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# A novel approach for low temperature bleaching and carbamoylethylation of cotton cellulose

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ABSTRACT

Simultaneous $H_2O_2$-bleaching and carbamoylethylation of cotton-containing fabrics were carried out at low temperature using the pad-wet-batch technique. Factors affecting both the efficiency of modification as well as the degree of whiteness of the treated substrates such as the concentration of $H_2O_2$, as a bleaching agent, acrylamide, as an etherifying agent, and NaOH, as a catalyst, as well as batching temperature and time have been studied. Optimum conditions for maximizing the efficiency of carbamoylethylation and achieving better degree of whiteness are 20 g/L $H_2O_2$, 25 g/L acrylamide, 10 g/L NaOH at 50 °C for 2 h. The reaction mechanism was investigated. The chemical structure of the modified substrates was investigated by FTIR, and the results verified the successful introducing of carbamoylethyl group onto/into the cellulose structure. Also, it was observed that dyeability with anionic dyes, Reactive Blue 113 and Acid Blue 351 was much better in comparison with the unmodified fabric samples. On the other hand, dyeing the bleached and modified fabric with Acid Blue 351 results in a significant improvement in both UVB-protection and the antibacterial functional properties.



## 1. Introduction

Cotton cellulose has excellent properties such as higher water absorbency and moisture, being comfortable, hygiene and elegance to wear. For these reasons, the apparel industry is predominantly cotton based (Karmakar, 1999).

Cotton is very nearly pure cellulose. The non-cellulosic components, e.g., hemicelluloses, protein, fats, waxes, minerals, etc., amount to up to 9.5%. Cellulose component is a polymer of glucose, and it is quite reactive because of the three functional groups, i.e., one primary and two secondary hydroxyl groups, on each β-anhydroglucose structure unit. Penetration of chemicals and dyes within the cellulose structure occur more capably in the disordered regions, i.e., amorphous regions (Segrl & Wakelyn, 1988).

On the other hand, pretreatment processes, i.e., desizing, scouring and bleaching, serve to prepare the textile material for the subsequent wet processes, i.e., coloration and/or finishing. To ensure successful results, it is necessary to attain the following properties: uniform extraction of impurities, uniform power of absorption, high and uniform whiteness, minimum damage of textile material along with the absence of creases, taking in consideration both the economical and environmental concerns (Coudhury, 2006).

Moreover, cotton etherification can be carried out via condensation, e.g. carboxymethylation etc., or addition reactions, e.g. carbamoylethylation etc., under alkaline conditions. These modification treatments provide cotton products with useful and durable functional properties (Mazewicz & Podlas, 1993).

In the present study, attempts have been made to enhance both the degree of whiteness as well as the extent of carbamoylethylation of the scoured cotton cellulose in one step using $H_2O_2$ as a bleaching agent. Besides searching for the proper conditions for attaining better degree of whiteness along with higher extent of modification, we examine the impact of the combined process on the dyeability with anionic dyes as well as on the UV-protection and antimicrobial function of the modified substrate.

## 2. Experimental

### 2.1. Materials

Greige100% woven cotton fabric (307 g/m$^2$) and grey cotton/polyester blended (50/50) fabric (160 g/m$^2$) were supplied by Misr Company for Spinning and Weaving, Mehala EL-Kubra, Egypt.

Sodium hydroxide, acrylamide, sodium sulphate, sodium carbonate and acetic acid were of laboratory grade chemicals. Hydrogen peroxide (35%), sodium silicate, non-ionic wetting agent namely Egyptol® (based on ethylene oxide condensate) and anionic wetting agent namely Espycon® (based on fatty acid) were

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of technical grade chemicals. Reactive Blue 113 and Acid Blue 351 were kindly supplied by Clariant and Bayer Co., respectively.

### 2.2. Desizing and scouring of cotton and cotton polyester fabrics

Loomstate fabrics were treated with an aqueous solution containing 5 g/L NaOH, 0.5 g/L ammonium persulphate, 2 g/L Egyptol® and 1 g/L Espycon using material to liquor ratio (LR) 1:30. The bath temperature was gradually increased to 95 °C for 30 min. The fabrics were washed twice with boiling water then with cold water and finally dried at ambient conditions.

### 2.3. Hydrogen peroxide and carbamoylethylation in one step

Scoured fabrics were padded in an aqueous solution containing (0–20 g/L) $H_2O_2$, NaOH (0–10 g/L), sodium silicate as stabilizing agent (1 g/L), Egyptol® (2 g/L), acrylamide (0–75 g/L). The treated fabric samples were then squeezed to wet pick up 100% then batched at (25–90 °C) in an oven for (1–4 h). At the end, the samples were washed several time with hot water then with cold water and dried at ambient conditions.

### 2.4. Dyeability with anionic dyes

#### 2.4.1. Acid dyeing

Bleached carbamoylethylated fabric samples were dyed with Isolan® Dark Blue S-GL (C.I. Acid Blue 351). The dyeing procedures was carried out as follows: the fabric was introduced in aqueous bath containing, 1% dye (owf), 5 g/L sodium sulphate, and 1 g/L Egyptol®. The pH was adjusted at 5–6 using diluted acetic acid keeping the liquor ratio LR 1:30. The bath temperature was gradually raised to 40 °C and the dyeing was proceeded for 45 min. At the end of dyeing the samples were rinsed several times with cold water soaped, rinsed and finally air dried.

