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Improving easy care properties of cotton fabric via dual effect of ester and ionic crosslinking

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ABSTRACT

To enhance the easy care finishing properties of cotton fabric along with maintaining its mechanical properties, a new route based on ionic crosslinking was employed. In this research work, pre-cationized cotton fabric was crosslinked using ammonium citrate in presence of sodium hypophosphite at 180 °C for 90 s. The effect of cationization level and ammonium citrate as well as silicon micro-emulsion softener concentrations on the performance properties of cotton fabric was determined. Results obtained show that the pre-cationization of cotton fabric having 0.09% nitrogen followed by crosslinking with 6% ammonium citrate brings about an enhancement in both dry and wet recovery angles along with a slight improvement in TS. Furthermore, the pre-cationized sample having the nitrogen content of 0.09% was characterized before and after ester crosslinking with 6% ammonium citrate (compared with an untreated sample) using thermo gravimetric analysis and Scanning Electron Microscope.

1. Introduction

Easy-care and durable press finishes are generally applied to cellulose and cellulose blend fabrics. Many chemical types of finishes have been used such as *N*-methylol compounds and polycarboxylic acids (Bajaj, 2002; Fahmy & Fouda, 2008; Fouda, El Shafei, Sharaf, & Hebeish, 2009). *N*-Methylol compounds are believed that they release formaldehyde which is a possible human carcinogen. Polycarboxylic acids cause yellowing as well as a remarkable loss in the mechanical properties of the finished fabrics (Schindler & Hauser, 2004). Many attempts were made to overcome these disadvantages (Bajaj, 2002). A novel approach has been conducted into novel chemical finishes based upon ionic crosslinking (El-Shafei, Fouda, Knittel, & Schollmeyer, 2008; Hashem, Ibrahim, Refaie, El-Shafie, & Hauser, 2009; Hashem, Refaie, Goli, Smith, & Hauser, 2009). Recently, PVP had been considered a new approach for crosslinking cellulosic fabrics (Fahmy, 2009; Fahmy, Abo-Shosha, & Ibrahim, 2009).

With the above in mind, the present work was undertaken with a view to enhance the ester crosslinking of cotton fabrics via ionic crosslinking.

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2. Experimental

2.1. Materials

Mill scoured and bleached cotton fabric (147 g/m^2) was used. The fabric was washed with an aqueous solution containing 2 g/L non ionic detergent for 30 min, thoroughly rinsed and dried at ambient conditions. 3-Chloro-2-hydroxypropyl trimethyl ammonium chloride (65%, w/w) under a commercial name (CR-2000), supplied by DOW Chemical Company, USA, was used as a cationizing agent for cotton fabric. Silicon-SLH® (silicon micro emulsion) (SME) – supplied by Texchem Egypt Co., Ltd.) were used. Ammonium citrate (AC), citric acid (CA), sodium hypophosphite monohydrate (SHP) and sodium hydroxide were of reagent grade.

2.2. Fabric treatments

Four sets of cotton fabrics were firstly cationized using pad-batch method where every set was padded in an aqueous solution containing a mixture of specific concentration of NaOH and CR-2000 followed by squeezing to 90% wet pick up, then stored in air tight plastic bags for 24 h at room temperature. The four concentrations of NaOH are 4.80, 9.56, 19.20 or 28.80 g/l whereas those of CR-2000 are 15.40, 30.80, 61.50 or 123.0 g/l respectively. The fabrics were then washed with distilled water to remove spent reactants and excess alkali, and then neutralized with acetic acid. It was found that the %N of the aforementioned treated four

