Egypt. J. Chem. **55**, No. 1, pp. 33- 56 (2012)

Synthesis of Core/Shell Nano Finish for Antimicrobial Cotton Fabrics

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SILVER loaded chitosan /methoxy polyethylene glycol chloro triazine (Ag/chit-MPEGT) core/shell nano particles were synthesized as a durable finish for cotton fabrics. Ag/chit-MPEGT was firstly synthesized by reaction of silver loaded chitosan (Ag-chit) with methoxy polyethylene glycol dichlorotriazine. The latter was prepared by reaction of MPEG with 2,4,6-trichloro-s-triazine in acetone and sodium carbonate. Silver loaded chitosan(Ag/chit) nanoparticles were prepared by Ionotropic gelatin method. The resulting Ag/chit-MPEGT core/shell nano-particles were characterized by IR-spectra, ^{1}H NMR spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM) and elemental spectroscopy imaging (ESI). The cotton fabric is treated with the prepared core/shell nanoparticles using the conventional and convenient pad-dry-cure techniques to impart the durable antimicrobial properties. Citric acid was used as a crosslinking agent to improve the morphology, the crease resistance and the durable press finishing of the treated fabric. The latter was tested for the fabric surface morphology, crease resistance, break tensile strength, elongation–at-break, air permeability and antimicrobial activity.

Today, textile materials are an area subject to rapid technological development. New materials with properties hither to not associate with textiles at all, hit the market each day. Some new materials have environmental and/or antimicrobial performance as a prerequisite for textile goods used in hospitals, hotels, sports, and personal care industries. However, there is an increasing public concern about the possible side effects of antibacterial finishing on environmental and biological systems.

An ideal textile antibacterial finishing should not only kill undesirable microorganisms and stop the spread of diseases but also fulfill three other basic requirements[(1)]. First, safety; the product should not be excessively toxic to human and the environment and should not cause skin allergy and irritation. Second, compatibility; the product must not present negative influences to textile properties or appearances and must be compatible with common textile processing. Third, durability; the product should be able to endure laundering,

drying, and leaching comfort. Researchers are now focusing on safe, durable, and environment-friendly natural substitutes.

Nanometer sized silver particles synthesized by inert gas condensation or condensation techniques showed antibacterial activity against *E. coli*[2]. Textile fabrics with antibacterial efficacy were easily achieved using nanosized colloidal silver particles (2–5 nm size), by padding process on cotton and polyesters. These fabrics showed laundering durability against *S. aureus* and *K. pneumonia*[3]. Similar results were achieved with nanosized colloidal silver particles on polyester nonwovens. The growth of bacteria colonies was absolutely inhibited with only 10 ppm colloidal silver when the mean diameter of the silver particles was 2–5 nm. Consequently, a smaller particle size yielded better bacteriostasis on silver-padded nonwoven fabrics[4].

Chitosan, β-(1/4)-linked polysaccharide of D-glucosamine, is an effective natural antimicrobial agent derived from chitin, the second most abundant natural polymer in the world, refined from the shells of crabs, shrimps, and other crustaceans. Its antimicrobial activity, at specific molecular weights [5], is due to the protonated amine groups[5]. Presence of the latter in chitosan inhibits the growth of microorganisms by holding negatively charged microorganism ions [5].

Many studies have examined chitosan as an antimicrobial finish for textile materials[5-8], either for production of low molecular weight chitosan followed by its application on textile fibers[9] or for co-spinning or co-casting of low molecular weight chitosan with cellulose molecules to make antimicrobial fibers and films[5,7]. However, these methods had to produce chitosan with specific molecular weights, which could considerably increase production costs.

In addition, insolubility of chitosan in neutral or alkaline conditions further limited its application. So, various studies were conducted to make water-soluble derivatives of chitin and chitosan by chemical modification techniques. However, chemical modifications change the fundamental skeleton of chitin and chitosan, the modified chitin and chitosan lose the original physicochemical and biochemical activities [10- 13]. On the other hand, the modification with a polymer may have an advantage, because the modification with a hydrophilic polymer would be expected to result in hydrophilic chitin or chitosan while keeping the fundamental skeleton intact. Some approaches for the graft copolymerization of hydrophilic polymer onto chitin and chitosan were reported as a technique to improve the affinity to water or organic solvents [14- 19].

Polyethylene glycol (PEG) is a polymer composed of repeating ethyleneoxy units $HO\text{-}(CH_2\text{-}CH_2O)_n\text{-}CH_2\text{-}CH_2\text{-}OH$ connected by ether linkage so that the polymer is relatively stable chemically and enzymatically. Only hydroxyl end group can be converted to other functionally. PEG is a polymer widely used as a pharmacological product of preferable hydrophilicity and biocompatibility with low biodegradability. PEG was grafted onto chitosan by different techniques

resulting in N-substituted chitosan derivatives[20-23]. Aly *et al*. have modified chitosan with PEG, to be used as finishing agent for cotton fabrics.

2,4,6-trichloro-1,3,5-triazine (Cyanuric chloride) is a heterocyclic organic compound commonly used for immobilization of proteins on various polymeric supports, such as cellulose [24] and agarose, as well as for modification of proteins[25], liposome[26] and natural polymers (*e.g.*, chitosan[27] and wool[28]). Trichlorotriazine derivatives have found extensive use in the synthesis of "activated" dyes, whiteners, herbicides, pharmaceuticals…, etc.[29]. Dichlorotriazine is not as reactive as the initial trichlorotriazine, but has a sufficient residual activity for attaching to biopolymers in weakly alkaline aqueous solutions at 35-40°C. Both mono-and dichlorotriazines exhibit biological activity and some carcinogenic properties[30]. Trichlorotriazine and its derivatives easily react with amines and alcohols (aromatic and aliphatic) in organic, organic/aqueous and aqueous solutions. Because of partial hydrolysis of trichlorotriazine and its derivatives in aqueous solutions, the use of organic media is preferable.

The present work aims at preparation of core/shell nanoparticles composed of silver loaded chitosan-polyethylene glycol cyanorate graft copolymer for impart durable, multipermement, anticrease properties and antimicrobial properties to the treated fabrics. At first, PEG was activated by 2,4,6-trichloro-s-triazine at room temperature in aceton[31] and sodium carbonate to give PEG-4,6-dichloro-s-triazine (MPEGT), which was used as a soluble electrophilic scavenger. The use of a non aqueous solution was essential and allowed to avoid hydrolysis of the product, which is common for 2,4,6-trichloro-s-triazine derivatives in aqueous solutions even at 4°C[31]. The complete activation of MPEG was confirmed by UV-Spectroscopy measuring absorbance at λ=234nm[32]. Secondary, silver loaded chitosan nanoparticles (Ag/chit) was synthesized by ionic gelatin with sodium tripolyphosphate. Finally, Ag/chit nanoparticles were reacted with MPEGT in presence of sodium carbonate to give Ag/chit-PEGT core/shell nanoparticles. The latter and the intermediate were separated from the reaction mixture and their structure was analyzed using IR-spectra, ^{1}H NMR spectroscopy, Chemical analysis and X-ray diffraction. The Ag/chit-MPEGT nanoparticles were confirmed by Transmission Electron Microscopy (TEM) and Elemental Spectroscopy Imaging (ESI). The silver nanoparticles formation is characterized by measuring the Plasmon resonance at 430nm using UV-Vis spectrophotometer. Cotton fabric was treated with Ag/chit-PEGT nanoparticles to impart multipermanent, antimicrobial and anticrease properties to the treated fabric in presence, as well as, in absence of citric acid and sodium hypophosphate as a crosslinking agent and catalyst, respectively. The Ag/chit-MPEGT nanoparticles incorporated in the treated fabrics were confirmed using SEM-EDS analysis and IR-Spectra.

