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Synthesis of poly (N-vinyl-2-pyrrolidone)/pyrodextrins adducts and their utilization in functionalization of cotton fabric

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Abstract : Poly (N-vinyl-2-pyrrolidone)/British Gum (PVP/BG) and Poly (N-vinyl-2-pyrrolidone)/Dexy84 (PVP/D84) adducts were prepared by polymerization of high concentrated aqueous solution of N-vinylpyrrolidone (VP) under different polymerization conditions in presence of two pyrodextrins namely British Gum and Dexy84 respectively as well as ammonium persulphate as an initiator. Upon the percent total conversion values, the prepared water-soluble PVP/BG hybrid with the total conversion of 99.2% was selected to be characterized via investigating its IR analysis. Treating cotton fabric with different easy care finishing formulations containing dimethyloldihydroxy ethylene urea as crosslinker and different concentrations of PVP/BG adduct imparts that fabric with stiffness properties. Furthermore, incorporation of TiO_2 or Ag nano-particles in the aforementioned finishing bathes results in durable stiffness as well as antibacterial properties of treated fabric.

Keywords: Pyrodextrins; British Gum; N-vinylpyrrolidone; Grafting; Functionalization.

1. Introduction

Starch is one of the most abundant storage polysaccharides in plants. Starch is consisting of a large number of glucose units linked together primarily by α-D-(1–4) glycosidic bonds. Pure starch is water insoluble white powder [1]. It consists of two types of molecules; the linear one is the amylose and the other is the branched amylopectin [2]. In general, starch contains 20 to 25% amylose as well as 80 to 75% amylopectin by weight. Many plants have high starch content such as potato, cassava, canna, peas, beans, corn, wheat, barley, etc [2]. Native starch, i.e. unmodified starches, is practically limited to its application in food. Modification of starch broadens its application form the food sector to other industrial sectors. Furthermore, starch can be modified physically, i.e. by pre-gelatinization, extrusion or re-drying, or chemically, i.e. by esterification, etherification, or oxidation [3,4,5].

The modified starch dextrins are produced by: (1) physical method using thermal treatments and (2) enzymolysis method using the amylase. These treatments change raw starches from the high molecular structure to low molecular structure giving rise to products having varied properties in solubility, viscosity, and film forming properties. The dry heat treatment for starch forms dextrins or more conveniently called "pyrodextrins" in this context. Dextrins are white to brown powders in color that are partially to fully water-soluble providing optically active solutions of low viscosities. White and yellow dextrins from starch roasted with little or no acid is called British gum. Industrially, dextrins are applied as a water-soluble glues in re-moistable envelope adhesives and paper tubes, as additives in froth flotation in the mining industry, in the foundry industry as green strength additives in sand casting, as printing thickener for batik resist dyeing, and as binders in gouache paint and also in the leather industry. In the field of textile finishing, white dextrins are used as coating agents to increase weight and stiffness of textile fabrics [6,7].

On the other hand, Poly (N-vinyl-2-pyrrolidone) (PVP) is a synthetic water-soluble polymer that is used in a wide range of applications. PVP polymers are film formers, protective colloid and suspending agents, dye-receptive agents, binders, stabilizers, detoxicants, complexing agents and have strong affinity for Ag or TiO_2 nano-particles [8].

Meanwhile, in the last decades, the customer's demands are constantly deriving the textile manufacturers towards innovative products having multi-functional and comfort properties. Functional finishing is performed for textiles to impart that textiles with one or multi-functional properties such as water and oil repellency, antimicrobial properties, pleasant smell, ultraviolet protective properties, self-cleaning, etc [9,10,11,12,13,14,15,16,17,18].

The present work was under taken with a view to establish the proper conditions of grafting some pyrodextrins with N-vinylpyrrolidone followed by incorporation of the synthesized adducts as functional additives during easy care finishing of cotton fabric.

2. Experimental

2.1. Materials

Mill scoured and bleached plain-weave cotton fabric (143 g/m^2) was used. Two maize starch based pyrodextrins (PDs) kindly supplied by the Egyptian Co. for starch and glucose, namely: i) British Gum (BG) (the starch is heat treated for a long period of time) and ii) Dexy84 (the starch is heat treated for 2h in the presence of an acid). Arkofix® NG, aqueous solution of dimethyloldihydroxyethylene urea (DMDHEU), kindly supplied by Clariant, Egypt, was used. Hostapal® CV-ET (a non-ionic wetting agent based on alkyl aryl polyglycol ether, clariant). N-vinylpyrrolidone (VP), supplied by MERCK-Schuchardt was used. Trichloromethane, methanol, hydroquinone, ammonium chloride, magnesium chloride and copper sulphate were laboratory grade chemicals.

2.2. Methods

2.2.1. Preparation of poly (N-vinyl-2-pyrrolidone)/pyrodextrins adducts

The polymerization of VP in presence of PDs was carried out under atmospheric oxygen in 30 ml polypropylene beaker at a specific liquor-to-pyrodextrin ratio (LR) as follows. A known concentration of ammonium persulfate aqueous solution was added to a beaker containing thermostatic mixture of VP aqueous solution and any of the above PDs, that are at specific liquor to material and molar ratios to each other, with rapid continuous stirring to form a uniform paste. The beaker was then kept in a thermostatic water bath for a period of time followed by cooling the sample at ambient conditions, addition of 500 ppm of hydroquinone and finally subjected to chemical analysis.

2.2.2. Purification of a prepared adduct for IR analysis

At optimum conditions of the polymerization reaction, the prepared PVP/PD adduct was poured into a beaker containing 300 ml of methanol. The product was then filtered and dried at 60 ^{O}C for 48 h. After that, the dried product was extracted with trichloromethane in a Soxhlet apparatus for 72 h to remove PVP homopolymer whereas the PVP-g-PD was dried and then stored over $CaCl_2$ in a desiccator for at least 48 hour before IR analysis [19].

2.2.3. Preparation of TiO_2 nanoparticles

Titanium dioxide nano-particles (TiO_2-NPs) were prepared as previously reported using titanium tetraisopropoxide precursor with 2-propanol and nitric acid [20].

