Carbohydrate Polymers xxx (2012) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

# Poly(acrylic acid)/poly(ethylene glycol) adduct for attaining multifunctional cellulosic fabrics

N.A. Ibrahim*, A. Amr, B.M. Eid, Z.E. Mohamed, H.M. Fahmy

*Textile Research Division, National Research Center, Cairo, Egypt*

ARTICLE INFO

*Article history:*
Received 29 February 2012
Received in revised form 21 March 2012
Accepted 23 March 2012
Available online xxx

*Keywords:*
Cellulose-containing fabrics
Acrylic acid
Polyethylene glycol
Polymerization
Adduct
Sizing
Functional finishes

ABSTRACT

Aqueous polymerization of partially neutralized acrylic acid (AA) along with polyethylene glycol (PEG-600) at AA/PEG-600 mass ratio 3/1 using ammonium persulfate as initiator under proper conditions results in formation of PAA/PEG-600 adduct. The structure of the adduct was confirmed by FT-IR spectra. The potential applications of the prepared adduct in: sizing, durable hand building of cotton cellulose, as well as in functional finishing of cellulose containing fabrics, i.e. cotton, viscose and cotton/polyester, with Ag- or $TiO_2$-nanoparticles were investigated. The modified substrates using the prepared adduct showed a remarkable improvement in their sizing, hand building and/or functional properties, i.e. antibacterial, anti-UV, and self cleaning, in addition to durability to wash. TEM images of the prepared nano-particles, SEM images of the untreated and treated substrates, as well as EDX spectra to analyze the surface elemental compositions were examined. The tentative mechanisms were also suggested.

## 1. Introduction

Innovative cellulose-based products with durable functional properties and high added value are greatly appreciated and find variety of potential applications to satisfy the ever-growing consumer demands (Ibrahim, Eid, & El-Batal, 2012).

At present, the use of nanomaterials and nanotechnology-based processes is growing in the field of textile applications, as a rout to impart new functionality and improved performance (Joshi & Bhattacharyya, 2011). Intensive research and development activities are also being dedicated to synthesis of inorganic nano-structured materials and their applications in imparting new functional properties to textiles such as anti-microbial, UV-blocking and self cleaning properties (Dastijerdi & Montazer, 2010; Ganesh, Raut, Nair, & Ramakrishna, 2011; Gladitz, Reinemann, & Radusch, 2009; Gupta, Jassal, & Agrawal, 2008; Ibrahim, Eid, Hashem, Refai, & El-Hossamy, 2010; Ibrahim, Refaie, & Ahmed, 2010; Mahltig, Haufe, & Böttcher, 2005; Qi et al., 2006; Thomas, Bajpai, & Bajpai, 2011) as well as easy care finishing (Chen & Wang, 2006; Yuen et al., 2009).

On the other hand, our previous studies have investigated the feasibility of using free radical polymerization of some vinyl monomers, e.g. acrylic acid, acrylamide, etc., in the presence of polysaccharides, e.g. Karaya gum, Tamarrind seed gum, Guar gum, British gum, gum Arabic, pyrodextrin, etc. or polylols, e.g. polyvinyl alcohol, polyethylene glycol, etc. to produce a variety of water-soluble hybrids that have useful potential applications especially in the textile fields. These applications include the utilization of the prepared and characterized hybrids or adducts in: cotton sizing (El-Sayed, Fahmy, Ibrahim, & Abo-shosha, 2004; Hebeish, Haggag, Abo-Shosha, & Ibrahim, 1989), textile printing (Abo-Shosha, El-Zairy, & Ibrahim, 1994; Abo-Shosha, Ibrahim, Allam, El-Zairy, & El-Zairy, 2006; Abo-Shosha, Ibrahim, Allam, & El-Zairy, 2008; Ibrahim, Abo-Shosha, Allam, El-Zairy, & El-Zairy, 2006; Ibrahim, Abo-Shosha, Allam, & El-Zairy, 2008, 2010), and in cotton finishing (Ibrahim, Abo-Shosha, Fahmy, El-sayed, & Hebeish, 2008; Mohammed, Abo-Shosha, & Ibrahim, 2009).

The objectives of the present study are to synthesis and characterize a new adduct based on polyacrylic acid/polyethylene glycol via free radical polymerization, as well as to investigate the potential applications of the prepared adduct in sizing and functional finishing of cellulose-based textiles.

## 2. Experimental

### 2.1. Fabrics

In this study, mill scoured and bleached: gauzy cotton fabrics (50 g/m$^2$), plain-weave cotton fabric (130 g/m$^2$), viscose fabric

---

* Corresponding author. Fax: +202 333 70931.
*E-mail address:* nabibrahim49@yahoo.co.uk (N.A. Ibrahim).

0144-8617/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2012.03.068

($110\,g/m^2$) and cotton/polyester blend fabric (50/50, $150\,g/m^2$) were used.

### 2.2. Chemicals

Glacial acrylic acid (AA), inhibited with 200 ppm hydroquinone monomethyl ether (Fluka Chemika, Switzerland), was used without distillation. Polyethylene glycol (PEG-600, Fluka Chemika), Fixapret® ECO (modified dimethyloldihydroxyethylene urea, BASF), Hostapal® CV-ET (a non-ionic wetting agent based on alkyl aryl polyglycol ether, clariant), and C.I. Basic Blue 9 (Merk) were used.

All other chemicals such as magnesium chloride hexahydrate ($MgCl_2{\cdot}6H_2O$), sodium hypophosphite monohydrate ($NaH_2PO_2{\cdot}H_2O$), ammonium persulfate [$(NH_4)_2\,S_2O_8$], citric acid, tri-sodium citrate, acetic acid, nitric acid, sodium hydroxide, 2-propanol and hydroquinone were of laboratory reagent grade. Both $AgNO_3$ (Sigma), and titanium tetraisopropoxide (Sigma) were of analytical reagent grade.

### 2.3. Methods

#### 2.3.1. Preparation of PAA/PEG adduct

Preparation of PAA/PEG adduct was carried out using the method described elsewhere (Abo-Shosha et al., 1994).

#### 2.3.2. Preparation of Ag-nanoparticles (Ag-NPs)

Ag-NPs were prepared using trisodium-citrate as a reductant as reported elsewhere (Sileikaite, Prosycevas, Puiso, Juraitis, & Guobiene, 2006).

#### 2.3.3. Preparation of $TiO_2$-nanoparticles ($TiO_2$-NPs)

$TiO_2$-nanoparticles were prepared as previously reported (Bozzi, Yuranova, & Kiwi, 2005) using titanium tetraisopropoxide precursor with 2-propanol and nitric acid.

#### 2.3.4. Utilization as a sizing agent

Strips of gauzy cotton fabrics were padded twice in a sizing bath containing aqueous solution of PAA/PEG-600 adduct at concentration of (10%) and a temperature of 60 °C to a wet pick-up of about 100%, followed by drying at 100 °C for 5 min. Finally, the obtained sized strips were conditioned at 65% relative humidity and 25 °C for 48 h before testing (Hebiesh, Fahmy, Ibrahim, & Abo-shosha, 2006).

#### 2.3.5. Size removal

The pre-weighted-sized samples were placed in cups of thermostatic Launder-Ometer containing water at 60 °C for 10 min, and a material to liquor ratio of 1/20, Finally the desized liquor was drained and the samples were thoroughly washed with water and dried to a constant weight.

#### 2.3.6. Utilization as a stiffening agent

Cotton fabric samples were padded twice in a solution containing the PAA/PEG-600 adduct (0–75 g/L), Fixapret® ECO (50 g/L), $MgCl_2{\cdot}6H_2O$ (5 g/L) and nonionic wetting agent (2 g/L) to 80% wet pickup, predried at 100 °C for 3 min, cured at 160 °C for 3 min, followed by after-washing at 50 °C/15 min in the presence of a nonionic wetting agent (2 g/L), drying and conditioning before testing (Ibrahim, Abo-Shosha, Fahmy, et al., 2008).

#### 2.3.7. Utilization in antibacterial finishing

Fabric samples were padded twice in a finishing formulation containing the prepared adduct (50 g/L), as a binding agent, the aqueous Ag-NPs solution (20 g/L), as antibacterial agent, Na-hypophosphite (15 g/L), as a catalyst, and nonionic wetting agent (2 g/L), to 80% wet pickup, predried at 85 °C/5 min and then cured at 180 °C for 2 min, followed by after washing at 50 °C in the presence of a nonionic wetting agent (2 g/L), rinsing, drying and conditioning before testing.

#### 2.3.8. Utilization in multifunctional finishing

To acquire stiffness, self cleaning, UV-protecting, and antibacterial in one step, the fabric samples were padded twice in a finishing formulation including the prepared adduct (50 g/L), the aqueous $TiO_2$-nano sol (5 g/L), as self-cleaning/anti-UV/antibacterial agent, Na-hypophosphite (15 g/L), as a catalyst, and a nonionic wetting agent (2 g/L), to 80% wet pick-up, predried at 85 °C for 5 min, and then cured at 180 °C for 2 min, followed by after-washing at 50 °C/5 min in the presence of a nonionic wetting agent (2 g/L), rinsing, drying and conditioning before testing.

#### 2.3.9. Basic dyeing

Basic dyeing of the treated and untreated fabric samples were carried out as previously reported (Ibrahim, Abo-Shosha, Elnagdy, & Gaffar, 2002).

### 2.4. Testing

The extent of polymerization, expressed as percentage total conversion, %TC, of the prepared adduct solutions was assessed as described elsewhere (Welcher, 1963). Determination of the prepared adduct components was determined as described elsewhere (Miller, 1964).

Size add-on as well as percent size removal were evaluated according to "boil-off" method (Slauson, Miller, & Rebenfeld, 1984).

Tensile strength (TS) and elongation at break (EB) in the warp direction were determined by the strip method according to ASTM Procedure D-2256-66T.

Stiffness of the treated and untreated samples was determined by DIN 53362.

Dry wrinkle recovery angle (WRA) was determined according to ASTM method S-1296-98.

