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An eco-friendly – novel approach for attaining wrinkle – free/soft-hand cotton fabric

Mohamed Hashem [a,*], Nabil A. Ibrahim [a], Amira El-Shafei [a], Rakia Refaie [a], Peter Hauser [b]

[a] *Textile Research Division, National Research Centre, Dokki, Cairo, Egypt*
[b] *College of Textile, North Carolina State University, Raleigh, NC, USA*

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ABSTRACT

A novel approach for upgrading both the wrinkle free and softness properties of cotton fabrics without adversely affecting their strength properties using an eco-friendly finishing regimes was investigated. Factors affecting the performance properties of the finished substrate such as pre-treatment, i.e., carboxymethylation (CMC) or ionic-crosslinking, post-treatment with amino functional silicone softener and its concentration, degree of carboxymethylation as well as thermofixation conditions were studied. The obtained results revealed that post-treatment with the amino based silicone micro emulsion (SiE) up to 30 g/L at pH 4 to a wet pickup of 100% followed by drying at 100 °C for 5 min and curing at 170 °C for 3 min results in a remarkable improvement in fabric resiliency (expressed as dry and wet wrinkle recovery angles), as well as in softness degree, without seriously affecting its retained strength. Improvement extent of the aforementioned properties is governed by the nature of the pre-treatment steps. Fixation of the amino-functional silicone softener onto/or within the modified cellulose structure is accompanied by a formation of semi-inter and/or intra-penetrated network (semi-IPN) thereby enhancing both the extent of crosslinking and networking as well as providing very high softness. FTIR analysis proved the formation of Si–O–Si–cellulose complex. Scanning electron micrograph shows that cotton, CMC and ionic crosslinked cotton fabrics treated with SiE shows higher surface smoothness and considerable reduction in protruding loose fibers, ditches and grooves compared with the untreated one.

1. Introduction

Cotton cellulose has excellent properties such as higher water absorbency and moisture, being comfortable to wear and easy to dye. For these reasons, the apparel industry is predominantly cotton based, and the share of cotton in total fibre consumption is about 50% (Karmakar, 1999).

Since the late 1980's, the market place has shown a steady increase in the demand for easy-care, wrinkle-resistant 100% cotton apparel. The ability of durable press cotton fabrics to combine comfort with easy care provides a full spectrum of benefits that a consumer could possibly expect (Schindler & Hauser, 2004).

Since the identification of formaldehyde as a probable human carcinogen, extensive efforts have been made to find formaldehyde-free crosslinking agents for cotton to replace the traditional *N*-methylol reagents (Clark & Andrewes, 1989; Ibrahim, Abo-Shosha, Elnagdy, & Gaffar, 2002; Lee & Kim, 2001; Peterson, 1983; Welch, 1992; Yang, Wei, & Lickfield, 2000). Recently, multifunctional carboxylic acids have been used as non-formaldehyde durable press finishing agents for cotton (Clark & Andrewes, 1989; Ibrahim et al., 2002; Lee & Kim, 2001; Welch, 1992; Yang et al., 2000). Severe tensile strength loss and yellowing have been the major obstacles for applications of polycarboxylic acids in durable press finishing processes of cellulose fabrics. On the other hand, crosslinking of cotton cellulose with polycarboxylic acids alters both chemical and physical properties of the cotton. Such chemical treatments eliminate or greatly restrict the ability of the cellulosic fibers to absorb dyes of various classes (Guan, Zheng, Mao, Gui, & Fu, 2007; Li, Jiang, Wang, Meng, & Qing, 2008; Patra, Arora, Arora, & Nigam, 2004; Schramm, Vukušic, & Katovic, 2002; Udomkichdecha, Kittinaovarat, Thanasoonthornroek, & Potiyaraj, 2003; Xiao, Zhang, Yang, & Huang, 2007; Yang, Wang, & Kang, 1997; Yang et al., 2000).

In our previous work (Hashem, Hauser, & Smith, 2003; Hashem, Refaie, & Hebeish, 2005; Hauser, Smith, & Hashem, 2004; Hebeish, Hashem, Abdel-Rahman, & El-Helw, 2006; Refaie, Hashem, & Hebeish, 2005; Hashem, Refaie, Goli, Smith, & Hauser, 2009) we have significantly improved wrinkle free properties of cotton fabric using ionic crosslinking principle. Cotton fabric is made anionic via carboxymethylation with monochloroacetic acid, or made cationic with 3-chloro-2-hydroy-propyltrimethyl ammonium chloride. Either form of ionic cellulose can be crosslinked in a second step by application of agents with the opposite ionic charge.

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* Corresponding author.
E-mail address: mhashem22@hotmail.com (M. Hashem).

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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 (Karmakar, 1999; Schindler & Hauser, 2004). Of the silicone softeners available, perhaps the most common in current industrial usage are the aminofunctional types (Fig. 1). These materials offer a range of handles depending on the relative size of *x* and the ratio of *x:y*. They may be supplied as surfactant-stabilized emulsions in water, either mechanical or microemulsions. Mechanical emulsions contain large droplets which tend to coalesce on the fabric, giving surface effects. The microemulsions, of much smaller droplet size, will tend to migrate into the yarn and give an overall softness to the whole structure (An, Li, Li, Jin, & Zhang, 2007; Habereder, 2002; Kulkarni, Deshpande, & Kushare, 2001; Schindler & Hauser, 2004; Teli, Paul, & Pardeshi, 2000).

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. They are commonly used in a micro-emulsion form, with a droplet size in the range of 40–150 nanometres. The emulsifier molecules surround the oil droplet and stabilize it (Kulkarni et al., 2001; Teli et al., 2000). 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 CMC (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; (b) antistatic properties of the amine functional groups.

The partially protonated amino groups of the SiE molecule ionically interact with negatively charged cotton cellulose or carboxymethylated cotton cellulose (CMC). This indeed promotes the idea behind the work discussed in this paper (An et al., 2007; Habereder, 2002; Kulkarni et al., 2001; Teli et al., 2000).

Accordingly, the research work presented here aimed essentially at, enhancement fabric resiliency and softness with minimal loss in strength properties taking into consideration the environmental aspects. Indeed, the latter impart cotton fabric a dual potential properties. SiE was applied onto the fabric using pad dry cure method. The effects of the process parameters were systematically investigated. These parameters include fixation temperature, fixation time, pH, degree of ionic crosslinking (expressed as carboxyl and nitrogen content of the fabric), and concentration of SiE. The treated fabrics will monitor for strength properties, wrinkle free properties, whiteness index and surface roughness. Selected samples are subjected to FTIR analysis.

