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ORIGINAL RESEARCH

Hyperbranched polymer–silver nanohybrid induce super antibacterial activity and high performance to cotton fabric

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Abstract Herein we present a novel approach for synthesis, characterization and application of a benign hyperbranched polyester amide–silver nanohybrid (Ag/HBPEA). The Ag/HBPEA is developed through three distinct steps. The first step involves amidation reaction of diethanol amine and maleic anhydride to yield AB2 monomer (adduct 1). The second step comprises reaction of adduct 1 with trimethylol propane in presence of catalyst to yield HBPEA. The third step entails reduction of silver nitrate by sodium borohydride reductant to effect in situ formation of AgNPs which are stabilized by HBPEA, leading ultimately to Ag/HBPEA nanohybrid. Both Ag/HBPEA nanohybrid and HBPEA are independently applied to cotton fabrics as per the conventional pad-dry-cure technique. To this end, through investigations into the structures of Ag/HBPEA nanohybrid and HBPEA stabilizer before and after application to cotton fabric using advanced techniques emphasize the Ag/HBPEA nanohybrid as multifunctional finishing agent rather than a super antibacterial activity of the cotton fabrics after treatment with Ag/HBPEA nanohybrid speaks of this. Current research generally addresses green chemistry because treatments involved therein are based on green basics and practices.

Keywords Hyperbranched polymer · Silver nanoparticles · Green chemistry · Cotton fabrics

Introduction

Dendrimers and hyperbranched polymers represent a new class of branched architectural polymers that attract much attention over the last decade by virtue of their unique structures. It is envisioned that such structures may grant unprecedented properties and lead to novel application (Paleos et al. 2010; Zheng et al. 2015; Zhou et al. 2010). Synthesis of dendreimers involves convergent or divergent growth through a repetitive multistep strategy. This is indeed the reasons behind the difficulties encountered in production of dendrimers on commercial scale as well as their high expenses. On the contrary, hyperbranched polymers are synthesized in one step process to bring about a mixture of linearly and fully branched AB repeating units. In as such, the as synthesized polymeric product is supposed to acquire properties similar to those of dendreimers polymers (Kim and

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Webster 1999). Thus highly branched materials find increasing industrial interest in a way that they are considered to be a good alternative to dendriemers. This is advocated by the very strong interest in structurally less perfect hyperbranched polymers with their easier and cheaper one-step synthesis (Gao and Yan 2004; Wilms et al. 2009; Yan et al. 2011; Zhou et al. 2010). They are also quite appropriate for large scale production. A wide variety of different monomers notably ABX monomers are used for synthesis of dendritic (Das et al. 2018; Rahman et al. 2017) and hyperbranched (Satoh 2012). Polyesters ABX monmers possess structures ranging from purely aliphatic (Gregorowicz et al. 2013; Lebarbé et al. 2014; Malek et al. 2015) to purely aromatic (Chen et al. 2015; Zhang and Jia 2006).

The properties of hyperbranched polymers can be adjusted to a large extent by chemical modification of the end groups due to the multi-functionality of these polymers (Segawa et al. 2010). Previous studies disclosed that the terminal groups of the hyperbranched polymers impacted significantly their physical properties such as glass transition temperature (Román et al. 2016) relaxation process (Gao and Yan 2004), viscosity (Mokhtari 2015), and solubility (Jinlian 2011) (Seiler 2006). Therefore, hyperbranched polymers offer very intrinsic properties which are of great potential values in application. They have found wide scope of successful applications in some industry products e.g. toughening additives (Marsh 2008), rheology modifiers (Tomuta et al. 2013) and low shrinkage restorative formulations (Dewaele et al. 2012). In recent years hyperbranched polymers have been applied in different coating technologies such as high solid alkyds, powder coatings and UV curable coatings (Asif and Shi 2004; Baumgart et al. 2011; Gao et al. 2011; Ibrahim et al. 2010; Lange and Wyser 2003). Developments of HBPEA based on commercially attractive monomers have been successfully achieved, this development afforded polymers with a high number of end groups, in particular, and multifunctionality on the same molecule. HBPEA can be modified with other various functionalities such as unsaturated groups, tertiary amines, or long alkyl chains in addition to hydroxyl and carboxylic groups. This means that, the concept of the synthesis allows a broad variety of structures and; the resulting properties like polarity or viscosity can be adjusted and fine-tuned for a wide scope of possible applications. As a consequence, HBPEA can be used in a variety of (potential) applications, such as crosslinkers in coatings, as toner resin, for dyeing polyolefin, as surfactants, or in cosmetics. Particularly notable is the disperse dyeing of polypropylene fibers, which has been a problem for decades. The development of coatings with antimicrobial properties has led to great commercial demand. Inorganic nanoparticles with antimicrobial activity are emerging as a new class of coating materials to fulfill the increasing general demands for hygiene in daily life.

Hyperbranched polymers were applied to cotton fabric for different functionality (Ibrahim et al. 2012; Klaykruayat et al. 2010; Zhang et al. 2013). Treatment of cotton with the amino-terminated hyperbranched polymers in the presence of citric acid as crosslinking agents prior to dyeing enhance the dyeability of the cotton fibre with reactive dyes (Li and Zhang 2010; Sadeghi-Kiakhani and Safapour 2015). Indeed, amino-terminated hyperbranched polymer (HBP-NH_2) grafted cotton fiber (HGCF) was prepared in order to achieve salt-free dyeing on cotton fiber with reactive dyes (Varadarajan and Venkatachalam 2016; Zhang et al. 2008).