Roughness of the treated and untreated fabric samples using roughness measuring instrument SE 1700α, Japan, according to JIS94 Standard.

The nitrogen content was determined by Kjeldhal method (Vogel, 1975).

Carboxyl content of the treated and untreated fabric samples was determined as described elsewhere (Cirino & Rowland, 1976).

Wettability of treated and untreated fabric samples was tested according to AATCC Test Method 39-1993.

The oily stain release rating (SRR) of the treated and untreated fabric samples was tested according to the AATCC Test Method 130-1974.

The color strength (*K*/*S*) values of the basic dyed fabric samples was determined from the reflectance measurement using Kubelka-Munk equation (Judd & Wyszecks, 1975)

$$\frac{K}{S} = \frac{(1-R)^2}{2R}$$

where *K*, *S* and *R* are the absorption coefficient, the scattering coefficient and the reflectance at the wave length of maximum absorbance of the used basic dye respectively.

FT-IR spectra were recorded on a Perkin-Elmer Spectrum 1000 Spectrophotometer using KBr disk technique.

Scanning electron microscope (SEM) images of the treated and untreated fabric samples were obtained with a JEOL JXA-840A electron probe microanalyzer, equipped with energy disperse X-ray spectroscopy (EDX) for the composition analysis (Ibrahim, Refaie, et al., 2010).

Please cite this article in press as: Ibrahim, N. A., et al. Poly(acrylic acid)/poly(ethylene glycol) adduct for attaining multifunctional cellulosic fabrics. *Carbohydrate Polymers* (2012), http://dx.doi.org/10.1016/j.carbpol.2012.03.068

The morphology and particles size of Ag-NP's and $TiO_2$-NP's were obtained by transmission electron microscope (TEM) using a JEOL, JEM 2100 F electron microscope at 200 kV.

The antibacterial activity against G+ve bacteria (*S. aureus*) and G−ve bacteria (*E. coli*) was evaluated according to AATCC Test Method 100-1999, and the reduction percent in bacteria (RPC) count was calculated.

The durability to wash (after 10 launder cycles) was determined according to AATCC Test method 135-2000.

UV-protection factor (UPF) was evaluated according to the Australian/New Zealand Standard (AS/NZS 4399-1996).

The self-cleaning action of the $TiO_2$-loaded substrates was assessed as described elsewhere (Ibrahim, Refaie, et al., 2010).

## 3. Results and discussion

### 3.1. Tentative mechanism

It would be helpful, if we consider, at the outset the tentative mechanism of the free radical polymerization of acrylic acid (AA), as a vinyl monomer, and polyethylene glycol (PEG-OH), as a substrate, in the presence of ammonium persulfate [$(NH_4)_2\,S_2O_8$] as initiator (Scheme 1)

i- Decomposition of $(NH_4)_2\,S_2O_8$

$$S_2O_8^{2-} \xrightarrow{\Delta} 2\,SO_4^{\bullet -} \tag{1}$$

$$2\,SO_4^{\bullet -} + H_2O \longrightarrow HO^{\bullet} + HSO_4^{-} \tag{2}$$

$$2\,HO^{\bullet} \longrightarrow H_2O_2 \longrightarrow H_2O + 1/2O_2 \tag{3}$$

ii- Initiation reaction

These radical species ($R^{\bullet}$) are capable of initiating the following reactions

$$AA + R^{\bullet} \longrightarrow AA^{\bullet} \quad \text{(activated monomer)} \tag{4}$$

$$PEG\text{-}OH + R^{\bullet} \longrightarrow PEG\text{-}O^{\bullet} + RH \tag{5}$$

iii- Homopolymerization reaction

$$n\,AA^{\bullet} \longrightarrow PAA \quad \text{(homopolymer)} \tag{6}$$

iv- Graft copolymerization reaction

$$n\,AA^{\bullet} + PEG\text{-}O^{\bullet} \longrightarrow PAA\text{-}g\text{-}PEG \tag{7}$$

Scheme 1. Suggested polymerization reactions

Thus, the mixture of polymerization products, i.e. unreacted PEG, PAA and PAA-g-PEG, all in a state of intimate entanglement, is referred to as the adduct product (Abo-Shosha et al., 2006; Ibrahim, Abo-Shosha, Fahmy, et al., 2008).

### 3.2. Major factors affecting the adduct formation

The effect of initiator concentration, polymerization temperature and time, degree of neutralization of AA as well as AA/PEG mass ratio on the extent of polymerization, expressed as %TC, and formation of PAA/PEG adduct was shown in Fig. 1 (from (a) to (e)) respectively.

#### 3.2.1. $(NH_4)_2\,S_2O_8$ concentration

Fig. 1(a) shows the effect of $(NH_4)_2\,S_2O_8$ concentration on the extent of polymerization, i.e. TC %. For a given set of polymerization conditions, it is clear that: (i) the %TC increased proportionally (from 60 to 83%) with increasing the initiator concentration in the polymerizing formulation from 0.25 to 1.5 g/L, and (ii) further increase in the initiator concentration than 1.5 g/L has practically a slight positive impact on the %TC. The enhancement in the %TC by increasing the initiator concentration, within the range examined, reflects its positive impacts on: stopping the inhibition action of hydroquinone monomethyl ether, creation of more free radical species ($R^{\bullet} = SO_4^{\bullet -}$ and/or $HO^{\bullet}$), formation of PEG-macroradicals and AA-activated monomer, supplying the system with adequate energy thereby resulting in promotion of homopolymerization and graft coplymerization reactions (Abo-Shosha et al., 2006; Hebeish et al., 1989; Ibrahim, Haggag, Abo-Shosha, & Hebeish, 1990).

On the other hand, the leveling of the %TC beyond 1.5 g/L could be discussed in terms of a shortage in AA monomer and/or the steric hindrance of the formed adduct (El-Sayed et al., 2004).

#### 3.2.2. Polymerization temperature

It is clear from Fig. 1(b) that increasing the polymerization temperature from 50 °C to 90 °C is accompanied by a remarkable increase in the %TC from 65.5 up to 93.5%. This could be attributed to the positive effect of temperature on overcoming the activation energy barrier, enhancing the decomposition of the used initiator as well as generation of more free radical species, minimizing the viscosity of the polymerization medium, improving mobility of free radicals as well as AA-activated monomer molecules,

Please cite this article in press as: Ibrahim, N. A., et al. Poly(acrylic acid)/poly(ethylene glycol) adduct for attaining multifunctional cellulosic fabrics. *Carbohydrate Polymers* (2012), http://dx.doi.org/10.1016/j.carbpol.2012.03.068

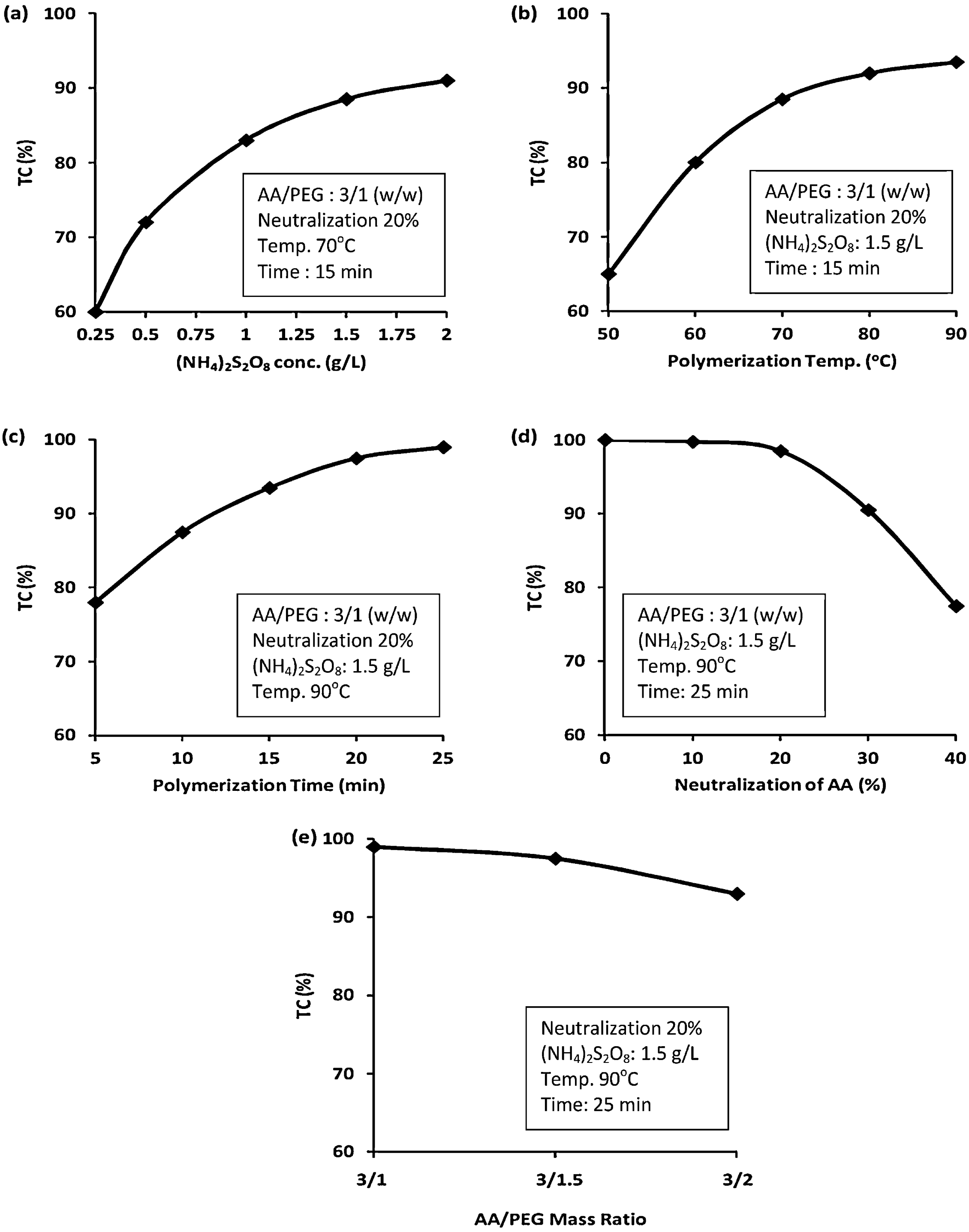


**Fig. 1.** Major factors affecting the extent of polymerization, expressed as total conversion-TC %. (a) Initiator concentration, (b) polymerization temperature, (c) polymerization time, (d) degree of neutralization of (AA), and (e) AA/PEG mass ratio.

and subsequently increasing the probability of their collisions and efficiency of formation of PAA/PEG adduct (Ibrahim, Abo-Shosha, Fahmy, et al., 2008).