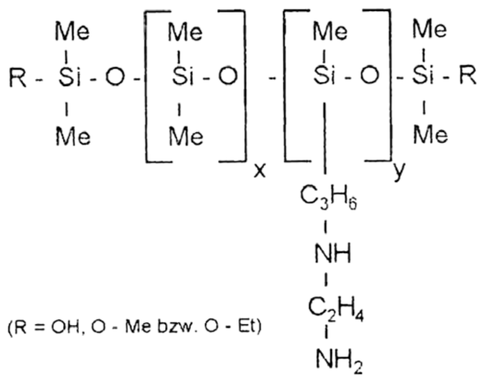


Fig. 1. Basic structure of aminosilicone softener (An et al., 2007; Habereder, 2002; Kulkarni et al., 2001; Schindler & Hauser, 2004; Teli et al., 2000).

2. Experimental

2.1. Materials

2.1.1. Cotton fabric

Mill desized, scoured and bleached print cloth, plain weave, style 400, 102 g/m^2 was supplied by Testfabrics, USA. The fabric was further purified in the laboratory by washing at 100 °C for 60 min using a solution containing 2 g/L, Na_2CO_3 and 1 g/L, Kierlon® NE (non-ionic surfactant). The fabric was then washed several times with boiling water then with cold water and finally dried at ambient conditions.

2.1.2. Chemicals

Sodium hydroxide, acetic acid, hydrochloric acid, monochloroacetic acid, sodium carbonate were of laboratory grade chemicals. 3-Chloro-2-hydroxypropyl trimethyl ammonium chloride (69%) of technical grade chemicals was kindly supplied under the commercial name CR-2000 by Dow Chemical Company, USA. Domosil® NY-ES (amino functional silicon softener, micro emulsion) (SiE) was kindly supplied form M. Dohmen Inc., Greenville, SC, USA.

2.2. Carboxymethylation of cotton fabric (CMC)

Cotton fabric was partially carboxymethylated (CMC) by a method similar to those previously reported (Hashem et al., 2003; Hashem et al., 2005; Hauser et al., 2004; Refaie et al., 2005). Hence, bleached cotton fabric samples were impregnated with 15 wt.% aqueous NaOH for 5 min at room temperature followed by squeezing to a wet pick up of 100% then dried at 60 °C for 5 min. The alkali treated samples were steeped in aqueous solution of ammonium salt of monochloroacetic acid (0–3 mol) for 5 min at room temperature. These samples were then squeezed to 100% wet pick up, sealed in plastic bags and heated at 80 °C for 1 h then washed and dried at room temperature. Blank, where the cotton samples were treated only with sodium hydroxide were also prepared.

2.3. Cationization of CMC fabric (formation of ionic crosslinking cotton fabric)

Cationization of carboxymethylated cotton fabric (CMC) was carried out using pad-dry-cure method (Hashem, Goli, & Hauser, 2009; Hashem et al., 2005; Hebeish et al., 2006; Smith, Hashem, & Hauser, 2007). Experimental procedure adopted was as follows, CR-2000 was mixed in solution with sodium hydroxide. CMC was padded through this mix and squeezed to wet pick-up of 100%. The fabric was dried at 40 °C for 15 min then cured at 120 °C for 15 min. At the end, the sample was washed with cold water and 1% acetic acid then washed several times with cold water and finally dried at ambient conditions.

2.4. Treatment of cotton and CMC fabric with silicon micro emulsion softener

Treatment of cotton fabric, carboxymethylated cotton fabric (CMC) or ionically crosslinked cotton fabric with amino functional silicon micro emulsion softener (SiE) was carried out using pad-dry-cure technique. The fabrics were treated with an aqueous solution of SiE (0–20%) at pH 4 (adjusted using 1% aqueous acetic acid) dried at 100 °C for 5 min the cured at (120–180 °C) for (3–10 min).

2.5. Testing and analysis

The anionic content of the carboxymethylated samples was quantitatively determined by acid base titration and is reported in the units of meq/100 g fabric. The method was adopted from previous work (Hashem et al., 2003; Hashem et al., 2005; Hauser et al., 2004; Refaie et al., 2005). Fabric pieces were cut from different parts into small species (3 mm × 3 mm). They were then soaked in 0.5% hydrochloric acid overnight. The sample pieces were then filtered off, washed several times with de-ionized water until free from chloride ions (indicated by the silver nitrate drop test). The sample was then dried at 105 °C for 3 h. Accurately 0.25 g from the dried sample soaked overnight at room temperature in 25 ml of 0.05 N NaOH. A blank experiment was also carried out. The samples were the titrated with 0.05 N aqueous HCl using phenolphthalein indicator.

$$\boxed{\text{Carboxymethyl content (meq/100g fabric)} = [V_{\text{blank}} - V_{\text{sample}}] \times \text{N}_{\text{HCl}}/\text{Sample weight}}$$

where V_{sample} is the titer for the sample, V_{blank} is the titer for the blank, and N_{HCl} is the normality of the HCl titrant.

- Nitrogen content of the samples was determined by the Kjeldhal method (Vogel, 1975).
- The wet and dry wrinkle recovery angles (WRA, DRA) were measured as per the AATCC standard test method 66-1998.
- Tensile strength of the samples was determined by the ASTM Test Method D5035. A Q-Test 1/5 tensile tester was used. Two specimens for each treated fabric were tested in the warp direction and the average value was recorded to represent the fabric breaking load (Lb).
- The whiteness index of the samples was determined by AATCC test method 110-2000 using Spectraflush SF600X a double beam spectrophotometer, manufactured by Data Color.
- Wettability was assessed in terms of drop disappearance, measured by allowing a drop of water to fall on the sample and recording the time required for drop disappearance (AATCC standard test method).
- All FTIR analysis in this work was obtained by using a Nicolet Nexus 470 – supplied with Germanium crystal. Software version is OMNIC 6.1. Interpretation of FTIR charts were carried out according to reports described elsewhere (Dean, 1995, Pavia, Lampman, and Kriz, 2001).
- Roughness was measured according to AATCC standard test method using a Surfacoder (1700a).
- Scanning Electron microscopy (SEM) was studied using a scanning electron probe microanalyzer (type JXA-840A) – Japan. The specimens in the form of fabrics were mounted on the specimen stabs and coated with thin film of gold by the sputtering method. The micrographs were taken at two magnifications, namely 1000 and 2500, using 30 kV accelerating voltage.

3. Results and discussion

3.1. Proposed reactions pathway and formation of semi-interpenetrate network

During the application process and the subsequent curing step, amino-silicones undergo two types of reactions. The first is ionic interaction between protonated amino groups of the amino silicon softener molecule and the negatively charged cotton or CMC fabric, which results in desired improvement in wet wrinkle recovery angle of the treated cotton fabric. The second reaction is between the silicone molecules themselves through their respective reactive groups, leading to a self-polymerized, cross-linked elastomeric network. The second reaction occurred during the curing step, (i. e. collapsed fabric state) which mean improvement the dry wrinkle recovery of the fabric. Both these reactions ensures durable higher wet and dry wrinkle recovery as well as permanent softness and hence the permanency to the overall treatment.