Experimental

Material

Chitosan with DA 95% was obtained from Aldrich Chemical Company. Polyethylene glycol monomethyl ether (Mn2000) was obtained from Fluka Chemical Company. Dyed fabric (100% cotton) (with 0.02N %) was kindly supplied by Misr Company for Spinning and Weaving, Elmahala-El-Kubra, Egypt. Cyanuric chloride, all commercially available solvents and reagents were used without further purification.

Methods

Silver loaded chitosan (Ag/chit) nanoparticles[39]

Chitosan was dissolved in 1% acetic acid solution at 60°C allowed by filtration to remove insoluble impurities. Once dissolved, the chitosan solution was diluted with distilled water to produce chitosan solution of concentration at 0.5% (W/V) with a solution pH of 6.0. Sodium tripolyphosphate(TPP) was dissolved in distilled water at the concentration of 0.5%(W/V). Then TPP solution was poured drop wise to the chitosan solution under magnetic stirring at 1000 rpm using stirring bar. Then the mixture was stirred for additionly 15 min. The formation of chitosan-TPP nanoparticles started spontaneously via the TPP initiated ionic gelation mechanism. The nanoparticles were formed at selected chitosan to TPP weight ratio of 5:1 at temperature of 25°C. Ag/chit nanoparticles were obtained by adding a solution of 0.118 mM silver nitrate to the chitosan nanoparticle suspension during chitosan nanoparticle synthesis before centrifugation and was stirred for another one hour. The nanoparticles were separated by centrifugation at 9000 rpm for 45 min. Then the supernatants were discarded. Nanoparticles were extensively rinsed with distilled water and dried at room temperature.

Preparation of MPEG-4,6-dichloro-s-triazine (MPEGT)

2, 4, 6-trichloro-s-triazine (5.5 g, 0.03 mol) was dissolved in acetone containing 10 g of anhydrous sodium carbonate. MPEG (19 g, 0.01mol) was added and the mixture was stirred overnight at room temperature. The solution was filtered, and diethyl ether was poured slowly into the filtrate under stirring. The obtained product was filtered off, reprecipitated several times from acetone to diethyl ether and dried in a vaccum oven.

Preparation of Ag/chit-g-MPEGT core shell nanoparticles

A mixture of Ag/chit (0.5 g) and MPEGT (7.6 g) in 100 ml DMF was heated at 50°C under magnetic stirring for 24hr. The solution was filtered, and diethyl ether was poured slowly into the filtrate under stirring.

It is well known that, chitosan is not soluble in dichloromethane whereas MPEGT is freely soluble. Therefore, unreacted MPEGT was removed by suspending the precipitated Ag/chit-PEGT in a large amount of dichloro methane

three times. Thereafter, the precipitate was collected by filteration and dried in air to give 3.2 g of Ag/chit-MPEGT.

Fabric treatment with Ag/chit-MPEGT

Cotton samples (5cm X 15cm) were padded with aqueous Ag/chit-MPEGT solution containing citric acid (CA) and sodium hypophosphite monohydrate (SHP) to give a wet pickup of 90%. The padded samples were dried at 90°C for 2 min and then cured in a laboratory oven for different time and temperatures. The treated fabrics were washed with tap water until neutral to pH paper and further washed in warm water using 1% acetic acid solution for 1hr, to remove unfixed Ag/chit-MPEGT, followed by washing with tap water and drying.

Characterization techniques

Structural characterization of Ag/chit-MPEGT core/shell nanoparticles

The characterization of the prepared product in each step and the performance properties of the treated fabrics were evaluated using published standard procedures including the following:

FTIR analysis: The infrared spectra were registered from 48 scannings at a resolution of 4 cm^{-1} by using JASCO FT/IR-6100 spectrophotometer (Japan).

^1H NMR spectral analysis: measured on a varian 400 MH Spectrometer for solutions in DMSO-d_6 using $SiMe_4$ as internal standard.

X-ray diffraction (X.R.D): Crystallinity of the reactants and Ag/chit-MPEGT nanoparticles were analysed with X-ray differaction using (BRUKUR D8 ADVANCE – Target CU kα with secondary monochromatic-ku= 40 Ma). Continuous scan mode was used in the range of $4° \leq 2\,0 \leq 60°$at 40kV and 30Ma.

Ultra violet–visible (UV–vis) spectra: By means of a 50 ANALYTIKA, JENA Spectrophotometer from 200 to 500 nm.

Transmission Electron Microscope (TEM): By a JEOL-JEM-1200 (Japan).

Scanning electron microscope (SEM): It was used using a scanning electron probe micro analyzer (JXA-840A, Japan). The specimen in the form of films were mounted on the specimen stabs and coated with thin film of gold by the sputtering method. The micrograph was taken at magnification of 1000 using (KV) accelerating voltage.

Analysis for C, H, and N was determined using an elemental Vario El-Elementar.

The nitrogen percent was estimated according to the microkjeldahl method (Vogel, 1975).

Performance testing of the cotton fabrics

Creasy recovery angle: Dry creasy recovery angle was determined according to AATCC Technical Manual test method (Vol.70, 1998).

Tensile strength: It was determined by the strip method according to ASTM method D2256-66T (ASTM Test Method, 1972).

Elongation- at- break: It was determined according to ASTM procedure D-2296-66T.

Air permeability: It was measured as per ASTM method 19996 D 737.

EDX analysis: Energy Dispersative X-ray by INCa (X Sight) (England).

Antimicrobial activity test disc diffusion method with some modification was used for screening the cotton fabric sample for antimicrobial activity (Ericson&Sherris, 1971). Nutrient agar for bacteria 0.1 ml of an appropriate dilution of the test culture was used. Cotton fabric samples (1-cm diameter) were placed on the surface of the incubated plates at 35°C for 24 hr. Diameter of plates inhibition zone (mm) including the disc diameter was measured for each treatment.