### 3.2.3. *Polymerization time*

For a given set of polymerization conditions and within the range examined (5–25 min), Fig. 1(c) shows that prolonging the polymerization time is accompanied by a gradual increase in the extent of polymerization, expressed as %TC, from 77.5% to 99%. This reflects the positive effect of proper time on: formation of free radicals and activated reactants as well as their mobility and diffuse-ability, and subsequent formation of PAA/PEG adduct, i.e. PAA, PEG and PAA-g-PEG entangled mixture (Abo-Shosha et al., 2006).

### 3.2.4. *Degree of neutralization*

Fig. 1(d) demonstrates the effect of degree of neutralization of AA, Na-form of AA, on the extent of formation of the PAA/PEG adduct, expressed as %TC. Within the range examined (0–40%) and for a given set of polymerization conditions, its clear that, (i)

Please cite this article in press as: Ibrahim, N. A., et al. Poly(acrylic acid)/poly(ethylene glycol) adduct for attaining multifunctional cellulosic fabrics. *Carbohydrate Polymers* (2012), http://dx.doi.org/10.1016/j.carbpol.2012.03.068

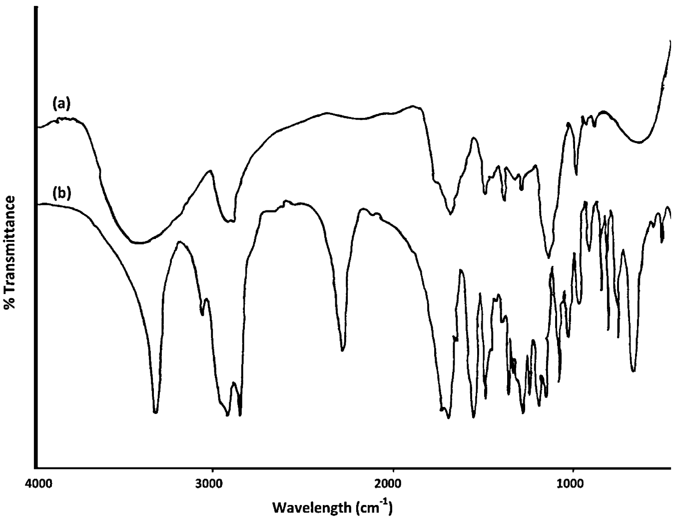


**Fig. 2.** FTIR spectrum of PEG-600 (a), the prepared PAA/PEG-600 adduct (b).

increasing the degree of neutralization from zero up to 20% has practically a marginal effect on the %TC, (ii) further increase in the % neutralization of AA up to 40% brings about a remarkable decrease in the %TC, from 99% down to 77.5%, and (iii) this remarkable decrease in %TC is attributed to the inhibition effect of abundant of $Na^+$ at higher degree of neutralization on the polymerization medium (Hebeish et al., 1989).

### 3.2.5. *AA/PEG mass ratio*

It is clear from Fig. 1(e) that, within the range examined 3/1 to 3/2 (w/w), decreasing the AA/PEG ratio from 3 down to 1.5 results in a gradual slight decrease in the %TC from 99% to 93%. This could be associated with lower AA component as well as higher viscosity of the polymerization medium due to the higher PEG-component. The ultimate effect of the aforementioned two factors is minimized the extent of polymerization.

## 3.3. *Characterization of PAA/PEG-600 adduct*

PAA/PEG-600 adduct with >99% total conversion was prepared by using the following proper polymerization conditions: PAA/PEG-600 (3/1 mass ratio), degree of neutralization of AA (20%); $(NH_4)_2S_2O_8$ (1.5 g/L); at 90 °C for 25 min. The prepared adduct was characterized by investigating its: visual appearance, water solubility, chemical analysis as well as FTIR spectra. The prepared adduct was white solid, water-soluble and contained 10.71% PAA, 88.69% PAA-g-PEG-600, along with other unreacted and/or by products.

On the other hand, The FTIR spectra of PEG-600 and PAA/PEG-600 adduct is shown in Fig. 2. The following bands are observed:

- In PEG-600 spectrum (a), there is a broad band in the region 3375 $cm^{-1}$ corresponds to OH stretching vibration, the methylene group is found around 2840 $cm^{-1}$, and the absorption around 1475 $cm^{-1}$ is due to binding vibration of —$CH_2$, also there are a strong bands around 1360 $cm^{-1}$ and 1290 $cm^{-1}$ due to C—O stretching vibration.
- In the PAA/PEG-600 adduct spectrum (b), the strong band around 3300 $cm^{-1}$ is related to hydroxyl groups (OH), the strong band at around 1710 $cm^{-1}$ is attributed to the carbonyl group C═O, and the two peaks around 2920 $cm^{-1}$ and 2875 $cm^{-1}$ are corresponded to aliphatic $CH_2$, also there are strong bands around 1210 $cm^{-1}$ and 1320 $cm^{-1}$ due to C—O stretch.
- The bands which are observed in spectrum (b) confirm the existence of carboxylic groups in the obtained adduct.

## 3.4. *Potential textile applications*

Because the main task of this part was to evaluate the potential textile applications of the prepared PAA/PEG-600 adduct in: sizing of cotton-cellulose, handle-modification, as well as in functional finishes of cellulose containing fabrics, i.e. anti-bacterial, UV-blocking and self-cleaning, a wide range of treatment formulations and conditions have been investigated.

### 3.4.1. *Cotton sizing*

For a given set of sizing conditions Fig. 3(a)–(c) shows that using the prepared PAA/PEG-600 adduct as a sizing agent brings about a significant increase in TS, from (22.5 kg up to 35 kg), a decrease in EB from (from 6.5% to 5.2%|) along with an outstanding increase in fabric stiffness (from 95 mg up to 7550 mg). This reflects the ability of the prepared adduct to coat and penetrate the treated fabric structure Fig. 3(d) in comparison with the unsized one, Fig. 3(c), thereby increasing coating and encapsulation of cellulose fibers and yarns cohesiveness which, in turn restricted fiber-slippage and yarn mobility (Hebiesh et al., 2006; Ibrahim, 1993; Ibrahim & Trauter, 1992).

On the other hand, desizing of the sized-fabric strips (size add on = 8.92%) at 65 °C/10 min using LR of 1/20 results in a complete removal of the used PAA/PEG-600 adduct. This most probably attributed to partial neutralization of AA in the monomeric or polymeric form along with the inclusion of the PEG, in the free or PAA-g-PEG form, in a state entanglement with other adduct components.

In summary, the obtained results clearly show that the using of the prepared PAA/PEG-600 adduct, as an efficient easily removable sizing agent, results in a significant improvement in the sizeability and desizeability of the sized fabric strips.

### 3.4.2. *Hand-builder finish*

The effects of inclusion of PAA/PEG-600 adduct (0–75 g/L) in the easy care finishing formulation of cotton fabric is given in Table 1. For a given set of finishing conditions, the following results were found: (i) increasing the adduct concentration within the range examined results in a significant increase in the carboxyl content from zero up to 82.1 meq/100 g sample, and a remarkable

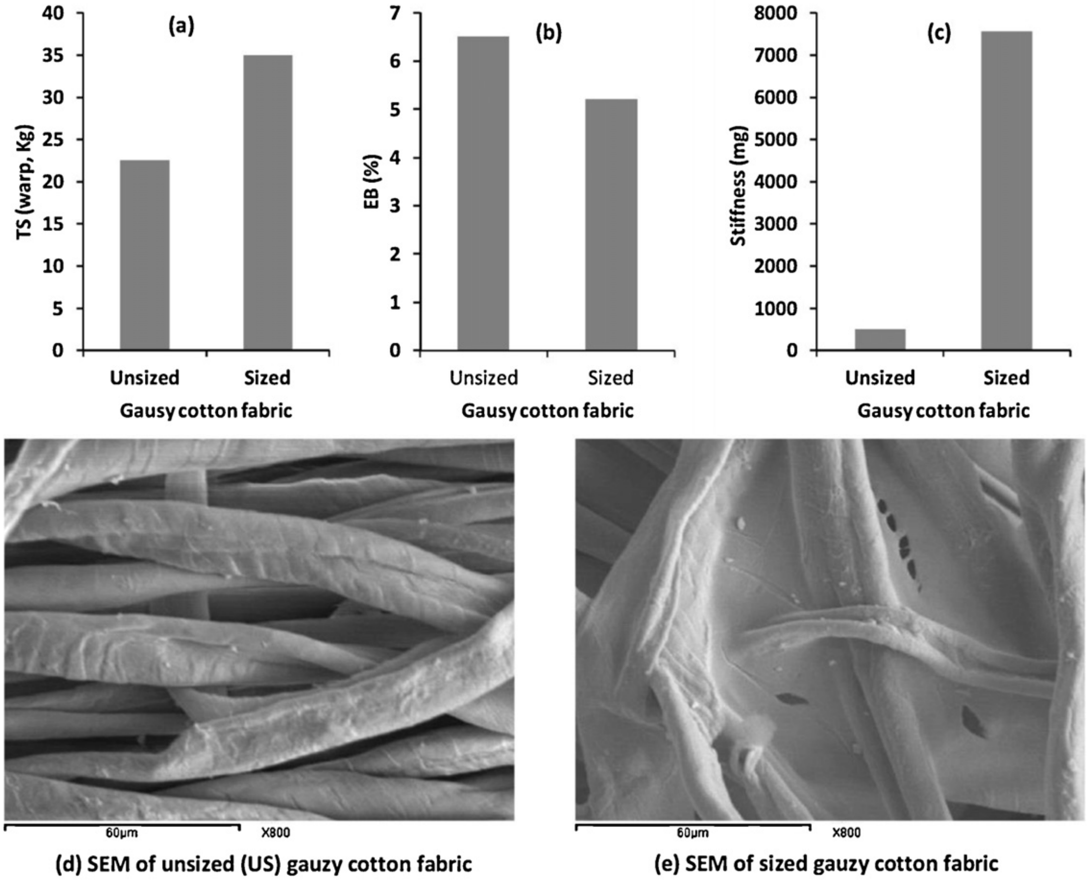
**Table 1**
Performance properties of easy care finished cotton fabric in the presence of PAA/PEG-600 adduct.

