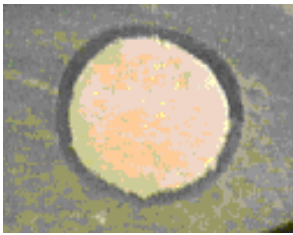

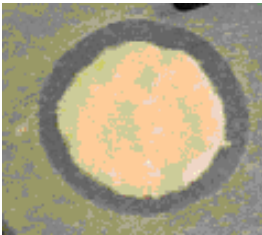
	Inhibition zone diameter (mm/1cm Sample)	
	Escherichia coli (G ⁻)	Staphylococcus aureus (G ⁺)
Blank	0.0	0.0
CMC cotton treated with SiME	15 mm/cm sample 	18 mm/cm sample 
CMC cotton treated with SiME/ AgNPs	17 mm/cm sample 	20 mm/cm sample 

Figure. 9 inhibition zone of CMC cotton treated with SiME /AgNPs

4.4. Effect of cationization of cotton on the application of silicon micro-emulsion loaded with silver nanoparticles

4.4.1. Physical properties of the treated cationized cotton fabric

The pre-cationized cotton sample having the nitrogen content of 0.09% was treated with different concentrations of silicone micro-emulsion softener SiME/AgNPs. Results obtained are set out in figure 10. Figure 10 shows that increasing the softener concentration enhance the, DRA along with a slight decreasing in TS. The basic function of a softener is to impart a particular handle to a textile surface to make the garment or fabric feel more appealing. Of the silicone softeners available, perhaps the most common in current industrial usage are the amino functional types. Amino-functional groups linked to polydimethylsiloxanes enable an improved orientation and substantively of the silicone on the substrate. This leads to an optimally soft handle and is often described by the term “super soft”. Amino silicones are by far the most extensively used functional silicones for textile finishing applications³¹. Actual surface modification is caused by specific properties of the silicone molecules and the functional groups attached.

These properties include, (a) lubrication and decreased frictional coefficient due to the lower intermolecular interactions between neighboring methyl groups, together with easy molecular rotation around the oxygen group of the silicone chain and (b) antistatic properties of the amine functional groups.

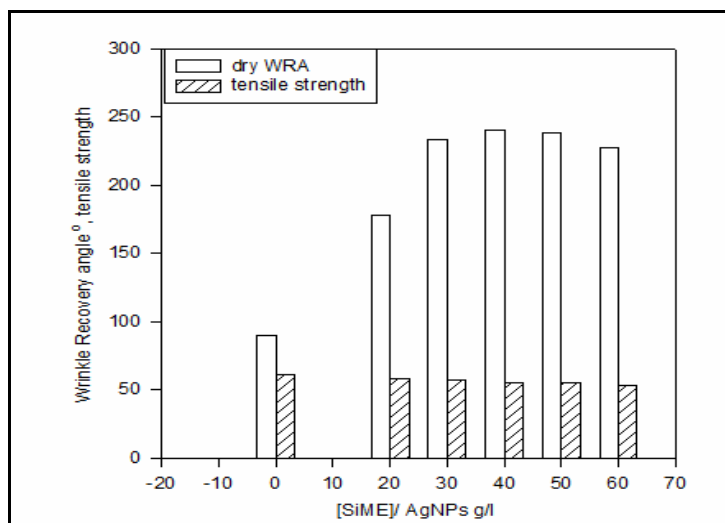


Figure.10 Effect of SiME concentration loaded with silver nanoparticles on physical properties of the treated cationized cotton fabric

4.4.2 Effect of Ag nanoparticles concentration on the roughness properties of SiME treated fabric

Table 2: Effect of Ag nanoparticles concentration on the roughness properties of SiME/AgNP's treated fabric

Sample / silver nanoparticles	Roughness ((μm))		
	Blank cotton	Carboxymethyl cotton	Cationized cotton
Zero	17.63	20.03	17.04
25ppm	15.46	17.77	17.29
50ppm	17.13	18.21	18.61

Table 2 show the effect of Ag nanoparticles concentration on the roughness properties of SiME/AgNPs treated cotton fabric as we can see there is a remarkable increase in roughness properties by increase concentration of silver nanoparticles in the treatment bath in case of cationized treated cotton fabric while the roughness of blank cotton fabric as well as Carboxymethyl cotton decrease by using the amount of silver nanoparticles, 25ppm while increase amount of silver nanoparticles up to 50ppm leads to increase in roughness properties of the surface cotton fabric whatever the post treatment .