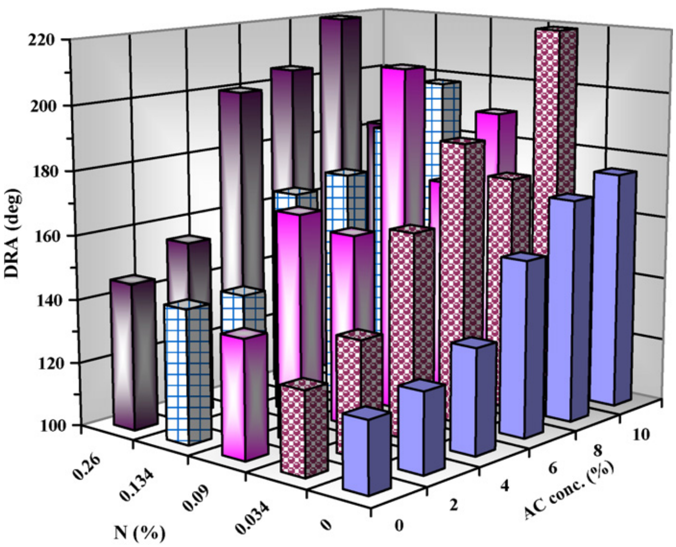


Fig. 1. Effect of ammonium citrate concentration and nitrogen content on dry wrinkle recovery angle of cotton fabric.

sets are 0.0342, 0.0891, 0.1304 and 0.2603% respectively (according to the used previous concentrations of NaOH and CR-2000). The second step consisted of padding pre-cationized cotton fabric (obtained in the first step) in aqueous solution containing ammonium citrate (AC) and sodium hypophosphite (SHP) with specific concentrations then squeezed to a wet pick up of 90%, dried in a circulating air oven at 85 °C for 3 min, and cured at 180 °C for 90 s. The cured cotton fabrics were then rinsed with distilled water at 40 °C for 10 min, dried and air-conditioned prior to evaluation.

2.3. Fabric evaluation

Nitrogen content was determined according to Kjeldahl method (Vogel, 1975). Carboxyl content was determined according to the Cirino method (Cirino & Rowland, 1976). Dry and wet wrinkle recovery angles (WRA) were determined by the ASTM method D-1296-67 using the iron recovery apparatus, type FF-07 (Metrimpex). The tensile strength (TS) was determined, in the warp direction, according to ASTM procedure D-2256-66T. CIE Whiteness Index (WI) was measured according to AATCC test method 110-1989 using a Milton Roy Color Mate spectrophotometer. Surface roughness (SR) was determined according to JIS 94 Standard test method using the surface roughness measuring instrument, SE 1700a. The absorbency test (W) was carried out according to AATCC test method 79-1992.

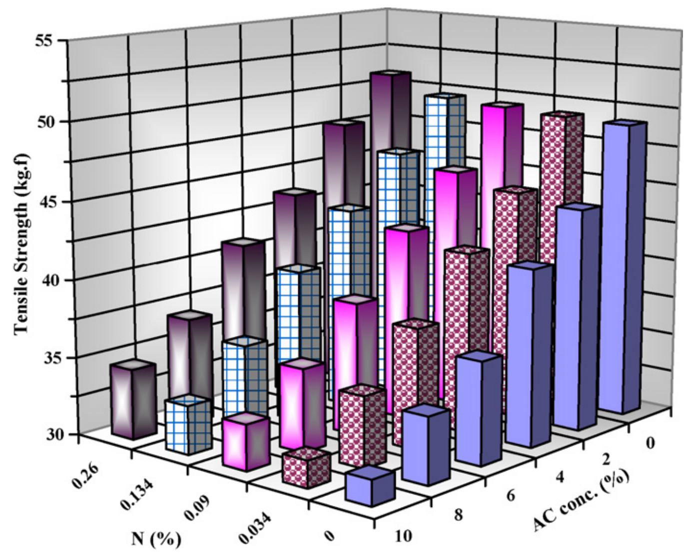


Fig. 3. Effect of ammonium citrate concentration and nitrogen content on the fabric tensile strength.