| PAA/PEG-600 adduct conc. (g/L) | %N | —COOH (meq/100 g) | TS (W, kg) | WRA (W+F)° | Stiffness (mg cm) | Roughness (μm) | Wetting time (s) | SRR | *K/S*[a] |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 0.98 | – | 45.2 | 232 | 750 | 16.0 | 4 | 2.0 | 1.06 |
| 25 | 0.80 | 35.42 | 48.5 | 215 | 1410 | 16.6 | 1 | 3.0 | 5.45 |
| 50 | 0.65 | 60.78 | 53.0 | 203 | 1728 | 17.4 | 1 | 5.0 | 6.88 |
| 75 | 0.54 | 82.10 | 56.2 | 185 | 2185 | 18.0 | 1 | 5.0 | 8.95 |
| Untreated | – | 1.30 | 58.0 | 115 | 530 | 15.0 | 2 | 2.5 | 0.65 |

*Finishing formulation*: PAA/PEG adduct (0–75 g/L); Fixapret® ECO (50 g/L); $MgCl_2{\cdot}6H_2O$ (5 g/L); wetting agent (2 g/L); wet-pickup (80%); drying at 100 °C/3 min, curing at 180 °C/3 min.

[a] Post-dyeing with C.I. Basic Blue 9 (3%).

Please cite this article in press as: Ibrahim, N. A., et al. Poly(acrylic acid)/poly(ethylene glycol) adduct for attaining multifunctional cellulosic fabrics. *Carbohydrate Polymers* (2012), http://dx.doi.org/10.1016/j.carbpol.2012.03.068



**(d) SEM of unsized (US) gauzy cotton fabric**

**(e) SEM of sized gauzy cotton fabric**

**Fig. 3.** Effect of using the prepared PAA/PEG-600 adduct on TS (a), EB (b), stiffness (c) as well as on surface morphology of sized substrate (e) compared with the unsized one (d) PAA/PEG-600 (10%) at 60 °C; wet pick up 100% drying at 100 °C.

improvement in: TS (from 45.2 up to 56.2 Kg), stiffness from (750 up to 2185 mg), as well as in roughness (16 up to 18 μm) of the treated fabric samples, (ii) inclusion of the prepared adduct brings about a noticeable decrease in the %N (from 0.98 down to 0.54%), in WRA (from 232° down to 185°) as well as wetting time (from 4 s down to 1 s), and (iii) incorporation of the PAA/PEG-600 adduct on finishing formulation, up to 75 g/L, along with other ingredients is accompanied by a significant improvement in SRR (from 2 up to 5) as well as in the post-dyeing with C.I. Basic Blue 9 dye, expressed as *K*/*S* values from 0.86 up to 8.95.

Based on the abovementioned results, the following tentative mechanism (Scheme 2) can illustrate the reactions and/or interactions among the cotton cellulose (Cell.OH), the prepared PAA/PEG-600 adduct ($\text{XOOC}\sim\text{PAA/PEG}\sim\text{OH}$, where X = Na or H), the unreactant PEG ($\text{PEG}\sim\text{OH}$) as well as the crosslinking agent ($\text{ROH}_2\text{CN}\sim\text{DMDHEU}\sim\text{NCH}_2\text{OR}$):

(i) Crosslinking of cotton cellulose

$$\text{Cell.OH} + \text{ROH}_2\text{CN-DMDHEU-NCH}_2\text{OR} + \text{HO.Cell} \xrightarrow[\Delta]{H^+} \text{Cell.O.H}_2\text{CN-DMDHEU-NCH}_2\text{.O.Cell} + 2\text{ROH} \quad \text{crosslinked cellulose} \tag{8}$$

thereby increasing the %N, WRA, roughness, wetting time and K/S values compared with the untreated cotton cellulose.

(ii) Fixation of the adduct-components onto/within the finish fabric matrix

$$\text{Cell.OH} + \text{ROH}_2\text{CN-DMDHEU-NCH}_2\text{OR} + \text{HO}\sim\text{PEG/PAA}\sim\text{COOX} \xrightarrow[\Delta]{H^+} \text{Cell.O.H}_2\text{CN}\sim\text{DMDHEU}\sim\text{NCH}_2\text{O.PEG/PAA}\sim\text{COOX} + 2\text{ROH} \tag{9}$$

Please cite this article in press as: Ibrahim, N. A., et al. Poly(acrylic acid)/poly(ethylene glycol) adduct for attaining multifunctional cellulosic fabrics. *Carbohydrate Polymers* (2012), http://dx.doi.org/10.1016/j.carbpol.2012.03.068

thereby enhancing the carboxyl content, TS, stiffness, roughness, wettability, SRR, as well as K/S values compared with the finished fabric without adduct.

$$\mathrm{Cell.OH + ROH_2CN\text{-}DMDHEU\text{-}NCH_2OR + PEG{\sim}OH \xrightarrow[\Delta]{H^+} Cell.OH_2CN\text{-}DMDHEU\text{-}NCH_2O{\sim}PEG + 2ROH} \tag{10}$$

thereby enhancing the wetting and dyeing properties.

On the other hand, fixation of PAA onto/within the finish matrix is achieved via formation of five membered cyclic anhydride intermediates (Martel, Weltrowski, Druffin, & Morcellet, 2002) that readily reacts with the hydroxyl groups of cellulose and/or PEG-OH by esterification and/or via formation of a coated film onto the treated substrate under thermal treatment (Ghosh & Das, 2000).

(iii) Formation of by products

$$\text{Finishing agent + PAA/PEG-adduct components} \xrightarrow[\Delta]{H^+} \text{Washable-unbound by product and/or insoluble coating film} \tag{11}$$

Scheme 2.Tentative reactions among (Cell.OH/DMDHEU/PAA-PEG)

It is worthy mentioned that the fixation of the prepared adduct-components and/or side interactions among the used ingredients is accompanied by a decrease in ether-crosslinking, expressed as %N and WRA values, along with an increase in other mechanical properties, i.e. TS, stiffness, and roughness.

This may be caused by the different crosslinks and/or deposition on/in the finish/fabric matrix, and their impacts on coating, encapsulation, cementing and restricting fibers/yarns mobility. This can led to a substantial increase in the extent of yarn cohesiveness as well as roughness along with a noticeable decrease in the yarn flexibility and finished fabric resiliency with the increase in the adduct concentration (El-Sayed et al., 2004).

Additionally, fixation of hydrophilic active sites, especially —COOH groups and PEG-moities, onto/within the finish/fabric matrix is responsible for the remarkable improve in hydrophilic properties of the treated fabric samples and, in turn SRR as well as *K*/*S*.

### 3.4.3. *Antibacterial/stiff hand finish*

The formation of Ag-NPs using trisodium citrate (TSC), as a reductant, proceeds according to the following chemical reaction (Kelly & Johnston, 2011):

$$2\mathrm{Ag}^{+} + \underset{\mathrm{TSC}}{\mathrm{Na_3C_6H_5O_7}} \rightarrow \underset{\mathrm{Ag\text{-}NP's}}{2\mathrm{Ag}^{\circ}} + \mathrm{Na_2C_5H_4O_5} + \mathrm{Na}^{+} + \mathrm{H}^{+} + \mathrm{CO_2} \tag{12}$$

Fig. 4(a) reports the UV–visible spectra of the prepared Ag-nanosol. The prepared sample shows a peak at around 427 nm due to the presence of Ag-NPs. Also, the TEM image, Fig. 4(b), shows that the formed Ag-NPs are <10 nm in size and are relatively homogenous. Moreover, the SEM of untreated and treated viscose images in Fig. 4(c) and (d) respectively showed that treated viscose fabric Fig. 4(d) was coated with the Ag°-PAA/PEG composite, and the existence of elementary silver on the fabric surface, as detected by EDX, confirm loading of the Ag-NP's onto the top layer and near surface layer of treated cotton fibers (Ag content = 0.21% w/w).

In this part, the prepared adduct was used to fix the prepared Ag-NP's onto/within the finish/fabric matrix to impart antibacterial and stiffness functional properties in one step.

