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A novel approach for adding smart functionalities to cellulosic fabrics

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ABSTRACT

A water soluble nanocomposite, based on Ag-nanoparticles (Ag-NPs) loaded on hyperbranched poly (amide–amine, HBPAA) was prepared, characterized and utilized in functional finishing as well as in combined reactive dyeing/and functional finishing of linen, cotton and viscose fabrics. Incorporation of the nanocomposite alone and in combination with reactive dyes in easy care finishing formulations brought about an outstanding antibacterial functionality of the finished and the dyed/finished fabrics even after 15 laundering cycles along with a slight negative impact on other performance properties. Improvement or decrement in the functional, comfort, and dyeing properties is governed by the type of cellulosic substrate.

1. Introduction

Cellulosic fabrics, i.e. linen, cotton and viscose are widely used in clothing fields for many reasons such as eco-friendly, renewability, hydrophilic properties, air permeability and comfortability (Ibrahim, Gouda, Husseiny, El-Gamal, & Mahrous, 2009; Ibrahim, Khalifa, El-Hossamy, &Twafik, 2010). However, these cellulosic fabrics are susceptible to attack by bacteria due to their large surface area and ability to provide proper conditions for the growth and accommodation of micro-organisms thereby causing irritation and odor problems along with fabric deterioration (Ibrahim et al., 2009; Ibrahim, Eid, & El-Zairy, 2011).

In response to the ever-growing consumer demands for safe healthy lifestyles, developing of innovative cellulose-based textiles with high added value and durable functional properties such as antibacterial, anti-UV, anti radiation, self cleaning and easy care has recently attracted the interest of R&D institutions and textile industry to cope with customer needs and to assure a share in the market (Bajaj, 2002; Holme, 2007; Schindler & Hauser, 2004).

Extensive research has been reported on enhancing the antimicrobial functions of cellulose based-textiles using different antimicrobial agents such as quaternary ammonium compounds (Gao & Cranston, 2008), N-halamines (Gouda & Ibrahim, 2008; Ibrahim, Aly, & Gouda, 2008; Ren, Kou, Liang, Worley, & Huang, 2008), chitosan (Öktem, 2003; Shanmugasundaram, 2006), immobilized enzymes (Ibrahim, Gouda, El-shafei, & Abdel-Fatah, 2007), polybiguanides (Blackburn et al., 2007; Chen-Yu, Eberhardt, & Kincade, 2007), halogenated phenols, e.g. triclosan (Orhan, Kut, & Gunesoglu, 2009; Simoncic & Tomsic, 2010), nanoparticles of noble metals and metal oxides (Dastjerdi & Montazer, 2010; Gorenšek & Recelj, 2007; Ibrahim, Eid, Hashem, Refai, & El-Hossamy 2010; Ibrahim, Refaie, & Ahmed, 2010), metal salts (Ibrahim, Mahrous, El–Gamal, Gouda, & Husseiny, 2010), hyperbranched polymer (Ibrahim, Abdel Rehim, & El-Batal, 2010; Ibrahim, Fahmy, Abdel Rehim, Sharaf, & Abo-Shosha, 2010; Zhang, Chen, Lin, & Zhang, 2009; Zhang, Zhang, Chen, & Lin, 2009), and metal nanoparticles stabilized polymer (Mahapatra & Karak, 2008; Zhang, Wu, Chen, & Lin, 2009), and polymer nanocomposites (Gowri et al., 2010).

The main goals of the present work are: (i) to prepare nanosilver (Ag-NPs) colloidal solution in one step by mixing $AgNO_3$ aqueous solution with hyperbranched poly (amide–amine, HBPAA) aqueous solution, in the presence of Na-borohydride ($NaBH_4$), as a reductant for silver cations, (ii) to characterize the obtained Ag-NPs colloidal solution, (iii) to apply the obtained Ag-NPs to cellulosic substrates in the presence of an eco-friendly crosslinking agent, Fixapret® ECO using the pad-thermofixation technique for imparting multifunctional durable properties, i.e. easy care, antibacterial and hydrophilicity functions, and (iv) to investigate the technical feasibility of multifunctional finishing and reactive dyeing in one step.

2. Experimental

2.1. Materials

In this study, 100% scoured and bleached plain weave linen (207 g/m^2), cotton (120 g/m^2) and viscose (110 g/m^2) fabrics were used.

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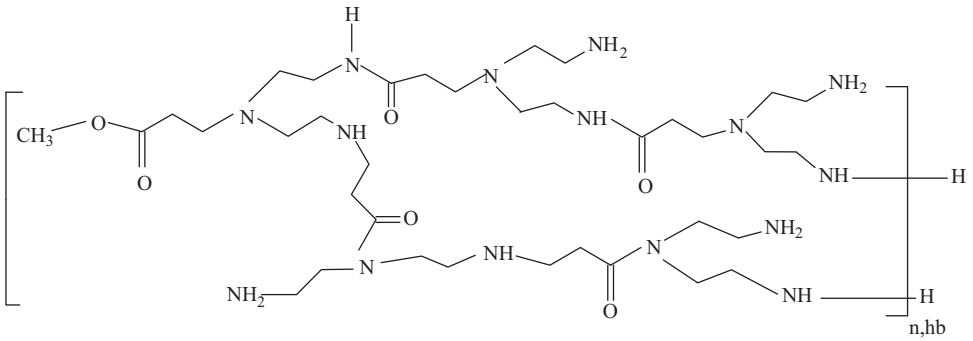


Fig. 1. Structure of hyperbranched poly (amide–amine).