We assumed that incorporation of ammonium based silicon softener in the structure of ionically crosslinked cotton fabric induces besides strong columbic forces, weaker forces such as dipole–dipole, hydrogen bonds, van der Waals interactions as well as ether crosslinking with cotton cellulose. The latter are formed in dry state (i.e., un-swelled state) of cotton fabrics (An et al., 2007; Habereder, 2002; Kulkarni et al., 2001; Teli et al., 2000).

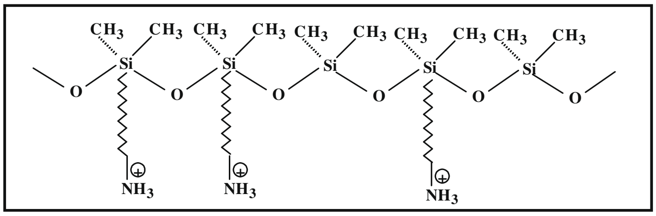
These interactions can be explained as follows.

Cotton cellulose reacts with monochloroacetic acid in presence of sodium hydroxide to bring about carboxymethylated cotton (CMC) as suggested by structure I.

$$\boxed{\textbf{Cell}-\text{O}-\text{CH}_2-\text{CO}\bar{\text{O}}\ \overset{+}{\text{Na}}}$$

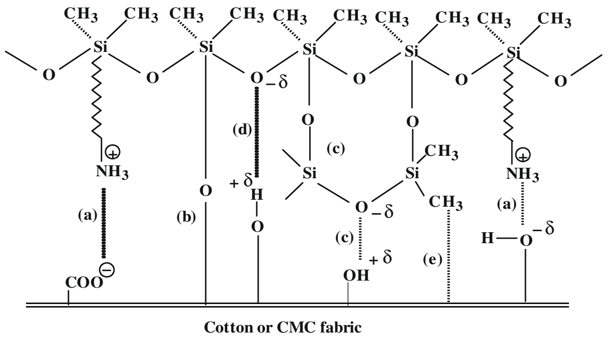
(Structure I, CMC).

In acidic medium the nitrogen atom in amino functional silicon micro-emulsion is protonated and converted to cationic as represented by structure II.



(Structure II, protonated amino silicon softener molecule).

CMC bearing the negatively charged carboxymethyl groups and the positively charged protonated amino group in SiE molecule may allow crosslinking when these groups are localized at two adjacent cellulose chains as suggested by structure III. The latter shows also the final proposed semi-interpenetrate network (semi-IPN) formed inside the cotton fibers. Once, structure III is achieved, the wet and dry wrinkle resistance properties as well as durable softness of cotton fabric may be realized. The magnitude of wrinkle resistance whether wet or dry, fabric softness and other fabric properties would rely on the degree of crosslinking, eventual location of the crosslinks, ratio of intra/inter-chain crosslinks, concentration of amino silicon softener, pH and state of cotton during crosslinking.



(a) Ionic interaction

(b) Covalent ether bond between cellulose and amino silicon molecule

(c) Covalent ether bond between amino silicon molecule themselves

(d) Hydrogen bond

(e) Van der Waal interaction

(Structure III, schematic representation show the final proposed semi-interpenetrate network (semi-IPN) obtained inside the cotton fibers. Ionic crosslinked, ether crosslinking, hydrogen bonding and van der Waal interaction are formed between cotton or carboxymethylated cotton fabric and amino silicon softener).

Table 1
Effect of curing temperature on performance properties of cotton and CMC fabrics treated with SME.

Fabric	Curing temp. (°C)	N (%)	DRA (°)	WRA (°)	W.I	Rou. (µm)	Wett. (s)	T.S (lbf)	El. (%)
Cotton fabric	Untreated	0.0	110	100	69	15.0	1	49	6.2
	120	0.05	90	130	67	14.9	10	48	6.1
	140	0.05	125	155	61	14.9	10	46	5.8
	160	0.05	138	160	58	14.8	15	46	5.9
	170	0.07	150	170	58	14.5	15	43	5.9
	180	0.08	150	160	53	14.5	15	40	5.5
CMC fabric	Untreated	0.0	90	105	65	15.0	1	79	27
	120	0.08	170	180	63	14.8	5	77	25
	140	0.09	210	200	63	14.6	4	75	23
	160	0.10	245	230	63	14.3	5	73	21
	170	0.12	260	250	61	14.3	5	72	21
	180	0.12	258	250	57	14.1	5	68	18

DRA, dry recovery angle; WRA, wet recovery angle; R.TS, retained tensile strength; Elon., elongation at break; wett., wettability, W.I, whiteness index.
Conditions used: [SME], 20 g/L, squeezing to wet pick up 100%, drying at 100 °C for 5 min, curing for 3 min, carboxyl content of CMC fabric, 65.5 meq/100 g fabric.

3.2. Effect of process parameters

3.2.1. Effect of curing temperature

Carboxymethylated cotton fabric (CMC fabric) was prepared as described in the experimental part. The fabric was then treated with an aqueous solution containing 20% Domosil® NY-ES (amino based silicon micro emulsion softener) (SiE) at pH 4. Cotton and CMC fabrics were padded in this solution in two dips and nips then squeezed to a wet pick-up of about 100%. The fabric was dried at 100 °C for 5 min and then cured at different temperatures for 3 min. Finally, the samples washed with cold water and monitored for nitrogen content, WRA, DRA, tensile strength and elongation at break, wettability, whiteness index, and roughness. Results obtained are set out in Table 1.

It is seen from Table 1 that: increasing the curing temperature from 120 to 170 °C is accompanied by an increase in fabric nitrogen content, wet and dry crease recovery angle. The surface roughness also improved as the curing temperature increased up to 170 °C. Further increase in curing temperature has practically no influence on the aforementioned properties. It is also observed that, wettability, tensile strength as well as elongation at break and whiteness index gradually decreased as the curing temperature increased. However, values of those properties remain at acceptable values admissible for easy care finishing for cotton fabric.

Salient feature observed in Table 1 is higher wet and dry wrinkle recovery angle of CMC fabric compared with cotton fabric when the both fabric are treated with the same concentration from SiE. Moreover, both fabric tensile strength and elongation at bleak are much higher for carboxymethylated cotton fabric compared with blank. Results of Table 1 make it clear that the optimum curing temperature for fixation of SiE onto cotton or CMC is 170 °C.

3.2.2. Effect of curing time

Table 2 shows the effect of curing time on the extent of SME fixation onto cotton and CMC fabric. The results signify that, for both fabrics, 3 min duration is enough for complete fixation of SiE. Further increases in reaction time have no effect on the extent of SiE fixation. A longer time provides better opportunity for better contact among the reactants and, therefore, a higher extent of reaction and fixation.