2.2.4. Preparation of silver nano-particles

Silver nano-particles (Ag-NPs) were prepared using trisodium-citrate as a reductant as reported elsewhere [21].

2.2.5. Poly (N-vinyl-2-pyrrolidone)/pyrodextrins adducts as functional finishes

The potential application of the prepared adducts as multifunctional finishes to impart cotton fabric with stiffness and antibacterial properties was studied. In that regard, cotton samples of 30X30 cm^2 were padded twice to a wet pick up of 100 % in finishing formulations containing 50 g/l of the adducts solutions, 60 g/l DMDHEU as crosslinker, 2 g/l non-ionic wetting agent, and 6 g/l of different salts as catalysts. To enhance the above mentioned functional properties of treated fabric, 3 g/l of TiO_2-NPs or 4 g/l of Ag-NPs may be added to the aforementioned finishing formulations. The padded samples were dried at 100 ^{O}C for 3 min and then cured at 160 ^{O}C for 3 min. The finished fabrics were washed at 50 ^{O}C for 15 minutes, thoroughly rinsed, and finally dried for testing.

2.3. Testing and analysis

- The extent of polymerization, expressed as percentage total conversion, % TC, was determined by assessing the unsaturation (double bonds) content before and after polymerization [22,23].
- Infra Red (IR) spectroscopy was carried out using Bruker IR Spectrometer.
- Nitrogen content was determined according to Kjeldahl method [24].
- Dry wrinkle recovery angle (WRA) was determined according to ASTM D-1296-98.
- The tensile strength (TS) of the finished fabric sample was tested in the warp direction according to ASTM D-2256-98.
- Stiffness (S) was determined in the warp direction according to ASTM D-1388-96 using Jika (Toyaseiki) apparatus.
- Surface roughness (SR) was measured using a Surfacoder 1700a.
- Wettability of treated and untreated fabric was determined according to AATCC Test Method 39-1993.
- Antimicrobial activity of control and finished cotton fabric were tested, expressed in the inhibition zone (IZ) per millimeters, according to the disc diffusion method, AATCC 147-2004. The antibacterial activities of the untreated blank as well as finished fabrics were tested against the following bacteria:
  Gram-positive bacteria: Staphylococcus aureus (SA).
  Gram-negative bacteria: Escherichia coli (EC).
- Durability to wash was assessed by subjecting the fabric to 10 laundering cycles. Each laundering cycle consists of washing for 10 min at 50 ^{O}C using 2 g/l nonionic surfactant followed by rinsing and air drying at ambient conditions.
- The morphology and particles size of the TiO_2-NPS and Ag-NPS emulsions was obtained by transmission electron microscope (TEM) using a JEOL, JEM 2100 F electron microscope at 200 kV.
- Scanning electron microscope (SEM) images of the treated and untreated fabric samples were obtained using SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 kV, magnification 14× up to 1,000,000 and resolution for Gun, FEI company, Netherlands.

3. Results and discussion

3.1. Tentative mechanism of PVP/PD adducts formation

Previous literatures [22,23,25] reported that ammonium persulfate decomposes in aqueous medium to generate $SO_4^{-\cdot}$ and $HO^{\cdot}$ free radical species ($R^{\cdot}$) that can initiate polymerization reaction of VP in presence of any of the aforementioned pyrodextrins, i.e. BG or D84, (PD-OH) as shown in the following equations:

$R^{\cdot} + VP \rightarrow VP^{\cdot} + RH$ ……………….… (1)

$VP^{\cdot} + n\,VP \rightarrow PVP$ ……..……….… (2)
(PVP homopolymer)

$PD\text{-}OH + R^{\cdot} \rightarrow PD\text{-}O^{\cdot} + RH$ ….... (3)
(PD macroradicals)

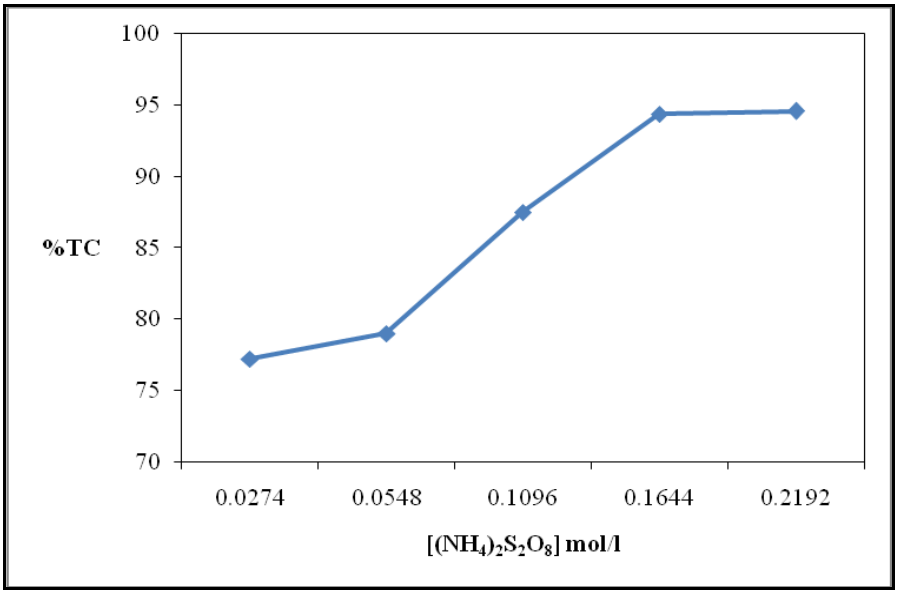
$PD\text{-}O^{\cdot} + nVP \rightarrow PVP\text{-}g\text{-}PD$ ....….. (4)
(PVP grafted PD)

Consequently, the final product of the polymerization reaction is a mixture of PVP homopolymer, PVP grafted PD and ungrafted PD (intact and oxidized) in a state of entanglement with each other. This mixture was referred as PVP/PD adduct.

Factors affecting the preparation of PVP/PD adduct were studied. These included ammonium persulfate concentration, temperature, time, VP concentration, BG to VP molar ratio and PD type,. Given below are the results with convenient discussion.