Fixapret® ECO (modified dimethyloldihydroxy ethylene urea – low formaldehyde reactant resin, DMDHEU, BASF), and Hostapal® CV-ET (nonionic wetting agent based on alkyl aryl polyglycol ether, Clariant) were of commercial grade.

Bifunctional reactive dyes namely Remazol® Red 3BS (C.I Reactive Red 239, $\lambda = 540$, DyStar) and Cibacron® Red FNR (C.I Reactive Red 238, $\lambda = 525$, Huntsman) were of commercial grade.

All other chemicals used during this study such as citric acid, sodium borohydride ($NaBH_4$), magnesium chloride hexahydrate ($MgCl_2{\cdot}6H_2O$), and silver nitrate ($AgNO_3$) were of laboratory reagent grade.

2.2. Methods

2.2.1. Synthesis of hyperbranched poly (amide–amine, HBPAA)

Synthesis and characterization of hyperbranched poly (amide–amine) (Fig. 1) were carried out using a procedure described by Ibrahim, Abdel Rehim, et al. (2010).

2.2.2. Preparation of Ag-nanoparticles in HBPAA matrix

Preparation of Ag-nanoparticles in HBPAA matrix was carried out using a reductive technique according to Mahapatra and Karak method (Zhang, Chen, et al., 2009). The typical one step preparation was as follows: 3 g of HBPAA with 100 ml distilled water was taken in a round bottle flask with continuous stirring. 5 ml solution of 0.1 g $AgNO_3$ in water and 5 ml solution of 0.1 g $NaBH_4$ in water were simultaneously added drop wise 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 Ag-colloid nanoparticles. The obtained solution was kept in a brown glass bottle for further studies.

2.2.3. Multi-functional finish

To enhance the easy care properties as well as to impart antibacterial functionality in one step, the cellulosic fabrics were padded twice in a finishing bath containing: Fixapret® ECO, as fixing and crosslinking agent, along with Ag-nano particles-containing HBPAA, as antibacterial agent, $MgCl_2{\cdot}6H_2O$/citric acid as a mixed catalyst, and a nonionic wetting agent, to 80% wet pick-up, predried at 85 °C/5 min and then cured, followed by rinsing and drying. Finishing formulations as well as curing conditions used were given in the text.

2.2.4. Combined functional finishing and reactive dyeing

To acquire easy care property, antibacterial activity with dyeability with reactive dyes in one step, the bleached cellulosic substrates were padded twice in a dyeing/finishing formulation including: Fixapret® ECO (75 g/L), nano-Ag/HBPAA (20 g/L), $MgCl_2{\cdot}6H_2O$ (7.5 g/L), citric acid (0.75 g/L) along with a nonionic-wetting agent (2 g/L), to give a wet pick up of 80%, followed by drying at 85 °C for 5 min, curing at 160 °C/3 min. After treatment, the dyed/finished cellulosic fabric were rinsed thoroughly in tap water, followed by rinsing at 50 °C for 5 min in the presence of 1 g/L Na_2CO_3 and 2 g/L nonionic wetting agent to remove excess and unfixed reactant and finally dried again at 85 °C/5 min.

2.3. Measurements

Nitrogen content (N%) was determined according to the Kjeldahl method. The Ag-content was quantitatively determined by using Flame Atomic Absorption Spectrophotometer, GBC-Avanta Australia.

Dry wrinkle recovery angle (WRA) was determined according to ASTM method D-1296-98. The wettability test (W) was carried using AATCC test method (39-1980). CIE whiteness index (WI) was determined according to ASTM standard test method (E313-98). The color strength (K/S) of the obtained reactive dyeings was measured at the wavelength of maximum absorbance using an automatic filter spectrophotometer and calculated by the Kubelka–Munk equation (Judd & Wyszecks, 1999): $K/S = (1 - R)^2/2R$, where K is the absorption coefficient, S is the scattering coefficient, and R is the reflectance of the dyed samples. Washing and rubbing fastness of the simultaneously dyed and finished cellulosic fabrics were evaluated according to AATCC test method (61-1989) and (8-1972). Air-permeability was determined according to ASTM standard test method (D737-96).

Anti-bacterial activity assessment against G+ve bacteria (*Staphylococcus aureus*) and G-ve bacteria (*Escherichia coli*) was evaluated according to AATCC Test Method (147-1988) and expressed as zone of growth inhibition (mm). Durability to washing was evaluated according to AATCC test method 124.

The morphology and particle size of nano Ag–(Ag-NPs) were obtained by transmission electron microscope (TEM) using a JEOL JEM 2100 F electron microscope at 200 kv.

The surface morphologies of the untreated and treated linen fabrics were observed with JEOL-JZA 840A scanning electron microscope, Japan, after the samples were plated with gold.