3. Results and discussion

It was believed that polycarboxylic acids, such as citric acid, can crosslink cellulosic fabrics through an anhydride intermediate mechanism (Fouda & Fahmy, 2011; Schindler & Hauser, 2004). To enhance the ester crosslinking of cotton fabrics along with minimizing the loss in the mechanical properties, cotton fabrics were pre-cationized then crosslinked with ammonium citrate. The effect of cationization level and citric acid concentration as well as

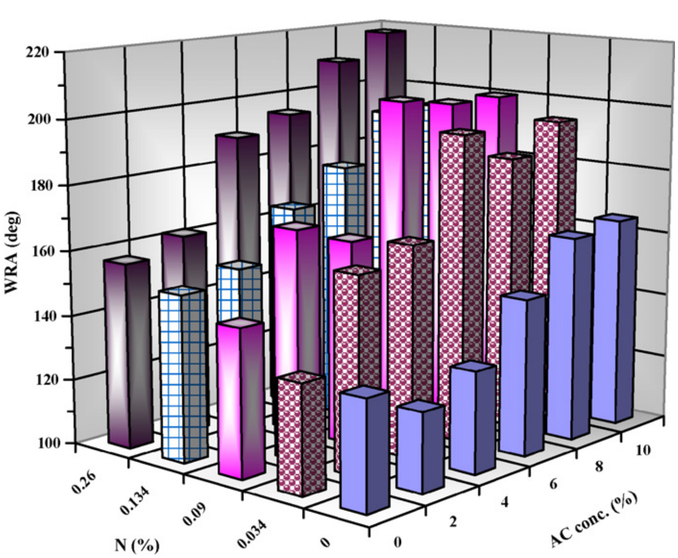


Fig. 2. Effect of ammonium citrate concentration and nitrogen content on wet wrinkle recovery angle of cotton fabric.

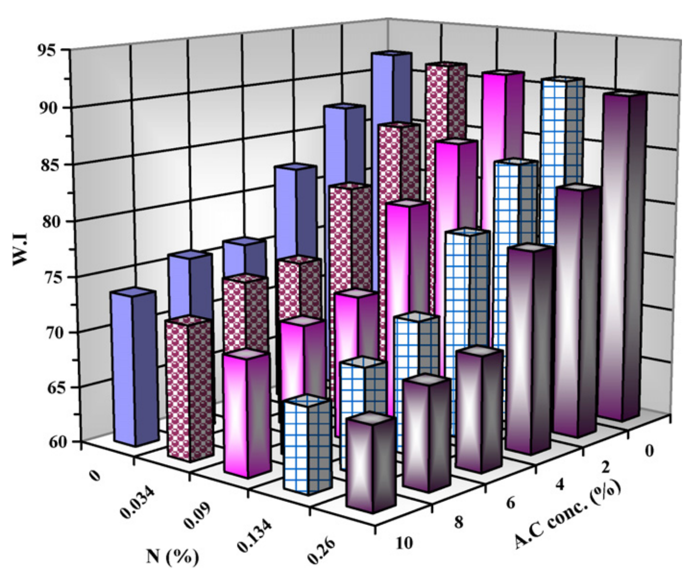


Fig. 4. Effect of ammonium citrate concentration and nitrogen content on the whiteness indices (WI) of treated cotton fabrics.

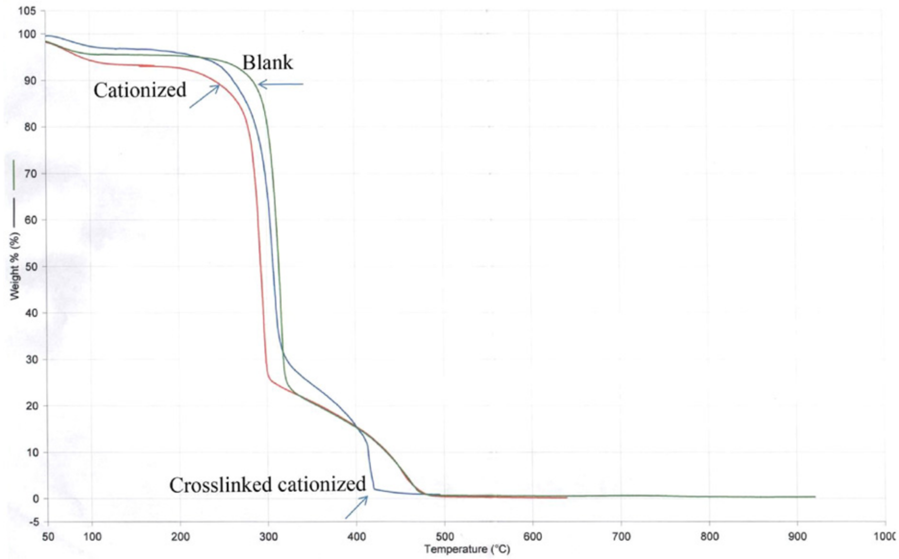


Fig. 5. TGA of untreated (blank), crosslinked and crosslinked pre-cationized cotton fabrics.