#### 2.4.2. Reactive dyeing

Bleached and carbamoylethylated fabric samples were dyed with reactive dye, namely Levafix Blue E3GA (C.I. Reactive Blue 113) using exhaustion method as follows: dyeing solution was first prepared using pasting technique with final dye concentration equal to 1% (owf) and LR 1: 30. The sample was introduced in the dye bath followed by addition of 25 g/L sodium sulphate and 15 g/L sodium carbonate with stirring. The dyeing temperature was gradually increased to 80 °C then another 25 g/L sodium sulphate and 15 g/L sodium carbonate was added and the dyeing process was continued for 45 min. At the end of dyeing process, the samples were thoroughly, soaped washed with hot water 10 min, then rinsed with cold water and finally dried at ambient conditions. Blank samples (i.e., bleached only without carbamoylethylation), was dyed using the same recipe.

### 2.5. Testing and analysis

- Whiteness index of the treated cotton fabrics were measured with Color-Eye 3100 spectrophotometer from SDL inter (Duff & Sinclair, 1989).
- Nitrogen content of the fabric samples was determined by the Kjeldahl method (Vogel, 1975).

efficiency percent ($F\%$) was calculated as per the following equation:

$$F\% = \frac{\text{Amount of nitrogen fixed (detected)}}{\text{Total amount of nitrogen of acrylamide applied}} \times 100$$

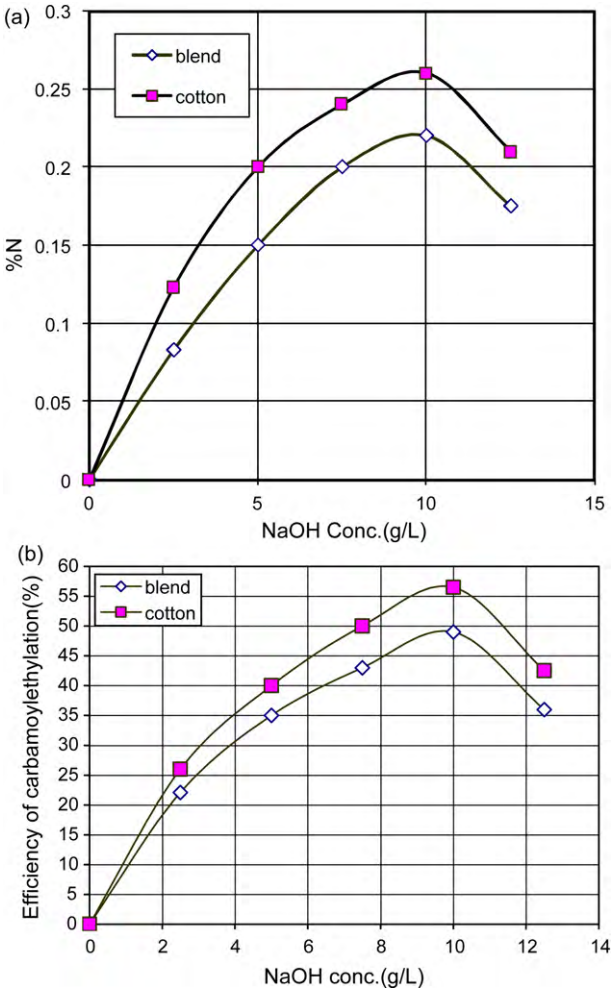



**Fig. 1.** Effect of NaOH concentration on the $N\%$ (a) and efficiency of carbamoylethylation (b) of the treated substrates.

- Determination of peroxy acids formed during the process was carried out after 5 min from mixing the path constituents according to Green and Mackellar procedure (Greenspan & MacKellar, 1948).
- Dyeability of treated and untreated fabric samples was determined by measuring $K/S$ values ($K$: absorption coefficient, $S$: scattering coefficient) at wave length of maximum absorbance for the used dyes, with Color-Eye 3100 Spectrophotometer supplied by SDL Inter. England (Duff & Sinclair, 1989).
- Antimicrobial Agar diffusion test according to AATCC Test Method 147-1988.
- UPF values were calculated according to the Australian/New Zealand Standard (AS/NZS 4399-1996).

## 3. Result and discussion

### 3.1. NaOH concentration

As far as the changes in the extent of carbamoylethylation of cotton cellulose, expressed as $N\%$ (Fig. 1a) and efficiency of etherification (Fig. 1b), of the modified/bleached substrates as a function of NaOH concentration, it is clear that:

(i) increasing NaOH concentration from zero up to 10 g/L is accompanied by a remarkable increase in both the $N\%$ and efficiency of etherification which reflects the positive role of NaOH

**Table 1**
Effect of NaOH concentration on the % formed peracid and degree of whiteness.

| NaOH conc. (g/L) | Formed peracid conc. (%) | W.I. | |
|---|---|---|---|
| | | Cotton/PET | Cotton |
| Blank | – | 20.2 | 19.2 |
| 0 | 2.1 | 45.8 | 44.7 |
| 2.5 | 2 | 39.3 | 38.5 |
| 5 | 1.8 | 37 | 35.9 |
| 7.5 | 1.6 | 35.3 | 33 |
| 10 | 1.8 | 46.6 | 45 |
| 12.5 | 1.6 | 42.6 | 42 |

Conditions used: $H_2O_2$, 5 g/L; acrylamide, 25 g/L; Egyptol®, 2 g/L; sodium silicate, 1 g/L; wet pick up 100% batched at 50 °C for 2 h in plastic bags.

in enhancing the extent of carbamoylethylation of the treated substrates (Mazewicz & Podlas, 1993);

$$\text{cell–OH} + CH_2{=}CH{-}CONH_2 \xrightarrow[\Delta]{OH^-} \text{cell–O–}CH_2CH_2CONH_2 \quad (1)$$