Current work's novelty addresses the basics and practical aspects of hyperbranched polyester amide (HBPEA) as the acting template during synthesis of hyperbranched polyester amide–silver nanohybrid (Ag/HBPEA). reaction involved in preparation of HBPEA embrace those among maleic anhydride (MA), diethanolamine (DEA) and trimethylol propane (TMP). By virtue of its polymeric nature, HBPEA induces stabilization of the nano-sized silver which is formed in situ under the action of sodium borohydride ($NaBH_4$) reductant on silver nitrate ($AgNO_3$). The ultimate result is hyperbranched polyester amide–silver nanohybrid (Ag/HBPEA). Major ultrafine characteristics of both the newly synthesized HBPEA stabilizer and Ag/HBPEA nanohybrid are performed using the state of the art tools. Independent application of those stabilizer (HBPEA) and the nanohybrid (Ag/HBPEA) to cotton fabrics and changes in fabric performance and antibacterial activity of the fabrics are examined. The work was extended to evaluate the antibacterial activities of the treated cotton fabric after 5, 10, 15 and 20 washing cycles.

Materials and methods

Materials

Mill scoured and bleached plain weave 100% cotton fabrics were used after being further purified in the laboratory. This purification involved treatment of the fabrics with a solution containing 1.5 g/l NaOH and 1.5 g/l wetting agent at the boil for 1 h. To this end the fabrics were thoroughly washed with hot and cold water. Maleic anhydride (MA), diethanol amine (DEA) and trimethylol propane (TMP) were purchased from Across Co. (Germany). 1,2,3,4-butantetracarboxylic acid (BTCA) was purchased from Across Co. Germany. Sodium borohydride ($NaBH_4$) and silver nitrate ($AgNO_3$) were purchased from Sigma-Aldrich Co. (USA). All chemicals used in current work were of laboratory reagent grade.

Methods

Synthesis of hydroxyl functionalized hyperbranched polyester amide

Hydroxyl functionalized hyperbranched polyester amide (HBPEA) was synthesized via pseudo-one step process.

Synthesis of AB2 monomer AB2 monomer was prepared by amidation reaction of DEA and MA at a molar ratio of 1/1 where 0.1 mol of MA was dissolved in 100 ml of chloroform in three-necked round-bottom flask at 25 °C, 0.1 mol of diethanolamine was rapidly poured into MA solution. The reaction mixture was stirred with a magnetic stirrer at 60 °C under reflux for 4 h and under nitrogen to obtain the AB2 monomer (Scheme 1).

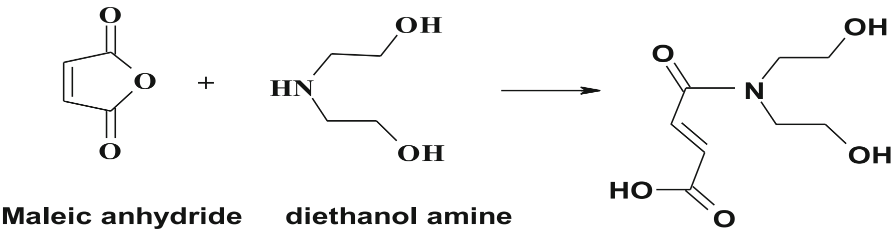
Synthesis of hyperbranched polyester amide (HBPEA) Hyperbranched polyester amide (HBPEA) was prepared in round bottom four necked reaction flask, each neck equipped with stirrer, thermocouple, nitrogen inlet, packed column condenser charged with a packing materials (glass peeds) connected with condenser and separator to collect the water coming out and a neck to charge the raw materials, using heating mantle as source for heating the flask. Adduct 1 (9 mol, 182.7 g), TMP (1 mol, 13.4 g) and 0.5 wt% of p-toluene sulphonic acid as catalyst were stirred and the reaction mixture temperature was increased gradually up to 140 °C. The unreacted residuals were removed by vacuum distillation. (Scheme 2).

Preparation of AgNPs in HBPEA matrix (Ag/HBPEA nanohybrid)

Preparation of Ag/HBPEA nanohybrid was carried out through inclusion of AgNPs in HBPEA matrix using a reductive technique. Different concentrations of HBPEA in 50 ml distilled water was taken in a round bottle flask with continuous stirring. 5 ml of 0.1 g $AgNO_3$ solution in water and 5 ml solution of 0.1 g $NaBH_4$ in water was simultaneously added drop wise into the polymer solution with vigorous stirring at 25 °C water was simultaneously added dropwise into the polymer solution with vigorous stirring at 25 °C until the color of the resultant solution turn light to dark yellow indicating the formation of AgNPs.

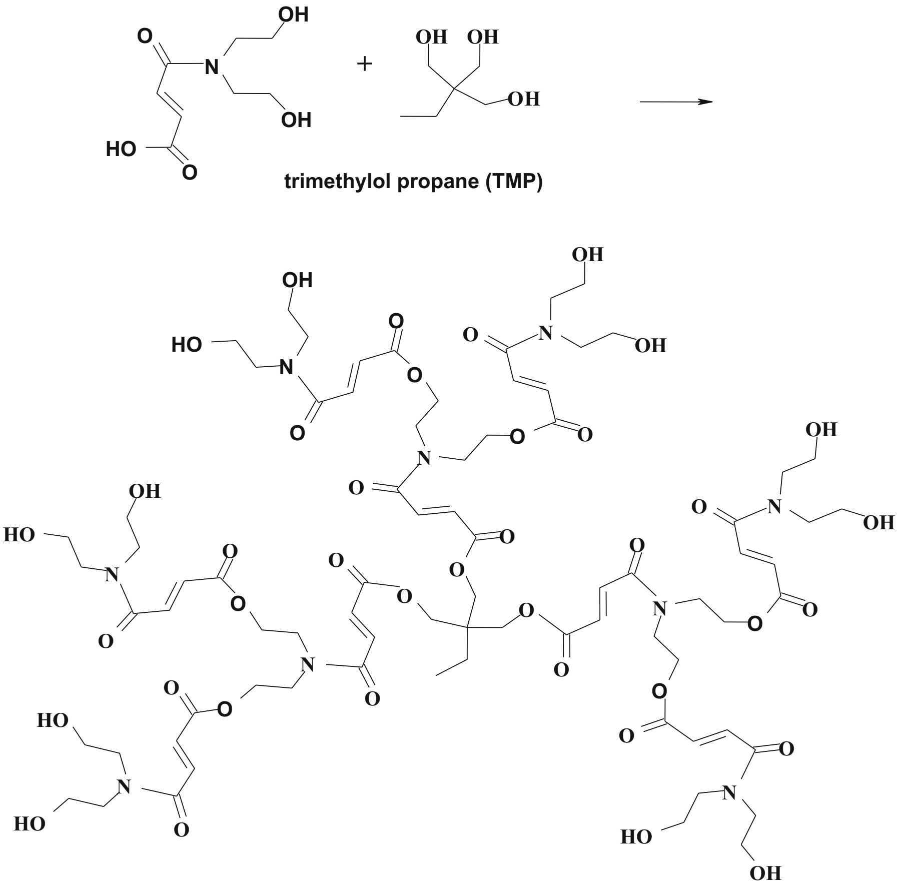
Application of HBPEA to cotton fabric

Fabric samples were impregnated for 5 min in pad baths containing different concentrations of HBPEA (3–10%) and BTCA (30 g/l) as a crosslinking agent