For a given set of treatment conditions, the data in Table 2 signify that: (i) incorporation of the prepared Ag-NPs along with the PAA/PEG adduct, as an esterifying and linking agent, in the presence of $\mathrm{NaH_2PO_2}$ as a catalyst results in a significant enhancement in the add-on, carboxyl content and Ag-content of top layer regardless of the used substrate, (ii) the variation in the aforementioned properties is determined by the type of substrate, i.e. surface area, cellulose content, amorphous/crystalline regions, extent of diffusion and penetration, as well as fabric structure, and follows the descending order: viscose > cotton > cotton/polyester, (iii) fixation of the prepared adduct via esterification and, in turn loading of the Ag-NP's onto/within the adduct/fabric matrix brings about remarkable improvement in both the stiffness properties and the antibacterial functionalities of the treated substrates along with a positive impact on their hydrophilicity, expressed as reduction in wetting time, (iv) the imparted significant stiffness properties, as compared with untreated ones, are attributed to the surface coating action of the utilized adduct as well as bridging of the fibers with the Ag-NP's, (v) addition of Ag-NP's to the finishing bath increases the probability of its binding to and loading onto the finish fabric matrix via the free carboxyl groups of the adduct, consequently increasing antibacterial efficacy of the treated fabric samples against G+ve and G−ve bacteria, (vi) the remarkable improvement in the antibacterial activity is attributed to the positive impacts of the loaded Ag-NP's on: damaging the bacterial membrane and finally leading to cell death, formation of Ag-ions taken into the cells, in the presence of moisture, bind to the bacterial DNA and finally causing their inactivation (Hoskins, Karanfil, & Serkiz, 2002),

$$\mathrm{O_{2(aq)}} + 4\mathrm{H_3O}^{+} + 4\mathrm{Ag_{(s)}} \rightarrow 4\mathrm{Ag}^{+}{}_{\mathrm{(aq)}} + 6\mathrm{H_2O} \tag{13}$$

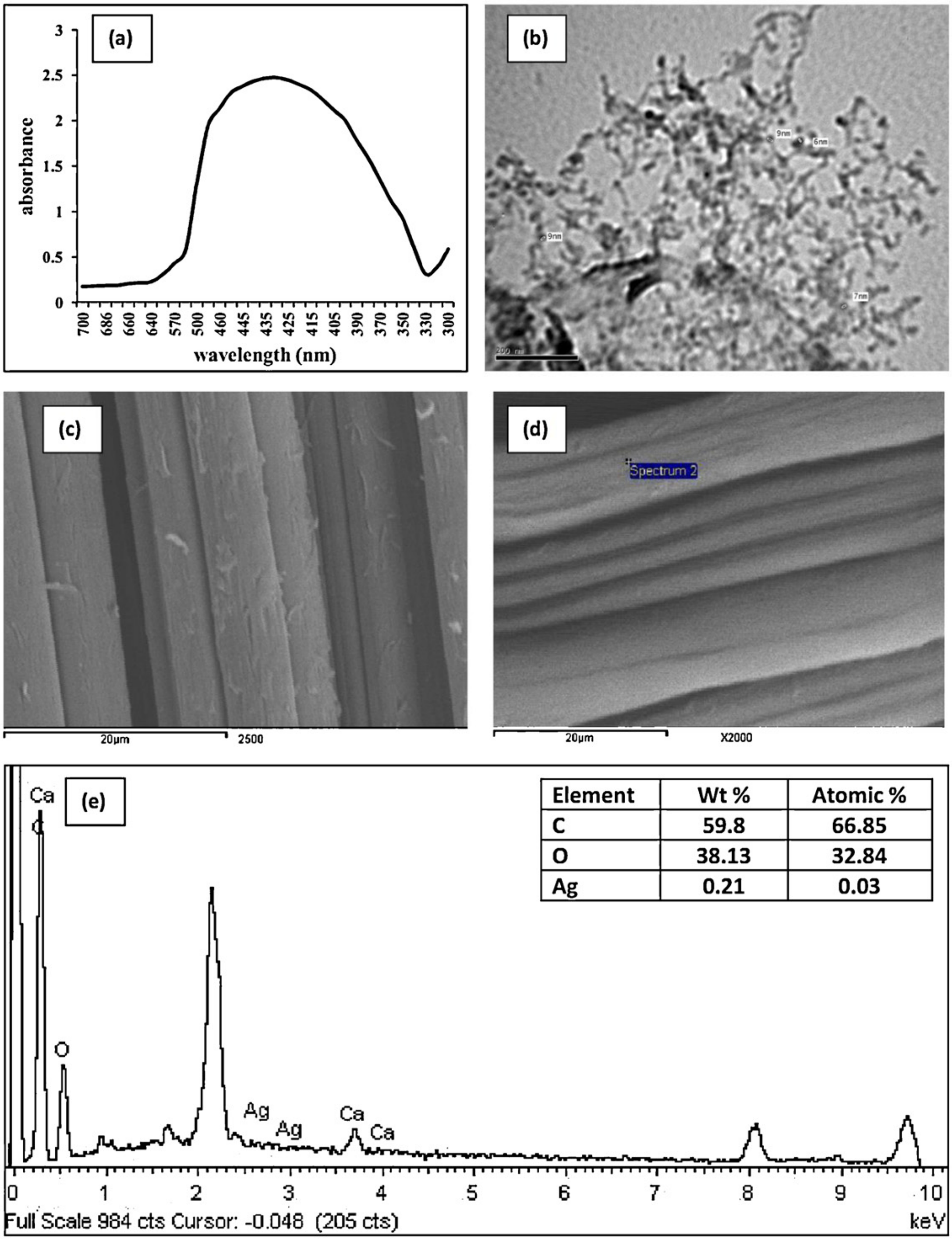
and/or producing of oxygen radicals that oxidize the molecular structure of bacteria (Ibrahim et al., 2012):

$$\mathrm{H_2O} + 1/2\mathrm{O_2} \xrightarrow{\mathrm{Ag}^{+}} \mathrm{H_2O_2} \rightarrow \mathrm{H_2O} + (\mathrm{O}) \tag{14}$$

and (vii) antibacterial activity against G+ve and G−ve bacteria follows the decreasing order G + ve > G−ve, regardless of the used substrate, most probably due to the differences in cell wall structure, amenability to disruption of the metabolic process and/or in response for inactivation to death (Ibrahim, Khalifa, El-Hossamy, & Tawfik, 2010).

On the other hand, the given data shows a noticeable retention in the imparted functional properties, i.e. stiffness and antibacterial properties, after 10 laundering cycles. This means that both the

Please cite this article in press as: Ibrahim, N. A., et al. Poly(acrylic acid)/poly(ethylene glycol) adduct for attaining multifunctional cellulosic fabrics. *Carbohydrate Polymers* (2012), http://dx.doi.org/10.1016/j.carbpol.2012.03.068



| Element | Wt % | Atomic % |
|---|---|---|
| C | 59.8 | 66.85 |
| O | 38.13 | 32.84 |
| Ag | 0.21 | 0.03 |

**Fig. 4.** (a) UV–visible spectra of Ag-NP's, (b) TEM image of Ag-NP's, (c) SEM of untreated viscose fabric, (d) SEM of treated viscose fabric, and (e) EDX image and element content of Ag-NP's loaded substrate.

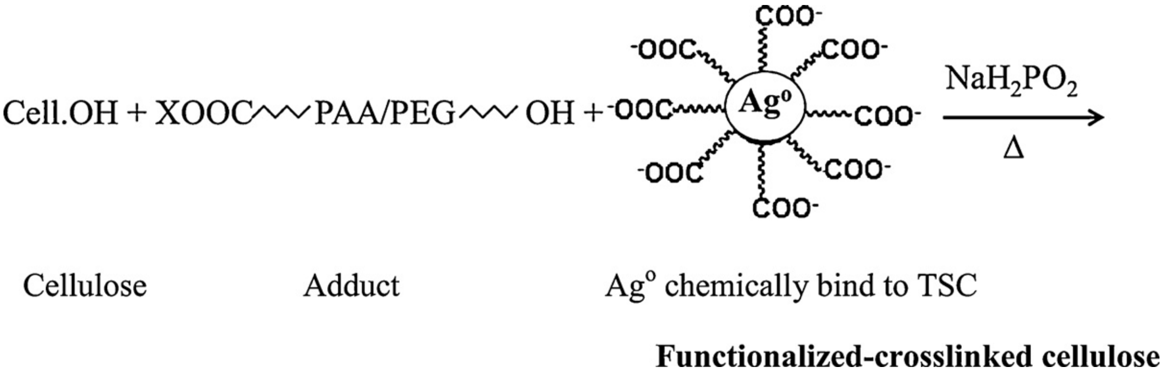
**Table 2**
Functionalization of cellulose-containing fabrics using PAA/PEG adduct along with Ag-NP's in the finishing formulation.

| Substrate | Treatment | Add-on (%) | Carboxyl content | Ag content (%) | Wetting time (s) | Stiffness (mg cm) | Reduction of bacteria (%) | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | *E. coli* (G−ve) | *S. aureus* (G+ve) |
| Cotton | Untreated | – | 1.30 | – | 2 | 530 | NR | NR |
| | Treated | 2.31 | 41.4 | 0.210 (0.181) | 1 | 2622 (2104) | 92.3 (88.0) | 94.5 (89.9) |
| Viscose | Untreated | – | 4.25 | – | <1 | 497 | NR | NR |
| | Treated | 3.14 | 48.6 | 0.282 (0.240) | <1 | 7279 (5810) | 95.3 (90.4) | 96.8 (92.2) |
| Cotton/polyester | Untreated | – | 0.85 | – | 4 | 427 | NR | NR |
| | Treated | 2.07 | 36.7 | 0.175 (0.154) | 2 | 2409 (1905) | 87.5 (82.0) | 89.9 (84.7) |

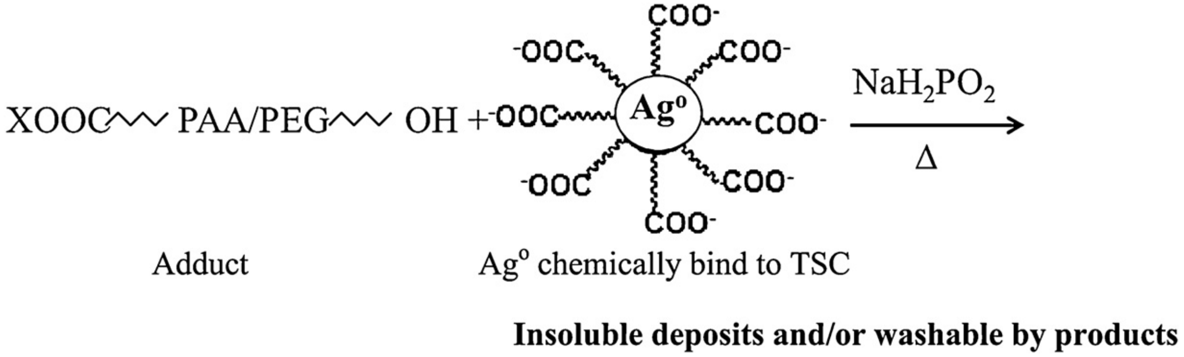
*Finishing formulation*: PAA/PEG adduct (50 g/L); $NaH_2PO_4$ (15 g/L), Ag-NP's (20 g/L of the stock solution); wet pick-up (80%); drying at 85 °C/5 min; curing at 180o C/2 min, NR: no reduction of bacteria.
Values in parentheses indicate retained functional after 10 laundering cycles.