(ii) further increase in NaOH concentration up to 12.5 g/L, has practically a negative impact on the extent of carbamolyethylation, most probably due to partial hydrolysis of $-CONH_2$ group to –COOH group (Hashem, Bach, Kesting, Hebeish, & Scholmeyer, 1995; Mazewicz & Podlas, 1993; Song, Zhou, Zhang, & Wu, 2008);

$$\text{Cell–O–}CH_2\text{–}CH_2\text{–CO–}NH_2 \xrightarrow[\Delta]{OH^-} \text{Cell–O–}CH_2\text{–}CH_2\text{–COOH} + NH_3 \quad (2)$$

and/or

$$CH_2{=}CH{-}CONH_2 \xrightarrow[\Delta]{OH^-} OH{-}CH_2CH_2CONH_2$$

$$\xrightarrow[\Delta]{OH^-} OH{-}CH_2CH_2 \cdot COONa \quad (3)$$

(iii) the extent of improvement in both *N*% and efficiency of etherification is determined by the cellulose content, i.e., 100% cotton > cotton/polyester;

(iv) treatment of the used two substrates with acrylamide and $H_2O_2$ in the absence of NaOH, under acidic conditions (Table 1), results in a sharp increase in the degree of whiteness from 19.2 to 44.7 (for cotton) and from 20.2 to 45.8 (for blend), most probably due to the generation of peracids (PA's $-CO_3H$) in the bleaching bath under acidic conditions and their spontaneous decomposition to give oxygen as bleaching agent (Chanra & Venkata, 2000; Hickman, 2002; Ibrahim, El-Hossamy, Hashem, Refai, & Eid, 2008; Sterine, 1995; Swern, 1970, Chapter VI);

$$CH_2{=}CH{-}COOR + H_2O_2 \rightarrow \underset{\text{per-propenic acid}}{CH_2{=}CHCO_3H} + R{-}OH \quad (4)$$

$$HO{-}CH_2CH_2{-}COOR + H_2O_2 \rightarrow \underset{\text{per-hydroxypropenic acid}}{HO{-}CH_2{-}CH_2{-}CO_3H} + R{-}OH \quad (5)$$

$$2CH_2{=}CHCO_3H \xrightarrow[40\,^\circ C]{pH>5} 2CH_2{=}CHCO_2H + \underset{\text{active oxygen}}{O_2} \quad (6)$$

$$2HOCH_2CH_2CO_3H \xrightarrow[40\,^\circ C]{pH>5} 2HOCH_2CH_2COOH + \underset{\text{active oxygen}}{O_2} \quad (7)$$

**Table 2**
Effect of $H_2O_2$ concentration on the % formed peracid and degree of whiteness.

| $H_2O_2$ conc. (g/L) | Formed peracid conc. (%) | W.I. | |
|---|---|---|---|
| | | Cotton | Cotton/PET |
| 0 | 0 | 19.2 | 20.2 |
| 5 | 1.8 | 45 | 46.6 |
| 10 | 2.1 | 55.3 | 58.2 |
| 15 | 2.2 | 65.8 | 70.2 |
| 20 | 2.2 | 75 | 76.1 |
| 25 | 2.2 | 75 | 76 |

Conditions used: NaOH, 10 g/L; acrylamide, 25 g/L; Egyptol®, 2 g/L; sodium silicate, 1 g/L; wet pick up 100%; batched at 50 °C for 2 h in plastic bags.

(v) increasing the extent of formation of peracids in the bleaching bath from zero up to 2.1% confirmed the above mentioned reactions mechanism;

(vi) increase NaOH concentration from 2.5 to 10 g/L results in an improvement in the whiteness index of both substrates (from 38.5 to 45 for cotton and from 39.3 to 46.6 for blend);

(vii) further increase in NaOH concentration, i.e., beyond 10 g/L, bring about a decrease in whiteness index values most probably due to lower stability of $H_2O_2$ at higher alkalinity,.

(viii) the degree of whiteness is determined by the polyester component in the fabric, i.e. cotton/polyester blend fabric > 100% cotton fabric;

(ix) the bleaching effect of $H_2O_2$ at alkaline conditions can be explained according to the following reaction mechanisms: (Schulz, 1990; Zeronian & Inglesby, 1995).

$$H_2O_2 \xrightarrow{OH^-} HO_2^- + H^+ \quad (9)$$

$$H_2O_2 + HO_2^- \rightarrow {}^\bullet OH + {}^\bullet OOH + OH^- \quad (10)$$

$$H_2O_2 + {}^\bullet OH \rightarrow {}^\bullet OOH + H_2O \quad (11)$$

$$\bar{O}H \text{ and/or } \bar{O}OH + \text{—C=C—} \longrightarrow \text{—C(OH)–C(OH)—} + \bar{O}H \quad (12)$$

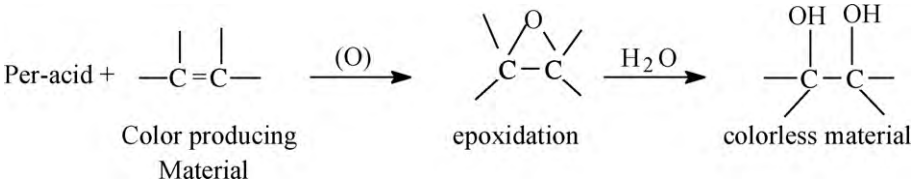
In conclusion, the optimal concentration of NaOH concentration for attaining higher efficiency of carbamoylethylation along with better degree of whiteness, regardless of the used substrate, is 10 g/L (0.25 mol) along with 25 g/L acrylamide (0.35 mol) under the given treatment conditions.