Scheme 1 Represent the formation of AB2 polymer from the reaction of maleic anhydride (MA) with diethanol amine (DEA)

Scheme 2 Chemical synthesis of highly functionalized hyperbranched polyesteramide (HBPEA)



with sodium hypophosphite (6%, w/w) as a catalyst. Cotton fabric samples were padded in the previously prepared solution in two dips and nips, then squeezed to a wet pick-up of 100%. Padded fabrics were dried at 80 °C for 5 min and then cured at 180 °C for 3 min. Treated fabrics were rinsed with hot water then with cold water and finally dried at room temperature.

Application of AgNPs/HBPEA nanohybrid to cotton fabric

The cotton fabric was padded in different solutions of AgNPs that were prepared using different HBPEA concentrations (3–7%) The fabric was then dried at 80 °C for 5 min.

Characterization techniques for nanohybrids preparation and cotton fabrics application

Fourier transform infrared (FTIR) spectroscopy of HBPEA was carried out using ATR-FTIR instrument. The latter was from SHIMADZU, Model IR prestige-21, Germany. Thermal gravimetric analysis TGA was carried out using TGA-50 shimadzu instrument, in the range 40–800 °C; the heating rate was 10 K/min and under nitrogen atmosphere.

UV–Vis spectra have been proved to be quite sensitive to the formation of silver colloids because AgNPs exhibit an intense absorption peak due to the surface Plasmon excitation which describes the collective excitation of conductive electrons in a metal. AgNPs were recorded in spectra 50 ANALYTIKA JENA spectrophotometer from 300 to 550. Distilled water was used as the blank. 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. SEM was studied using a scanning electron—JSM-5400 instrument (Jeol, Japan). The specimens in the form of fabrics were mounted on the specimen stabs and coated with thin film of gold by the sputtering method. The elemental analysis was performed using EDX, which is an attachment to the scanning electron microscopy. The spectra obtained during EDX studies were used for carrying out the quantitative analysis.

Roughness was measured according to AATCC standard test method using a Surfacoder (1700a). Tensile strength (TS) and elongation at break were determined according to ASTM standard test Method, D 1682-94, 1994.

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 cm^2 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.

Results and discussion

The first target of the current work was designed to prepare a highly functionalized hyperbranched polyester amide (HBPEA) to be used as efficient stabilizing agent for AgNPs due to the presence of huge numbers of hydroxyl and amide groups. The synthesis was performed as per the pseudo-one step. The first scheme involved reacting MA with DEA to yield AB2 monomer (Scheme 1) which in turn, was reacted with TMP as a core monomer in presence of P-toluene sulfonic acid as a catalyst to form HBPEA (Balkan et al. 2017) as displayed in Scheme 2.

FTIR and thermal stability of the as synthesized HBPEA

Figure 1a shows the FTIR spectra of HBPEA polymer. It reveals the appearance of strong absorption band of hydroxyl group at 3457 cm^{-1}, ester group stretching at 2089 cm^{-1} and the absorption band of amide carbonyl groups at 1635 cm^{-1}. The band at 1046 cm^{-1} is attributed to = C–H bending and those at 1130, 1184, and 1290 cm^{-1} are attributed to C–O and C–N stretches. Figure 1b shows TGA of the as prepared HBPEA. The results imply that HBPEA displays excellent thermal stability even at high temperature. The weight loss attains the value of only 8.452% up to 282 °C. whereas it reaches a value of 42.5% when the temperature was raised to 383.61 °C. On the other hand, HBPEA loses almost its weight 98.9% at 653 °C.

UV–Vis spectroscopy of HBPEA and Ag/HBPEA nanohyprids

Figure 1c, d shows UV–Vis spectra of HBPEA and Ag/HBPEA at different concentrations of HBPEA aqueous solution. The HBPEA aqueous solution has only one absorption peak at 292 nm as displayed in Fig. 1c and exhibits yellow and transparent color after reaction with silver nitrate as represented in Fig. 1d. It is observed that another absorption peak at 414 nm appeared which demonstrates the formation of AgNPs. Furthermore, the absorbance of AgNPs increases with increasing the concentration of HBPEA confirming that increasing HBPEA concentration leads to enhancement of the stability of the generated AgNPs which, in turn, increases the number of AgNPs in a nanoform (Hebeish et al. 2013, 2014, 2016). Concurrently, the solution turned from transparent to semitransparent. AgNPs were further observed by TEM technique to determine shape and particle distribution.

Particle size shape and size distribution of AgNPs stabilized with different concentrations of HBPEA

Figure 2 shows the TEM image and size distribution of the AgNPs in AgNPs/HBPEA hybrid prepared using different concentrations of HBPEA. The ability of HBPEA to adsorption on the surface of AgNPs alter the relative growth rate in different crystallography planes thereby resulting in the formation of AgNPs. The obtained particles are spherical-shaped and highly dispersed.