4.4.3. Antibacterial activity of the treated cationized cotton fabric

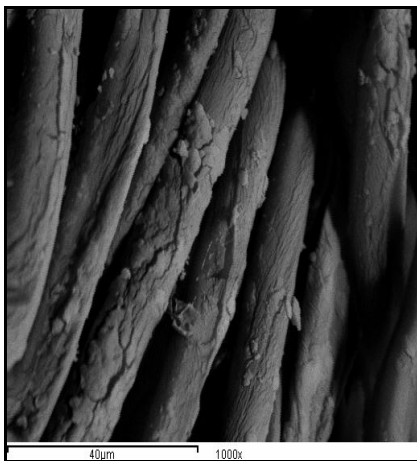
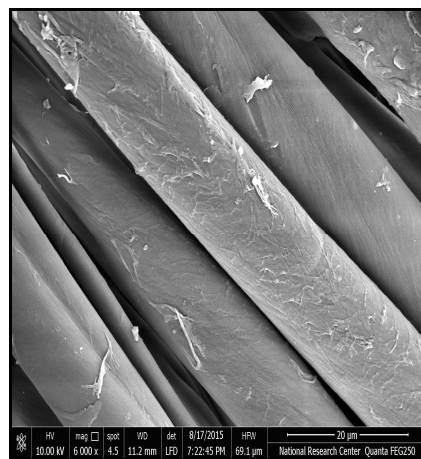
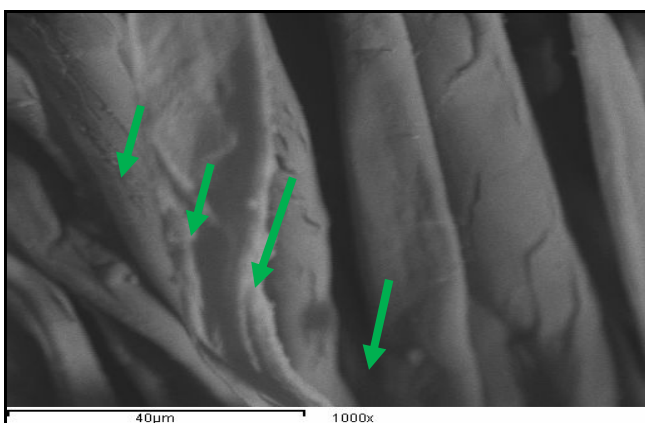
Cotton fabric with good antibacterial activity is obtained by the cationization of cotton using Quat-188 (*3-Chloro-2-hydroxypropyl trimethyl ammonium chloride*) in the presence of alkali and loaded with SiME/AgNPs. The antibacterial activity of the treated cotton fabrics are evaluated against *E. coli* and *S. aureus*. The activity of the cells of both microorganisms decreased by increasing the cationization of the cotton in comparison with the control, hence, the antibacterial activity of the treated cotton fabrics increased. The antibacterial activity of Cationized cotton treated with SiME /AgNPs was also evaluated, and the results in table 3 show that the activity of the cells decreased by increasing the concentration of cationized cotton treated with SiME /AgNPs. There is proposed mechanism for the antibacterial activity. the cationized cotton, interact with the negative charged residues present at the cell wall of bacteria leading to alteration of the cell wall permeability, consequently, interfere with the bacterial metabolism and result in the death of cells.