Results and Discussion

Charaterization of the reactants,intermediate nanoparticles

Chitosan contains two hydroxyl groups and one amino group in every monosaccharide residue and potentially is able to undergo many reactions of alcohols .One of the most common reactions of alcohols is etherification or nucleophilic substitution (SN^2) reaction. It takes place between OH groups of alcohols or between the OH group of an alcohol and the halogen group of an alkyl halide. Alkyl halides (methyl chloride, ethyl chloride…, etc) are the reactants for etherification of cellulose in strongly alkaline aqueous solutions.

Ag/chitosan–MPEGT were synthesized as presented in Scheme1.The intermediate and final products were separated from the reaction mixtures and their structures were confirmed and characterized using IR, ^{1}H NMR spectroscopy, TEM and X-ray diffraction, as presented below:

Spectral characterization

FTIR- spectroscopy: IR Spectra of chitosan and chitosan derivatives are summarized in Fig. 1a-c. It was found that distinctive absorption bands at 3378 cm^{-1} for (-OH group), 2874 cm^{-1} (-CH group) aliphatic 1661 cm^{-1} (amide I), 1599 cm^{-1} (amide II NH_2), and 1050-1160 cm^{-1} (C-O-C bridge) for chitosan (Fig. 1a).

In Ag/chit nanoparticles, the band at 1643 cm^{-1} disappears and a new band at 1635 cm^{-1} appears, the intensity of amine bending at 1635 cm^{-1} goes down; which could be attributed to the linkage between tripolyphosphate group of TPP and

ammonium group of chitosan nanoparticles. A new band appears at 1218 cm^{-1} due to P=O stretching in chitosan nanoparticles which is absent in bulk chitosan.

Binding of silver with N of the amine and amide group results in decreasing of intensity of amine and amide band at 1661 cm^{-1}. Division of combined band of amine and amide at 1633 cm^{-1} and 1573 cm^{-1} also indicates the binding of Ag with O and N of those groups[39].

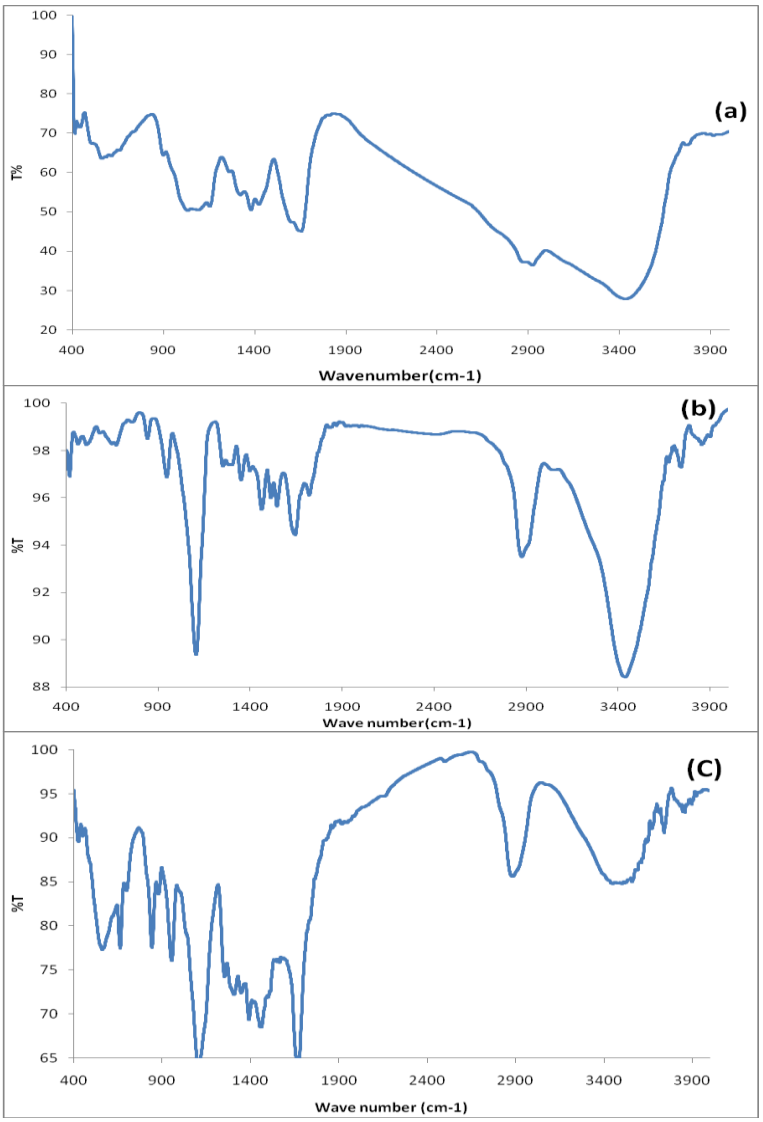


Fig. 1. FTIR spectra of (a) chitosan; (b) PEGT; (C) Ag/chit-PEGT.

Also, the band intensities in between 1000 cm^{-1} and 1350 cm^{-1} due to C-N stretching and bending is very less in silver loaded chitosan nanoparticles because of the complexation of chitosan with silver.

In case of IR spectrum of MPEGT (Fig. 1b), compared to the spectrum of initial MPEG, exhibits a new absorption band at 1546 cm^{-1}, which is attributed to the triazine ring[35].

In case of IR- spectra Ag/chit –PEGT nanoparticles (Fig. 1c) show a new absorbance band at 1546 cm^{-1}, which is attributed to the triazine ring[35, 39]. The bands characteristic both of chitosan and MPEGT with a much higher absorbance of the PEGT groups are shown and clarify that the degree of substitution of MPEGT to chitosan monosaccharide residue is high. Distinct absorption bands at 1110 cm^{-1} (C-O stretching) and 2886 cm^{-1}(C-H stretching) appear and the band at 3400 cm^{-1} (O-H stretching) declines. It is expected that the Ag loaded chitosan backbone may compose an inner-core while MPEGT may form an outer-shell of core/shell nanoparticles.

Characterization by X-ray diffraction: Chitosan is semicrystalline polymer, whereas PEG is highly crystalline with defined crystal structure[33].

The X-ray patterns of chitosan, MPEGT, and Ag/Chit-MPEGT are shown in Fig. 2a, b and c, respectively. It is seen (Fig. 2a) that chitosan powder has reflaction at $2\theta = 20.0°$, and relative weak reflection at $2\theta = 10.2°$, which were in good agreement with earlier published data [34]. The diffraction diagram of Ag loaded chitosan nanoparticles shows sharp peak at $2\theta = 44.3°$ which is due to the face centered cubic crystalline structure of silver[36].

The diffraction diagram of Ag/chit-MPEGT graft copolymer (Fig. 2c) shows two reflection falls around $2\theta=23.24°$ and $2\theta=19.0°$ which are very sharp and narrow, suggesting a copolymer with a high crystalline structure. This confirms that, whereas chitosan backbones are amourphous, the Ag/chit- MPEGT grafts form a regular structure. No significant differences between the intensities of peaks in X-ray diffraction patterns of Ag/chit-MPEGT graft copolymers and MPEGT were observed (Fig. 2b).