The size of AgNPs with narrow size distribution is ranging from 8 to 18.1 nm in case of using lower concentrations of HBPEA (3% to 5%), AgNPs with smaller size ranging from 1 to 6.7 nm generated in aqueous medium and the size is still small as even by rising the concentration up to 7% HBPEA, a point

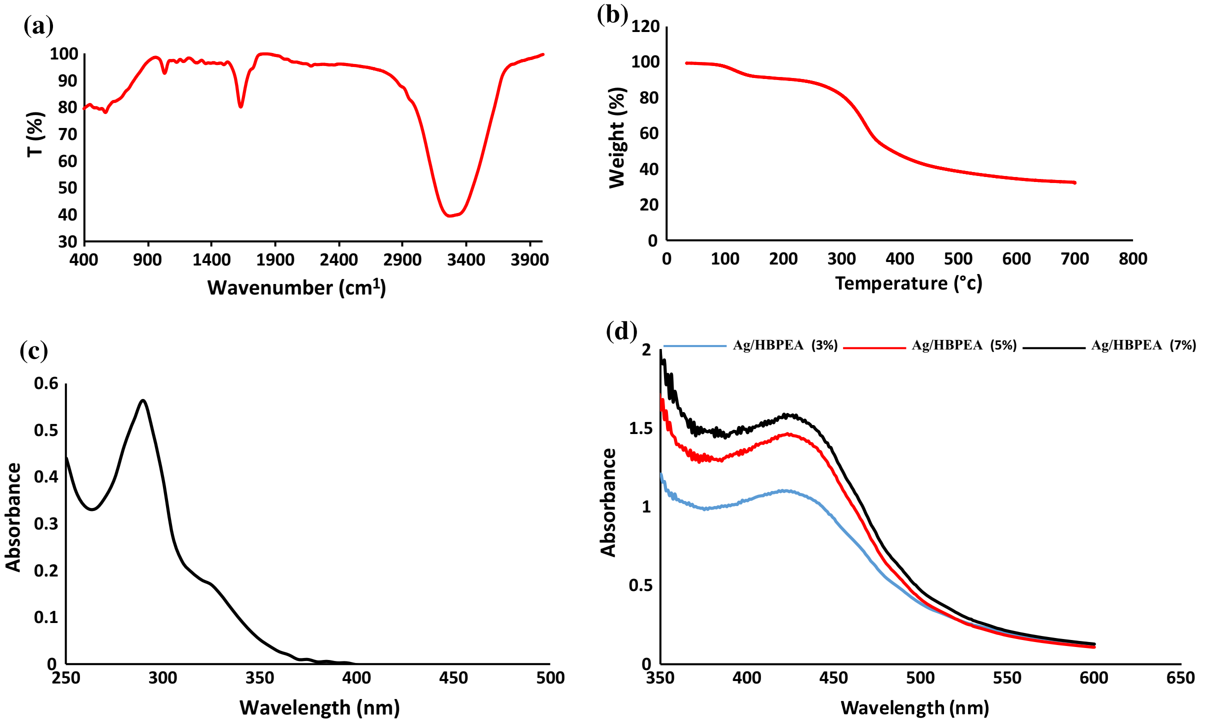


Fig. 1 **a** FT-IR spectra, **b** TGA analysis of HBPEA, **c** UV–Vis spectra of HBPEA and **d** UV–Vis spectra of Ag/HBPEA nanohybrid using different concentrations of HBPEA (3%, 5% and 7%)

which could be attributed to the adsorption of more HBPEA on AgNPs which prevents them to grow to bigger clusters.

Hydrodynamic average size and surface charge of AgNPs stabilized with different percentages of HBPEA

For further confirmation about the particle size and zeta potential (surface charge) of the formed AgNPs stabilized with different concentrations of HBPEA, particle size analyzer and zeta potential via dynamic light scattering (DLS) technique was performed. Figure 3a–c represent the graphs for the hydrodynamic size and polydispersity index (PdI) of Ag/HBPEA nanohybrid. It is observed that the average hydrodynamic size of the as synthesized AgNPs stabilized using 3, 5 and 7% of HBPEA is very small ranged from 7 nm, 9 nm and 11 nm respectively. Additionally, PdI of these three nanohybrid is less than 0.5 which confirms the monodispersity of the formed AgNPs with more homogeneity.

On the other hand, Zeta potential graphs of the formed nanohybrid based on AgNPs stabilized via different concentrations of HBPEA is plotted in Fig. 3d–f. It is noted that the zeta potential for the three samples is above − 30 (− 31 mv, − 39 mv and − 54 mv for the formed AgNPs using 3% HBPEA, 5% HBPEA and 7% HBPEA respectively) indicating that the formed AgNPs is well stabilized via hydroxyl groups of the used stabilizing agent (HBPEA) (El-Naggar et al. 2018a, b). Moreover, as observed from the graphs, the zeta potential value increases by increasing the concentration of HPPEA used as stabilizing agent. Current promising results advocate the HBPEA as an excellent candidate for stabilization of AgNPs against agglomeration.

Application of the formed nanohyprid onto cotton fabrics to impart antibacterial properties

The second target of the present work is to apply the formed nanohybrid of AgNPs solution stabilized via different concentrations of HBPEA to cotton fabrics. Morphological and mechanical properties of the nanohybrid treated cotton fabrics were evaluated and compared with the cotton fabrics treated with HBPEA. Given below is the surface morphology and