3.2. Factors affecting the preparation of PVP/PD adducts

3.2.1. Ammonium persulfate concentration

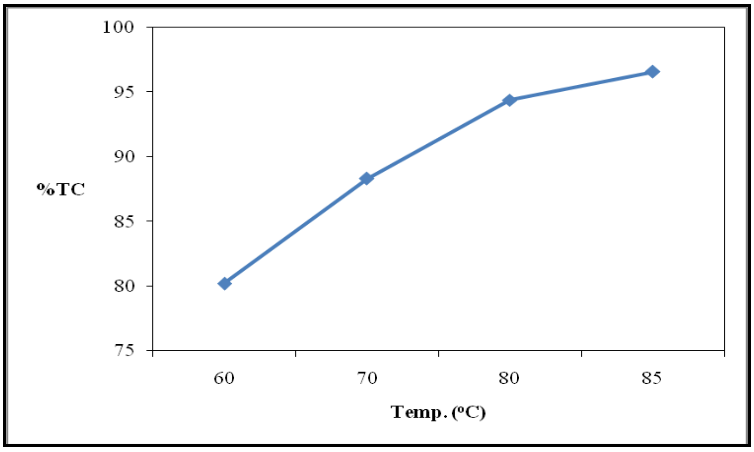


[VP], 3.1042 mole/l; VP/BG molar ratio, 0.5; temperature, 80 ^{O}C; time, 50 min.; LR, 1 l/kg.

Figure 1: Effect of ammonium persulfate concentration on the percent total conversion of PVP/BG adduct.

Figure 1 shows the effect of ammonium persulfate concentration on the extent of polymerization of VP monomers in presence of BG expressed as %TC. It is clear that increasing the ammonium persulfate concentration from 0.0274 to 0.1644 mole/l is accompanied by a gradual increasing in the % TC reflecting the role of ammonium persulfate as a source for generation of free radical species that cause an initiation and propagation of the polymerization reaction [15,23,25]. Further increasing of ammonium persulfate concentration, i.e. beyond 0.1644 and up to 0.2192 mole/l, practically has no effect on the % TC suggesting an abundance of free radicals at persulfate concentrations higher than0.1644 mole/l that causes a faster rate of termination [23,25].

3.2.2. Temperature

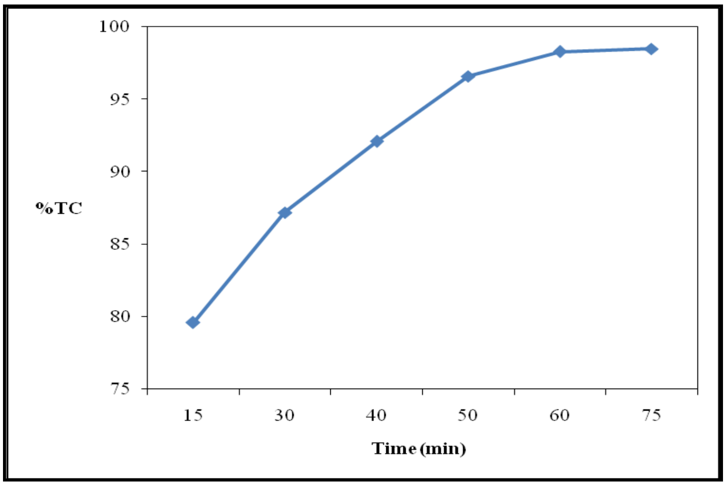


[VP], 3.1042 mole/l; VP/BG molar ratio, 0.5; [$(NH_4)_2S_2O_8$], 0.1644 mole/l; time, 50 min; LR, 1 l/kg.

Figure 2: Effect of temperature on the percent total conversion of PVP/BG adduct.

Figure 2 shows the effect of polymerization reaction temperature on the percent total conversion. The results reveal that the total conversion increases significantly by increasing the polymerization temperature within the range studied. This is a direct consequence for: i) the fast rate of the initiator decomposition that results in generation of more free radical species, ii) increasing of the mobility of VP molecules, and iii) increasing of the rate of initiation and propagation of polymerization. Hence and as a result of these factors, the extent of the polymerization reaction will be enhanced expressed in increasing of %TC [15,23,25].

3.2.3. Time



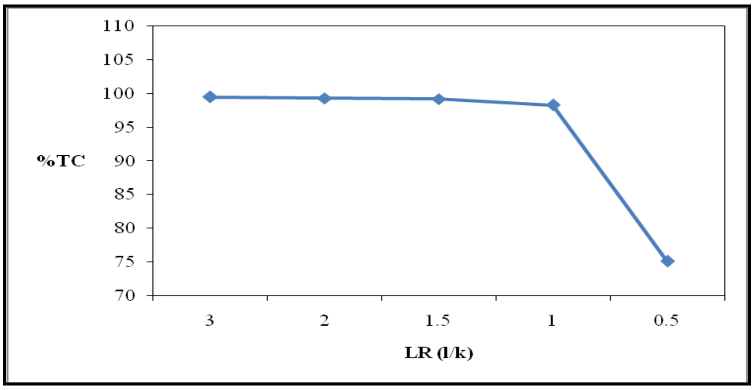
[VP], 3.1042 mole/l; VP/BG molar ratio, 0.5; [$(NH_4)_2S_2O_8$], 0.1644 mole/l; temperature, 85 ^{O}C; LR, 1 l/kg.

Figure 3: Effect of time on the percent total conversion of PVP/BG adduct.

Figure 3 shows the effect of the polymerization time on the extent of total conversion. It is well seen that prolonging of the polymerization reaction from 10 to 60 min results in an enhancement in the percent total conversion reflecting that at the initial stages of the polymerization reaction the reactants are present in abundance in addition to the induced energy to the polymerization system by virtue of the exothermic nature of the reaction.

Longer time than 60 and up to 75 min practically does not affect the total conversion suggesting the depletion in both the monomer and initiator concentrations as well as increasing of the reaction medium viscosity that in turn impedes the mobility of unreacted molecules and consequently minimizes the extent of the polymerization reaction by time [15,23,25].