^{1}H NMR spectroscopy: ^{1}H NMR of chitosan, MPEGT and Ag/chit-MPEGT are shown in Fig. 3a & c, respectively. With ^{1}H NMR of chitosan (Fig. 3a) there is a chemical shift at 4.68-4.99 ppm (1H, b.d, H-1), 3.99 ppm (br.s., H-3,H-4, and H-6), 3.75 ppm (br., H-5, H-6), 3.19 ppm (br.s.H-2) and 2.05 ppm (br.,s.CO-CH_3). ^{1}H NMR of MPEGT (Fig. 3b) shows the strong peak of oxymethyl group PEG at 3.2-3.8 ppm and methoxy groups (3.28-3.36 ppm) of MPEGT. In ^{1}H NMR of Ag/chit-MPEGT (Fig. 3c)they are 4.2-4.74 ppm (1H, br.d. H-1), 3.82 ppm (H-3, H-4, H-6'), 3.71ppm (H-5, H-6, and OCH_2), 3.33 (OCH3), 2.84 ppm (-NH-CH2-CH2-O), 2.03 ppm (1H.br.s,-COCH3). A new very strong signal appeared at δ = 3.50-3.60 ppm, which is attributed to the oxyethylene groups

present in the grafts. Ag/chit-MPEGT contain dominant signal at 3.50-3.60 ppm, confirming high density of MPEGT graft.

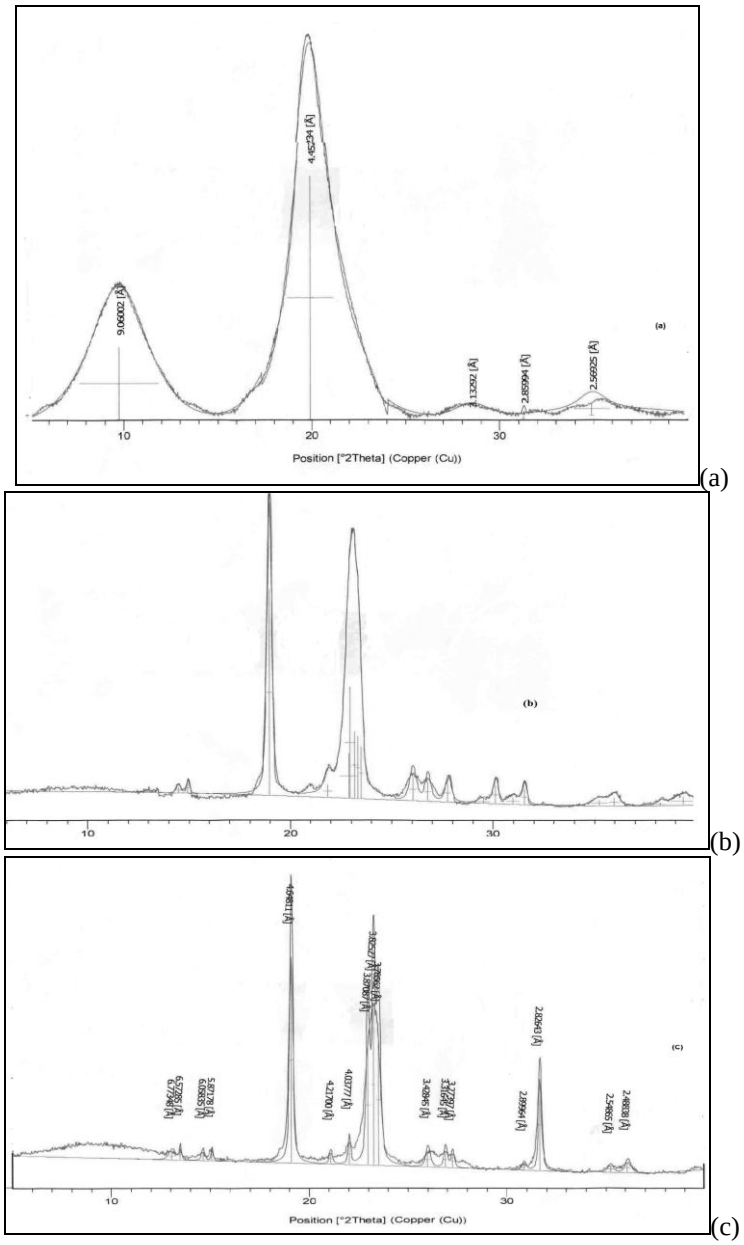


Fig. 2. X-ray of :(a) chitosan; (b) MPEGT; (c) Ag/chit-PEGT.

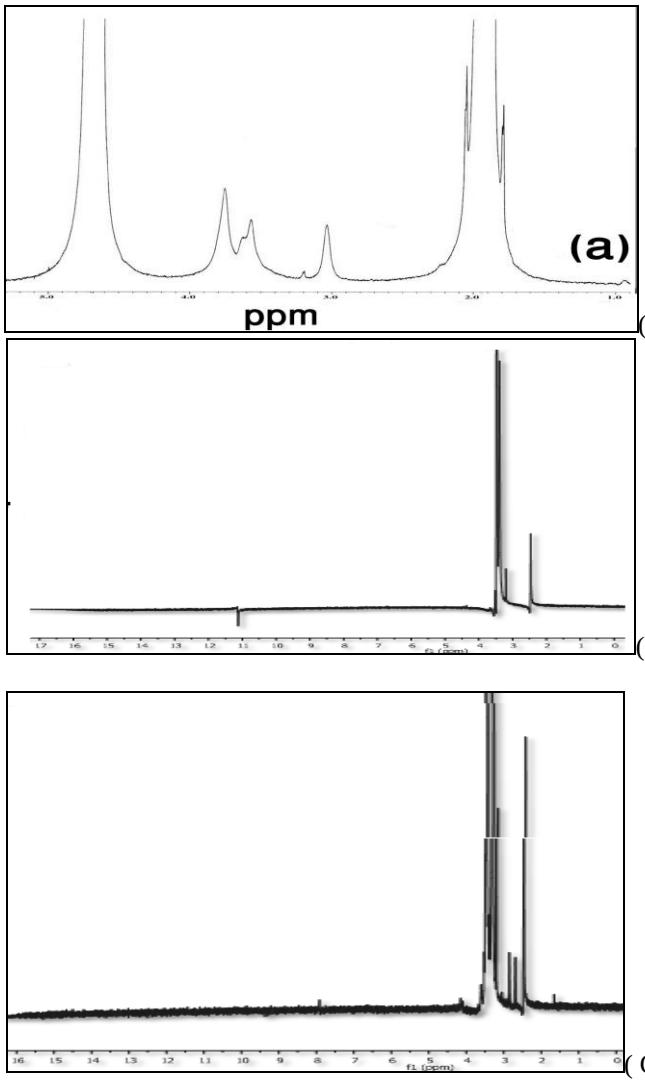


Fig. 3. ^{1}H NMR of: (a) chitosan; (b) PEGT; (c) Ag/chit-PEGT.