Please cite this article in press as: Ibrahim, N. A., et al. Poly(acrylic acid)/poly(ethylene glycol) adduct for attaining multifunctional cellulosic fabrics. *Carbohydrate Polymers* (2012), http://dx.doi.org/10.1016/j.carbpol.2012.03.068

Ag-NP's and PAA/PEG adduct are firmly bound to the treated substrate according to following equations (Kelly & Johnston, 2011):

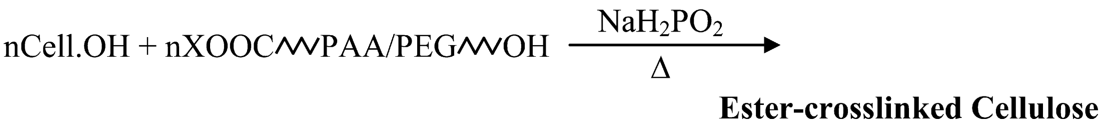


(15)



(16)

and



(17)

where X = Na or H.

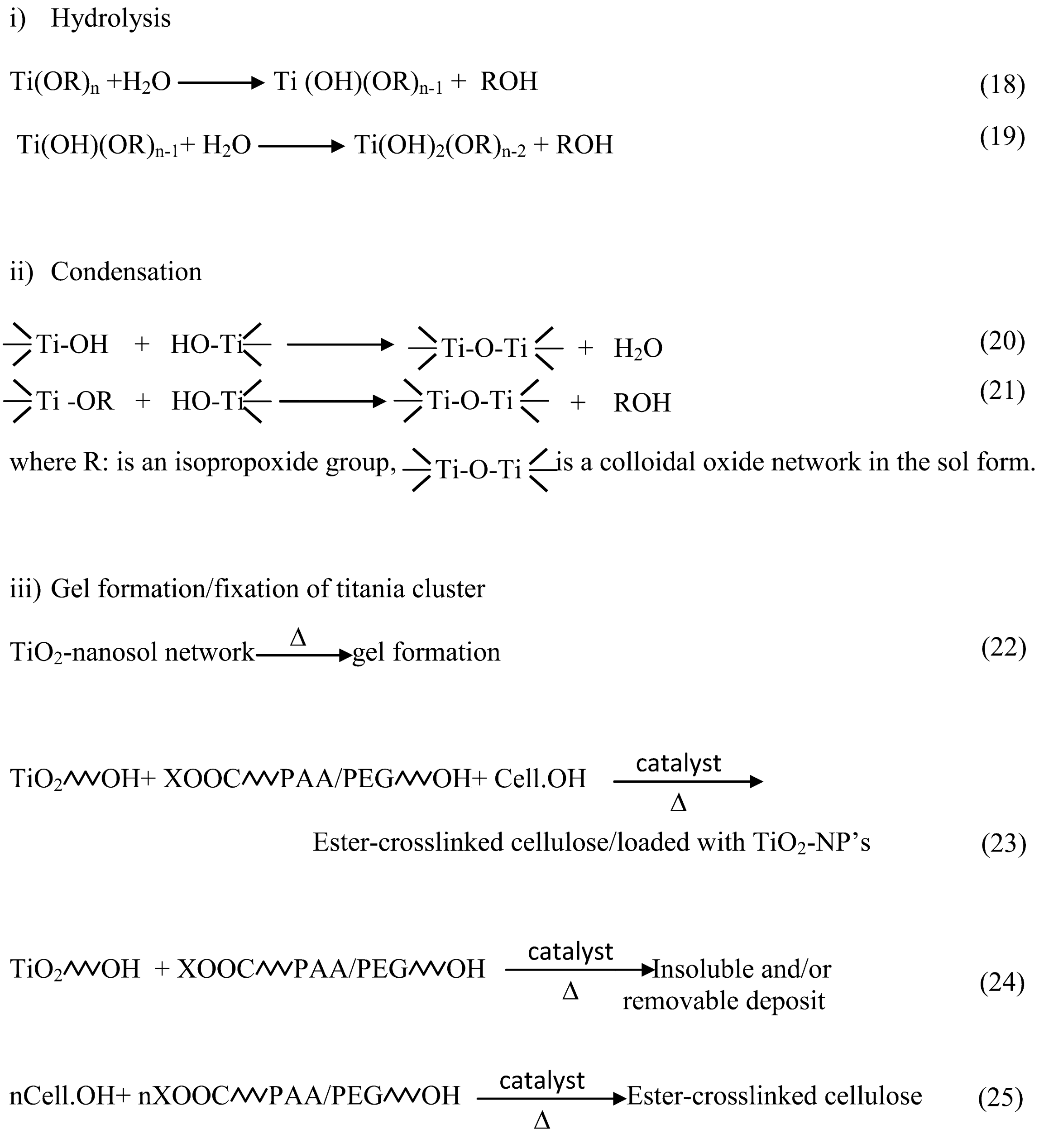
**Table 3**
Functionalization of cellulose-containing fabrics using PAA/PEG adduct along with Ti-NP's in the finishing formulation.

| Substrate | Treatment | Add-on (%) | Carboxyl content | Ti-content (%) | Wetting time (s) | Stiffness (mg cm) | UPF | ZI | | SRR | | *K*/*S* | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | *E. coli* (G−ve) | *S. aureus* (G+ve) | Exposure time | | Exposure time | |
| | | | | | | | | | | 0 | 8 | 0 | 8 |
| Cotton | Untreated | – | 1.30 | – | 2 | 530 | 8 | – | – | 2 | 2 | 0.65 | 0.55 |
| | Treated | 2.57 | 47.81 | 0.130 (0.106) | 1 | 2708 (2180) | 38 (30) | 9 (6) | 11 (9) | 3 | 5 | 5.23 | 0.38 |
| Viscose | Untreated | – | 2.31 | – | 1 | 497 | 5 | – | – | 2 | 2 | 1.15 | 0.96 |
| | Treated | 3.45 | 26.32 | 0.203 (0.164) | <1 | 7306 (5603) | 52 (42) | 15 (13) | 18 (15) | 3 | 5 | 8.22 | 0.56 |
| Cotton/polyester | Untreated | – | 3.14 | – | 4 | 427 | 18 | – | – | 2 | 2 | 0.42 | 0.30 |
| | Treated | 2.30 | 40.78 | 0.112 (0.093) | 3 | 2503 (2078) | 45 (36) | 11 (9) | 13 (11) | 3 | 5 | 3.43 | 0.28 |

*Finishing formulation*: PAA/PEG adduct (50 g/L); Na− hypophosphite (15 g/L), Ti-nanosol (2.5 g/L); wet pick-up (80%); drying at 85 °C/5 min; curing at 180 °C/2 min, UPF: UV-Protection Factors; ZI: Inhibition Zone; SRR: Stain Release Rating; *K*/*S*: Color Strength of the basic dyed samples (dye: 3% owf); exposure time 8 hrs to sunlight.
Values in parentheses indicate retained functional after 10 laundering cycles.

### 3.4.4. *Multifunctional finish*

The chemical reactions that occur during the formation of $TiO_2$-NP's using a mixture of titanium tetraisopropoxide (TIP) as a precursor along with 2-propanol and nitric acid as well as their fixation onto/in the finish/fabric matrix via the free carboxylic groups of the PAA/PEG adduct are demonstrated in Scheme 3 (Gupta et al., 2008; Ibrahim, Refaie, et al., 2010; Karimi, Mirjalili, Yazdanshenas, & Nazari, 2010; Li, Deng, & Zhao, 2009)