3.3. Effect of carboxyl content and SiE concentration on performance properties of cotton and CMC fabric

A close examination of results in Tables 1 and 2 indicated that the extent of interaction with nominated silicone softener expressed as %N follows the descending order CMC > untreated cotton fabric. This is may be due to the higher negatively charged surface of CMC and its higher affinity towards the cationic protonated SiE (structures I and II). Therefore, in order to optimize the application of SiE onto cotton or CMC fabric a series of studies were carried out aiming at investigate the effect of SiE and carboxyl content onto performance properties of the treated fabric. Results obtained are set out in Figs. 2–7 and Table 3.

Fig. 2 shows the effect of SiE concentration and carboxyl content on final nitrogen content of the treated fabric. It is seen from Fig. 2 that, at the same SiE concentration, increasing the carboxyl content was accompanied by slightly increase in the nitrogen content of the treated cotton fabrics. It is further noted that at the same carboxyl content, increasing SiE concentration is accompanied by increasing in nitrogen content of the treated fabric.

Figs. 3 and 4 shows the effect of SiE concentration and fabric carboxyl content on dry and wet wrinkle recovery angle of the

Table 2
Effect of curing time on performance properties of cotton and CMC fabrics treated with SME.

Fabric	Curing time (min)	N (%)	DRA (°)	WRA (°)	W.I	Rou. (µm)	Wett (s)	T.S (lbf)	El. (%)
Cotton fabric	Untreated	0.0	110	100	69	15.0	1	49	6.2
	1	0.04	138	136	68	14.8	10	49	5.9
	2	0.04	144	154	61	14.7	10	46	5.5
	3	0.07	150	170	58	14.5	15	43	5.9
	5	0.07	150	172	55	14.5	15	39	5.4
CMC fabric	Untreated	0.0	90	105	65	15.0	1	79	27
	1	0.09	200	220	64	14.6	5	77	25
	2	0.09	244	230	63	14.3	5	75	22
	3	0.12	260	250	61	14.3	5	72	21
	5	0.12	262	250	61	14.2	5	69	17

DRA, dry recovery angle; WRA, wet recovery angle; R.TS, retained tensile strength; El., elongation at break; wett., wettability, W.I, whiteness index.
Conditions used: [SME], 20 g/L, squeezing to wet pick up 100%, drying at 100 °C for 5 min, curing temp., 170 °C, carboxyl content of CMC fabric, 65.5 meq/100 g fabric.

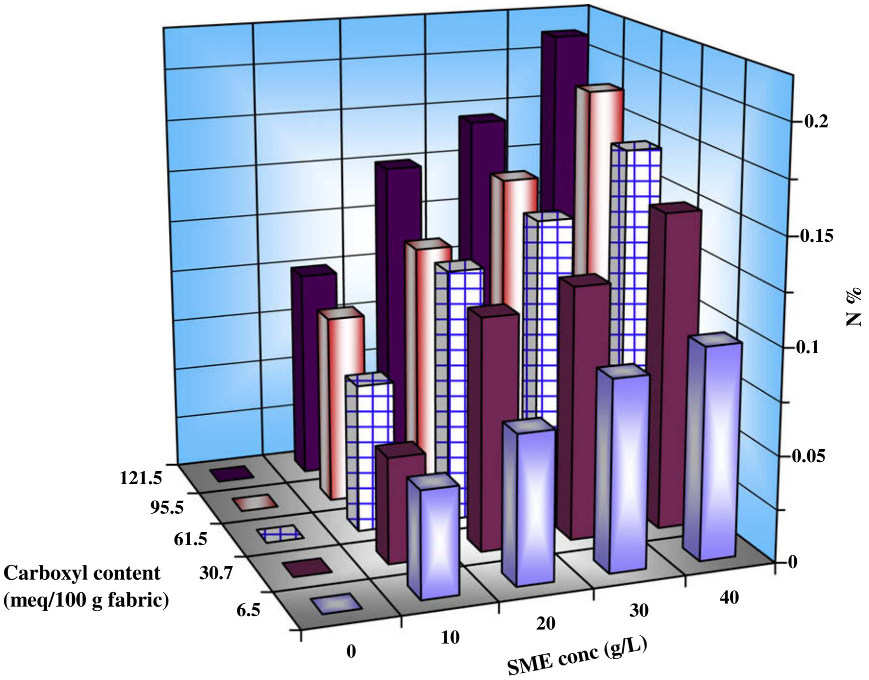


Fig. 2. Effect of carboxyl content and SME concentration on nitrogen content of the treated fabric. Conditions used: Squeezing to wet pick up 100%, drying at 100 °C for 5 min, curing temp., 170 °C, curing time, 3 min. The value of carboxyl content equal to 6.5 meq/100 g fabric represents the carboxyl content of the blank sample before carboxymethylation.

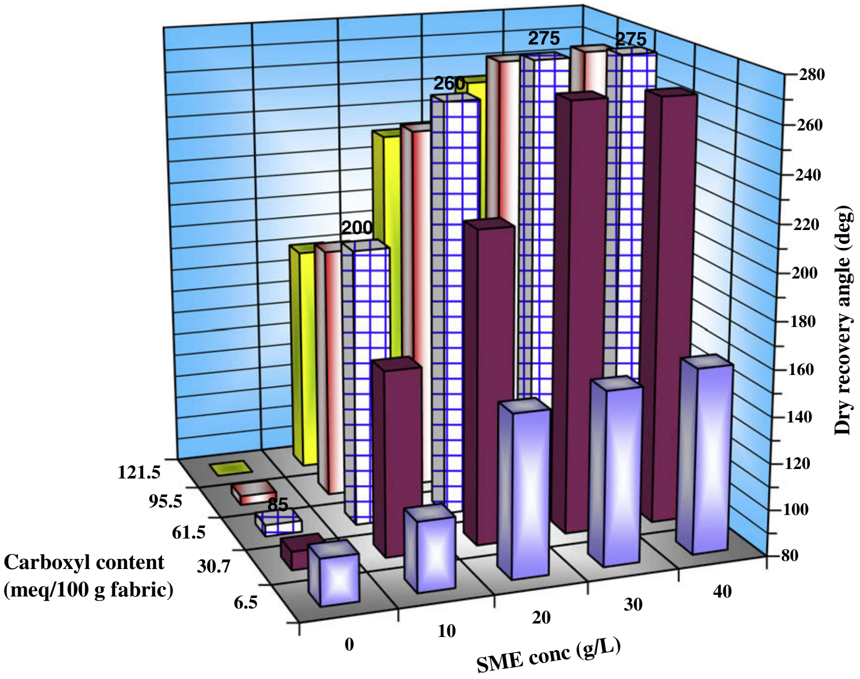


Fig. 3. Effect of carboxyl content and SME concentration on dry wrinkle recovery angle of the treated fabric. Conditions used: Squeezing to wet pick up 100%, drying at 100 °C for 5 min, curing temp., 170 °C, curing time, 3 min. The value of carboxyl content equal to 6.5 meq/100 g fabric represents the carboxyl content of the blank sample before carboxymethylation.