3.2.4. Liquor-to-BG Ratio (LR)

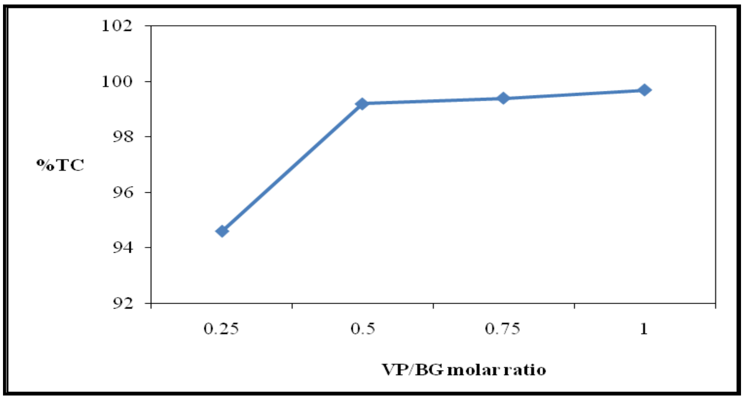


[VP], 3.1042 mole/l; VP/BG molar ratio, 0.5; [$(NH_4)_2S_2O_8$], 0.1644 mole/l; temperature, 85 ^{O}C; time, 60 min.

Figure 4: Effect of liquid-to-BG ratio on the percent total conversion of PVP/BG adduct.

Figure 4 depicts the variation in the %TC of the prepared adducts upon altering the LR in the polymerization reaction medium. It was visually observed that the paste formed at a ratio of 0.5 l/k before starting the reaction was not homogenous as the used amount of liquid was not sufficient for complete wetting of BG whereas ratios of 1, 2 and 3 l/k results in formation of homogenous pasts, i.e. BG was completely wetted. However, it was noticed that increasing of the LR has a positive impact on the %TC suggesting that the liquid phase is necessary for formation of BG macro-radicals and their collisions with VP molecules to form PVP-g-BG [15,25]. Moreover, increasing the LR beyond 1 and up to 3 l/k is accompanied by leveling off the %TC. It seems that increasing of the reaction medium viscosity, until solidification, at LR of 2 and 3 l/kg hinders more collisions between VP molecules and macroradicales of BG and thereby the leveling off of the %TC [15,23,25].

3.2.5. VP/BG molar ratio



[VP], 3.1042 mole/l; [$(NH_4)_2S_2O_8$], 0.1644 mole/l; temperature, 85 ^{O}C; time, 60 min; LR, 1.5 l/kg.

Figure 5: Effect of VP/BG molar ratio on the percent total conversion of PVP/BG adduct.

Figure 5 shows the effect of VP to BG molar ratio on the extent of polymerization, expressed as percent total conversion. It is clearly seen that, increasing VP/BG molar ratio up to a value 0.75 is accompanied by an enhancement in total conversion. Higher values of these ratios have practically no effect on total conversion, i.e. the percent conversion is leveling off. The data in Figure 5 suggests that two factors oppositely govern the magnitude of the total conversion. The first is increasing the availability of VP molecules in the reaction medium which indeed will enhance the polymerization reaction, i.e. increases the total conversion. The other factor is thickening of the reaction medium as the polymerization reaction proceeds that hinders the mobility of

VP molecules and consequently decreases the molecular collisions among reactants in the reaction medium; the matter that certainly lead to the decreasing of total conversion. However, the results depicts that the first factor is the predominant. Leveling off the percent conversion beyond molar ratio of 0.75 reflects the solidification of the reaction product that hinders further polymerization reactions despite of increasing of VP concentration in the reaction medium [15,25].

3.2.6. Pyrodextrin type

Table 1: Effect of pyrodextrin type on the percent total conversion of PVP/PD adduct.

Pyrodextrin type	%TC
British Gum	99.2
Dexy84	97.9

[VP], 3.1042 mole/l; VP/BG molar ratio, 0.75; [$(NH_4)_2S_2O_8$], 0.1644 mole/l; temperature, 85 ^{O}C; time, 60 min; LR, 1.5 l/kg.

The effect of using different types of PDs that are BG and D84 on the %TC of the prepared hybrids is shown in Table 1. It is clear that the %TC in case of BG is the higher than D84, suggesting that initiation and propagation stages of the polymerization reaction is faster in case of BG than that of D84. However, the %TC is very high for both types of the used PDs, suggesting that once the initiation and propagation start, the reaction proceeds almost to completion due to the presence of highly concentrated VP in the reaction medium [15,25].

3.3. Characterization of PVP/BG adduct

The PVP/BG adduct that prepared with total conversion of 99.2% using the following polymerization conditions: [VP], 3.1042 mole/l; VP/BG molar ratio, 0.75; [$(NH_4)_2S_2O_8$], 0.1644 mole/l; temperature, 85 ^{O}C; time, 60 min and LR, 1.5 l/kg, was water-soluble and characterized via investigating its IR analysis.

3.3.1. FTIR analysis of the PVP/BG adduct

The FTIR spectrum of BG and purified PVP/BG adduct, i.e. the adduct resulted after the removal PVP homopolymer, are represented by Figures 6 and 7 respectively. It is clear that, the most characteristic bands in spectrum of BG are 3350 cm^{-1} corresponding to OH stretch due to glucosidic ring, 2943 cm^{-1} corresponding to C-H aliphatic stretching, 1430-1377 cm^{-1} corresponding to C-H bending, 1160 cm^{-1} and 1021cm^{-1} for C-O and C-C stretching respectively. On the other hand, the FTIR spectrum of PVP/BG adduct includes almost the same bands of BG except a band at 1665 cm^{-1},which is not present in Figure 6, confirming the presence of PVP in the form of PVP-g-BG in the prepared adduct [26,27,28].