Table 1
Comparative study on the effect of ammonium citrate vis a vis citric acid.

Type of finishing treatment	DRA (°)	WRA (°)	TS (kgf)	EB (%)	WI	Carboxyl content (mequiv./100 g)
Untreated (blank)	122	133	49.1	10.0	92.0	3.1
Cationized cotton	137	145	49.4	10.2	91.1	2.9
Citric acid	180	172	32.1	4.6	79.9	66
Citric acid plus cationization	225	240	35.3	6.3	78.4	64
Ammonium citrate	155	148	36.5	6.8	76.1	49
Ammonium citrate plus cationization	209	203	38.5	7.1	73.2	46

The nitrogen content of cationized cotton fabric equal 0.0891%; [ammonium citrate], 6%; [SHP], 6%; AC/SHP molar ratio, 1; wet pick-up, 100%; drying, 100 °C/3 min; curing, 180 °C/90 s.

reaction time and temperature on the performance properties of cotton fabric was determined. Results obtained along with appropriate discussion is given below.

3.1. Crosslinking of pre-cationized cotton fabrics: effect of process parameters

3.1.1. Effect of ammonium citrate concentration

Figs. 1 and 2 show the dependence of dry and wet recovery angle, respectively of cotton fabrics on degrees of cationization (expressed as nitrogen content of the fabric) and ammonium citrate concentrations. It is obvious that: (i) regardless of the cationization level, the crosslinking of cotton fabrics enhances the dry resiliency of treated fabrics, (ii) the ester crosslinking of cationized fabrics enhances the dry resiliency of treated fabrics with higher extents compared with than the un-cationized samples, and (iii) both dry and wet recovery angle of cationized and crosslinked fabric attained highest values when the cationized cotton fabric having 0.09% nitrogen content was crosslinked with 6% ammonium citrate.

Higher resiliency of crosslinked cationized cotton fabric can be explained in the light of additional crosslinking resulted from ionic interaction between the negatively charged carboxyl groups (imparted to the fabric after the crosslinking with ammonium citrate) and the positively charged quaternary amino groups. Higher resiliency was achieved when the all negatively charged groups located intra/inter the cotton cellulose are mostly ionically interact with the positively charges cationic groups.Scheme 1 can explain the mechanism of both the ester as well as ionic crosslinking of cationized cotton fabrics (Hashem, Hauser, & Smith, 2003).

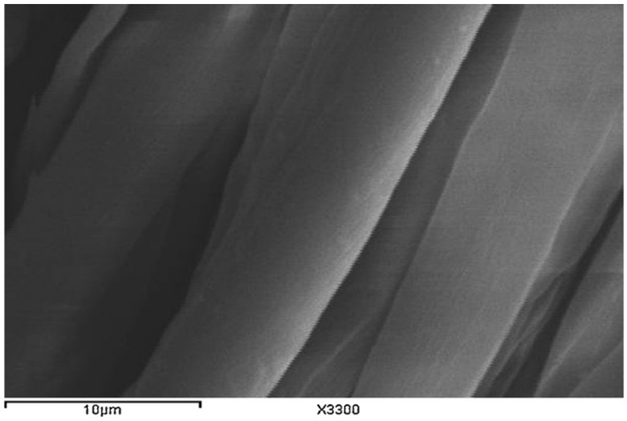
Structures I and/or II may explain the additional extents of crosslinking when cationized cotton samples are esterified with citric acid. The second step in the above mechanism may explain the improvement in wet WRA of cotton samples, where ionic bonds are formed in the wet state during the finishing with citric acid.