All determinations were done in triplicate and the average was taken as final results.

3. Results and discussion

Since the main task of the present research work is to prepare Ag-NPs using HBPAA, as a reducing, stabilizing and capping agent, along with $NaBH_4$, as a reductant, in one step, and subsequently to utilize the prepared Ag-NPs colloidal solution in multifunctional treatments of linen, cotton and viscose cellulosic fabrics for imparting antibacterial activity, and enhancing their easy care and reactive dyeing properties without adversely affecting their high level of comfort, a wide range of experimental parameters have been

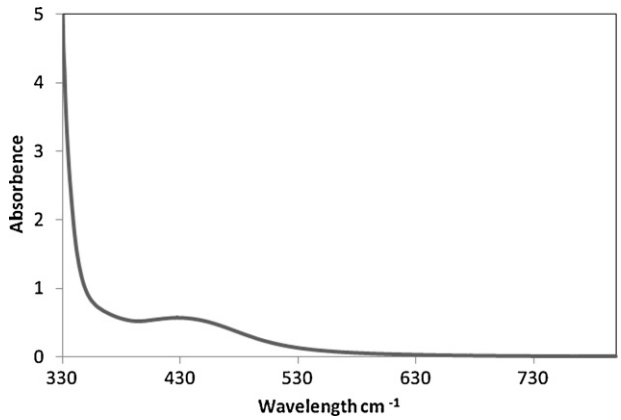


Fig. 2. UV–vis spectra of the silver colloid nanoparticles.

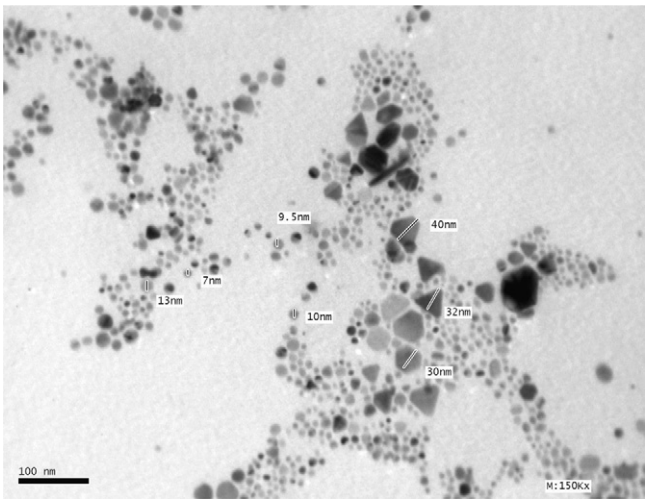


Fig. 3. TEM of prepared silver nano-particles.

investigated. Results obtained along with their appropriate discussion were followed.

3.1. Formation and characterization of the colloid Ag-NPs

Presence of $AgNO_3$, HBPAA and $NaBH_4$ in aqueous solution under vigorous mixing would be expected to promote the following reactions: (i) reduction of Ag^+ to form Ag° (Ag-NPs) using $NaBH_4$ and HBPAA as follows (Sastry, Patil, & Sainkar, 1998):

$$4Ag^+ + BH_4^- + 4OH^- \rightarrow 4Ag^\circ \downarrow + BH_2(OH)_2^- + 2H_2O \quad (1)$$

and in situ reduction of Ag^+ via complexation with HBPAA active groups, i.e. $-NH_2$ groups, to form Ag colloidal NPs, and (ii) subsequent adsorption of a large amount of HBPAA via its positive charges on the Ag-NPs surface thereby preventing the formed Ag-NPs from aggregation, i.e. high strong stability (Barnickel, Wokaun, Sager, & Eicke,1992; Zhang, Chen, et al., 2009).

The formation of Ag-NPs in HBPAA matrix is observed by UV–vis absorption (Fig. 2) and supported by TEM (Fig. 3). Fig. 2 exhibits an absorption peak in the range of 434 nm, a typical Plasmon resonance band of Ag-NPs (Mahapatra & Karak, 2008; Sastry et al., 1998; Zhang, Chen, et al., 2009). On the other hand, TEM (Fig. 3) study confirmed that Ag-NPs are not agglomerated, well dispersed with particle size in the range of 7–40 nm. The prepared Ag-NPs colloidal solution is highly stable and shows no signs of aggregation after six months of storage.

3.2. Functional finishes

3.2.1. Reactant resin concentration

Table 1 demonstrates the variation in the performance and functional properties of the treated cellulosic fabrics as a function of reactant resin concentration (0–100 g/L) and in the presence of the prepared Ag-NPs colloidal solution (20 g/L). For a given treatment conditions, it is evident that increasing the crosslinking agent concentration in the finishing formulation results in: (i) a significant improve in the %N, Ag-content, wrinkle recovery angles as well as a remarkable enhancement in the antibacterial activity of the treated fabric samples against G+ve and G-ve bacteria, and (ii) a slight or no negative impact on wetting time, whiteness index as well as on the air permeability, regardless of the used substrate.