treated fabric respectively. It is seen from Figs. 3 and 4 that, at the same SiE concentration, increasing the carboxyl content up to 65.5 meq/100 g fabric, was accompanied by a higher increase in the wet and dry wrinkle recovery angle. Further increase in carboxyl content, decreased both the DRA and WRA. At the same carboxyl content, increasing SiE concentration from zero to 30 g/L was accompanied by an increase in both DRA and WRA. Further increased in SiE concentration up to 40 g/L, has practically no influence on the DRA and WRA of the treated cotton fabrics. Obviously, maximum DRA and WRA were obtained at SiE concentration equal 30 g/L SiE and the fabric carboxyl content should not increase more than 61.5 meq/100 g fabric.

Fig. 5 shows the effect of SiE concentration and fabric carboxyl content on whiteness index (W.I) of the treated fabric. It is seen from Fig. 5 that, at the same SiE concentration, increasing the carboxyl content of the fabric was accompanied by a gradual decrease in fabric W.I, the same holds true when SiE was increased.

The amino group undergo oxidation under the effect of high curing temperature and air oxygen. This would account the decrement of fabric whiteness index upon increasing the concentration of SiE.

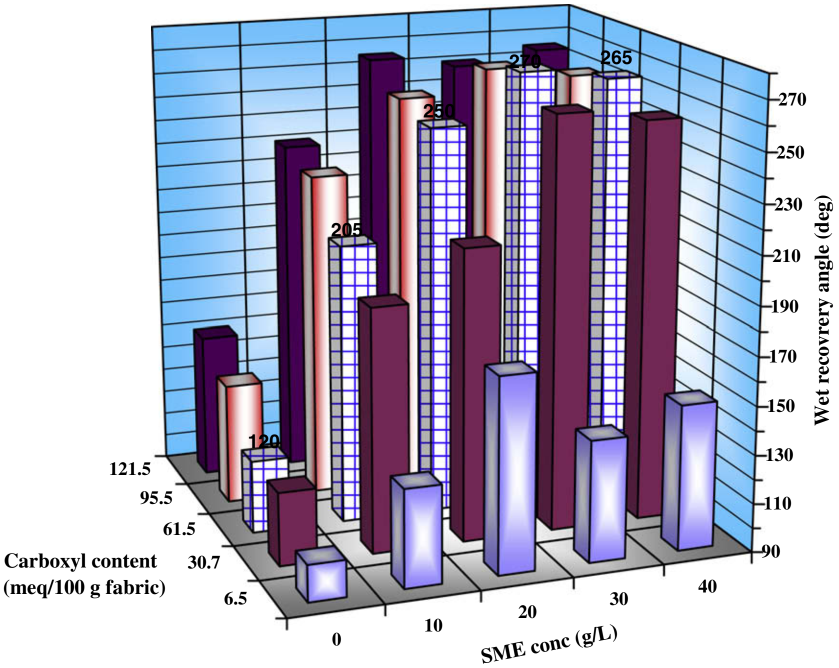


Fig. 4. Effect of carboxyl content and SME concentration on wet wrinkle recovery angle of the treated fabric. Conditions used: Squeezing to wet pick up 100%, drying at 100 °C for 5 min, curing temp., 170 °C, curing time, 3 min. The value of carboxyl content equal to 6.5 meq/100 g fabric represents the carboxyl content of the blank sample before carboxymethylation.

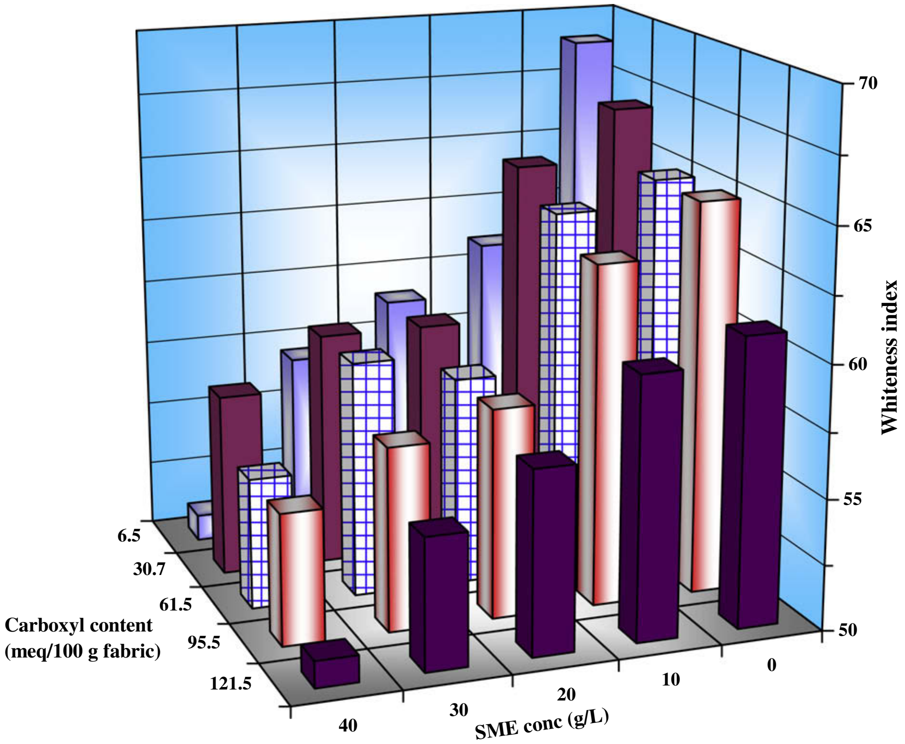


Fig. 5. Effect of carboxyl content and SME concentration on whiteness index of the treated fabric. Conditions used: Squeezing to wet pick up 100%, drying at 100 °C for 5 min, curing temp., 170 °C, curing time, 3 min. The value of carboxyl content equal to 6.5 meq/100 g fabric represents the carboxyl content of the blank sample before carboxymethylation.