Table 3 inhibition zone of Cationized cotton treated with SiME /AgNPs

Sample treated	Inhibition zone diameter (mm/1cm Sample)			
	25ppm		50ppm	
	S.aureus (+ve)	E.coli (-ve)	S.aureus (+ve)	E.coli (-ve)
Blank	0.0	0.0	0.0	0.0
Cationized Cotton treated with SiME /AgNPs	17	15	21	16.5
Cationized cotton treated with SiME	15	13	17	14

4.4.4. SEM Characterization of the treated cationized cotton fabric

Figure. 11a shows scanning electron micrograph of cationized cotton fabric. It is evident that the fibres show harsh surfaces whereas concave grooves are still appear. Fig. 11c shows scanning electron micrograph of Cationized cotton treated with SiME /AgNPs. It is evident form micrograph that, the fibres are swelled and show flat ridges, concave grooves, few protruding fibrils and harsh fibre surface. From micrograph (Fig11 a,b,c), we can see that the change in the structure of fibres surface is comparatively notable. After cationization treatment the surface of cellulose fibres become rough, loose and striated. The external fibrillation of modified cellulose fibres was also exfoliated partially. In addition, the surface of cellulose fibres shows some helical ditches orientated along the direction of micro-fibril. Fibre swelling is due to the higher sodium hydroxide concentration used during the cationization reaction. While image in Fig 11(b) shows very smooth surface due to treatment with softener

**Figure 11 (a) SEM of the cationized cotton****Figure 11(b) Cationized cotton treated with SiME****Figure 11(c) Cationized cotton treated with SiME /AgNPs.**

The image of Fig 11(c) presents a photograph at 1000 times magnification. it can be observed clearly that relatively monodisperse silver nanoparticles are embedded into fiber networks. The presence of silver nanoparticles confirmed by the presence of visible spherical particles shapes throughout the surface of fibers

4.4.5.XRD of Cationized Cotton treated with SiME/AgNPs

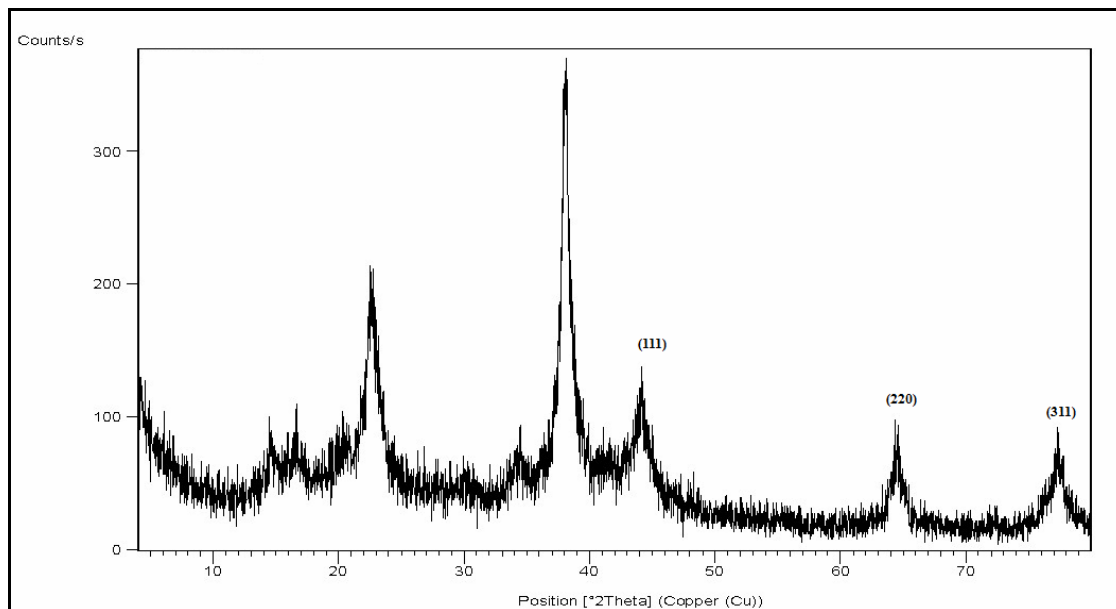


Figure 12: XRD of cationized cotton treated with SiME/AgNPs

For further confirmation, XRD diffraction patterns for AgNPs loaded cotton fabric composite were performed and shown in Figure 12, The latter Figure shows, that the XRD pattern of the cotton fibers are coated with silver nanoparticles. Three obvious peaks at $2\theta = 44^\circ$, 64° , and 77° correspond to (111), (200), (220), and (311) crystallographic planes of silver crystal (JCPDS cards 4-0783), respectively. This analysis confirms the face centered cubic (fcc) structure of pure silver crystal.