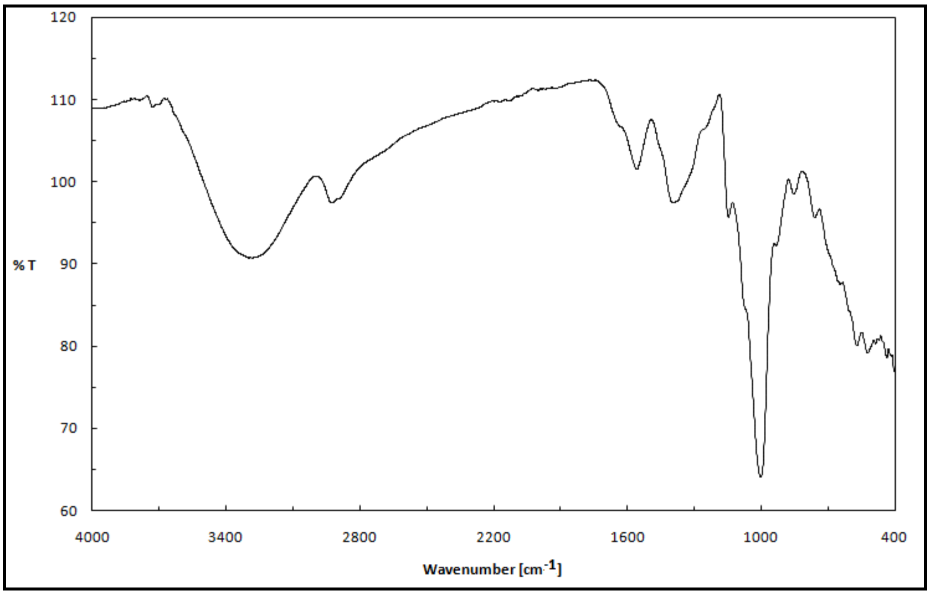


Figure 6: FTIR spectrum of BG.

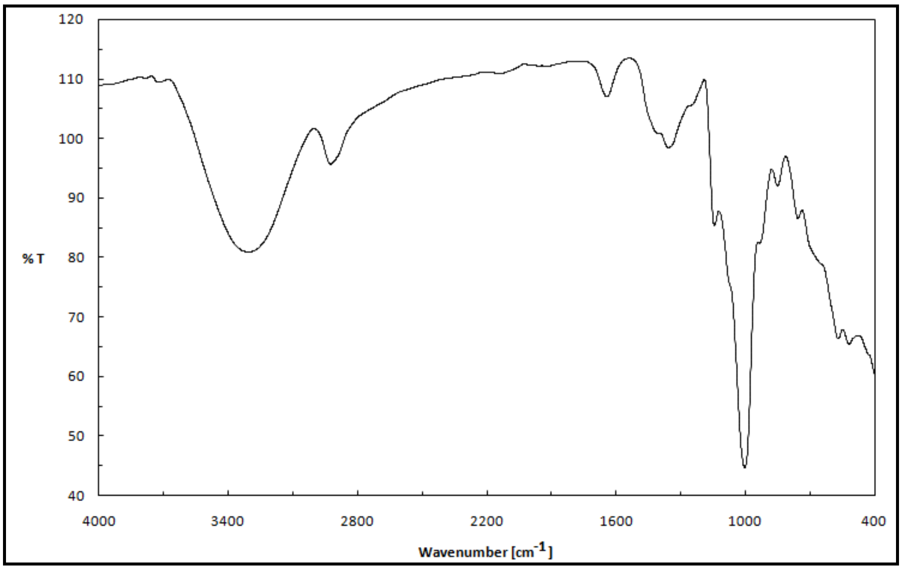
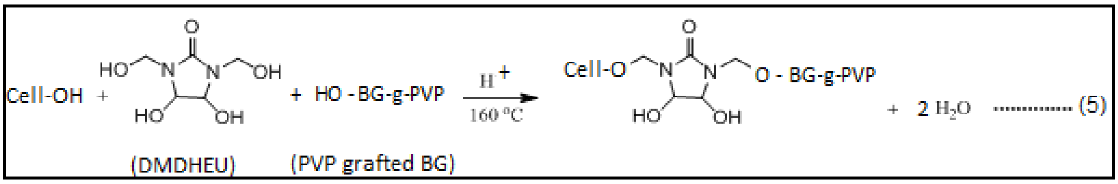


Figure 7: FTIR spectrum of PVP/BG adduct.

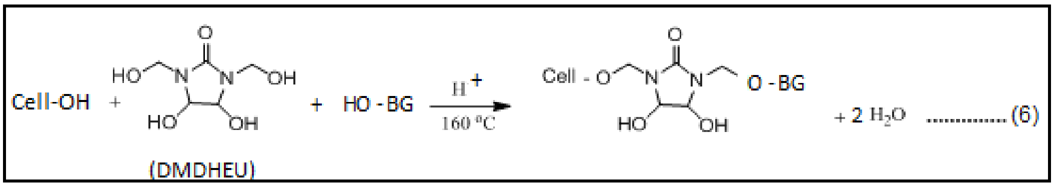
3.4. The potential application of PVP/BG adduct as functional additive in textile finishing

It was reported that PVP forms coordination bonds with TiO_2 and Ag nano-particles as well as Cu^{+2} ions [29,30,16]. Thus, to multi-functionalize cotton fabric, i.e. impart that fabric with stiffness as well as antibacterial properties, the prepared PVP/BG adduct was incorporated in different easy care finishing formulations containing Ag or TiO_2 nano-particles (Ag or TiO_2-NPs) or copper sulphate as a catalyst. Moreover, the presence of the DMDHEU as a crosslinker in the above finishing formulations certainly will enhance the fixation of such adduct ingredients into the finished fabric structure as follows [31]:

i) Binding of PVP/BG adduct to cellulose structure

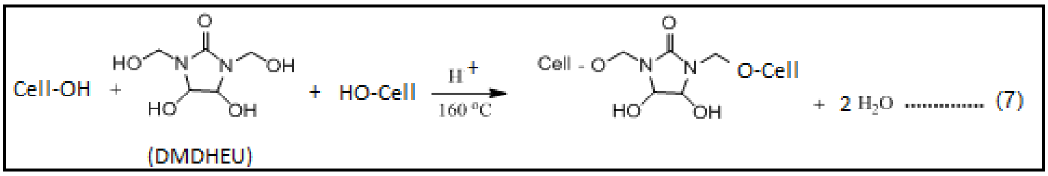


ii) Binding of ungrafted BG to cellulose structure



On the other hand, the following competitive reaction may be also occurred as follows:

iii) crosslinking of cellulose structure



iv) formation of washable crosslinked products

$$\text{DMDHEU + HO-BG or HO-BG-g-PVP} \xrightarrow[160\ ^{o}C]{H^{+}} \text{Washable unbound crosslinked by products} \quad \text{.........} (8)$$

3.4.1. PVP/BG adduct as a hand builder finish

Table 2: Effect of PVP/BG adduct concentration on some performance properties of treated fabric.