Table 3 shows the effect of SiE concentration and fabric carboxyl content on tensile strength and elongation at break of the treated fabric. It is seen from Table 3 that, at the same SiE concentration, increasing the carboxyl content of the fabric was accompanied by higher increase in both tensile strength and elongation at break. It is also seen that, irrespective to the carboxyl content, increasing

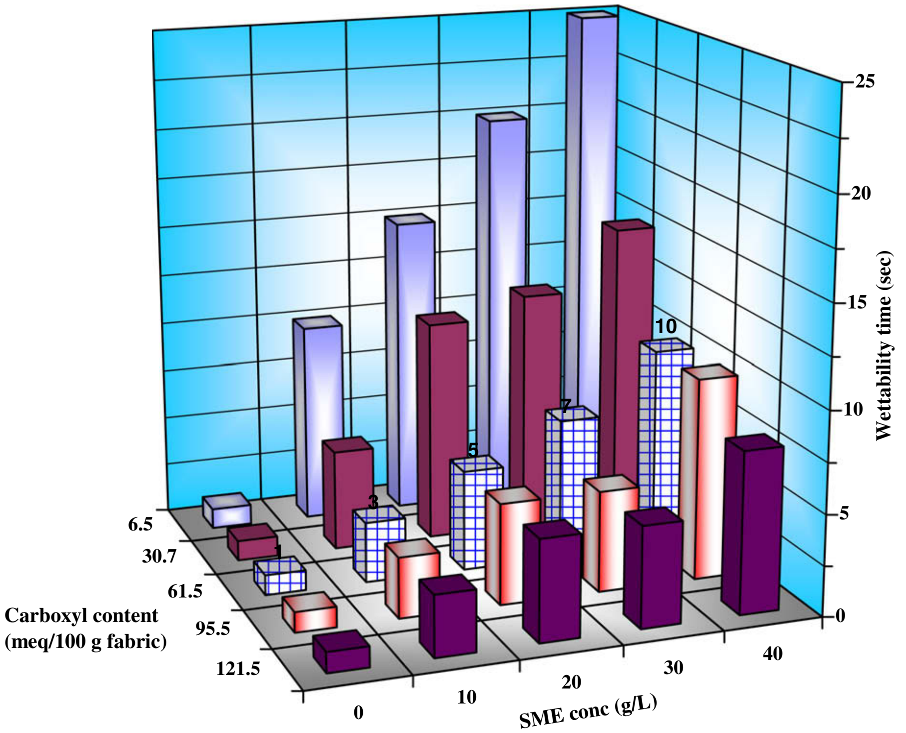


Fig. 6. Effect of carboxyl content and SME concentration on the fabric wettability before and after treatment. Conditions used: Squeezing to wet pick up 100%, drying at 100 °C for 5 min, curing temp., 170 °C, curing time, 3 min. The value of carboxyl content equal to 6.5 meq/100 g Fabric represents the carboxyl content of the blank sample before carboxymethylation.

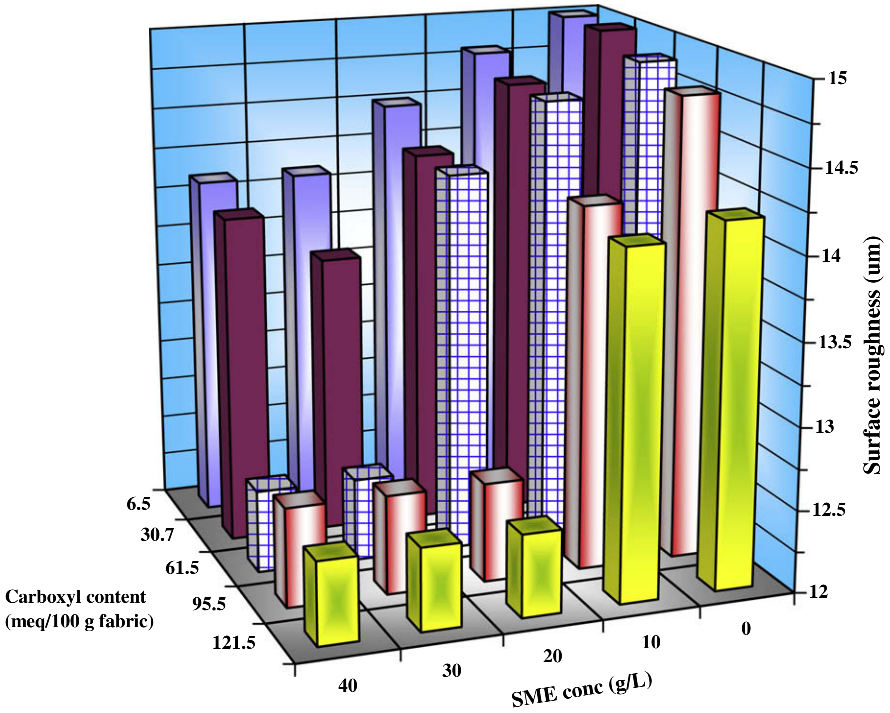


Fig. 7. Effect of carboxyl content and SME concentration on the surface roughness of the treated fabric. Conditions used: Squeezing to wet pick up 100%, drying at 100 °C for 5 min, curing temp., 170 °C, curing time, 3 min. The value of carboxyl content equal to 6.5 meq/100 g Fabric represents the carboxyl content of the blank sample before carboxymethylation.

SiE concentration is accompanied by a marginal decrease in tensile strength. However, CMC fabric having carboxyl content equal to 61.5 meq/100 g shows a value of tensile strength and elongation at break equal to 71 lbf and 20% respectively. This value is much higher than that obtained with cotton fabric treated with the same SiE concentration but lower than that obtained with carboxymethylated fabric without SiE treatment. A point which indicated that, although, there were a decrement in tensile strength and elongation at break upon treatment with SiE, pre-carboxymethylation greatly improved the fabric tensile strength and elongation at break.

Fig. 6 shows the effect of SiE concentration and the carboxyl content on wettability of the treated fabric. It is seen from Fig. 6 that, at the same SiE concentration, increasing the carboxyl content of the fabric was accompanied by an increase in wettability of the treated fabric. It is also seen that, at the same carboxyl content, increasing SiE concentration is accompanied by a decrease in fabric wettability due to the hydrophobic nature of the deposited silicone film onto the treated fabric cotton samples. However, the wettability show permitted values (7–10 s) at carboxyl content equal to 61.5 meq/100 g whatever the concentration of SME used.

Fig. 7 shows the effect of SiE concentration and the carboxyl content on surface roughness of the treated cotton fabric. It is seen from Fig. 7 that, at the same SiE concentration, increasing the carboxyl content of the fabric was accompanied by an improvement in fabric roughness after treatment. It is also seen that, at the same carboxyl content, increasing SiE concentration is accompanied by improvement in surface roughness of the treated fabric samples. Higher fabric softness was observed at SiE concentration equal to 30 g/L and fabric carboxyl content equal 65 meq/100 g fabrics.

Table 3
Effect of carboxyl content and SME concentration on tensile strength and elongation at break of the treated fabric.