5. Conclusion

This research work has shown that: (i) the optimum condition for fixation of SiME loaded with AgNPs onto the CMC Cotton and Cationized cotton fabric involve treatment of the fabric with an aqueous solution containing 50 g/L SiME, (ii) the performance properties of the treated cotton fabric depend on the fabric carboxyl content and SiME/AgNPs concentration, (iii) maximum DRA and WRA were obtained with those fabric pre-ionic crosslinked then treated with SiME, (iv) the surface roughness of the fabric was greatly improved after SiME/AgNPs treatment, the improvement was pronounced with CMC fabric or ionic crosslinked fabric, (v) the tensile strength of CMC fabric or cationized cotton fabrics was slightly improved (vi) The Scanning electron micrograph show that, post-treatment with SiME /AgNPs results in remarkable changes in surface properties regardless of the used substrate i.e., cotton, CMC or cationized cotton .

A cationized cotton fabric enhances dry recovery angles in presence of SiME/AgNPs. Scan electron morphologies (SEMs) of cationized cotton fabric, and those samples cationized followed by application of SiME/AgNPs reveal that, the fibres show smooth surfaces whereas concave grooves are still appear. Evaluation of the treated fabric either CMC or cationized were evaluated against bacterial and they give promising results express as inhibition zone. This improved that the stability of the nanoparticles in the softener emulsion give promising data which can used in the field of textile industrial.