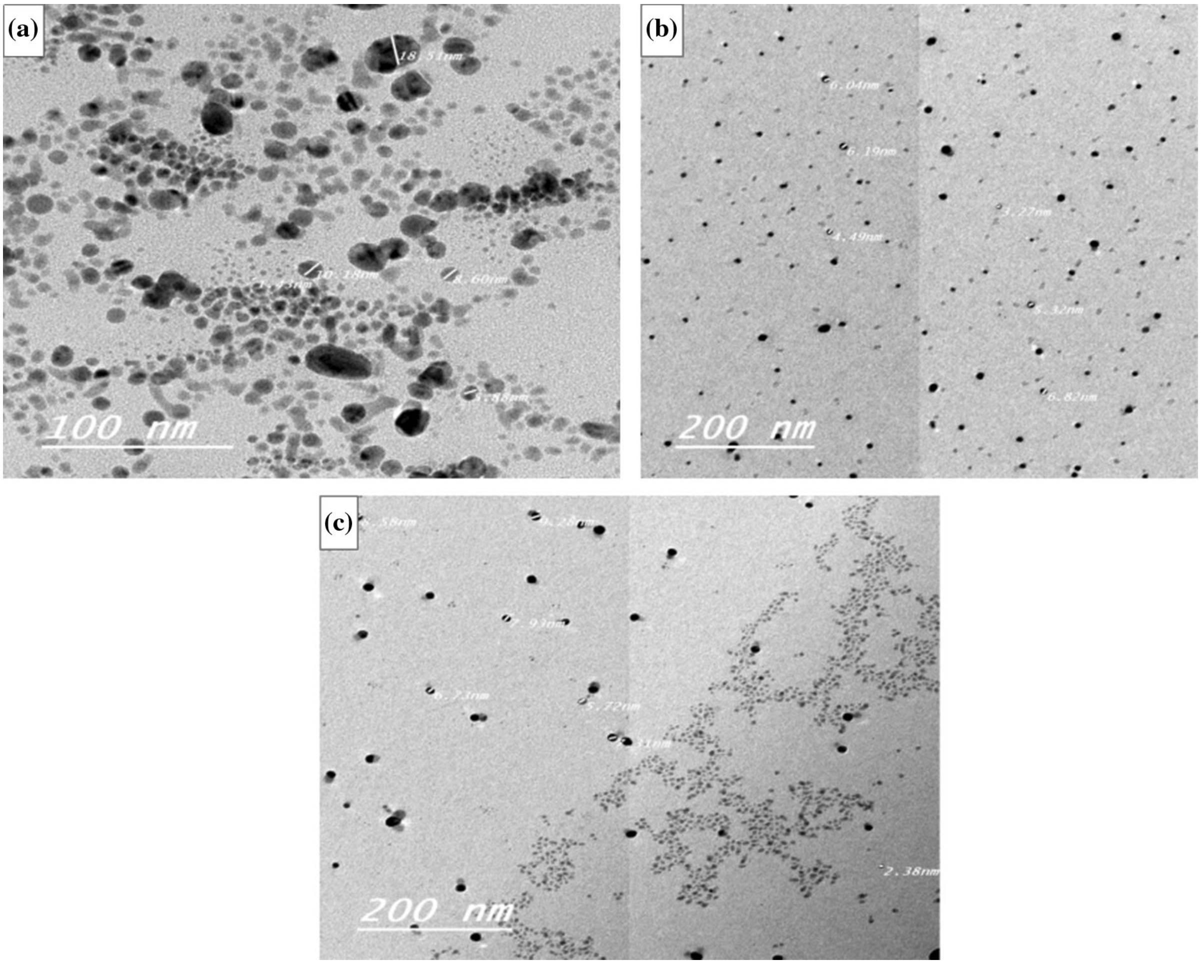


Fig. 2 TEM images of AgNPs prepared with **a** 3% HBPEA, **b** 5% HBPEA, **c** 7% HBPEA

mechanical properties such as roughness, tensile strength and elongation) of the treated cotton fabrics.

Morphological structure and elemental analysis of the treated cotton fabrics

Figure 4a shows the surface morphology of cotton treated with HBPEA. It is seen that the treated cotton fabrics exhibit a smooth surface. HBPEA seems to form homogenous film which is uniformly distributed on cotton fabric.

Figure 4b, d, f shows SEM of cotton fabrics treated with AgNPs stabilized with 3%, 5% and 7% of HBPEA respectively. On the other hand, EDX figures as represented in Fig. 4c, e, g shows the elemental analysis of each sample of cotton fabric treated with these three formula of AgNPs that were prepared using different concentrations of HBPEA. Obviously increasing the concentration of HBPEA causes more homogeneity in HBPEA film coating. Results of EDX depict that increasing the amount of HBPEA used in preparation of AgNPs from 3 to 7% is accompanied by increased AgNPs on the cotton fabric. Indeed, this is verified by EDX results that reveal increment in the nitrogen content which, in turn, expresses HBPEA content on the cotton fabric.

Mechanical performance of Ag/HBPEA treated cotton fabric

The mechanical properties of untreated and cotton fabrics treated with Ag/HBPEA nanohybrid was performed to clarify the effect of such treatments on the mechanical attributes of cotton fabric. Table 1 depicts the mechanical performance of cotton fabrics treated with Ag/HBPEA nanohybrid using HBPEA at different concentrations. Table 1 also discloses the effect of increasing HBPEA concentration in only its own solution on the mechanical performance of cotton fabric treated thereof as well as those of the untreated fabric (control). As is evident the untreated cotton fabric (control) exhibits a tensile strength of 65 kgf. Involvement of AgNPs with HBPEA at a concentration of 3% in a nanohybrid vis-à-vis only 3% HBPEA solution reveals, after being applied to the fabric, tensile strength of 44 kgf with strength loss of 32% and 56 kgf with strength loss of 1% respectively. This implies that nanohybrids have much less degradative effect than pure HBPEA solution. Movement restriction of molecular and fibrillar structure of cotton cellulose (i.e. rigidity) along with chemical degradation occurring during crosslinking by BTCA may account for the observed losses in tensile strength. Increasing the HBPEA concentration alone or in the nanohybrid acts in favor of the tensile strength but with the certainty that the nanohybrid displays higher tensile strength than does the pure HBPEA. Indeed the tensile strength obtained with fabric treated with Ag/HBPEA (7%) (61 kgf) lower in value than that of blank cotton by only 4%, reflecting the advantage of the nanohybrid. It is understandable that the enhancement in tensile strength by increasing HBPEA concentration is a manifestation of extra strength conferred on the fabric by HBPEA film which is stronger at higher concentration of HBPEA.