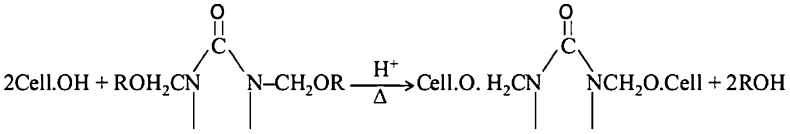
Table 1
Effect of finishing agent concentration on some performance and functional properties of treated cellulosic fabrics.

Substrate	Finishing agent conc. (g/L)	N%	Ag-content (mg/100 g fabric)	Wet (s)	WI	WRA (w + f)°	AP L/m²/s	Antibacterial activity (ZI, mm)	
								G + ve	G-ve
Linen	Untreated	0.05	–	5	65.5	110	18.4	0.0	0.0
	0	0.12	171	<1	63.2	128	17.5	2.8	2.0
	25	0.19	236	<1	60.8	165	16.6	6.3	5.4
	50	0.30	290	1	58.6	216	16.2	7.9	7.0
	75	0.48	324	2	55.5	245	15.6	11.4	10.2
	100	0.56	340	4	52.3	267	14.4	13.1	11.9
Cotton	Untreated	0.00	–	2	78.8	125	45.1	0.0	0.0
	0	0.15	190	<1	74.9	136	43.6	4.0	2.7
	25	0.24	280	<1	71.2	198	41.3	7.3	6.5
	50	0.37	312	<1	68.6	235	39.9	10.2	9.0
	75	0.59	343	1	65.0	265	36.6	13.4	11.6
	100	0.68	372	2	62.2	283	33.4	15.0	13.3
Viscose	Untreated	0.00	–	<1	95.5	152	82.2	0.0	0.0
	0	0.25	209	<1	91.4	170	76.3	5.1	4.4
	25	0.33	310	<1	87.6	250	73.2	9.8	7.9
	50	0.48	345	<1	83.8	268	71.6	14.1	13.0
	75	0.64	372	<1	80.6	280	68.5	16.4	15.5
	100	0.75	392	1	77.3	300	62.9	19.5	18.2

Finishing formulation: finishing agent (0–100 g/L); $MgCl_2.6H_2O$ (7.5 g/L); citric acid (0.75 g/L); Ag-NPs/HBPAA colloid solution (20 g/L); nonionic wetting agent (2 g/L); wet-pick up (80%); drying at 85 °C/5 min; curing at 160 °C/3 min, followed by after washing.
N%: nitrogen content; Wet: wetting time; WI: whiteness index; WRA: wrinkle recovery; AP: air permeability; ZI: zone of inhibition.

The enhancement in the %N, Ag content, WRA, and antibacterial functionality of the finished fabric samples against G+ve and G-ve bacteria reflects the positive role of the finishing agent in:

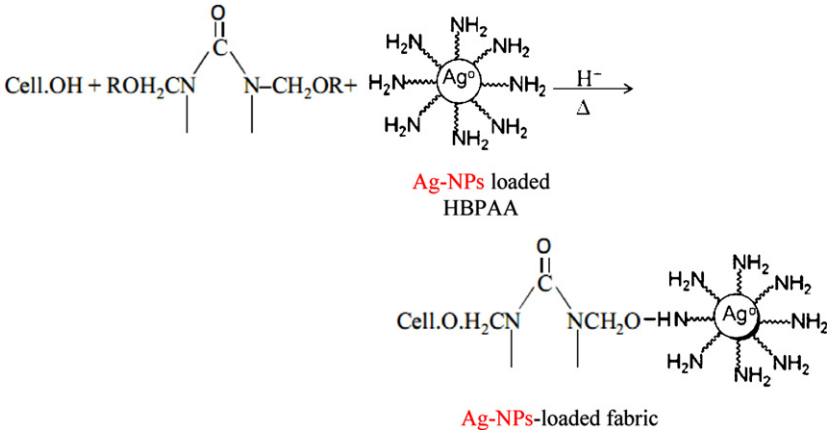
i) increasing the extent of crosslinking of adjacent cellulose chains via formation of ether-links as follows:



(2)

thereby enhancing both the %N and WRA, and

ii) enabling the fixation of Ag-NPs onto/within the crosslinked cellulose structure via fixation of Ag-NPs loaded HBPAA onto/within the finish/fabric matrix thereby enhancing the extent of fixation Ag-NPs-loaded HBPAA, i.e. higher %N and Ag-content as follows (Ibrahim, Abdel Rehim, et al., 2010):



(3)

The increase in wetting time, as in case of using linen susbstrate, and the decrease in whiteness index (WI), as well as air permeability (AP) properties of the finished fabrics most probably attributed to the formation and deposition Ag-NPs colloid/reactant resin film [Eq. (3)] onto/within the finish/fabric matrix, thereby leading to a slight decrease in wettability, whiteness index along with restricting the air flow through the finished fabric structure (Ibrahim, Eid, et al., 2010).

Table 1 reveals also that incorporation of the prepared Ag-NPs colloid (20 g/L) in the finishing formulation and in the absence of reactant resin brings about an improvement in %N, Ag-content, WRA as well as antibacterial activity, along with a decrease in other performance properties. This reflects the ability of the prepared Ag-NPs colloid, via its active sites: imino and terminal $-NH_2$ groups, to interact with active groups of the bleached cellulosic substrates, e.g.–OH, –COOH, –CHO groups under the given finishing conditions. Fixation of Ag-NPs colloid onto and/or within the cellulose structure exhibits antibacterial functionality against G+ve and G-ve bacteria strains.