The dependence of tensile strength (TS) of the cationized and crosslinked cotton fabric on both ammonium citrate concentration and cationization level (expressed as nitrogen content) is shown in Fig. 3. It is clear that, pre-cationization of the ester crosslinked

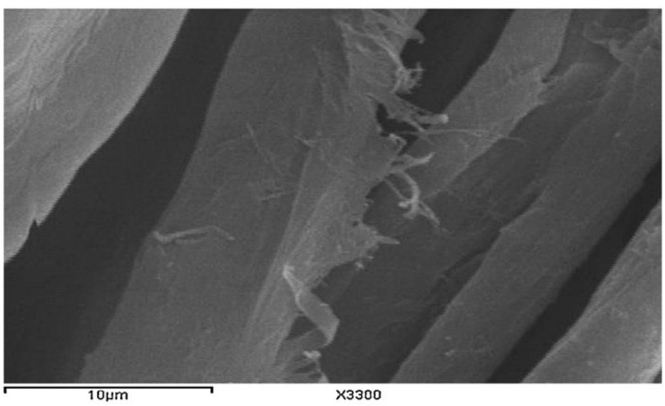
Table 2
Effect of concentration of SME on the performance properties of treated cotton fabrics.

SR	WI	Wettability (s)	TS (kgf)	DRA (°)	Nitrogen content (%)	SME conc. (g/l)
14.32	92	2.28	49.1	122	–	Untreated
14.89	73.2	3.21	38.5	209	0.0812	Control
14.11	70.3	29	35.2	228	0.1266	10
12.86	68.1	79	33.4	249	0.1431	20
12.42	66.8	89	31.8	263	0.1623	30

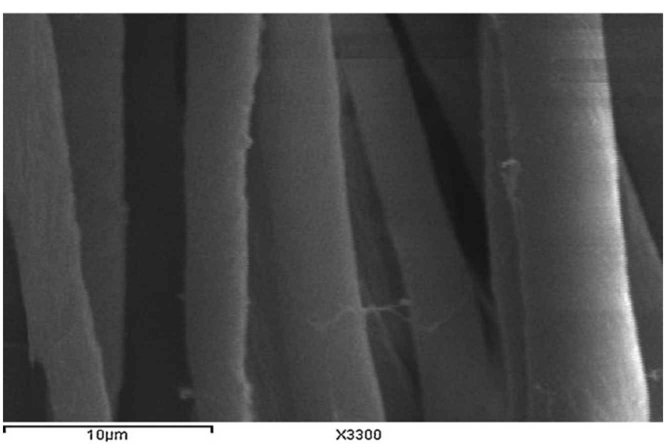
The nitrogen content of cationized cotton fabric equal 0.0891%; [ammonium citrate], 6%; [SHP], 6%; AC/SHP molar ratio, 1; wet pick-up, 100%; drying, 100 °C/3 min; curing, 180 °C/90 s. Control sample is the cationized sample which have nitrogen content of 0.0891% then crosslinked with 6% ammonium citrate.



(a) SEM of untreated cotton fabric



(b): SEM of cotton fabric crosslinked with ammonium citrate.



(c): SEM of crosslinked pre-cationized cotton fabric

Fig. 6. SEM of (a) untreated cotton fabric; (b) cotton fabric crosslinked with ammonium citrate; (c) cotton fabric cationized followed by crosslinking with ammonium citrate.

cotton samples brings about a slight enhancement in the TS and that enhancement increases with increasing the cationization level. This can be attributed to the extra force imparted to the fabric by ionic interaction between the negatively charged carboxyl groups and the positively charged quaternary amino groups (Fahmy, 2004; Hashem, Refaie, et al., 2009).

Fig. 4 shows the effect of ammonium citrate concentration and degree of cationization (expressed as nitrogen content) on the whiteness of the cotton fabric. The data in Fig. 4 signify that esterification of the uncationized samples is accompanied by decrease in WI which is a direct consequence of the partial dehydration of citric acid and formation of unsaturated acids (Schindler & Hauser, 2004). Moreover, the esterification of the pre-cationized samples leads to decrement in fabric WI. However, the values of WI remain at acceptable level if the degree of cationization remains at lower level.