W (s)	S (mg)	SR (µm)	TS (KG)	WRA $(W+F)^{O}$	%N	PVP/BG adduct (%)
1	570	15.4	45.6	143	0	**Untreated**
3	1459	16.9	33.5	198	0.491	**40**
4	1780	17.6	39.7	211	0.539	**60**
4	2243	18.1	42.4	223	0.647	**80**

Fabric finishing conditions: [DMDHEU], 60 g/l; [$MgCl_2$], 6 g/l; wet pick up, 100 %; drying, 100 ^{O}C/3 min; curing, 160 ^{O}C/3 min. WRA: wrinkle recovery; TS, tensile strength; SR, surface roughness; S, stiffness; W, wettability; WI, whiteness index.

Table 2 shows the performance properties of cotton fabric treated with finishing formulations containing different concentrations of PVP/BG adduct (40-80 g/l), 60 g/l of DMDHEU and 6 g/l magnesium chloride. It is obvious that increasing such adduct concentration from 40 to 80 g/l is accompanied by increasing of percent nitrogen, tensile strength, surface roughness and stiffness of the finished fabric along with a reduction in resiliency and wettability of that fabric. This is may be a result for the gradual increasing in the finishing bath viscosity that impedes the diffusion of DMDHEU inside the fabric structure, i.e. reduces the number of fabric crosslinks, as well as fixation of such adduct polymers onto fabric cellulose structure (equations 5 and 6) [31].

3.4.2. PVP/BG adduct as an antibacterial/stiff hand finish

Table 3: Effect of catalyst and nano-particle type on the antibacterial properties of treated fabric.

Finishing formulation	IZ (mm)	
	G-ve	G+ve
Untreated	0	0
BG/DMDHEU/$MgCl_2$	0	0
Adduct/DMDHEU/$MgCl_2$	0	0
BG/DMDHEU/$CuSO_4$	10(5)	8(3)
Adduct/DMDHEU/$CuSO_4$	13(9)	10(7)
BG/DMDHEU/NH_4Cl/TiO_2-NPs	15(8)	12(6)
Adduct/DMDHEU/NH_4Cl/TiO_2-NPs	19(16)	15(11)
BG/DMDHEU/NH_4Cl/Ag-NPs	13(6)	10(4)
Adduct/DMDHEU/NH_4Cl/Ag-NPs	16(13)	13(9)

Fabric finishing conditions: [PVP/BG adduct or BG], 60 g/l; [DMDHEU], 60 g/l; [$MgCl_2$, NH_4Cl or $CuSO_4$], 6 g/l; [Ag-NPs], 4 g/l; [TiO_2-NPs], 3 g/l; wet pick up, 100 %; drying, 100 ^{O}C/3 min; curing, 160 ^{O}C/3 min. Ammonium chloride was used as a catalyst in case of the finishing formulations containing Ag- or TiO_2-NPs. ZI: zone of inhibition; G+ve: St. aurous; G-ve: E. coli. Values in parentheses indicate durability of treated fabric to washing after 10 washing cycles.

To impart cotton fabric with antibacterial properties, copper sulphate as a catalyst or Ag or TiO_2 nano-particles as functional additives were utilized in different easy care finishing formulations containing BG/DMDHEU or Adduct/DMDHEU The antimicrobial properties of the treated fabrics are shown in Table 3. For a given set of finishing conditions, it is clear that:

i) among the above mentioned used catalysts, $CuSO_4$ imparts a stiff hand cotton fabric with antimicrobial properties and these properties are enhanced in presence of the prepared adduct, most probably due to the chelation of the Cu^{2+} cations by PVP [16,26,30], ii) incorporation of TiO_2- or Ag-NPs in easy care finishing formulations containing either BG or the prepared adduct remarkably enhances the antibacterial properties of treated fabric, iii) the extent of the improvement in the antibacterial properties of the finished fabric follows the descending order: Adduct/TiO_2- or Ag-NPs > BG/TiO_2- or Ag-NPs which can be explained by the ability of PVP to bind these nano particles via coordination bonds [16,26,30], and iv) the differences in the magnitudes of the aforementioned antibacterial properties of treated fabric are governed by the differences between the above cations or nano particles in the molecular weight, particle size, location, fixation and extent of distribution, and ability to bind to specific sites in the DNA in the bacterial cells and/or form high oxidative radicals on the nano-particles loaded fabric [15,16,26,30] hence inactivate and destroy bacteria. On the other hand, Table 3 reveals also that Adduct/TiO_2- or Ag-NPs is more durable for washing than that BG/TiO_2- or Ag-NPs up to 10 washing cycles.

3.4.3. Characterization of Ag- or TiO_2-NPs as well as Adduct/Ag-NPs, Adduct/ TiO_2-NPs or Adduct/Cu^{2+} treated fabric

The particle size of the prepared Ag- or TiO_2-NPs is characterized by investigating their TEM images. Moreover, fabric samples treated with easy care finishing formulations containing Adduct/Ag-NPs, Adduct/TiO_2-NPs or Adduct/Cu^{2+} were also characterized by investigating their SEM and EDX images.