In addition to that, the reduction in whiteness index of the treated substrates is most probably due to the presence of Ag-NPs and/or free $-NH_2$ groups on/within the fabric structure.

The remarkable increase in the loaded Ag-NPs, by increasing the reactant resin concentration, which in turn significantly affects the antibacterial activity of the treated fabrics most probably due to: (i) the reaction of Ag-NPs (Ag°) with the sulfur-containing proteins in/outside the cell membrane thereby inhibiting enzyme functions and affecting cell viability, (ii) releasing of (Ag^{+}) ions from (Ag°) which in turn can interact with phosphorous-moities in DNA thereby inactivating DNA replication (Gupta, Bajpai, & Bajpai, 2008) and/or (iii) generation of hydroxyl and other oxyradicals and their responsibility for damaging the bacteria's cell and inhibiting the multiplication of microorganisms cannot be ruled out (Dastjerdi, Montazer, & Shahsavan, 2009). On the other hand, the inactivation of G+ve was more efficient than G-ve bacteria most probably due differences in their cell wall structure, outer membrane as well as in amenability to inhibition of enzyme functions and/or inactivation of DNA replication (Gouda & Ibrahim, 2008; Gupta et al., 2008).

Additionally, the differences in the performance and functional properties of the treated cellulosic fabrics reflect the variations among the nominated substrates in surface area, cellulose content, amorphous to crystalline regions, availability and accessibility of the –OH active sites, other functional groups, e.g. –COOH, CHO, porous structure, fabric construction, cellulose content as well as pretreatment history.

3.2.2. Ag-NPs–loaded HBPAA concentration

As far as the change in the performance and functional properties of Ag-NPs colloid concentration, the data in Table 2 reveal that increasing its concentration up to 20 g/L results in a remarkable increase in the %N, Ag-content, as well as in the antibacterial activity, regardless of the treated substrate. The significant improve in the aforementioned properties could be discussed in terms of higher extent of fixation of the prepared Ag-NPs colloid onto/or within the finish/fabric matrix [Eq. (3)], thereby enhancing %N, Ag-content, hydrophilicity as a direct consequence of introducing new hydrophilic sites such as $-NH_2$ and –NH groups loaded with Ag-NPs and hence exhibit greater inhibiting power against the G+ve and G-ve bacterial strains as compared to Ag-NPs-unloaded cellulosic fabrics. It is clear from Table 2 that the greater the amount of Ag-NPs colloid-loaded onto/within the fabric, the higher the antibacterial

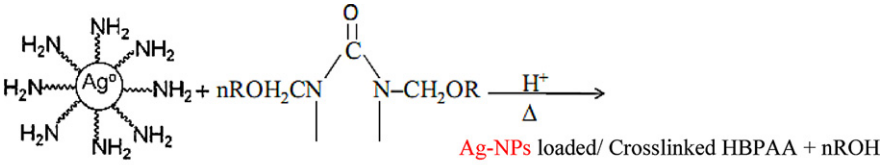
Table 2
Effect of incorporation of Ag-NPs/HBPAA colloidal solution into the finishing formulation on some performance and functional properties of treated cellulosic fabrics.

Substrate	Ag-NPs/HBPAA conc. (g/L)	N%	Ag-content (mg/100 g fabric)	Wet (s)	WI	WRA (w + f)°	AP L/m²/s	Antibacterial activity (ZI, mm)	
								G + ve	G-ve
Linen	Untreated	0.05	–	5	65.5	110	18.4	0.0	0.0
	0	0.26	–	6	60.9	265	16.5	1.3	0.9
	10	0.39	157	4	57.8	256	15.9	6.5	5.1
	20	0.48	324	2.5	55.5	245	15.6	11.4	10.2
	30	0.54	341	1.0	48.3	235	15.3	12.9	11.8
Cotton	Untreated	0.00	–	2	78.8	125	45.1	0.0	0.0
	0	0.34	–	3	71.6	278	41.8	1.8	1.3
	10	0.48	198	2	67.3	270	38.2	8.5	6.8
	20	0.59	343	1	65.0	265	36.6	13.4	11.6
	30	0.66	365	<1	57.4	254	35.4	14.0	12.8
Viscose	Untreated	0.00	–	<1	95.5	152	82.2	0.0	0.0
	0	0.43	–	2	87.2	295	77.1	2.6	1.9
	10	0.56	225	1	83.8	286	74.3	9.4	7.4
	20	0.64	372	<1	80.6	280	68.5	16.4	15.5
	30	0.73	398	<1	77.9	270	67.4	17.0	16.3

Finishing formulation: finishing agent (75 g/L); $MgCl_2.6H_2O$ (7.5 g/L); citric acid (0.75 g/L); Ag-NPs/HBPAA colloid solution (0–30 g/L); nonionic wetting agent (2 g/L); wet-pick up (80%); drying at 85 °C/5 min; curing at 160 °C/3 min, followed by after washing.
N%: nitrogen content; Wet: wetting time; WI: whiteness index; WRA: wrinkle recovery; AP: air permeability; ZI: zone of inhibition.

functionality, expressed as large area of inhibition zone, regardless of the used substrate.