3.1.2. Comparative study on the effect of ammonium citrate vis a vis citric acid

Table 1 shows a comparative study on the effect of ammonium citrate vis a vis citric acid for ester-crosslinking of both the uncationized and cationized cotton fabrics. The results in Table 1 reveal that, upon using citric acid as a crosslinker, both wet and dry wrinkle recovery angles were higher compared with those obtained with ammonium citrate as crosslinker. The same holds true for whiteness index (WI) and carboxyl content whereas, a value of tensile strength (TS) is higher than that of the citric acid as a crosslinker. This order reflects the differences between these crosslinkers in: (a) the reactivity, (b) activation energy, (c) functionality, (d) structure as well as thermal stability, (e) level and extent of esterification, and (f) location, number and length of crosslinks (Fahmy, 2004).

3.1.3. Soft finishing of crosslinked pre-cationized cotton fabric

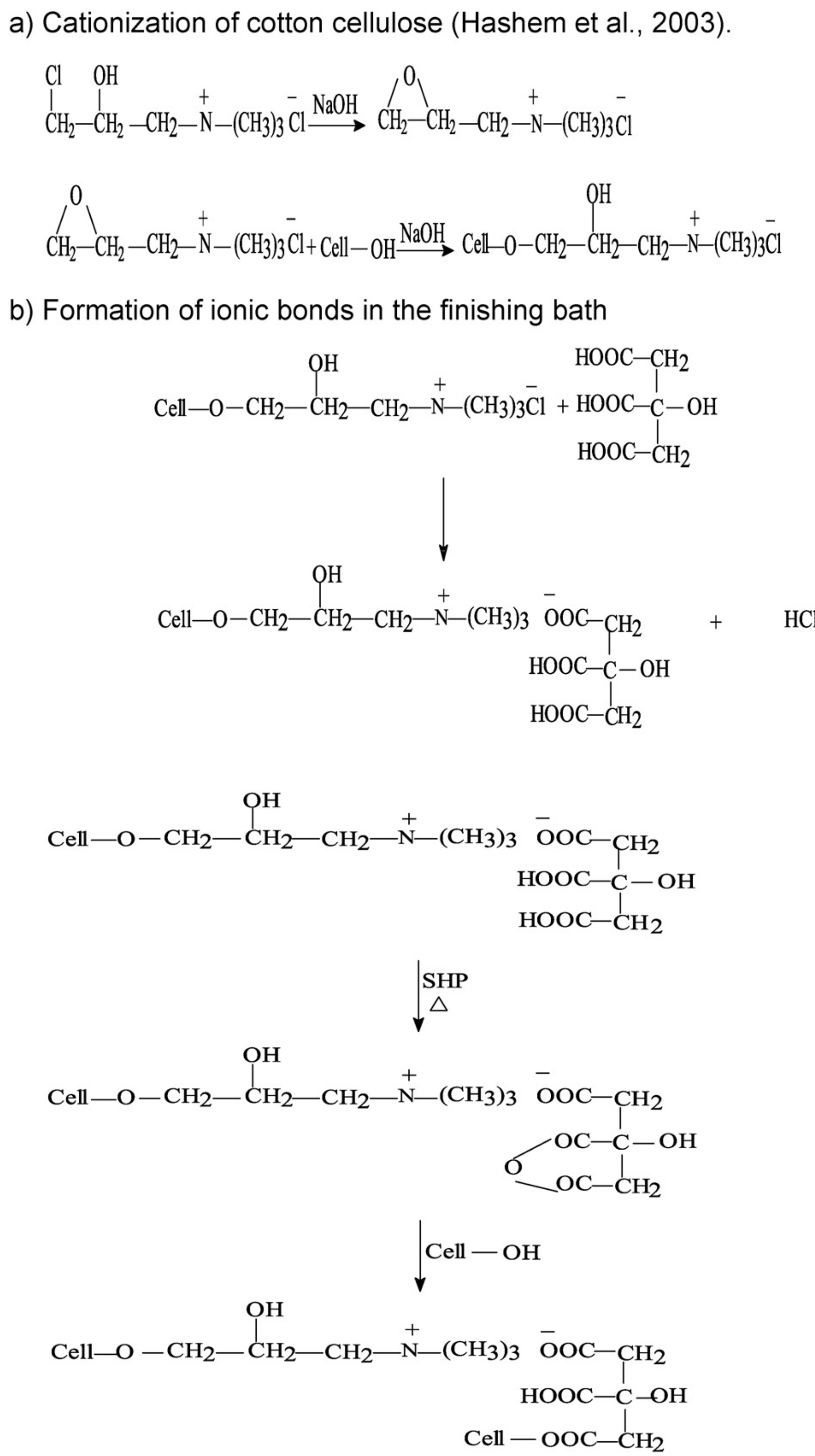
The pre-cationized cotton sample having the nitrogen content of 0.09% and crosslinked with 6% ammonium citrate was treated with different concentrations of silicone microemulsion softener (0–30 g/l). Results obtained are set out in Table 2. Table 2 shows that increasing the softener concentration enhances the N%, DRA as well as SR along with a slight decreasing in both TS and WI. The basic function of a softener is to impart a particular handle to a textile surface to make the garment or fabric feel more appealing. Of the silicone softeners available, perhaps the most common in current industrial usage are the amino functional types. Amino-functional groups linked to polydimethylsiloxanes enable an improved orientation and substantively of the silicone on the substrate. This leads to an optimally soft handle and is often described by the term "super soft". Amino silicones are by far the most extensively used functional silicones for textile finishing applications. These emulsions exhibit a positive surface charge and thus get attracted by the negatively charged fabric surface, leading to a strong sorption. Such favourable charge distribution facilitates superior molecular distribution and higher sorption at lower solution concentrations, leading to favourable process economics. Thus by virtue of their positive surface charge, these emulsions are the best choice for most cellulose fabrics such as cotton or ester crosslinked cotton with polycarboxylic acid (Habereder, 2002).