Fig. 4 **a** SEM of cotton fabric treated with HBPEA, SEM and EDX of cotton fabric treated with AgNPs prepared using, **b**, **c** 3% HBPEA, **d**, **e** 5% HBPEA and **f**, **g** 7% HBPEA respectively ▶

Results of the elongation at break (Table 1) shed insight on two major features. Firstly, the elongation at break acquires higher values in case of cotton fabrics treated with the Ag/HBPEA nanohybrid than those treated with HBPEA solution. Secondly, the elongation at break enhances by increasing HBPEA concentration up to 3–5% and decreases thereafter. It is certain, however, that the values of elongation at break observed with higher HBPEA concentration (i.e. 7%) are much more than that of the control.

Table 1 set up also the results of surface roughness of cotton fabric before and after being treated with AgNPs alone or in Ag/HBPEA nanohybrid. The results figure out roughness average value of 13.59 for fabrics treated with Ag/HBPEA nanohybrid. Inclusion of AgNPs in HBPEA. adversely affect, but to low extent, the softening properties of HBPEA. In

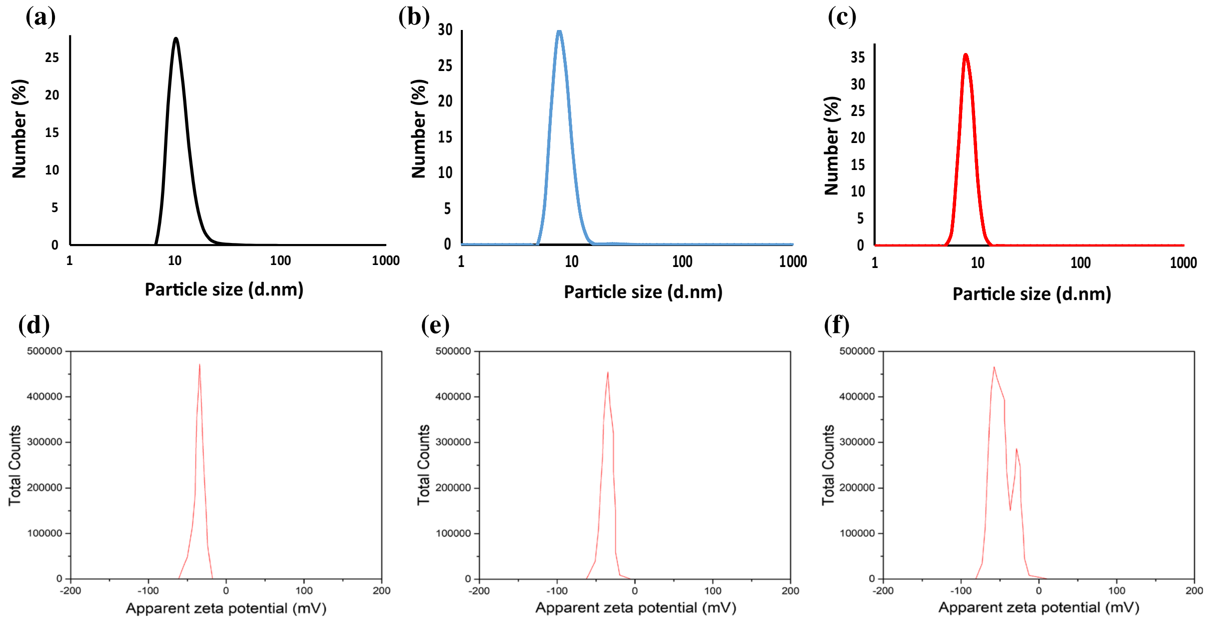
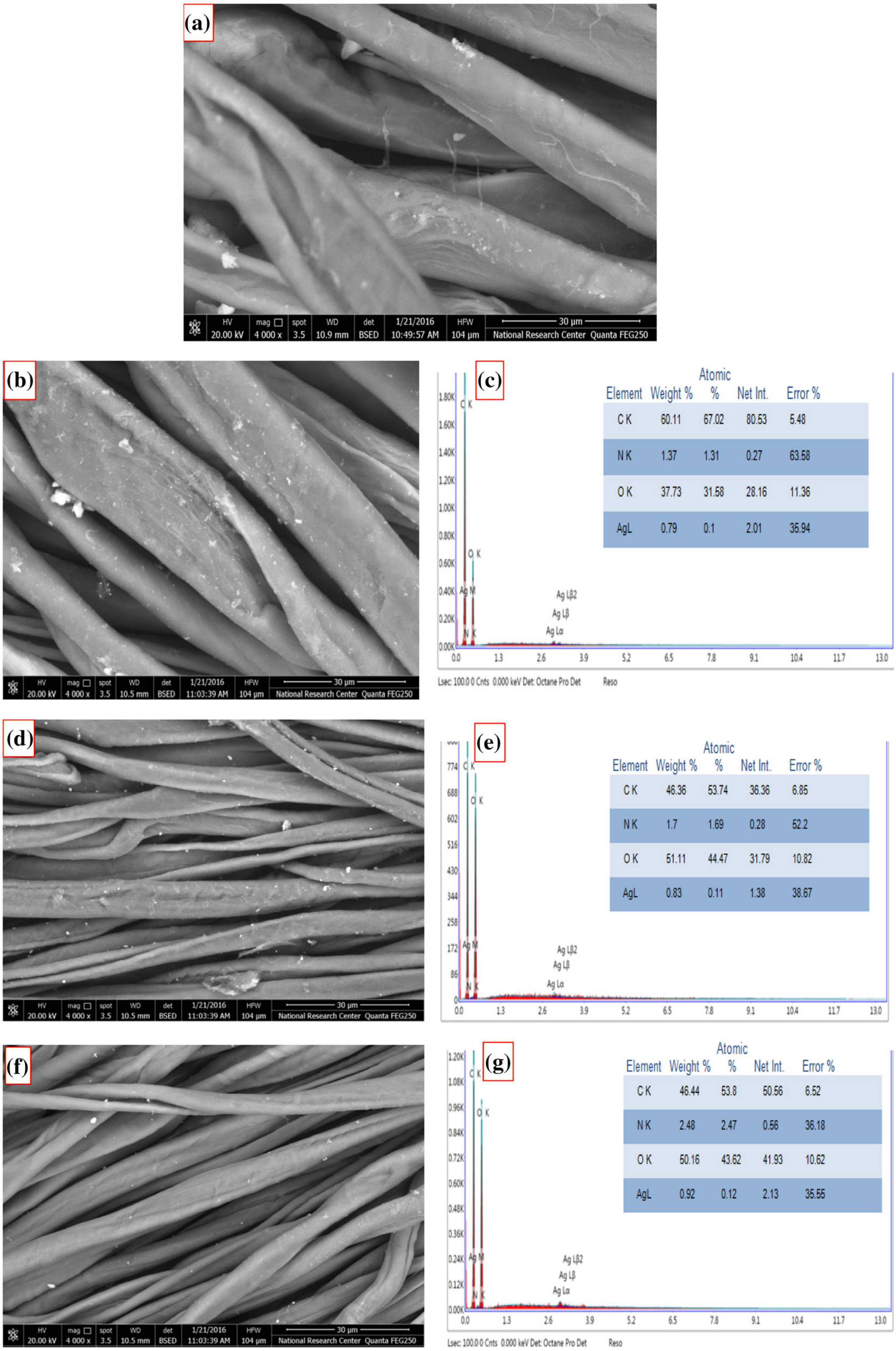