Solubility of Ag/chit- MPEGT nanoparticles: MPEGT was prepared by the reaction of MPEG with 2,4,6-trichloro-s-triazine at room temperature in dry acetone. The use of a non-aqueous solution was essential and allowed to avoid hydrolysis of the product. MPEGT was confirmed by UV- spectroscopy measuring absorbance at λ=234 nm[32] and was used as electrophilic scavenger. The latter was reacted with hydroxyl and amino groups of chitosan loaded silver

nanoparticles. The obtained Ag/chit MPEGT nanoparticles, like oligomer or low molecular weight substance are soluble of wide pH range within short time and the viscosity of the solution is very low. Low viscosity of Ag/chit- MPEGT nanoparticles could be related to hydrogen bonding and aggregation phenomena. Poor solubility of chitosan and high viscosity of its solutions is explained by partially crystalline structure of this polymer and very tight hydrogen bonding between amino and hydroxyl groups[40]. Grafting of PEG chains separates chitosan backbones, collapses order characteristic to chitosan solutions and drastically decreases hydrogen bonding. It is known also[41] that macromolecules of chitosan-PEG copolymer may form aggregates in an aqueous solutions. Compacticity of these aggregates depends on density of PEG chains and possibly reaches maximal value at moderate DS. Aliphatic hydrocarbons, carbon tetrachloride and diethyl ether are non solvents for the nanoparticles (Table 1).

TABLE 1. Solubility of Ag/chit-PEGT with different solvents.

Solvent	Solubility
H_2O	Completely soluble
DMF	Completely soluble
aceton	Partial soluble
DMSO	Compeletly soluble
ethyle alc.	Partial soluble
ethyle acetate	Completely soluble
benzene	Completely soluble

UV-spectroscopy: Figure 4 shows the UV-Vis absorption spectra of Ag/chitosan without TPP (Fig. 4a), Ag/chit with 0.25gm TPP (Fig. 4b) and Ag/chit with 0.5 gm TPP (Fig. 4c) nanoparticles. It is well known that the size and amount of nano particles affect both the band width and intensity of the Plasmon absorption band[37]. Furthermore, dielectric materials containing nano-clusters present optical absorption bands, named surface Plasmon absorption bands (SPB), which depend on both the characteristics of nanoparticles and the refractive index of the surrounding medium. It is reported that the surface Plasmon excitation of Ag nanoparticles has an intense absorption peak around 400 nm[38]. In our results, the absorption peaks approximate at 430 nm (Fig. 4) attributed to the surface Plasmon absorption of silver nanoparticles was generally observed.

Imaging and histograming of nanoparticles by TEM

Figure 5(a-d) shows representation TEM images of Ag/chit nanoparticles with TPP (Fig. 5a) and Ag/chit-MPEGT (Fig. 5b) as well as TEM histograms of

Ag/chit (Fig. 5c) and Ag/chit-MPEGT (Fig.5d). The results indicated that most of the nanoparticles are spherical with a mean particle size of 18 nm, 16 nm, and 6 nm for Ag/chit with TPP as crosslinking agent and Ag/chit- MPEGT nanoparticles, respectively (Fig. 5a-d). The decrease in mean size and multishape formation may be due to the high swellability of non-crosslinked chitosan rather than the crosslinked chitosan. Therefore, the non-crosslinked chitosan, in absence of TPP, is in swelled stage resulting in higher size of the particles. In the TEM images of Ag/chit-MPEGT nanoparticles (Fig. 5b) no aggregation with a similar nono-metric dimension is observed. Furthermore, the particle size distribution of Ag/chit-MPEGT nanoparticles is relatively in narrow-size distribution (Fig. 5d).

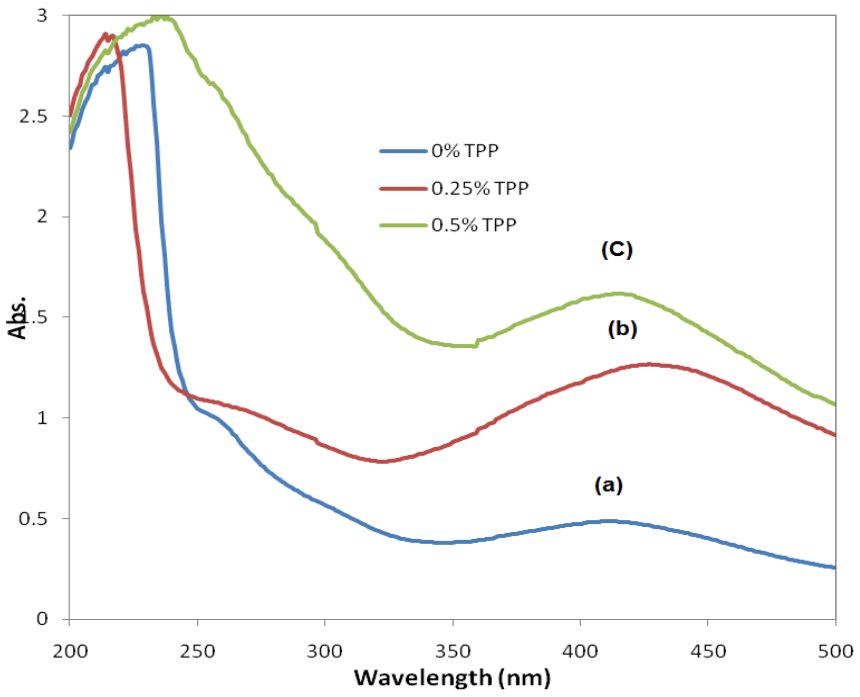


Fig. 4. UV-Spectra of: Ag/chit without TPP, (a); Ag/chit with 0.25%TPP, (b); Ag/chit with 0.5% TPP, (c).