### 3.2. $H_2O_2$ concentration

For given treatment conditions, the obtained data (Fig. 2 and Table 2) signify that:

(i) increasing $H_2O_2$ concentration for zero up to 20 g/L has practically a negative impact on both the *N*% (Fig. 2a) and the efficiency of carbamoylethylation (Fig. 2b) of the treated fabric samples, regardless of the used substrate;

(ii) the decrease in the aforementioned properties most probably due to the decrement in the alkalinity of the treatment bath, partial oxidation of acrylamide into peracids [Eqs. (6) and (7)], or side interaction among the monomer molecules via addition

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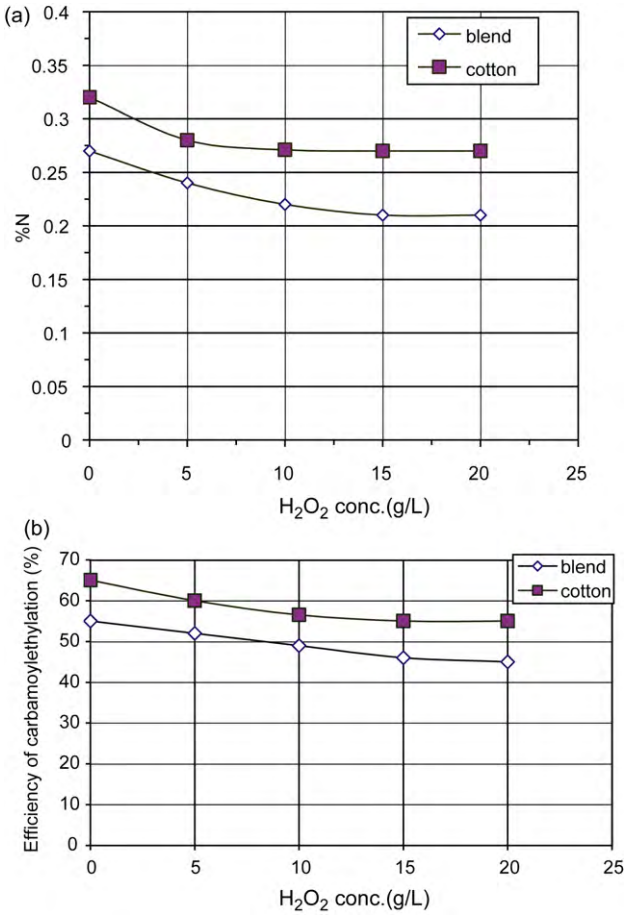


**Fig. 2.** Effect of $H_2O_2$ concentration on the *N*% (a) and efficiency of carbamoylethylation (b) of the treated substrates.

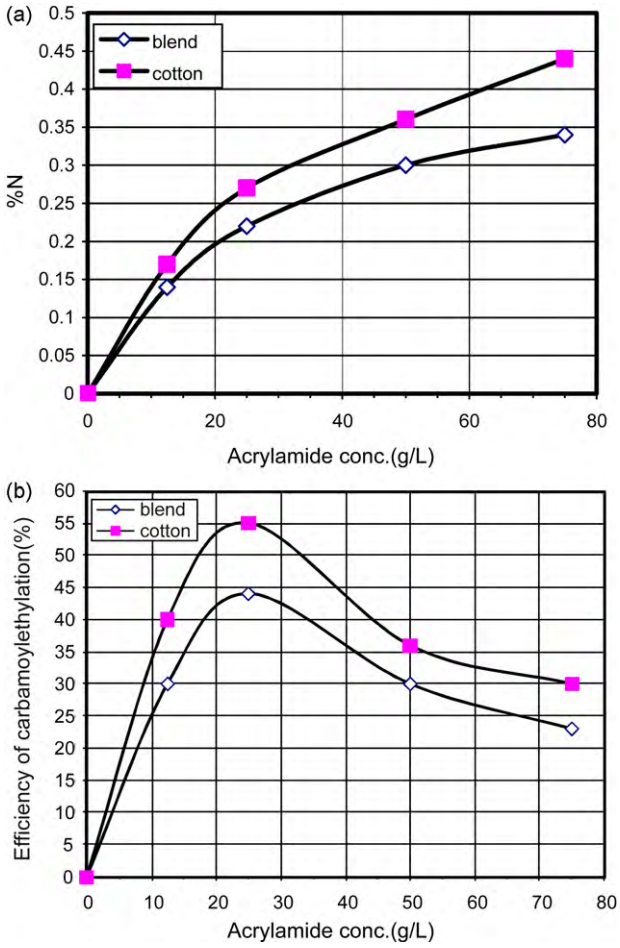


**Fig. 3.** Effect of acrylamide concentration on the *N*% (a) and efficiency of carbamoylethylation (b) of the treated substrates.

reaction and/or partial hydrolysis of carbamoylethyl group of modified cellulose [Eq. (2)];

$$CH_2{=}CH{-}CONH_2 + H_2O \xrightarrow{OH^-} OH{-}CH_2CH_2CONH_2 \quad (13)$$

$$NH_2{-}CO{-}CH{=}CH_2 + OH{-}CH_2{-}CH_2{-}CO{-}NH_2$$

$$\xrightarrow{OH^-} \underset{\text{acrylamide-diethylether}}{NH_2{-}CO{-}CH_2{-}O{-}CH_2{-}CH_2{-}CO{-}NH_2} \quad (14)$$

(iii) increasing $H_2O_2$ concentration up to 20 g/L has a positive impact on both the extent of peracids formation as well as on the whiteness index of the treated fabric samples (Table 2), most probably due to the greater destructive effect of the colored matters at higher $H_2O_2$ concentration (Karmakar, 1999; Segrl & Wakelyn, 1988);
(iv) practically no increase in the abovementioned properties was observed beyond 20 g/L $H_2O_2$.