References

1. Prasad A.K., "Novel Effects in Garment Processing and Value Added Finishes", *J. Textile Assoc.*, 2007, 39-43.
2. Weber R., *New Aspects in Softening*. CHT R. *Beitlin GMBH*, 1999: 30 p.
3. Guo J., *The Effect of Household Fabric Softeners on the Thermal Comfort and Flammability of Cotton and Polyester Fabrics Thesis Blacksburg, Virginia* May, 2003: 121 p.
4. Frotsher H., *Chemistry and Physical Chemistry of Subsidiary Materials for Textiles Veb Verlag Technology Berlin*, 1953: 203 p. (in German).
5. Juodsnukytė D., Gutauskas M., Krauledas Influence of Fabric Softeners on Performance Stability of the Textile Materials S. ISSN 1392–1320 *Materials Science (MEDŽIAGOTYRA)*. 2005, 11, 2.
6. Soane D, Offord D & W Ware in *Nanotechnology: Global Strategies, Industry Trends and Applications*, edited by J Schulte (John Wiley & Sons Ltd, New York) 2005, 149.
7. Hebeish A., El-Shafei A., Sharaf S. and Zaghloul S.; Novel Precursors for green synthesis and application of silver nanoparticles in the realm of cotton finishing. *Journal of Carbohydrate Polymers* 2011, 84, 605–613.
8. Hebeish A., El-Shafei A., Sharaf S., Zaghloul S., In situ formation of silver nanoparticles for multifunctional cottoncontaining cyclodextrin *Carbohydrate Polymers* 2014, 103 ,442– 447.
9. Hebeish A., El-Shafei A., Sharaf S., Zaghloul S., Development of improved nanosilver-based antibacterial textiles viasynthesis of versatile chemically modified cotton fabrics *Carbohydrate Polymers* 2014, 113, 455–462.
10. Farouk A., Sharaf S., Abd El-Hady M.M. Preparation of multifunctional cationized cotton fabric based on TiO₂ nanomaterials *International Journal of Biological Macromolecules* 2013, 61, 230– 237.
11. Xin J H, Daoud W A & Kong Y Y, A new approach to UV- blocking treatment for cotton fabrics, *Text Res J*, 2004,74 , 97–100.
12. Fei B, Deng Z, Xin J H, Zhang Y & Pang G, Room temperature synthesis of rutile nanorods and their applications on cloth, *Nanotechnology*, 2006,17 ,1927–1931.
13. Vigneshwaran N, Kumar S, Kathe A A, Varadarajan P V & Prasad V, Functional finishing of cotton fabrics using zinc oxide-soluble starch nanocomposites, *Nanotechnology*, 2006, 17, 5087–5095.
14. Qi K., Chen X., Liu Y., Xin J H, Mak C L & Daoud W A, Facile preparation of anatase/SiO₂ spherical nanocomposites and their application in self cleaning textiles, *J Mater. Chem.* 2007, 17, 3504–3508.
15. Baglioni P., Dei L., Fratoni L., Lo Nostro P & Moroni M., Preparation of nano- and micro-particles of group II and transition metals oxides and hydroxides and their use in the ceramic, textile and paper industries, *WO Pat* 2,003,082,742, 2003.
16. Yadav A, Prasad V, Kathe A A, Raj S, Yadav D, Sundaramoorthy C & Vigneshwaran N, Functional finishing in cotton fabrics using zinc oxide nanoparticles, *Bull Mater Sci*, 2006, 29, 641-645.
17. Wong Y W H, Yuen C W M, Leung M Y S, Ku S K A & Lam H L I, Selected applications of nanotechnology in textiles, *AUTEX Res J*, 2006, 6 (1) 1-10.
18. Abd El-Hady M.M., Farouk A., Sharaf S. Flame retardancy and UV protection of cotton based fabrics using nano ZnO and polycarboxylic acids *Carbohydrate Polymers* 2013, 92, 400-406.
19. Hashem M., Refaie, R., Goli K., Smith B., & Hauser, P., Enhancement of wrinkle free properties of carboxymethylated cotton fabric via ionic crosslinking with poly(vinylpyrrolidone). *Journal of Industrial Textile.* (2009). doi: 10.1177/1528083709102934.
20. Thirumalai Arasu, V, Prabhu, D, Soniya, M: Stable silver nanoparticle synthesizing methods and its applications. *J. Bio. Sci. Res.*, 2010, 1, 259-270.
21. Bozzi A., Yuranova T., I. Guasaquillo, Laubb D., Kiwi J., Self-cleaning of modified cotton textiles by TiO₂ at low temperatures under daylight irradiation *Journal of Photochemistry and Photobiology A: Chemistry*, 2005, 174, 156–164.
22. Refaie, R., Hashem, M. M., & Hebeish, A.. Inducing durable press performance to ionically crosslinked cotton fabric. *Research, RJTA*, 2005, 9 (2), 47.
23. Hebeish A.A., El-Rafie M.H., Abdel-Mohdy F.A., Abdel-Halim E.S., Emam H.E. Carboxymethyl cellulose for green synthesis and stabilization of silver nanoparticles *Carbohydrate Polymers*: 2010, 82, 933–941.
24. An, Q., Li, L., Li, M., Jin, Y., & Zhang, X. Film morphology and orientation of Nb-aminoethyl-c-aminopropyl-polysiloxane on cellulose: (2007). *Model structure. AATCC Review*, 36.

25. Teli, M. D., Paul, R., & Pardeshi, P. D. Softener in textile industry: Chemistry, classification and application. *Colourage*, 2000, 17.
26. Choi, H. AATCC Review, March: (2002), 42–45.
27. Hashem, M., Hauser, P., & Smith, B. Wrinkle recovery for cellulosic fabric by means of ionic crosslinking. *Textile Research Journal*, 2003, 73(9), 762–766.
28. Ibrahim, N. A., Abo-Shosha, M. H., Elnagdy, E. I., & Gaffar, M. A. Eco-friendly durable press finishing of cellulose-containing fabrics. *Journal of Applied Polymer Science*, (2002), 84, 2243.
29. Karmakar, S. R. *Textile science and technology. Chemical technology in the pre-treatment processes of textiles* ((1999), 12, 3-44). New York: Elsevier.
30. Awwad A., Salem N. and Abdeen A. ,Green synthesis of silver nanoparticles using carob leaf extract and its antibacterial activity *International Journal of Industrial Chemistry* 2013, 4-29.
31. Haberer, P. Silicon softeners: structure effect relationship. *Melliand International*, (2002), 8, 143-146.