Carboxyl content (meq/100 g)	SME concentration (g/L)				
	0.0	10	20	30	40
Untreated cotton (6.5)	49 (6.2)*	46 (6.1)	44 (5.9)	43 (5.5)	40 (5.3)
30.7	61 (12)	59 (17)	57 (16)	55 (15)	54 (15)
61.5	75 (19)	73 (23)	72 (21)	71 (20)	68 (19)
95.5	77 (23)	75 (25)	74 (25)	73 (22)	71 (20)
121.5	79 (27)	77(26)	75 (25)	75 (25)	73 (23)

Conditions used: Squeezing to wet pick up 100%, drying at 100 °C for 5 min, curing temp., 170 °C, curing time, 3 min.
* Values in brackets represent elongation at break.

Table 4
Performance properties of cotton, CMC, and ionic crosslinked cotton before and after treatment with SiME.

Fabric	N (%)	DRA (°)	WRA (°)	W.I	Rou. (μm)	Wett. (s)	T.S (lbf)	El. (%)
Untreated blank	0.0	110	100	69	15	2	49	6.2
Cotton fabric treated with SME	0.09	155	140	57	14.1	20	43	5.5
CMC untreated	0.0	85	120	65	14.5	1	78	25
CMC treated with SME	0.14	275	265	59	12.5	7	71	20
Ionic crosslinked untreated	0.38	225	265	61	14.6	1	65	19
Ionic crosslinked treated with SME	0.44	278	285	57	12.7	5	61	20

DRA, dry recovery angle; WRA, wet recovery angle; R.TS, retained tensile strength; Elon., elongation at break; wett., wettability; W.I, whiteness index.
Conditions used: [SME], 30 g/L, squeezing to wet pick up 100%, drying at 100 °C for 5 min, curing at 170 °C for 3 min carboxyl content of CMC fabric, 61.5 meq/100 g fabric. Ionic crosslinked cotton fabric was prepared as descried in the experimental part.

3.4. Type of substrate vs. performance properties

Cotton, CMC and ionic crosslinked cotton were treated with an aqueous solution containing 30 g/L SiE at pH 4 then squeezed to a wet pick up of 100%, dried at 100 °C for 5 min, followed by curing

Table 5
Peaks assignment of cotton and CMC fabrics.

Cotton (Fig. 1)		CMC (Fig. 2)	
Peak cm^{-1}	Assignment	Peak cm^{-1}	Assignment
–	–	3382	Carboxylic –OH stretching
3339	Alcoholic –OH stretching	3340	Alcoholic–OH stretching
2900	Aliphatic –CH_2 stretching	2895	Aliphatic –CH_2 stretching
–	–	1731	–C=O stretching of carboxylic acid
1650	Absorbed water and hydrogen bond	–	–
–	–	1591	Carboxylate anion-symmetric stretching
1428	Aliphatic –CH_2 bending	1425	Aliphatic –CH_2 bending
1367	–CH bending (deformation stretching)	1367	–CH bending (deformation stretching)
1338	–OH in plane bending	1337	–OH in plane bending
1316	–CH wagging	1316	–CH wagging
1161	–C–O–C–asymmetric bridge stretching	1156	–C–O–C–asymmetric bridge stretching
1110	–C–O–H bending of secondary alcoholic	–	–
1057	Asymmetric in plane ring stretching	1059	Asymmetric in plane ring stretching
1033	–C–O stretching	1026	–C–O stretching
902	Asymmetric out-of-phase ring stretch –C_1–O–C_4 β-glucosidic bond	896	Asymmetric out-of-phase ring stretch –C_1–O–C_4 β-glucosidic bond
–	–	707	–O–C=O bending in carboxylic acid

Table 6
Peaks assignment of CMC fabrics treated with SME.

SME (Fig. 3)		CMC treated with SME (Fig. 4)	
Peak cm^{-1}	Assignment	Peak cm^{-1}	Assignment
	–	3400	Carboxylic –OH stretching
		3394	Alcoholic –OH stretching
3380	–NH and –$^{\oplus}NH_3$ stretching	3380	–NH and –$^{\oplus}NH_3$ stretching
–	–	2905	Aliphatic –CH_2 stretching
–	–	1728	–C=O stretching of carboxylic acid
1642	–$^{\oplus}NH_3$ deformation	1642	–$^{\oplus}NH_3$ deformation
		1425	Aliphatic –CH_2 bending
		1368	–CH bending (deformation stretching)
		1337	–OH in plane bending
		1316	–CH wagging
1261	Si–CH_3 in silanes –CH_3 symmetric deformation	1260	Si–CH_3 in silanes CH_3 symmetric deformation
1094	Si–O–Si in siloxanes Si–O–Si antisym. stretch	1156	–C–O–C–asymmetric bridge stretching
		1059	Si–O–Si in siloxanes Si–O–Si antisym. stretch
		1026	–C–O stretching
		896	Asymmetric out-of-phase ring stretch –C_1–O–C_4 β-glucosidic bond
–	–	798	–O–C=O bending in carboxylic acid

at 170 °C for 3 min. The fabrics were monitored for their performance properties before and after the treatment. Results obtained are set out in Table 4. The results depict that, the treatment route greatly affects the performance properties of the treated fabric and the following featured arose:

(i) Maximum DRA and WRA were obtained with those fabric pre-ionic crosslinked then treated with SiE where the fabric shows DRA and WRA as high as 278° and 285° respectively, then come the CMC treated with the same SiE concentration (DRA & WRA equal 275° and 265° respectively). Untreated ionic crosslinked fabric acquired DRA equal 225°. This result evidenced the role of SiE in formation of semi-interpenetrate network (semi-IPN) in and/or onto the cotton fibers. Although there was some improvement in both WRA and DRA of cotton fabric after treatment with SiE, the values are much lower than that required for easy care finishing of cotton fabrics.

(ii) The fabric whiteness index decreased in all treatment compared with the untreated fabric but the decrement was