3.4.3.1. TEM, SEM and EDX images

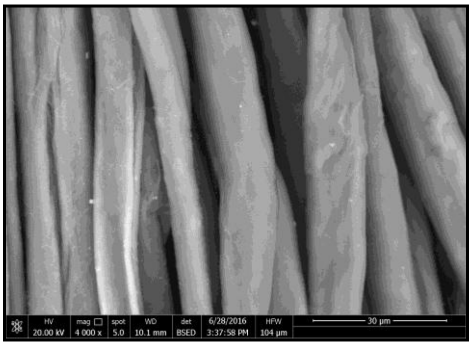


Figure 8(a): SEM of untreated cotton fabric.

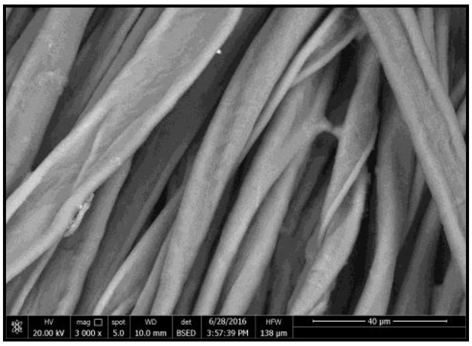


Figure 8(b): SEM of PVP/BG adduct treated cotton fabric.

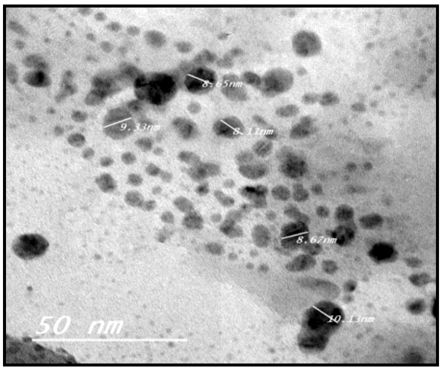
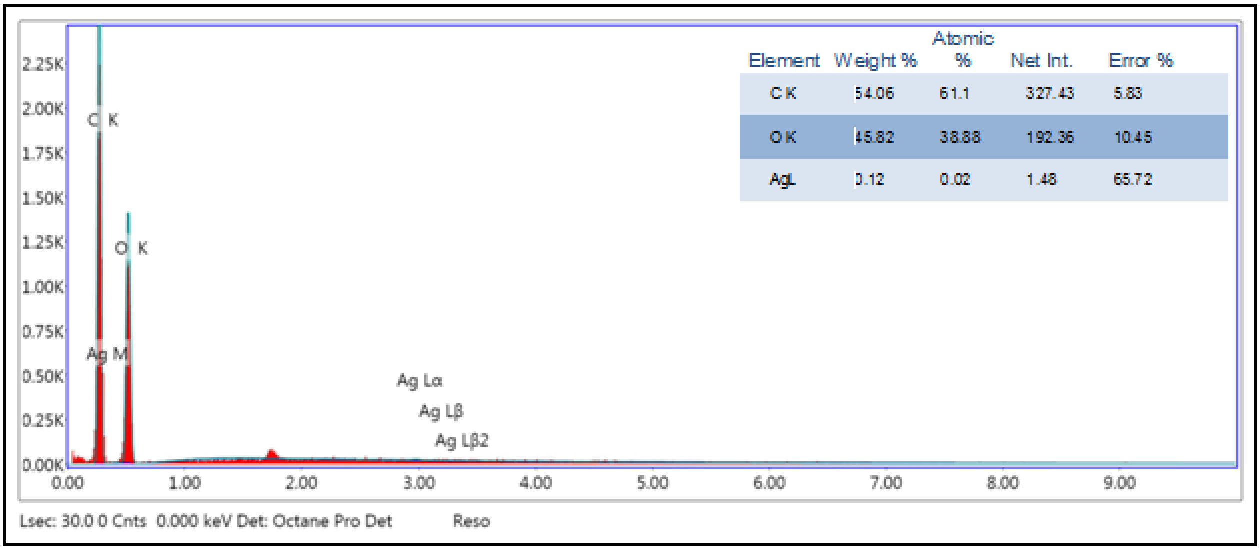


Figure 9 (a): TEM image of Ag-NPs.



Element	Weight %	Atomic %	Net Int.	Error %
C K	54.06	61.1	327.43	5.83
O K	45.82	38.88	192.36	10.45
AgL	0.12	0.02	1.48	65.72

Figure 9(b): EDX image of cotton fabric treated with PVP/BG adduct loaded with Ag-NPs.