On the other hand, Table 2 also shows that, increasing the Ag-NPs colloid concentration brings about a noticeable decrease in wetting time as well as a decrease in whiteness index, WRA and air-permeability of the treated cellulosic substrates. This is a direct consequence of introducing new active sites onto the finish fabric matrix, $-NH_2$ and NH groups, in the free form and/or blocked with Ag-NPs thereby: (i) increasing the hydrophilicity of the crosslinked cellulose structure, i.e. better wettability, (ii) interacting with the reactant resin, i.e. lowering extent of crosslinking cellulose and hence lowers WRA [Eq. (4)], and (iii) restricting the air flow through the cellulose structure via formation of Ag-NPs deposits onto the surface and/or entrapment into the porous structure of the fabric, i.e. lower whiteness and air permeability properties.



(4)

Results in Table 2 also show that further increase in Ag-NPs colloid concentration, i.e. beyond 20 g/L, results in further improve in %N, Ag content, wettability along with further decrease in whiteness index, WRA and air-permeability properties of the finished cellulosic substrates variation in the value of the aforementioned performance and functional properties of the treated substrates reflects the differences among them in fabric structure, composition, modification extent, amorphous/crystalline region ratio etc., as mentioned before.

It is also evident, Table 2, that finishing of the cellulosic substrate, in the absence of Ag-NPs colloid, is accompanied by a remarkable increase in %N, WRA, along with an improve in the antibacterial activity of the finished fabric samples as a direct consequence of enhancing the extent of crosslinking of cellulose structure via formation of ether links [Eq. (2)] thereby enhancing fabric resiliency, acting as a low formaldehyde source thereby interacting with the cytoplasmic constituents, e.g. nucleic acids, and/or as a barrier against microorganism, as well as (Ibrahim, Refaie, et al., 2010; Maillard, 2002) reducing slightly the hydrophilicity, whiteness and air permeability of the finished fabric compared to the untreated ones.

3.2.3. Curing conditions

As is evident, Tables 2 and 3, the optimal concentration of the reactant resin and Ag-NPs/HBPAA colloid are 20 g/L and 75 g/L respectively taking in consideration the negative impacts on some physic-mechanical properties of the treated substrates.

As far as the changes in the performance and functional properties of the treated cellulosic substrates as a function of curing condition, the data in Table 3 signify that variation of the thermofixation conditions of the treated fabric from 120 °C/5 min to 160 °C/3 min results in: (i) an enhancement in the %N, Ag-content, WRA as well as in antibacterial activity, regardless of the used substrate, as a direct consequence of enhancing the extent of crosslinking [Eq. (2)], fixation of Ag-NPs/HBPAA colloid onto/within the finish fabric matrix [Eq. (3)] and (ii) a marginal or slight reduction in the hydrophilic property, whiteness and air permeability of the treated substrates.

It is also evident (Table 3) that: (i) the variation in the aforementioned properties is determined by the nature of the substrate, extent of its modification as well as fixation of Ag-NPs/HBPAA colloid, and (ii) the remarkable improvement in the imparted antibacterial properties of the cured fabric samples at 160 °C/3 min can be ascribed to both the higher extent of loading both the Ag-NPs along with binding of cationic active sites onto/within the finish/fabric matrix (Maillard, 2002), thereby disrupting the power function of the cell, e.g. permeability and respiration . . .etc., and causing damage of the cells via interaction of Ag-NPs with phosphorous and sulfur-containing DNA, in addition to ionic interaction between the cytoplasm membrane of the bacteria and the introduced cationic active sites and/or producing of oxygen radicals that

Table 3
Effect of curing conditions on some performance and functional properties of treated cellulosic fabrics.

Substrate	Curing conditions (°C/min)	N%	Ag-content (mg/100 g fabric)	Wet (s)	WI	WRA (w + f)°	AP L/m²/s	Antibacterial activity (ZI, mm)	
								G + ve	G-ve
Linen	120°/5	0.26	212	1	66.9	212	16.3	7.4	6.5
	140°/4	0.41	247	2	60.4	230	15.9	9.6	8.4
	160°/3	0.48	324	2.5	55.5	245	15.6	11.4 (10.0)*	10.2 (8.5)*
Cotton	120°/5	0.34	243	<1	74.4	244	41.0	10.0	8.8
	140°/4	0.49	305	1	69.6	252	38.2	11.5	10.0
	160°/3	0.59	343	1	65.0	265	36.6	13.4 (12.5)	11.6 (10.6)
Viscose	120°/5	0.43	278	<1	91.6	252	74.0	11.0	10.4
	140°/4	0.56	332	<1	86.0	268	70.5	13.9	13.0
	160°/3	0.64	372	<1	80.6	280	68.5	16.4 (15.1)	15.5 (14.0)

Finishing formulation: finishing agent (75 g/L); $MgCl_2.6H_2O$ (7.5 g/L); citric acid (0.75 g/L); Ag-NPs/HBPAA colloid solution (20 g/L); nonionic wetting agent (2 g/L); wet-pick up (80%); drying at 85 °C/5 min; curing at 160 °C/3 min, followed by after washing.
N%: nitrogen content; Wet: wetting time; WI: whiteness index; WRA: wrinkle recovery; AP: air permeability; ZI: zone of inhibition.
*Values in parentheses indicate retained antibacterial after 15 laundering cycles, according to the AATCC Test Method 147-1988.