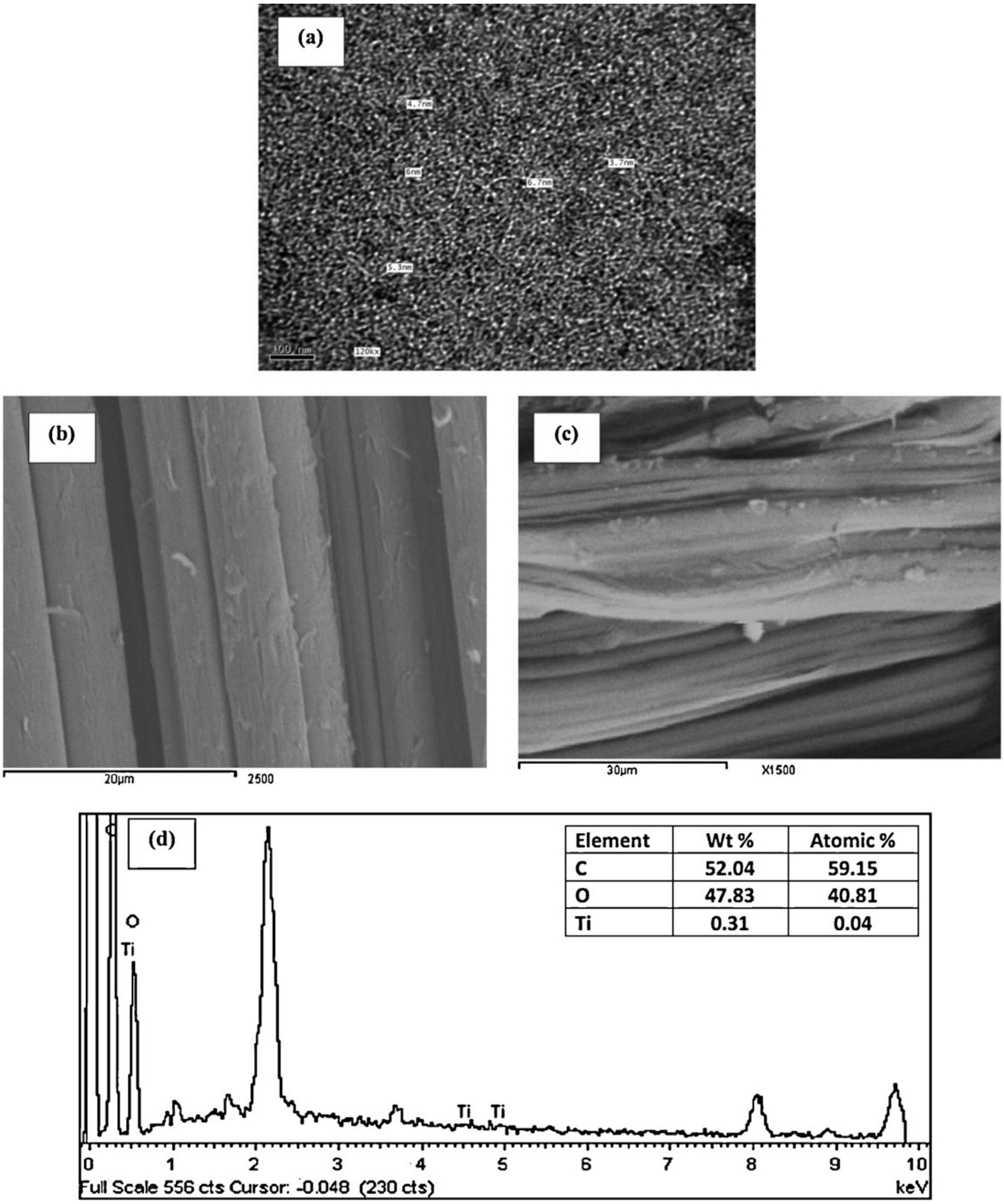


Scheme 3. Formation of $TiO_2$-NP's and their fixation onto cellulosic substrate

For confirming the abovementioned tentative mechanism, the image of the formed $TiO_2$-nanosol, the image of $TiO_2$-NP's'loaded viscose fabric, using the PAA/PEG adduct as an ester-crosslinker and as a binder, as well as the existence of elementary titanium on the fabric surface were investigated and detected [Fig. 5(a)–(d)] respectively. As depicted in Fig. 5(a) the size of nano-sol $TiO_2$, observed by TEM, is less than 10 nm with uniform distribution. On the other hand Fig. 5(b) and (c) show the images of the treated and untreated viscose samples respectively. From the image it can be observed that the untreated one has a fuzzy surface, whereas the treated one Fig. 5(b) is smooth due to the presence of $TiO_2$-NP's dispersed/loaded coating film onto the PAA/PEG finish/fabric surface. EDX measurements, Fig. 5(d), also reveal the loading of titanium on PAA/PEG/finish cotton fabric surface (Ti-content = 0.13 w/w).

Table 3 shows variations in performance and functional properties of cotton, viscose and cotton/polyester blend fabric samples as a function of $TiO_2$-nano incorporation (2.5 g/L), as a functional additive, PAA/PEG adduct (50 g/L), as a binding agent and ester-crosslinking agent, and Na-hypophosphite (15 g/L), as a an esterifying catalyst. From Table 3, it can be seen that treatment

Please cite this article in press as: Ibrahim, N. A., et al. Poly(acrylic acid)/poly(ethylene glycol) adduct for attaining multifunctional cellulosic fabrics. *Carbohydrate Polymers* (2012), http://dx.doi.org/10.1016/j.carbpol.2012.03.068



| Element | Wt % | Atomic % |
|---|---|---|
| C | 52.04 | 59.15 |
| O | 47.83 | 40.81 |
| Ti | 0.31 | 0.04 |

**Fig. 5.** (a) TEM image of Ti-NP's, (b) SEM of untreated viscose fabric, (c) SEM of treated viscose fabric, and (d) EDX image and element content of Ti-NP's loaded substrate.

with the abovementioned finishing formulation has a remarkable influence on the % add on, carboxyl content, % Ti-content and hydrophilic properties, regardless of the used substrate. The extent of improvement in the aforementioned properties is governed by: (i) type of substrate, e.g. nature of fiber, cellulosic component, amorphous/crystalline ratio, fabric structure, functional groups, etc., (ii) extent of modification by the PAA/PEG adduct, e.g. estercrosslinking, esterification, location and distribution onto/within the modified structure, availability and accessibility of the introduced carboxyl groups, etc., and (iii) extent of fixation of the $TiO_2$-NP's onto/within the finish fabric matrix, chemically via the free carboxyl groups of the adduct and/or physically via entrapment onto/within the finished fabric structure. In addition, the given results clearly indicate that treatment with PAA/PEG adduct along with $TiO_2$-NP's significantly affects the fabric handling. The higher the add on, the greater the stiffness of the fabric, viscose > cotton > polyester/cotton, as a direct consequence of estercrosslinking as well as deposition of the PAA/PEG/$TiO_2$-NP's film onto the fabric surface.

Additionally, the results also indicated that, fixation of the $TiO_2$-NP's, via the used adduct onto/within the finish/fabric matrix brings about a remarkable improvement in UV-protection, expressed as UPF values, compared with the untreated ones, and the anti-UV efficiency is governed by nature substrate, extent of modification of its structure as well as extent of loading $TiO_2$-NP's. This enhancement in UPF values reflects the scattering/absorption ability of the $TiO_2$-NP's – loaded/finished fabric surface samples (Ibrahim, Refaie, et al., 2010).

On the other hand, Table 3 shows that fixation of the $TiO_2$-NP's onto/within the finished fabric imparts a significant anti-bacterial properties against G−ve (*E. coli*) and G+ve (*S. auereus*) bacteria, regardless of the finished substrate. This reflects

Please cite this article in press as: Ibrahim, N. A., et al. Poly(acrylic acid)/poly(ethylene glycol) adduct for attaining multifunctional cellulosic fabrics. *Carbohydrate Polymers* (2012), http://dx.doi.org/10.1016/j.carbpol.2012.03.068

the higher-antibacterial activity of $TiO_2$-NP's with UV-irradiation through generation of extremely reactive species, e.g. superoxide ions, hydroxyl radicals, etc., according to the following equations (Chen, Wang, & Yeh, 2010; Ibrahim, Refaie, et al., 2010),

$$TiO_2 \xrightarrow{UV} e_{cb}{}^{-} + h_{vb}{}^{+} \tag{26}$$

$$h_{vb}{}^{+} + HO_{abs}{}^{-} \rightarrow HO^{\bullet} + TiO_2 \tag{27}$$

$$h_{vb}{}^{+} + H_2O_{abs} \rightarrow HO^{\bullet} + H^{+} + TiO_2 \tag{28}$$

$$O_2 + e_{cb}{}^{-} \rightarrow O_2{}^{\bullet} + H^{+} \rightarrow HO_2{}^{\bullet} \tag{29}$$

$$2HO_2{}^{\bullet} \rightarrow O_2 + H_2O_2 \tag{30}$$

thereby attacking the bacterial cell membrane, losing of its essential functions and destroying it.

The photocatalytic effect activity of $TiO_2$-NP's loaded on the cellulose-containing fabrics using the PAA/PEG adduct as a linking agent was investigated by the degradation of oil-satin and discoloration of C.I. Basic Blue 9 under sunlight (Table 3). For a given treatment conditions, it is clear that, exposure of the stained fabric samples to the sunlight for 8 h is accompanied by a significant improvement in the SRR. Regardless of the used substrate, i.e. higher self-cleaning performance compared with the untreated ones using stain release replica. In addition, the extent of discoloration of basic dyed/finished fabric samples is far greater than the untreated ones, regardless of the used substrate. These results clearly signify that the $TiO_2$-NP's loaded fabric samples posses a remarkable photocatalytic power compared with untreated ones, suggesting the generation of high oxidative radicals on the $TiO_2$-NP's loaded fabric surface, e.g. $HO^{\bullet}$, $HO_2{}^{\bullet}$ and consequence photocatalytic degradation of the stain and the basic dye due to the visible light irradiation (Qi, Wang, & Xin, 2011).

Moreover, the data in Table 3 also indicated that the imparted properties, i.e. stiffness, anti-UV, antibacterial as well as self cleaning, are still enough durable even after 10 washing cycles.

## 4. Conclusions

- A new water-soluble poly (acrylic acid)/poly (ethylene glycol) adduct was successfully prepared, characterized and used as a sizing agent, as stiffening agent and as binding agent for fixation of Ag-NP's and $TiO_2$-NP's independently on the cellulose containing fabrics to impart multifunctional properties.
- The prepared adduct proves to be an efficient-easily removable sizing agent for cotton cellulose.
- It's utilization as an additive in easy care finishing formulation results in imparting a durable stiffness properties along with better hydrophilic properties, i.e. wettability, stain release, dyeability with basic dyes.
- Its application as an ester-crosslinker as well as a binder for nano-materials, i.e. Ag-NP's and $TiO_2$-NP's in the presence Na-hypophosphite as catalyst brings about a significant improvement in the functional properties of the treated cellulose-containing fabrics.
- The extent of improvement in the imparted functional properties is governed by the type of substrate, extent of modification as well as type of nano-materials.
- Repeated washing cycles (10 cycles) of the treated fabric samples slightly decrease the gained functional properties.

## References

Abo-Shosha, M. H., El-Zairy, M. R., & Ibrahim, N. A. (1994). Preparation and rheology of new synthetic thickeners based on polyacrylic acid. *Dyes & Pigments*, *24*, 249–257.

Abo-Shosha, M. H., Ibrahim, N. A., Allam, E., El-Zairy, M. R., & El-Zairy, E. M. (2006). Synthesis and characterization of polyacrylic acid/dexy 85 and polyacrylic acid/gum arabic adducts. *Journal of Applied Polymer Science*, *101*, 4290–4300.

Abo-Shosha, M. H., Ibrahim, N. A., Allam, E., & El-Zairy, E. (2008). Preparation and characterization of polyacrylic acid/karaya gum and polyacrylic acid/tamarind seed gum adducts and utilization in textile printing. *Carbohydrate Polymers*, *74*, 241–249.