### 3.3. Acrylamide concentration

As far as the changes in the *N*% (Fig. 3a) and efficiency of carbamoylethylation of cellulose component (Fig. 3b) as a function of acrylamide concentration, keeping acrylamide (0.35 mol)/NaOH (0.25 mol) molar ratio at 1.4 fixed, the obtained data signify that:

(i) increasing acrylamide concentration, within the range examined is accompanied by a significant increase in the *N*% of the treated fabric samples (Fig. 3a);
(ii) increasing acrylamide concentration up to 25 g/L results in a significant increase in the extent of carbamoylethylation from zero up to 55% for cotton and up to 44% for blend (Fig. 3b);
(iii) a significant decrease in the efficiency of etherification was observed beyond 25 g/L acrylamide most probably due to the side interactions explained by [Eqs. (13) and (14)] thereby forming acrylamide-diethyl ether rather than formation of cellulose ether (Hashem et al., 1995).

On the other hand, the data in Table 3 show that, increasing acrylamide concentration up to 25 g/L results in a remarkable increase in the extent of formation of peracids in the bleaching bath thereby enhancing the extent of bleaching of the treated substrates, i.e. higher degree of whiteness. Further increase in acrylamide concentration has practically no significant effect on the degree of whiteness.

**Table 3**
Effect of acrylamide concentration on the % formed peracid and degree of whiteness.

| Acrylamide conc. (g/L) | Formed peracid conc. (%) | W.I. | |
|---|---|---|---|
| | | Cotton | Cotton/PET |
| Blank | – | 19.2 | 20.2 |
| 0 | 0 | 20.8 | 22.8 |
| 25 | 2.2 | 75 | 76.1 |
| 50 | 2.5 | 75.8 | 78.7 |
| 75 | 2.7 | 74.3 | 76.3 |

Conditions used: $H_2O_2$, 20 g/L; acrylamide/NaOH molar ratio was kept at 1.4; Egyptol®, 2 g/L; sodium silicate, 1 g/L, wet pick up 100%; batched at 50 °C for 2 h in plastic bags.

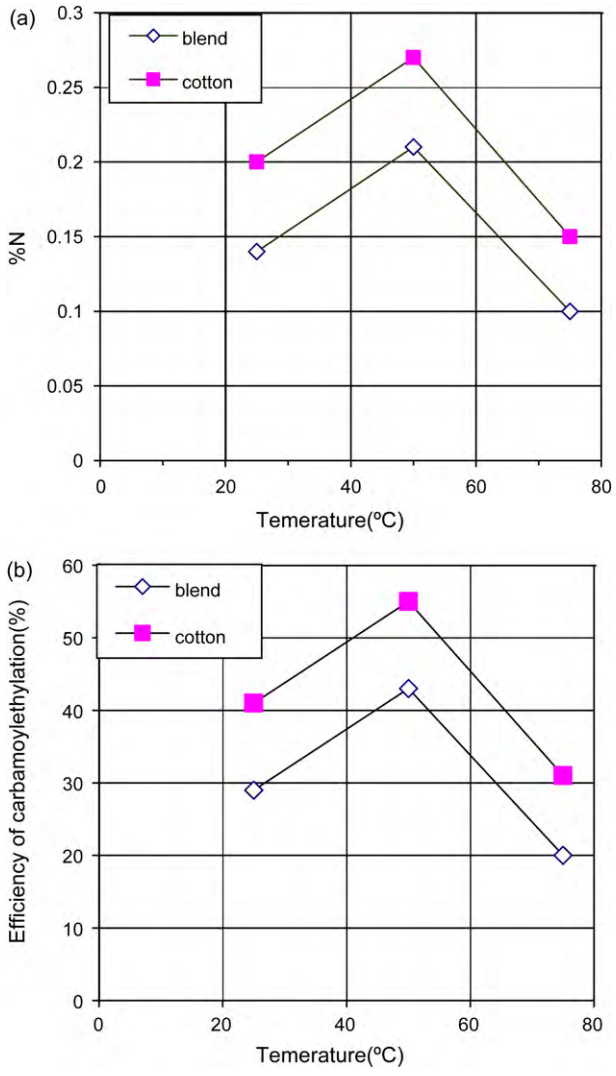


**Fig. 4.** Effect of batching temperature on the *N*% (a) and efficiency of carbamoylethylation (b) of the treated substrates.

Therefore, the optimal acrylamide concentration for attain higher extent of etherification along with better degree of whiteness, keeping in mind material conservation is 25 g/L.

### 3.4. Batching temperature

Studies on the effect of batching temperature on *N*% and efficiency of carbamoylethylation are shown in Fig. 4a and b respectively. It is clear that:

(i) raising the batching temperature from 25 to 50 °C, keeping other variable prefixed, is accompanied by a significant increase in *N*% (Fig. 4a) and the efficiency of carbamoylethylation (Fig. 4b), regardless of the used substrate;
(ii) the increase in the aforementioned properties reflects the positive impact of increasing batching temperature on enhancing: the swellability of the cellulose structure, the availability and accessibility of active sites, i.e. OH groups as well as the extent of penetration and diffusion of reactants within the cellulose structure thereby enhancing the extent of carbamoylethylation; and
(iii) use of higher batching temperature, i.e., 75 °C, impairs the extent of modification most probably due to partial hydrolysis of carbamoylethyl groups at high temperature under the used alkaline conditions [Eqs. (2)–(5)], i.e. lower *N*% and reaction efficiency.

**Table 4**
Effect of batching temperature on the % formed peracid and degree of whiteness.

| Temperature (°C) | Formed peracid conc. (%) | W.I. | |
|---|---|---|---|
| | | Cotton | Cotton/PET |
| Blank | – | 19.2 | 20.2 |
| 25 | 2.1 | 54.7 | 58.8 |
| 50 | 2.2 | 75 | 76.1 |
| 75 | 2.2 | 76.8 | 77.8 |

Conditions used: NaOH, 10 g/L; $H_2O_2$, 10 g/L; acrylamide, 25 g/L; Egyptol®, 2 g/L; sodium silicate, 1 g/L, wet pick up 100%; batched for 2 hrs in plastic bags.