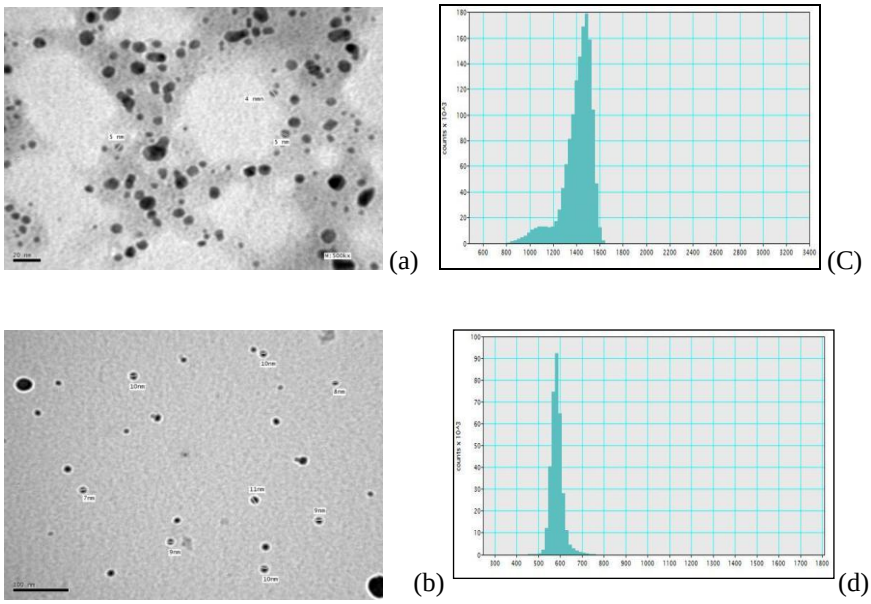


Fig 5. TEM for: Ag/chit, (a); Ag/chit-PEGT, (b); Histogram of Ag/chit, (c); Ag/chit-PEGT, (d).

Application of Ag/chit-MPEGT nanoparticles for cotton fabrics treatment

The application of chitosan as multifunctional finishing agent for textiles was reported[42]. Chitosan shows its biological activity only in acidic medium because of its poor solubility above pH 6.5. However, the use of chitosan as an antimicrobial agent in textile is limited because the hand of fabric is adversely affected by treating with chitosan, especially of high molecular. Low laundering durability of the chitosan treated fabrics is another problem to be solved.

Ag/chit-MPEGT copolymer with expectable multifunctional finishing effects when used for treatment of treated cotton fabrics along without as well as with citric acid and sodium hypophosphite monohydrate in the finishing bath was studied. Factors affecting the treatment such as Ag/chit-MPEGT and citric acid concentration, presence of sodium hypophosphite as well as temperature and curing time on performance and chemical properties of the treated fabrics are discussed below.

Curing temperature: Table 2 shows the effect of the curing temperature on the amount of Ag/chit-MPEGT copolymer (expressed by nitrogen percent) fixed on the cotton fabric. The nitrogen percent was calculated before and after washing. It is observed that, the increment of nitrogen percent at temperature lower than 120°C in absence of citric acid (CA) as crosslinking agent and sodium hypophosphite (SHP) as catalyst refers to the reaction of residual active

chlorine in the Ag/chit-MPEGT with hydroxyl group of cotton fabrics. On the contrary, significant interaction takes place at 160°C beyond which the extent of the interaction increases by increasing the curing temperature within the range studied. Based on these findings, it is logical to conclude that beside the reaction of residual active chlorine in the triazine with the cotton fabric there is also esterification reaction between the Ag/chit-MPEGT and cotton fabric in presence of citric acid. The latter acts as a bridge between the Ag/chit- MPEGT and cotton cellulose. In substantiation with this is that the temperature of the interaction is fulfilled at 160°C and above which are indeed required for efficient catalysis using SHP.

TABLE 2. Effect of curing temperature.

Temp. (°C)	N% before	N% after	Roughness (μm)	CRA (degree)	T.s (Kg)	Air permability ($cm^3/cm^2/sec$)
120°	0.18	0.10	15	102	64	19.3
140°	0.22	0.17	12.5	112	78	25
160°	0.28	0.21	13	119	45	24
180°	0.32	0.29	14.2	128	38	26

[core shell],1%; citric acid,5%; [SHP],3%;drying,80°C for 10 min; curing time, 2 min.

It is as well to emphasize that by virtue of their structural similarity and their possessiveness of plenty of hydroxyl groups, Ag/chit-MPEGT and cotton cellulose are hold in an intimate association after curing at higher temperatures (160°C and above) by physical forces, hydrogen bonding in particular.

In combination with this is the already mentioned chemical bonding. That is, fixation of Ag/chit- MPEGT on the cotton fabric entails chemical and physical attachments.

Other performance properties of the multifinishing fabrics are also given in Table 2. The latter shows that the effect of rising of curing temperature up to 160°C is to bring about substantial increment in the crease recovery of the treated fabrics. Curing temperature higher than 160°C causes a decrement in the crease recovery most probably because of breaking-down cross-links under the effect of high temperature (180°C) under the highly acidic condition used.

Results of Table 2 refer that the tensile strength decreases with increasing the curing temperature but the decrease is apparent only at temperature higher than 160°C. This could be ascribed to molecular degradation of the cotton fabrics. The treated fabrics acquire increased air permeability and decreased roughness at higher temperature of curing as can be realized from Table 2. Needless to say

that decrement in roughness is a manifestation of improved smoothness and, therefore, comfort.

Ag/chit-MPEGT core/shell nanoparticles concentration: Table 3 shows the dependence of the interaction of Ag/chit-MPEGT copolymer with cotton fabric in presence of CA as a crosslinking agent and SHP as a catalyst on Ag/chit-MPEG core shell nanoparticles concentration.

Obviously, the extent of the reaction, expressed by N%, increases by increasing the Ag/chit-MPEGT concentration in the padding bath within the range studied. The favorable effect of Ag/chit-MPEGT concentration could be ascribed to abundance of its molecules in the vicinity of the accessible cellulose hydroxyl groups at higher concentrations. That is, greater availability of Ag/chit-MPEGT in the proximity of cellulose hydroxyls at its higher concentrations provides more proper environment for the interaction of Ag/chit-MPEGT with cotton cellulose.

Table 3 shows that the nitrogen percent values are higher before than after washing, this is most probably due to removal of unreacted and loosely adhered finish from the fabric surface.

TABLE 3. Effect of core shell concentration.

[core shell]	N% before	N% after
0.25	0.15	0.13
0.5	0.18	0.16
0.75	0.21	0.17
1.0	0.28	0.21
1.5	0.29	0.22
2.0	0.31	0.24

[citric acid], 5%; [SHP],3%; drying, 80°C for 10 min; curing temp.160°C; curing time, 2 min.

Effect of citric acid concentration: Cotton fabrics were treated with Ag/chit-MPEGT to evaluate the effect of citric acid concentration as cross linking agent on the amount of Ag/chit-MPEGT fixed on the cotton fabrics. The effect of citric acid concentrate on the reaction efficiency expressed by nitrogen percent and on the performance property of the treated fabrics was recorded in Table 4. It seems that the increase in the concentrate of CA leads to increase in the nitrogen content to 5% CA and marginally decrease above CA 7%. The increase in the nitrogen percent is attributed to the fact that in a complex system such as Ag/chit-MPEGT graft copolymer/CA/SHP/H_2O, reaction and, therefore, fixation of the copolymer to the fabric is a manifestation of bridging through the polycarboxylic acid (CA) of the cellulose hydroxyls as one end of the bridge and chitosan hydroxyls on the other end

of the bridge. In both cases, bridging occurs via esterification reactions. The data also indicate that the concentration of CA has adverse effect on the tensile strength of the treated fabrics where the latter acquire tensile strength values lower than the unfinished fabrics. Such significant losses in tensile strength are associated with molecular degradation of cotton cellulose under the action of CA and catalyst along with rigidity conferred on cellulose structure under the onset of cross-linking. Table 4 also shows that the air permeability decreased with increasing the concentration of CA. A decrease in air permeability might decrease the comfort of the hygienic product. This is not occurring in current products because of the presence of PEG in the copolymer used.