Actual surface modification is caused by specific properties of the silicone molecules and the functional groups attached. These properties include, (a) lubrication and decreased frictional coefficient due to the lower intermolecular interactions between neighbouring methyl groups, together with easy molecular rotation around the oxygen group of the silicone chain and (b) antistatic properties of the amine functional groups.

The partially protonated amino groups of the silicone microemulsion molecule ionically interact with negatively charged cotton cellulose or residual carboxyl groups imparted to the cotton fabric after ester crosslinking with AC. This indeed promotes the idea behind the work discussed in this paper (An, Li, Li, Jin, & Zhang, 2007; Habereder, 2002; Kulkarni, Deshpande, & Kushare, 2001; Teli, Paul, & Pardeshi, 2000).

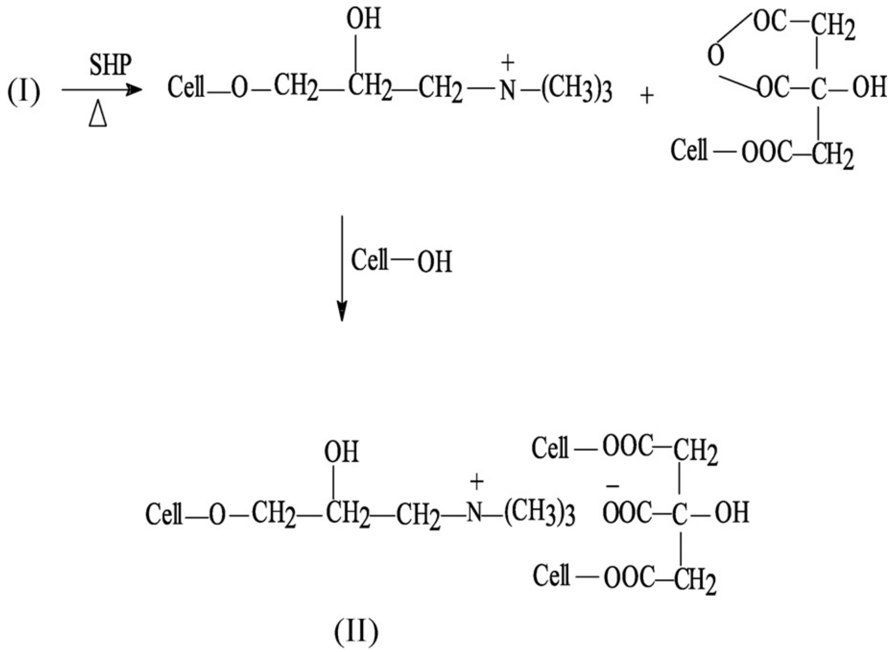
3.2. Characterization of crosslinked pre-cationized cotton fabric