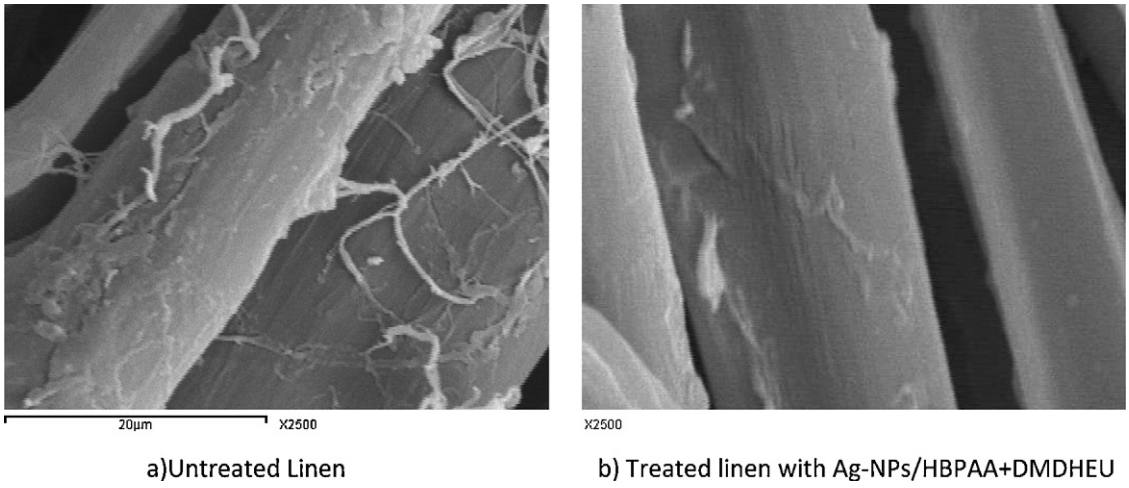


Fig. 4. SEM of untreated and treated line fabric samples.

oxidize the molecular structure of bacteria [Eq. (5)], i.e. highly efficient antibacterial functionality (Dastjerdi et al., 2009; Zhang, Peng, Huang, Zhou, & Yan, 2008)

$$H_2O + \frac{1}{2}O_2 \xrightarrow{\text{Metal ion}} H_2O_2 \rightarrow H_2O + (O) \quad (5)$$

Furthermore, experimental results shown in Table 3 also indicate that, increasing laundering cycles up to 15 only has not a remarkable negative impact on the retained antibacterial activity of the Ag-NPs/HBPAA-loaded cellulosic fabrics, regardless of the used substrate. This means that incorporation of Ag-NPs/HBPAA colloid in the finishing formulation is accompanied by significant

Table 4
Performance, functional and dyeing properties of simultaneously reactive dyed/functional finished cellulosic fabrics.

Substrate	Reactive dye	N%	K/S	Wet (s)	WRA (w + f)°	AP L/m²/s	Antibacterial activity (ZI, mm)		WF		RF	
							G + ve	G-ve	St.	Alt.	Dry	Wet
Linen	None	0.48	–	2.5	245	15.6	11.4 (10.0)*	10.2 (8.3)*	–	–	–	–
	C.I. Reactive Red 239 λ_{max} = 540	0.54	16.74	<1	238	16.0	11.0	10.0	4–5	4–5	4–5	4
	C.I. Reactive Red 238 λ_{max} = 525	0.59	18.04	<1	229	17.9	10.8	9.6	4	4–5	4	3–4
Cotton	None	0.59	–	1	265	36.6	13.4 (12.5)	11.6 (10.6)	–	–	–	–
	C.I. Reactive Red 239 λ_{max} = 540	0.63	17.38	<1	256	38.4	13.0	11.1	4–5	4–5	4–5	4
	C.I. Reactive Red 238 λ_{max} = 525	0.68	19.31	<1	250	39.8	12.5	10.4	4	4–5	4	3–4
Viscose	None	0.64	–	<1	280	68.5	16.4 (15.1)	15.5 (14.0)	–	–	–	–
	C.I. Reactive Red 239 λ_{max} = 540	0.70	19.75	<1	270	71.8	15.6	14.8	4–5	4–5	4–5	4
	C.I. Reactive Red 238 λ_{max} = 525	0.76	22.31	<1	268	72.3	14.9	13.2	4–5	4	4	3–4

Dyeing/finishing formulation: finishing agent (75 g/L); $MgCl_2.6H_2O$ (7.5 g/L); citric acid (0.75 g/L); Ag-NPs/HBPAA colloid (20 g/L); nonionic wetting agent (2 g/L); reactive dye (10 g/L); wet-pick up (80%); drying at 85 °C/5 min; curing at 160 °C/3 min, followed by after washing.
K/S: color strength; WF: washing fastness; RF: rubbing fastness; St: staining on cotton; Alt: alteration.
*Values in parentheses indicate retained antibacterial after 15 laundering cycles.