Fig. 3 **a–c** Particles size and **d–f** zeta potential of AgNPs prepared using different concentrations of HBPEA (3%, 5% and 7%) respectively



(c)

Element	Weight %	Atomic %	Net Int.	Error %
C K	60.11	67.02	80.53	5.48
N K	1.37	1.31	0.27	63.58
O K	37.73	31.58	28.16	11.36
AgL	0.79	0.1	2.01	35.94

(e)

Element	Weight %	Atomic %	Net Int.	Error %
C K	46.36	53.74	36.36	6.85
N K	1.7	1.69	0.28	52.2
O K	51.11	44.47	31.79	10.82
AgL	0.83	0.11	1.38	38.67

(g)

Element	Weight %	Atomic %	Net Int.	Error %
C K	46.44	53.8	50.56	6.52
N K	2.48	2.47	0.56	36.18
O K	50.16	43.62	41.93	10.62
AgL	0.92	0.12	2.13	35.55

conclusion, the Ag/HBPEA nanohybrid is much more advantageous in producing cotton fabrics with higher mechanical performance than HBPEA alone.

Table 1 Roughness, elongation and tensile strength of untreated and treated cotton fabrics with Ag/HBPEA nanohybrid using different concentrations of HBPEA

Fabric substrate	Concentration of HBPEA (%)											
	0			3			5			7		
	Roughness (μm)	Tensile strength (kgf)	Elongation at break (%)	Roughness (μm)	Tensile strength (kgf)	Elongation at break (%)	Roughness (μm)	Tensile strength (kgf)	Elongation at break (%)	Roughness (μm)	Tensile strength (kgf)	Elongation at break (%)
Cotton fabric (control)	13.58	65	9	15.03	44	18	13.60	47	16	13.60	54	14
Cotton fabric treated with Ag/HBPEA nanohybrid	13.58	65	9	15.03	56	18	15.04	58	20	15.14	61	17

Evaluation of Antibacterial activities of cotton fabrics treated with HBPEA alone as well as Ag/HBPEA nanohybrid

The antimicrobial activity of cotton samples treated by the newly synthesized compound containing silver nanoparticles (i.e. Ag/HBPEA) which are formed with the aid of HBPEA as stabilizer was evaluated using an agar disk diffusion assay. Parallel to this, solution contains only HBPEA at different concentrations were used in treatment of cotton fabric for the sake of comparison. The antimicrobial activities of the treated fabrics were tested against two bacteria and two fungi. The bacteria are gram positive (*staphylococcus aureus)* and gram negative (*Escherichia coli).* While *Aspergillus flavus* and *Candida albicans* are used as fungus species. The results obtained are shown in Fig. 5a, b for cotton fabrics treated with HBPEA only and that treated with Ag/HBPEA nanohybrid respectively. Obviously, treated fabric using HBPEA (3%) exhibits no antibacterial activity as revealed from Fig. 5a. Increasing the concentration of HBPEA to 5% is accompanied by a significant increase in the antibacterial activity of the treated fabric against staphylococcus aureus, *Escherichia coli* and Candida albicans.

The antibacterial activity of the treated fabrics continued to increase and improve by increasing concentration of used HBPEA to attain maximum at a concentration of 10% as evidenced by the increase in the inhibition zone diameter. Figure 5b shows the effect of increasing concentration of HBPEA used in preparation of AgNPs on the antibacterial activity of cotton fabrics treated with Ag/HBPEA nanohybrid. In contrast with treatment with HBPEA alone, treatment of cotton fabric with Ag/HBPEA (3%) nanohybrid induces antibacterial activity which is rather excellent and could be attributed to the presence of AgNPs in the treating agent, i.e. the nanohybrid. Treatment of fabric with Ag/HBPEA (5%) nanohybrid enhances the antimicrobial activity of cotton fabric against all tested microorganisms including Aspergillus flavus (fungus). It is also observed from Fig. 5a, b that HBPEA and HBPEA/AgNPs treated cotton fabric have a better antibacterial resistance against *E. coli*