On the other hand, raising the batching temperature from 25 to 50 °C, has practically a marginal effect on the percentage of formed peracid (the formed peracid increased from 2.1 to 2.2%) along with a remarkable positive impact on the whiteness index of the treated substrates (W.I. increased from 54.7 to 75 for cotton fabric and from 58.8 to 76.1 for blend fabric) as shown in Table 4. Further increase in the batching temperature has practically no effect. It is therefore concluded that, the remarkable improvement in the degree of whiteness, using the nominated ingredient, depends mainly on the strong bleaching action of the generated peracid, especially at low temperature, in combined with less bleaching effect of $H_2O_2$-active species under the used conditions (Brooks & Moore, 2000; Zeronian & Inglesby, 1995).

### 3.5. Batching time

For a given treatment conditions, the obtained results signify that:

(i) prolonging the batching time up to 2 h at 50 °C results in a significant improvement in *N*% (Fig. 5a), extent of carbamoylethylation (Fig. 5b) along with a remarkable enhancement in the degree of whiteness of the treated substrates (Table 5) without significantly affecting the improvement the percentage of formed peracid;
(ii) further lengthening of batching time has practically marginal effect on the aforementioned properties; and
(iii) current data show that, the optimal batching time for attaining acceptable efficiency of chemical modification along with higher degree of whiteness is 2 h.

### 3.6. FTIR analysis

FTIR analysis was carried out onto bleached cotton fabric (blank), bleached fabric in the presence of acrylamide and acrylamide (Figs. 6–8 respectively)

The summary of band position and their assignments (Dean, 1995; Pavia, Lampman, & Kriz, 2001) for each spectrum are set out in Table 6. It is clear that:

**Table 5**
Effect of batching time on the % formed peracid and degree of whiteness.

| Time (h) | Formed peracid conc. (%) | W.I. | |
|---|---|---|---|
| | | Cotton | Cotton/PET |
| Blank | – | 19.2 | 20.2 |
| 1 | 2.1 | 32.5 | 26.5 |
| 2 | 2.2 | 75 | 76.1 |
| 3 | 2.2 | 75.1 | 76.3 |

Conditions used: NaOH, 10 g/L; $H_2O_2$, 20 g/L; acrylamide, 25 g/L; Egyptol®, 2 g/L; sodium silicate, 1 g/L, wet pick up 100%; batched at 50 °C in plastic bags.

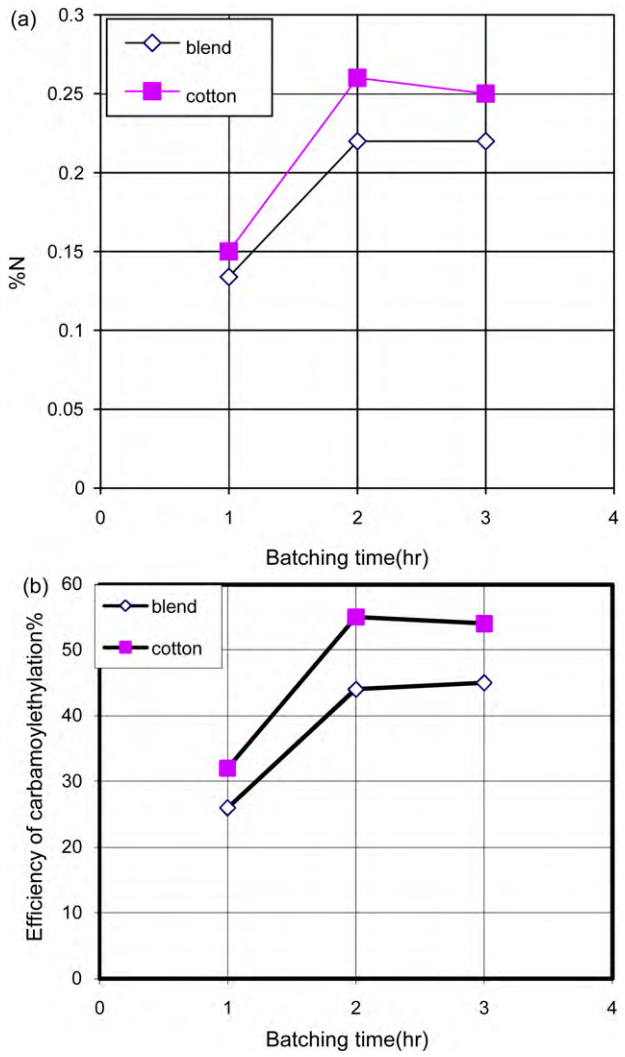


**Fig. 5.** Effect of batching time on the *N*% (a) and efficiency of carbamoylethylation (b) of the treated substrates.

- A broad strong peak at 3355 $cm^{-1}$ is attributed to stretching vibration of –NH groups. This peak was not observed in spectrum of cotton fabric bleached in the absence of acrylamide.
- In spectrum of cotton fabric bleached in the presence of acrylamide, there is a medium peak at 1655 $cm^{-1}$ assigned for –C=O stretching vibration of carboxylic groups. This peak was also not observed in the spectra of cotton fabrics bleached in the absence of acrylamide.
- In spectrum of cotton fabric bleached in the presence of acrylamide a medium peak at 1241 $cm^{-1}$ is assigned for –C–N stretching. This band is not observed in spectrum of cotton fabric bleached in the absence of acrylamide.