The pre-cationized cotton sample having the nitrogen content of 0.09% and crosslinked with 6% ammonium citrate was characterized before and after ester crosslinking with 6% ammonium


a) Cationization of cotton cellulose (Hashem et al., 2003).
NaOH
NaOH
b) Formation of ionic bonds in the finishing bath
HCl
SHP
Cell — OH

(I)

Scheme 1.



Scheme 1. (*Continued.*)

citrate using thermo gravimetric analysis and Scan Electron Microscope (SEM). Untreated cotton samples were also investigated for comparison.

3.2.1. Thermo gravimetric analysis (TGA)

Fig. 5 shows three curves representing the TGA of cationized, crosslinked cationized as well as untreated cotton samples. It is clear that all curves are consisting of three parts; the first part represents dehydration stages which start from 50 °C to about 200, 210 and 262 °C with percent loss of weights of 5.584, 3.83 and 5.072% for cationized, crosslinked cationized as well as untreated cotton samples respectively. The second part represents the first stage of the thermal degradation as a result of the pyrolysis of all samples which start from 200, 210 and 262 °C and ends at about 318, 348 and 344 °C with percent weights loss of 68.873, 70.546 and 72.092% for the aforementioned samples respectively. The third part represents the conversion of the remaining materials to carbon residues. This stage ends at 639, 494 and 491 °C with weights loss of 23.698, 24.272 and 20.966% for these samples respectively.

3.2.2. Scanning Electron Microscope (SEM)

Scanning electron morphologies (SEMs) of untreated cotton fabric, pre-cationized cotton fabric, and pre-cationized cotton samples followed by crosslinking with 6% AC are shown in Fig. 6(a–c). In this study, we investigated the effects of pre-cationization and the crosslinking with AC on cotton fabrics by comparing their micrographs. Examination of bleached cotton fabric micrograph (Fig. 6a) shows typical fibres with twisted, wrinkled and that was produced when fibres from the boll dehydrate upon boll opening. It is also seen characteristic parallel ridges fibril with smooth ridges, concave grooves spiralling around the fibre at an acute angle to its axis and protruding fibrils.

Fig. 6b shows scanning electron micrograph of cationized cotton fabric. It is evident that the fibres show harsh surfaces whereas concave grooves are still appear.

Fig. 6c shows scanning electron micrograph of pre-cationized cotton samples followed by crosslinking with 6% AC. It is evident form micrograph that, the fibres are swelled and show flat ridges, concave grooves, few protruding fibrils and harsh fibre surface. From micrograph (Fig. 6a–c), we can see that the change in the structure of fibres surface is comparatively notable. After cationization treatment the surface of cellulose fibres become rough, loose and striated. The external fibrillation of modified cellulose fibres was also exfoliated partially. In addition, the surface of cellulose fibres shows some helical ditches orientated along the direction of micro-fibril. Fibre swelling is due to the higher sodium hydroxide concentration used during the cationization reaction.

4. Conclusion

Ester crosslinking of cationized cotton fabrics enhances both dry and wet recovery angles and the highest values were obtained when the cationized cotton fabric having 0.09% nitrogen content was crosslinked with 6% ammonium citrate. It is noted also that, pre-cationization of cotton fabric followed by ester crosslinking bring about a slight enhancement in the TS and that enhancement increases with increasing the cationization level. Scan electron morphologies (SEMs) of pre-cationized cotton fabric, and those sample pre-cationized followed by crosslinking with 6% AC reveal that, the fibres show harsh surfaces whereas concave grooves are still appear.

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