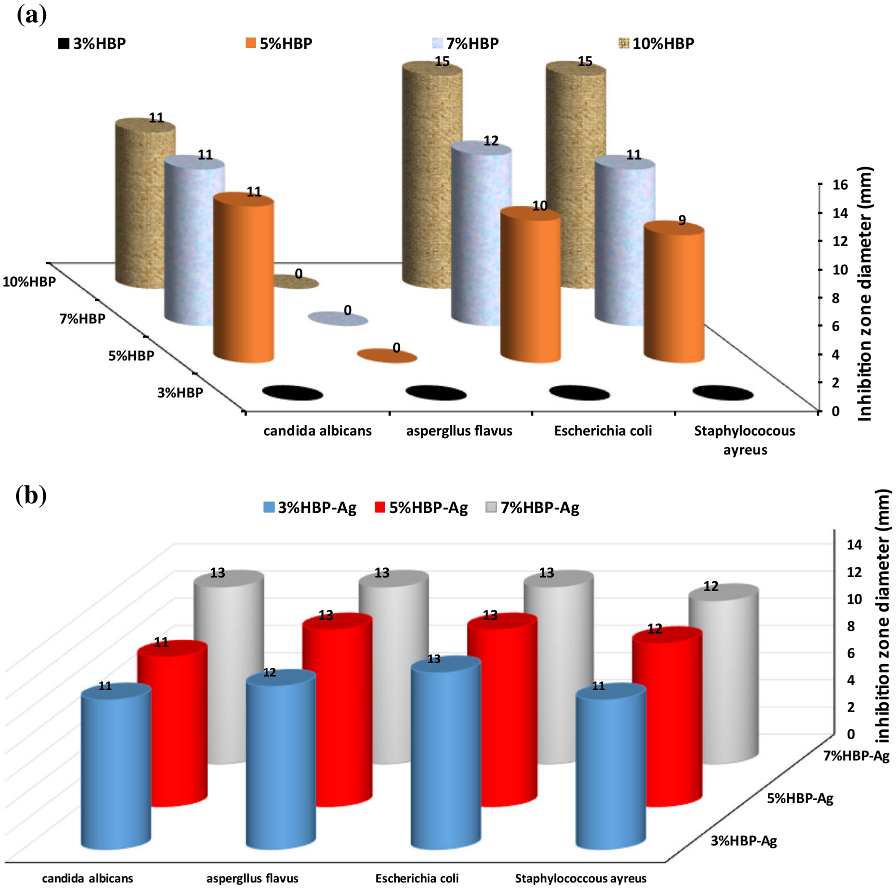


Fig. 5 Inhibition zone (mm) of cotton fabric treated with different concentrations of **a** HBPEA, **b** Ag/HBPEA nanohybrid prepared using 3%, 5% and 7% of HBPEA

(Gram negative) than staphylococcus aureus (Gram positive); this difference could be attributed to the difference in structure of the cell walls of both bacteria. Previous reports revealed that the layer of peptide glycan in gram positive bacteria is thicker than in gram negative bacteria (Hebeish et al. 2011).

Durability of treated cotton fabrics against washing cycles

The cotton fabrics treated with nanohybrid of Ag/HBPEA (3%) was chosen for evaluation of the durability against washing cycles (5, 10, 15 and 20). It is observed that the durability is still excellent and there is no noticeable loss for the percentage of AgNPs and the inhibition zone in nm is above 8 mm even after 20 washing cycles (Fig. 6).

This action could be attributed to the strong bond between HBPEA and cellulosic chains of cotton fabrics. Based on the promising data, the antimicrobial cotton fabrics treated with this environmental compound of Ag/HBPEA nanohybrid is considered to be fantastic fabrics to be used in medical textiles especially for hospitals textiles.

Conclusion

Experiments of current research work were designed to achieve two targets. The first is concerned with the synthesis and characterization of hyperbranched polyester amide (HBPEA) stabilizer and hyperbranched polyester amide–silver nanohybrid (Ag/HBPEA). the stabilizer (HBPEA) was fabricated through reaction of diethanol amine (DEA) with maleic anhydride (MA) to yield adduct 1 which, in turn, reacted with trimethanol propane (TMP) to yield HBPEA stabilizer. Meanwhile, synthesis of Ag/HBPEA nanohybrid was fulfilled via in situ formation of AgNPs in a system containing HBPEA stabilizer,

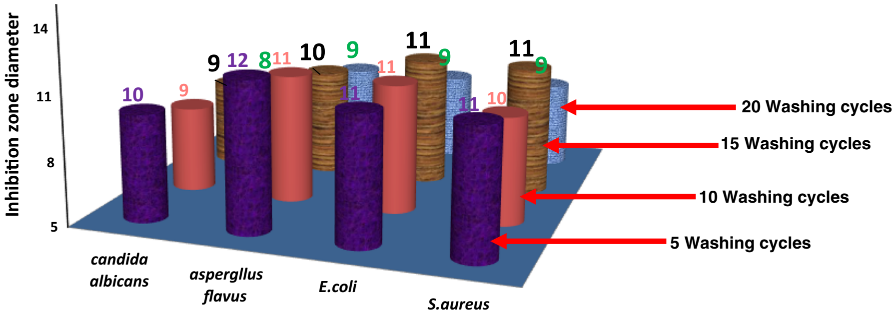


Fig. 6 Inhibition zone (mm) of cotton fabric treated with Ag/HBPEA nanohybrid using 3% of HBPEA after washing cycles

sodium borohydride ($NABH_4$) reductant and silver nitrate ($AgNO_3$). Evidently, $AgNO_3$ is converted to AgNPs under the reducing action of $NaBH_4$, in presence of HBPEA which inevitably invites AgNPs for interaction leading to Ag/HBPEA nanohybrid. AgNPs is formed homogenously on the interaction with the stabilizer. AgNPs are spherical-shaped and highly dispersed. The hydrodynamic size of the currently synthesized AgNPs stabilized using 3%, 5% and 7% of HBPEA is very small ranged from 7 nm, 9 nm and 11 nm respectively. On the other hand, the second target is the application of HBPEA stabilizer and Ag/HBPEA nanohybrid independently to cotton fabrics followed by thorough assessment of thus treated fabrics using the state of art tools, e.g.; UV–Vis spectral analysis, TEM, SEM connected with EDX, FTIR, zeta potential and particle size analyzer, etc. Fabrics treated with HBPEA exhibits smooth surface. Increase the concentration of the nanohybrid (Ag/HBPEA) from 3 to 5%, induces excellent antimicrobial activity against staphylococcus aureus, *Escherichia coli* and Candida albicans even after 20 washing cycles. Treatment of the cotton fabric with HBPEA or Ag/HBPEA is accompanied by small losses in the mechanical properties with the certainty that Ag/HBPEA nanohybrid acquires lesser harm effect than does HBPEA. Indeed, results of current work are promising and pursue further developmental work, scaling up and mill trials.

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