TABLE 4. Effect of citric acid.

Citric acid (%)	N% before washing	N% after washing	Roughness (µm)	CRA (degree)	T.S (Kg)	Air permability ($cm^3/cm^2/sec$)
0	0.20	0.08	17.8	95	51	51
1	0.24	0.16	15.2	96	45	50.8
3	0.28	0.19	14.6	97	42	42.7
5	0.28	0.21	13.7	105	40	36
7	0.30	0.25	13.6	93	39	33

[Ag/chit-MPEGT],1%; [SHP],3%;drying,80°C for 10 min; curing temperature,160°C; curing time,2 min.

Effect of curing time: Table 5 shows the effect of curing time on the performance of cotton fabrics. The latter was padded to 90% wet pick up in Ag/Chit- MPEGT solution in presence of 5% CA and 3% SHP, dried at 80°C for 10 min and cured at 160°C for different durations. It is observed that the curing time appears to have a significant influence on the amount of nitrogen percent. The latter increases by increasing the curing time before and after washing. The data also indicate that the curing time has the highest impact on the wrinkle resistance (expressed by CRA) and tensile strength of the treated fabrics. An increase in the curing time has the most significant effect on the improvement in CRA of the finished fabrics and loss in fabric tensile strength.

TABLE 5. Effect of curing time.

Time (min)	N% before	N% after	Roughness (µm)	CRA (degree)	T.S (Kg)
0.5	0.20	0.19	13.2	95	64
1	0.22	0.19	13.6	81	59
2	0.28	0.21	11.6	102	50
3	0.31	0.23	13	101	43

[core shell],1%; citric acid,5%; [SHP],3%;drying,80°C for 10 min; curing temp.,160°C.

Characterization of the treated fabrics using SEM-EDS

Ag/chit-MPEGT core shell nanoparticles were synthesized and used as multifinishing agent for cotton fabrics. The latter were subjected to multifinishing under the optimal condition arrived at from studies that have been detailed in the foregoing sections. Specifically, the cotton fabric was padded to 90% wet pick up in a treating bath containing 1% Ag/chit-MPEGT in presence of 5% citric acid as crosslinking agent and 3% SHP as a catalyst and cured at 160°C for 2 min.

Figure 6 (a & b) are SEM micrographs of cotton fabrics before (Fig. 6a) and after the treatment (Fig. 6b). Compared with the one before the treatment, the treated surface did not show much difference. Both treated and untreated cotton displayed smooth fiber appearances. No individual particles or deposits were found even under high SEM magnifications. All these evidences implied that during the particle condensation, the nanosized particles were packed closely to form a thin film on fabric surface instead of individual particles.

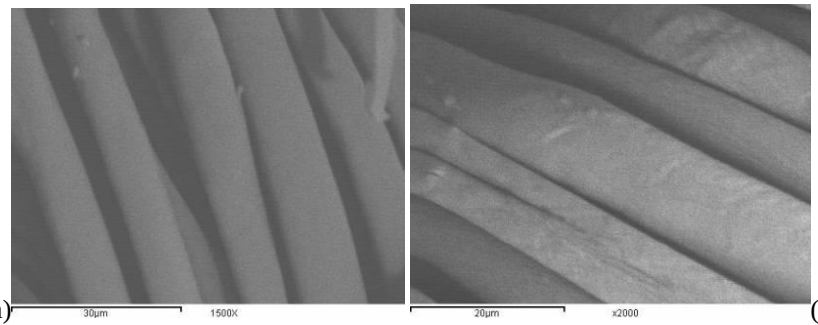


Fig. 6. SEM of: (a) untreated fabric; (b) treated fabric with Ag/chit-PEGT.

Energy dispersive X-ray spectroscopy (EDS) analysis was carried out on INCa (xSight) scanning electron microscope (SEM) equipped with an EDS instrument. It is used to determine the composition of element particles incorporated on the surface of the treated fabrics.

The results of EDS analysis are presented in Fig. 7 and the elements percentage were listed in Table 6. From these results we can show that there are peaks at around 3Kev characteristic for silver nanoparticles.

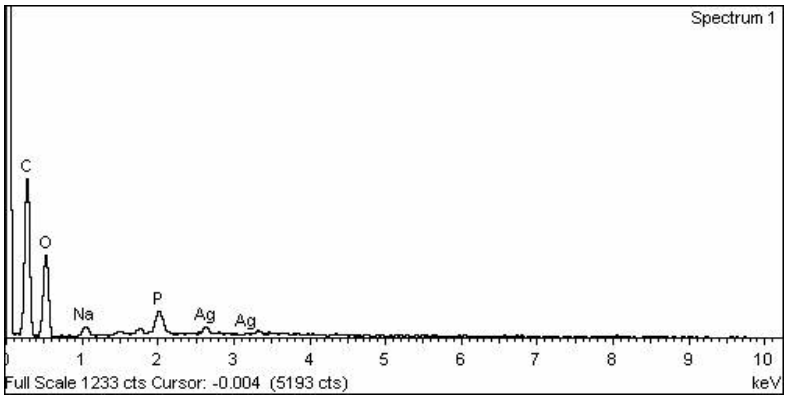


Fig. 7. EDS of treated fabric with Ag/chit-PEGT.

TABLE 6. EDS for treated fabric.

Element	Weight%	Atomic%
C K	52.27	59.91
O K	44.99	38.71
Na K	1.34	0.80
P K	1.28	0.57
Ag L	0.12	0.02
Totals	100.00	

Antimicrobial activity of Ag/chit-PEGT treated fabric

MIC means the minimum inhibition concentration of agent needed to inhibit bacterial growth; therefore, the lower the MIC value of an agent, the higher the antimicrobial activity that can be expected. The MIC value of Ag/chit-MPEGT was 280µg/ml.

Several works are used to impart antibacterial properties to fabrics. Cho and Cho (1997) conducted a study on a dual functional finishing, using the antibiotic gentamincin as antibacterial agent and a fluoro chemical as a blood repellence agent on surgical gowns fabric. The results show 98% reduction of gram-positive and gram-negative. Lim and Hudson (2004) reported that the growth of *S. aureus* was inhibited by chitosan derivative, Aly *et al.* (2007) also observed a similar trend by treating the cotton fabrics with quaternary chitosan.