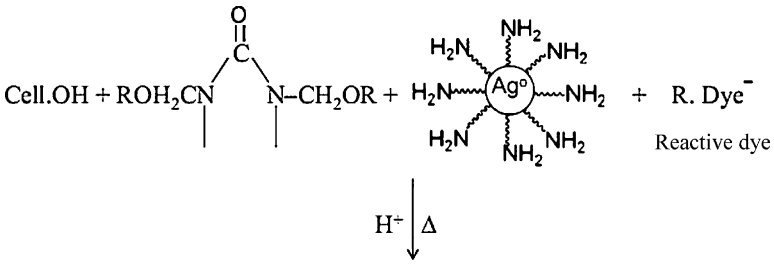
fixation of the grafted Ag-NPs/HBPAA colloid onto/within the cellulose structure, i.e. high durability against repeated laundering cycles.

On the other hand, the SEM of untreated and treated linen images in Fig. 4 showed that treated linen fibers (Fig. 4b) were coated by a homogenous distributed finishing formulation layer resulted in disappearing of the linen fibrils on the fabric surface compared with the untreated ones (Fig. 4a).

3.3. Combined reactive dyeing and functional finishing

In this part, the feasibility of carrying out simultaneous reactive dyeing and functional finishing of the used cellulosic substrates was investigated.

For the given set of dyeing/finishing conditions, the data in Table 4 signify that incorporation of the nominated heterobifunctional reactive dyes in the finishing formulation is accompanied by an increase in %N, an improve in wettability, a remarkable enhancement in the *K*/*S* values, a slight decrease in WRA values along with an improve in air-permeability of the treated fabric samples. The change in the aforementioned properties is ascribed to the fixation of the added reactive dyes onto/within the finish/fabric matrix thereby introducing triazine-moieties, hydrophilic/solubilising groups along with a chromogene, responsible for the color, onto the cellulose structure, via ionic interaction between the abundant cationic active sites of the grafted Ag-NPs/HBPAA colloid, i.e. imino and terminal $-NH_2$ groups, and the anion groups of the used reactive dyes under the used acidic conditions, as follows (Ibrahim, Abdel Rehim, et al., 2010; Zhang, Zhang, et al., 2009):



Reactive dyed/functionalized/crosslinked cellulose structure (6)

The slight decrease in WRA values and the improve in air permeability property of the dyed finished cellulosic substrates are a direct consequence of decreasing the extent of the crosslinking of the cellulose chain-active groups, –OH groups, especially in the amorphous regions of the cellulose structure, which may be attributed to side interactions with the finish and/or with Ag-NPs/HBPAA colloid.

Table 4 also shows that, inclusion of the used reactive dyes in the functional finishing formulations brings about a slight decrease in the antibacterial activity against the G+ve and G-ve strains, regardless of the used substrate, most probably due to a slight decrease in the extent of Ag-NPs/HBPAA loaded colloid, i.e. less loaded-Ag-NPs, and/or the capping of positively charged cationic active sites of the fixed HBPAA by the anionic dye negative groups (Ibrahim, Abdel Rehim, et al., 2010; Zhang, Zhang, et al., 2009), i.e. less antibacterial activity. On the other hand, repeated laundering (15 cycles) of the dyed/finished substrates results in a slight decrease in the antibacterial activity, i.e. higher retention of antibacterial efficacy, as a direct consequence of the high durability of the functional finish.

On the other hand, the dyeing, performance and functional properties given in Table 4 are determined by the nature of the cellulosic substrate as well as the type of reactive dye, e.g. molecular size, functionality, extent of fixation and interaction, hue as well as stability under the used treatment and fixation conditions.

4. Conclusions

- A water-soluble Ag-NPs colloid was prepared by using hyperbranched poly (amide–amine, HBPAA) as an effective self-reducing, stabilizing and binding agent along with $NaBH_4$, as a co-reductant, in aqueous solution at room temperature. The size of the prepared Ag-NPs ranged from 7 to 40 nm.
- Incorporation of the prepared Ag-NPs-colloid (20 g/L) in easy care finishing formulation along with other additives such as the reactant resin, Fixapret® ECO (7.5/0.75 g/L), and the mixed catalyst, $MgCl_2{\cdot}6H_2O$/citric acid and application to the used cellulosic substrates by the pad-dry-cure (160 °C/3 min) technique resulted in fixation the nanocomposite onto the finish/fabric matrix thereby imparting durable antibacterial activity to the finished substrates against G+ve (*S. aureus*) and G-ve (*E. coli*) bacteria strains even after 15 consecutive home laundering cycles, and with minimal negative impacts on other performance properties.
- It is feasible to obtain reactive dyeings with easy care, antibacterial, comfort and good to very good fastness properties via simultaneous dyeing and functional finishing of the cellulosic substrates in one step under the given proper treatment conditions.
- The extent of modification, functionalization as well as dyeing is determined by the type of cellulosic substrate, i.e. viscose > cotton > linen.

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