Bozzi, A., Yuranova, T., & Kiwi, J. (2005). Self-cleaning of wool-polyamide and polyester textiles by $TiO_2$-rutile modification under daylight irradiation at ambient temperature. *Journal of Photochemistry and Photobiology A: Chemistry*, *172*, 27–34.

Chen, C. C., & Wang, C. C. (2006). Crosslinking of cotton cellulose with succinic acid in the presence of titanium dioxide nano-catalyst under UV-Radiation. *Journal of Sol–Gel Science and Technology*, *40*, 31–38.

Chen, C. C., Wang, C. C., & Yeh, J. T. (2010). Improvement of odor elimination and anti-bacterial activity of polyester-fabrics finished with composite emulsions of nanometer titanium dioxide-silver particles – water-brone urethane. *Textile Research Journal*, *80*, 291–300.

Cirino, O. V., & Rowland, S. P. (1976). Effect of poly (sodium acrylate) finish on moisture related properties of cotton-containing durable press fabrics. *Textile Research Journal*, *46*, 272–277.

Dastijerdi, R., & Montazer, M. (2010). A review on the application of inorganic-structured materials in the modification of textiles: Focus on antimicrobial properties. *Colloids and Surfaces B: Biointerfaces*, *79*, 5–18.

El-Sayed, Z., Fahmy, H. M., Ibrahim, N. A., & Abo-shosha, M. H. (2004). Preparation of polyacrylic acid/pyrodextrins adducts and utilization in cotton sizing. *Egyptian journal of Chemistry*, *47*, 641–655.

Ganesh, V. A., Raut, H. K., Nair, A. S., & Ramakrishna, S. (2011). A review on self-cleaning coatings. *Journal of Material Chemistry*, *21*, 16304–16322.

Ghosh, P., & Das, D. (2000). Modification of cotton by acrylic acid (AA) in the presence of $NaH_2PO_4$ and $K_2S_2O_8$ as catalysts under thermal treatment. *European Polymer Journal*, *36*, 2505–2511.

Gladitz, M., Reinemann, S., & Radusch, H. J. (2009). Preparation of silver nanoparticles dispersions via a dendritic–polymer template approach and their use for antibacterial surface treatment. *Macromolecular Materials and Engineering*, *294*, 178–189.

Gupta, K. K., Jassal, M., & Agrawal, A. (2008). Sol-gel derived titanium dioxide finishing of cotton fabric for self cleaning. *Indian Journal of Textile Research*, *33*, 443–450.

Hebeish, A., Haggag, K., Abo-Shosha, M. H., & Ibrahim, N. A. (1989). Polymerization of carboxylic-containing monomers with chemical initiators. Part I. Polymerization of acrylic acid. *Acta Polymerica*, *40*, 719–723.

Hebiesh, A., Fahmy, H. M., Ibrahim, N. A., & Abo-shosha, M. H. (2006). Preparation of a chemical polyblend sizing agent via polymerization of acrylic acid with polyvinyl alcohol. *Polymer-Plastics Technology & Engineering*, *45*, 309–315.

Hoskins, J. S., Karanfil, T., & Serkiz, S. M. (2002). Removal and sequestration of iodide using sliver-impregnated activated carbon. *Environment Science & Technology*, *36*, 689–784.

Ibrahim, N. A. (1993). Optimization of desizing water-soluble sizes. V. Desizing of CMC-size. *American Dyestuff Reporter*, *82*, 18–24.

Ibrahim, N. A., & Trauter, J. (1992). Optimization of the desizability of water soluble sizes. III. Effect of size formulation. *Melliand Textilbericht*, *73*, 377–379+E169.

Ibrahim, N. A., Haggag, K., Abo-Shosha, M. H., & Hebeish, A. (1990). Polymerization of carboxylic-containing monomers with chemical initiators. Part II. Polymerization of methacrylic acid. *Acta Polymerica*, *41*, 59–63.

Ibrahim, N. A., Abo-Shosha, M. H., Elnagdy, E. I., & Gaffar, M. A. (2002). Eco-friendly durable press finishing of cellulose-containing fabrics. *Journal of Applied Science*, *84*, 2243–2253.

Ibrahim, N. A., Abo-Shosha, M. H., Allam, E., El-Zairy, M. R., & El-Zairy, E. M. (2006). New thickening agents for reactive printing of cellulosic fabrics. *Journal of Applied Polymer Science*, *101*, 4430–4439.

Ibrahim, N. A., Abo-Shosha, M. H., Allam, E. A., & El-Zairy, E. M. (2008). Effective acid printing of protein and nylon-6 fabrics using new thickening agents. *Polymer-Plastics Technology & Engineering*, *47*, 389–397.

Ibrahim, N. A., Abo-Shosha, M. H., Fahmy, H. M., El-sayed, Z. M., & Hebeish, A. A. (2008). Hybrids for finishing cotton fabric with durable handle performance. *Journal of Materials Processing Technology*, *200*, 385–389.

Ibrahim, N. A., Eid, B. M., Hashem, M. M., Refai, R., & El-Hossamy, M. (2010). Smart options for functional finishing of linen-containing fabrics. *Journal of Industrial Textiles*, *39*, 233–265.

Ibrahim, N. A., Abo-Shosha, M. H., Allam, E. A., & El-Zairy, E. M. (2010). New thickening agents based on tamarind seed gum and karaya gum polysaccharides. *Carbohydrate Polymers*, *81*, 402–408.

Ibrahim, N. A., Khalifa, T. F., El-Hossamy, M., & Tawfik, T. M. (2010). Effect of knit structure and finishing treatments on functional and comfort properties of cotton knitted fabrics. *Journal of Industrial Textiles*, *40*, 49–64.

Ibrahim, N. A., Refaie, R., & Ahmed, A. F. (2010). Novel approach for attaining cotton fabric with multi functional properties. *Journal of Industrial Textiles*, *40*, 65–83.

Ibrahim, N. A., Eid, B. M., & El-Batal, H. (2012). A novel approach for adding smart functionalities to cellulosic fabrics. *Carbohydrate Polymers*, *87*, 744–751.

Joshi, M., & Bhattacharyya, A. (2011). Nanotechnology – a new route to high performance functional textiles. *Textile Progress*, *43*, 65–83.

Judd, D., & Wyszecks, G. (1975). *Color in business science and industry* (3rd edition). New York: John Wiley & Sons.

Karimi, L., Mirjalili, M., Yazdanshenas, M. E., & Nazari, A. (2010). Effect of nano $TiO_2$ on self cleaning property of cross-linking cotton fabric with succinic acid under UV-irradiation. *Photochemistry & Photobiology*, *86*, 1030–1037.

Kelly, F. M., & Johnston, J. H. (2011). Colored and functional silver nanoparticle-wool fiber composites. *Applied Materials & Interfaces*, *3*, 1083–1092.

Please cite this article in press as: Ibrahim, N. A., et al. Poly(acrylic acid)/poly(ethylene glycol) adduct for attaining multifunctional cellulosic fabrics. *Carbohydrate Polymers* (2012), http://dx.doi.org/10.1016/j.carbpol.2012.03.068

Li, H., Deng, H., & Zhao, J. (2009). Performance research of polyester fabric treated by nano titanium dioxide (Nano-$TiO_2$) anti-ultraviolet finishing. *International Journal of Chemistry*, *1*, 57–62.

Mahltig, B., Haufe, H., & Böttcher, H. (2005). Functionalisation of textiles by inorganic sol-gel coatings. *Journal of Material Chemistry*, *15*, 4385–4398.

Martel, B., Weltrowski, M., Druffin, D., & Morcellet, M. (2002). Polycarboxylic acids as crosslinking agents for grafting cyclodextrins onto cotton and wool fabrics: Study of the process parameters. *Journal of Applied Polymer Science*, *83*, 1449–1456.

Miller, M. L. (1964). Acrylic acid polymers. In *Encyclopedia of polymer science and technology*. New York: John Wiley & Sons Inc., pp. 1, 209.

Mohammed, Z. E., Abo-Shosha, M. H., & Ibrahim, N. A. (2009). Preparation of polyethylene glycol/polyacrylamid adduct and utilzation in cotton finishing. *Carbohydrate Polymers*, *75*, 479–483.

Qi, K., Daoud, W. A., Xin, J. H., Mak, C. L., Tang, W., & Cheung, W. P. (2006). Self-cleaning cotton. *Journal of Material Chemistry*, *16*, 4567–4574.

Qi, K., Wang, X., & Xin, J. H. (2011). Photocatalytic self-cleaning textiles based on nano crystalline titanium dioxide. *Textile Research Journal*, *81*, 101–110.

Sileikaite, A., Prosycevas, I., Puiso, J., Juraitis, A., & Guobiene, A. (2006). Analysis of silver nanoparticles produced by chemical reduction of silver salt solution. *Material Science*, *12*, 287–289.

Slauson, S. D., Miller, B., & Rebenfeld, L. (1984). Physicochemical properties of sized yams. Part I: Initial studies. *Textile Research Journal*, *54*, 655–664.

Thomas, V., Bajpai, M., & Bajpai, S. K. (2011). In situ formation of silver nanoparticles within chitosan–attached cotton fabric for antibacterial property. *Journal of Industrial Textiles*, *40*, 229–245.

Vogel, A. I. (1975). *Elementary practical organic chemistry. Part 3: Quantitative organic analysis* (2nd edition). London: Longman Group Ltd., p. 652.

Welcher, F. J. (1963). *Standard method of chemical analysis. Part A*. New York: Nostrand Co., Inc., p. 475.

Yuen, C. W. M., Ku, S. K. A., Li, Y., Cheng, Y. F., Kan, C. W., & Choi, P. S. R. (2009). Improvement of wrinkle-resistant treatment by nanotechnology. *Journal of the Textile Institute*, *100*, 174–180.

Please cite this article in press as: Ibrahim, N. A., et al. Poly(acrylic acid)/poly(ethylene glycol) adduct for attaining multifunctional cellulosic fabrics. *Carbohydrate Polymers* (2012), http://dx.doi.org/10.1016/j.carbpol.2012.03.068