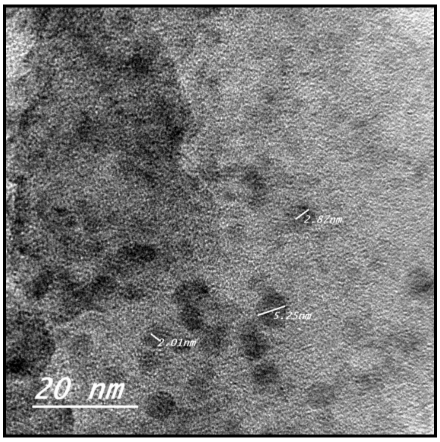
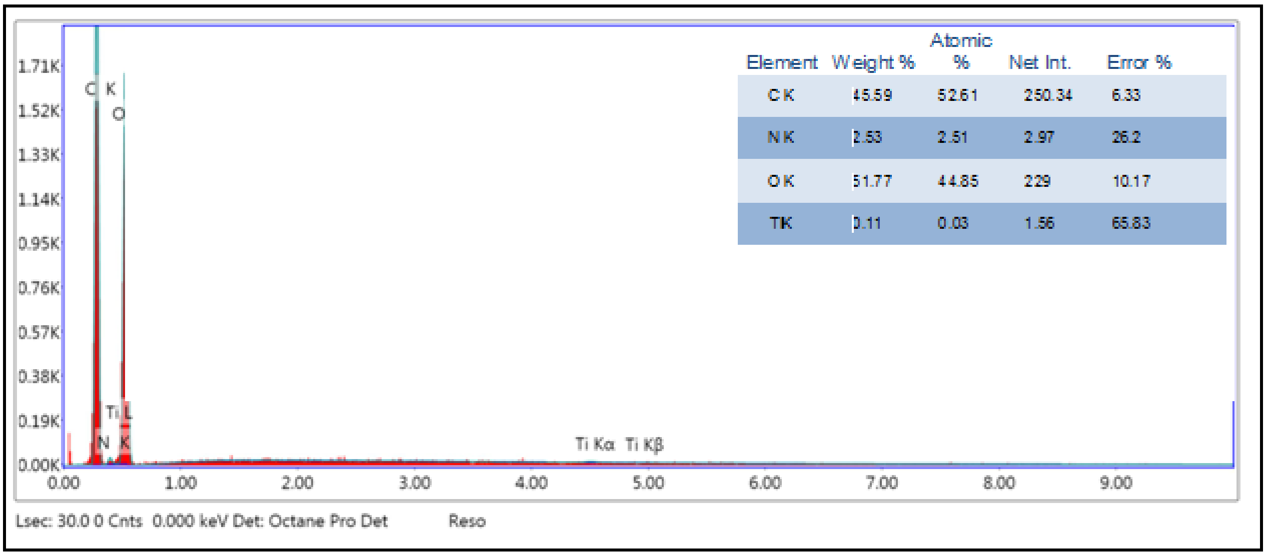
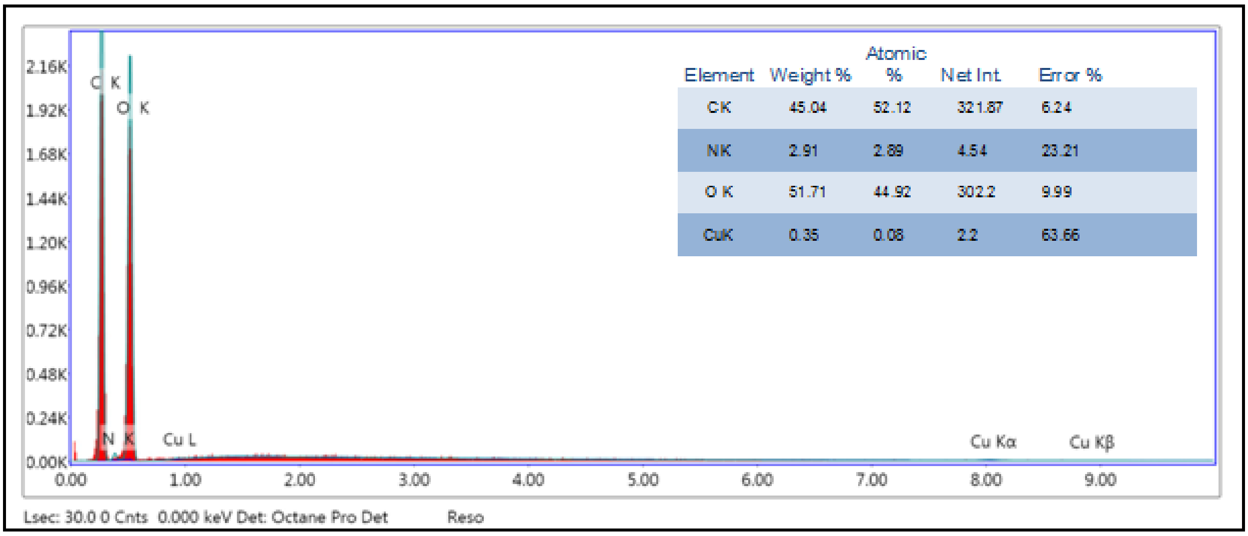


Figure 10(a): TEM image of TiO_2-NPs.



Element	Weight %	Atomic %	Net Int.	Error %
C K	45.59	52.61	250.34	6.33
N K	2.53	2.51	2.97	26.2
O K	51.77	44.85	229	10.17
TiK	0.11	0.03	1.56	65.83

Figure 10(b): EDX image of cotton fabric treated with PVP/BG adduct loaded with TiO_2-NPs.



Element	Weight %	Atomic %	Net Int.	Error %
CK	45.04	52.12	321.87	6.24
NK	2.91	2.89	4.54	23.21
O K	51.71	44.92	302.2	9.99
CuK	0.35	0.08	2.2	63.66

Figure 11: EDX image of cotton fabric treated with PVP/BG adduct loaded with Cu^{2+}.

Figure 8 (b) shows SEM of the PVP/BG adduct treated cotton fabric where a deposited film of the PVP/BG adduct can be seen on the surface of that fabric compared with that of the untreated sample (Figure 8 (a)). Figure 9 (a) shows the TEM image of Ag-NPs. It can be seen that these particles are well distributed and less than 10 nm in size. Moreover, Figure 9 (b) shows EDX image of cotton fabric treated with PVP/BG adduct loaded with Ag-NPs which confirms the presence of Ag-NPs in the treated fabric structure with a content of 0.12% (w/w). On the other hand, Figure 10 (a) shows the TEM image of TiO_2 NPs where these particles are not aggregated and of size less than 10 nm. Furthermore, Figure 10(b) shows EDX image of cotton fabric treated with PVP/BG adduct loaded with TiO_2-NPs which confirms the presence of TiO_2-NPs in the treated fabric structure with a content of 0.11% (w/w). Additionally, EDX of cotton fabric sample treated with the prepared adduct and loaded with Cu^{2+} is represented by Figure 11 confirming the presence of these cations with a content of 0.11% (w/w) in that fabric structure.

3.5. Conclusions

A new water-soluble PVP/BG adduct was prepared with a total conversion of 99.2% by polymerization of VP (3.1042 mole/l) in presence of BG at a molar ratio of VP/BG 0.75 and LR of 1.5 l/kg using $(NH_4)_2S_2O_8$ (0.1644 mole/l) at 85 ^{O}C for 60 min. At optimum polymerization reaction conditions, the prepared adduct was characterized via investigating its IR analysis and utilized in different easy care finishing formulations using dimethyloldihydroxy ethylene urea as crosslinker as a hand builder to impart cotton fabric with stiffness properties. Moreover, combination of such adduct with TiO_2 or Ag nano-particles in the aforementioned finishing bathes results in durable stiffness as well antibacterial properties of treated fabric.

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