The above findings indicate the formation of carbamoylethyl cotton cellulose during its bleaching in the presence of acrylamide.

### 3.7. Post-dyeing and functional finishing

The impact of pre-modification on subsequent anionic dyeing or functional finishing of cotton and cotton/polyester blend fabrics was investigated. The results are showed in Table 7. It shows that:

(i) introduction of $CH_2$–$CH_2CONH_2$ moieties onto and/within the cellulose structure via modification brings about a significant increase in dyeability with reactive and acid dyes used, regardless the type of substrate;
(ii) the higher the cellulose content, the higher is the extent of modification, i.e., *N*%, and depth of shade, i.e., *K*/*S*, of the obtained dyeings;
(iii) the extent of post-dyeing is determined by number, location and availability of active sites, i.e. –OH and –$CONH_2$ groups, as well as on the type and nature of the used dye, e.g., dye molecular size, functionality, fiber-dye capacity, mode of interaction and fixation (via covalent dye-fiber bond as in case of reactive dyeing or ionic and/or physical bonds as in case of acid dyeing) (EL-Hilw & Hebeish, 1999; Ibrahim, 1995);
(iv) subsequent dyeing of the modified substrates with Acid Blue 351 (chrome containing dye) results in or remarkable improvement in the UVB-protection, expressed as UPF value., and the UPF values follow the decreasing order: modified cotton fabric followed by acid dyeing > modified cotton fabric > bleached fabric reflecting the higher UVB-absorption capacity imparted