Table 7 Shows the antimicrobial activity of the Ag/chit-MPEGT treated fabrics against four types of bacterial (*Bacillus subtilis*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*) compared to standard antibacterial agent (*e.g* tetracycline). All Ag/chit-MPEGT treated fabrics showed very high activity for all kind of bacteria higher than the tetracycline antibacterial agent.

TABLE 7. Antimicrobial activity of Ag/chit-PEGT.

Sample		**Inhibition zone diameter (mm/mg sample)**			
		***Bacillus subtilis* (G+)**	***Escherichia coli* (G-)**	***Pseudomonas aeruginosa* (G-)**	***Staphylococcus aureus* (G+)**
Standard	Tetracycline antibacterial agent	32	32	34	30
X		12	13	14	13

There are many proposed mechanisms of antimicrobial activity by the multifinishing treatment. In one mechanism, poly cationic nature of chitosan component in Ag/chit-MPEGT graft copolymer interferes with bacterial metabolism by sticking at all the surfaces. The second mechanism is the binding of chitosan with DNA to inhibit mRNA synthesis. The third mechanism depends on the fact that the high ability of chitosan is to bind heavy metals and trace elements. The coordination capability of chitosan is related to the free content of NH_2 groups. The degree of protonation of NH_2 in chitosan is constant at given pH values[43]. When the pH value is high, the degree of protonation of NH_2 groups in chitosan is low. Because the antimicrobial test is exposed in sterile-distilled water, the amino groups are free and have strong coordination capability of chitosan toward metals. A fourth mechanism may be attributed to the antimicrobial activity of this chitosan; graft copolymer can be closely correlated to the formation of hydrophobic microareas[44]. At pH 7 the degree of protonation of NH_2 is very low; thus, the repulsion of NH_3^+ is weak, so the strong intermolecular and intramolecular hydrogen bond results in the formation of hydrophobic micro areas in the polymer chain[44]. At the same time, the polymer chain of PEG in the Ag/chit-MPEGT graft copolymer is highly hydrophilic and hydrophobic parts. This amphiphilic structure provides structure affinity between the all walls of bacteria and the CTS derivatives.

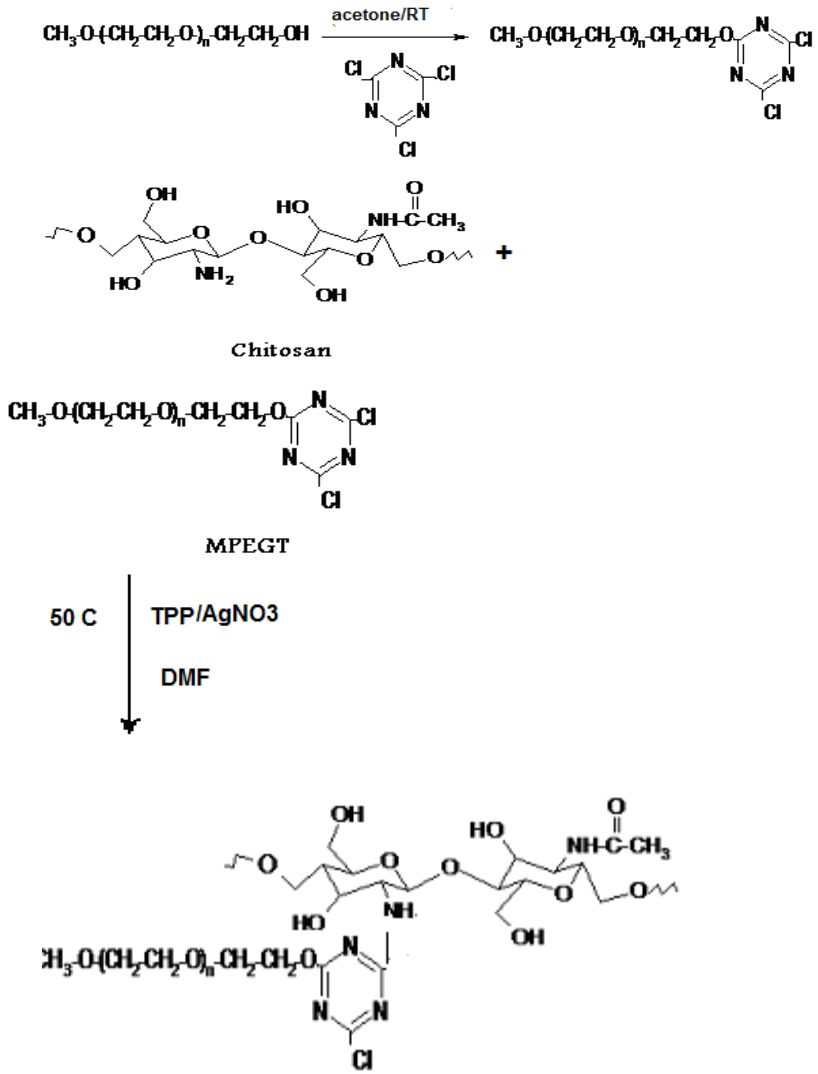
One of the biggest concerns of antimicrobial finish in textile industry is durability. An ideal antimicrobial finish should be effective for the entire lifetime of a textile article. Generally, if a textile material can maintain at least 75% of its inhibitory activity after twenty times of home laundering, it will be acceptable as a durable antimicrobial finish.

The antimicrobial efficiency was determined by measuring the fabric microbial reduction after 1, 5, 10 and 20 repeated wash cycles (Table 8).

It is obvious (Table 8) that the treated fabrics still have high reduction percent of bacteria, higher than standard antibacterial agent (tetracycline), even after 20 wash cycles.

TABLE 8. Effect of washing cycle.

Cycle of washing	*Staphylococcus aureus* (G+)	*Escherichia coli* (G-)
0	30	32
1	22	29
3	19	25
5	17	23
10	13	19



Scheme1. Preparation of Ag/chit-MPEGT.

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(*Received* 26/9/2011 ;
accepted 2/10/2011)

تخليق مادة تجهيز نانومترية لاكساب اقمشة القطن خاصية مقاومة الميكروبات

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يتناول هذا الجزء بالدراسة امكانية تحضير وتوصيف جزيئات الفضة النانومترية المحملة على الكيتوزان مع الميثوكسى بولى ايثيلين جليكول ترايازين وتطبيقه على الالياف القطنية بطريقة امنه بيئيا. وقد تم ذلك من خلال تحضير كلا من الكيتوزان المحمل بجزئيات الفضة النانومترية، كما تحضير الميثوكسى بولى ايثيلين جليكول داى كلورو ترايازين. ثم يلى ذلك تفاعل كل من المركبين السابقين ليعطى مركبا امنا بيئيا يستخدم لتجهيز الاقمشة القطنية بغرض اكسابه خاصية مقاومة البكتيريا.