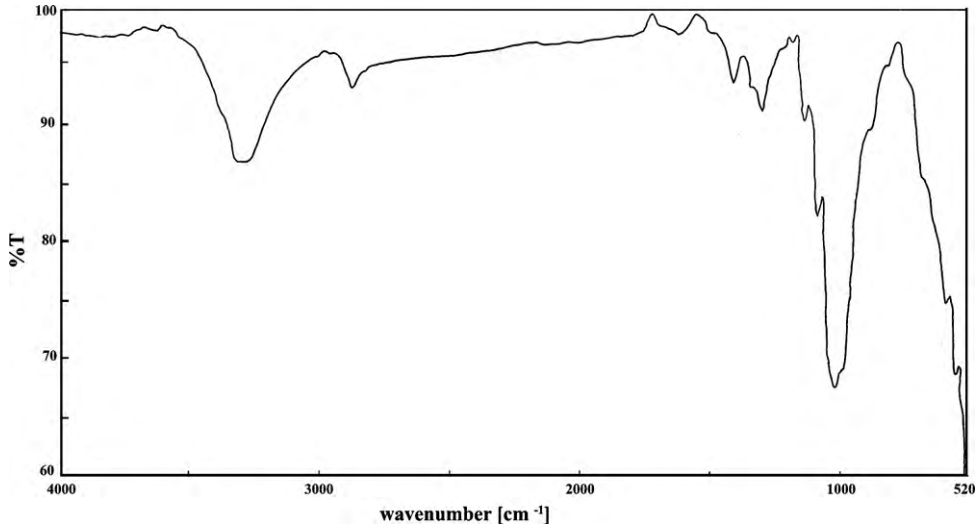


**Fig. 6.** Cotton.

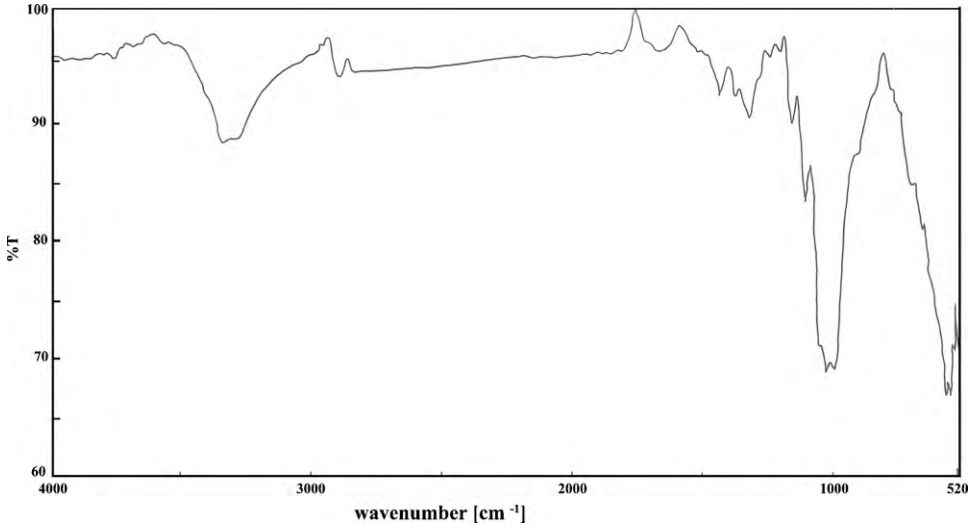


**Fig. 7.** Modified cotton.

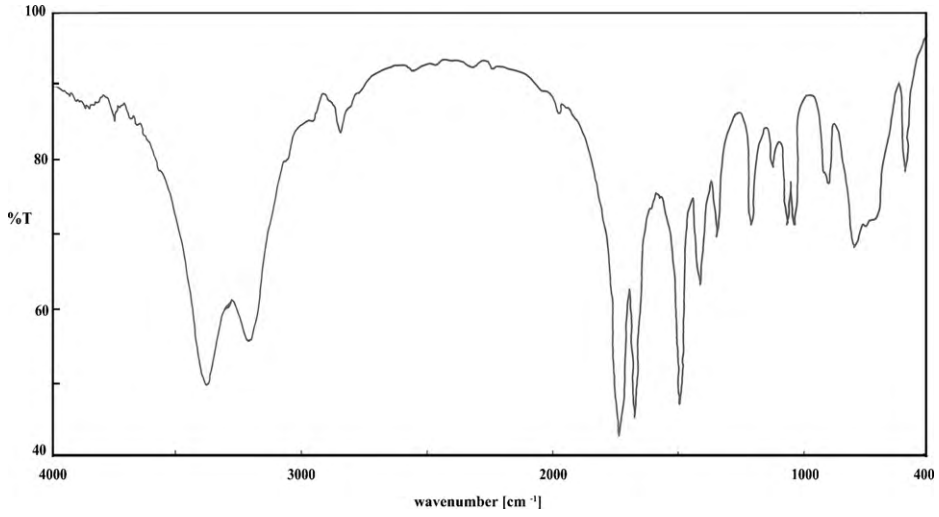


**Fig. 8.** Acrylamide.

to the fabric by the used acid dye (Ibrahim, Eid, Hashem, Refai, & El-Hossamy, 2010; Ibrahim, Mahrous, El–Gamal, Gouda, & Husseiny, 2010);

(v) post-dyeing of modified substrates using Acid Blue 351 dye is accompanied by upgrading the antibacterial activity of the obtained dyeing, against gram positive bacteria (*Staphylococcus aurous*) and gram negative bacteria (*Escherichia coli*); and

(vi) the antibacterial activity is determined by the extent of dyeing of modified substrate i.e. cotton > blend, as well as the type of

**Table 6**
Peaks assignment of bleached cotton in the absence (Fig. 6) and presence of acrylamide (Fig. 7) as well as acrylamide alone (Fig. 8).

| Bleached cotton in the absence of acrylamide (Fig. 6) | | Bleached cotton in the presence of acrylamide (Fig. 7) | | Acrylamide (Fig. 8) | |
|---|---|---|---|---|---|
| Peak ($cm^{-1}$) | Assignment | Peak ($cm^{-1}$) | Assignment | Peak ($cm^{-1}$) | Assignment |
| – | – | 3355 | –NH stretching | 3355 | –NH stretching |
| 3331 | Alcoholic –OH stretching | 3300 | Alcoholic –OH stretching | 3188 | C=C–H stretching |
| 2891 | Aliphatic $-CH_2$ stretching | 2888 | Aliphatic $-CH_2$ stretching | 2814 | Aliphatic $-CH_2$ stretching |
| – | – | 1655 | C=O stretching of amide | 1674 | C=O stretching vibration |
| | | | | 1612 | C=C stretching vibration |
| 1428 | Aliphatic $-CH_2$ bending | 1427 | Aliphatic $-CH_2$ bending | 1428 | C–CH in plan bending |
| 1365 | –CH bending (deformation stretching) | 1364 | –CH bending (deformation stretching) | 1350 | C–H bending vibration |
| 1338 | –OH in plan bending | 1337 | –OH in plan bending | 1278 | –C–N bond stretching |
| 1318 | –CH Waging | 1315 | –CH Waging | 989 | Out of plan C=C–H bending |
| 1154 | –C–O–C– asymmetric bridge stretching | 1241 | –C–N bond stretching | 961 | Out of plan C=C bending |
| 1103 | –C–O–H bending of secondary alcoholic | 1155 | –C–O–C– asymmetric bridge stretching | | |
| 1024 | –C–O stretching | 1105 | –C–O–H bending of secondary alcoholic | | |
| 905 | Asymmetric out-of-phase ring stretch $-C_1-O-C_4$ β-glucosidic bond | 1024 | –C–O stretching | | |

**Table 7**
Effect of pre-modification on dyeability and functionality of the modified substrates.

| Substrate | *N* (%) | Efficiency (%) | UPF | Inhibition clear zone (mm) | | Dyeability (*K*/*S*) | |
|---|---|---|---|---|---|---|---|
| | | | | *E. Coli* (G −ve) | *St. aureus* (G +ve) | Reactive Blue 113 | Acid Blue 351 |
| Cotton | | | | | | | |
| Bleached | – | – | 8 | 0 | 0 | 3.28 | 0.0 |
| Modified | 0.24 | 55 | 15 | 0.9 | 1.1 | 24.7 | 6.0 |
| Modified dyed with Acid Blue 351 | 0.24 | 55 | 121 | 14 | 15 | – | 6.0 |
| Blend | | | | | | | |
| Bleached | – | – | 14 | 0 | 0 | 2.33 | 0.0 |
| Modified | 0.22 | 44 | 22 | 0.5 | 0.7 | 8.7 | 2.5 |
| Modified dyed with Acid Blue 351 | 0.22 | 44 | 89 | 12 | 14 | – | 2.5 |

bacteria, G +ve > G −ve, most probably due to the difference in the susceptibility of the cell wall to damage as well as in response to inactivation and/or inhibition (Ibrahim, Eid, et al., 2010; Ibrahim, Mahrous, et al., 2010).

## 4. Conclusions

This paper described the technical feasibility of carrying out $H_2O_2$-bleaching and carbamoylethylation of cotton cellulose in one step process using the pad-wet-batch technique. The extent of etherification and the whiteness index of the treated substrates depend on reactant concentration, the batching conditions as well as cellulose content of the fabric, i.e. cotton or cotton/polyester. The net advantage in case of using this combined process include lower temperature, shorter time, better whiteness, as well as higher reactivity of modified cotton cellulose. The modified substrates showed a much higher *K*/*S* value than the unmodified ones after subsequent dyeing with reactive or acid dyes. The obtained acid dyeings, using Acid Blue 351, showed a significant improve in their UVB-protection values as well as in their antibacterial activities against gram positive and gram negative bacteria in comparison the un-dyed ones.

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