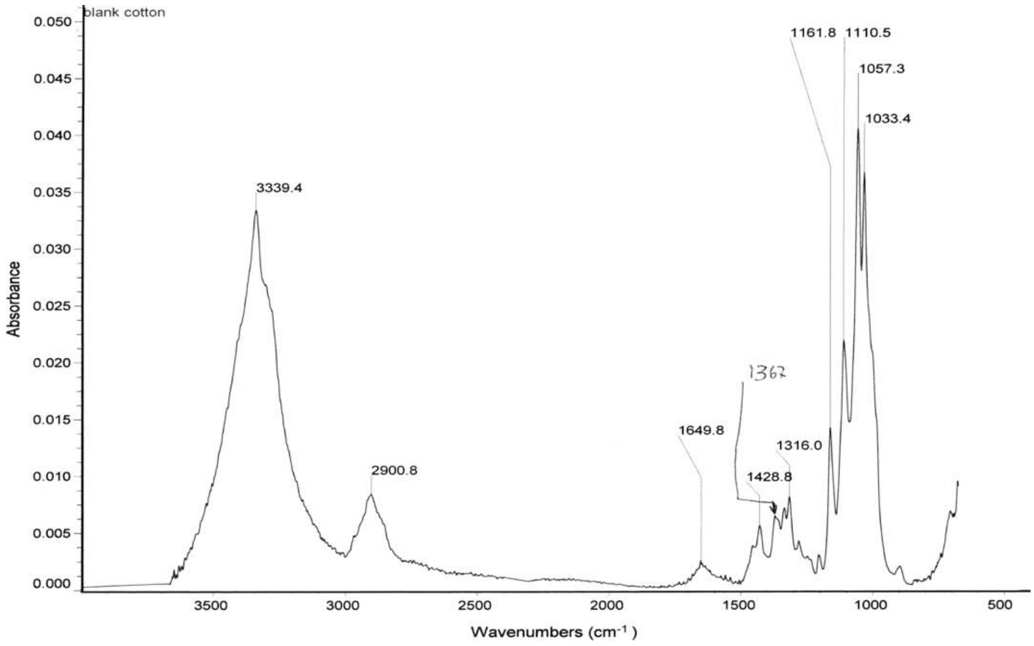


Fig. 8. FTIR of untreated cotton fabric.

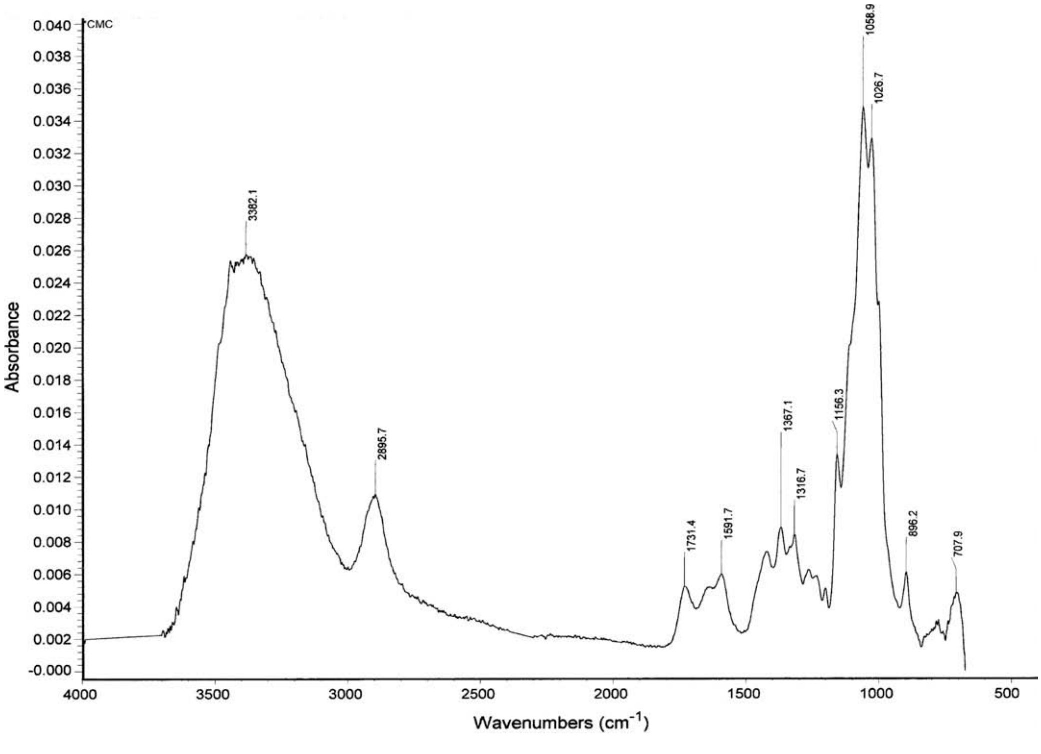


Fig. 9. FTIR of carboxymethylated cotton fabric (CMC).

higher with those post treated with SiE. However, values of W.I remain at acceptable values admissible for easy care finishing for cotton fabric.

(iii) The surface roughness was greatly improved after SiE treatment and followed the descending order: CMC treated with SiE > Ionic crosslinked treated with SiE > Cotton fabric treated with SiE > CMC untreated > Ionic crosslinked untreated > Untreated blank.

(iv) The fabric wettability decreased after SiE treatment. Such decrement is pronounced with untreated cotton fabric treated with SiE, whereas the decrement was marginal if CMC or ionic crosslinked fabric treated with SiE.

(v) The nitrogen content largely depends on the treatment prior to application of SiE. For example, pre-carboxymethylation enhances the fabric nitrogen content. The higher nitrogen content observed with ionic crosslinked cotton fabric is

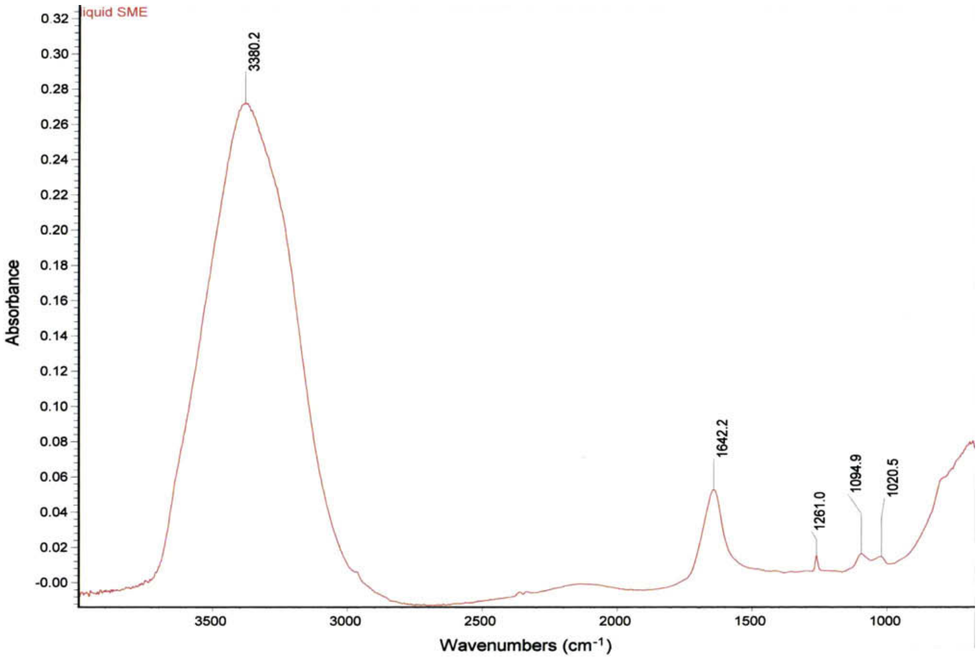


Fig. 10. FTIR of SME aqueous solution at pH 4.

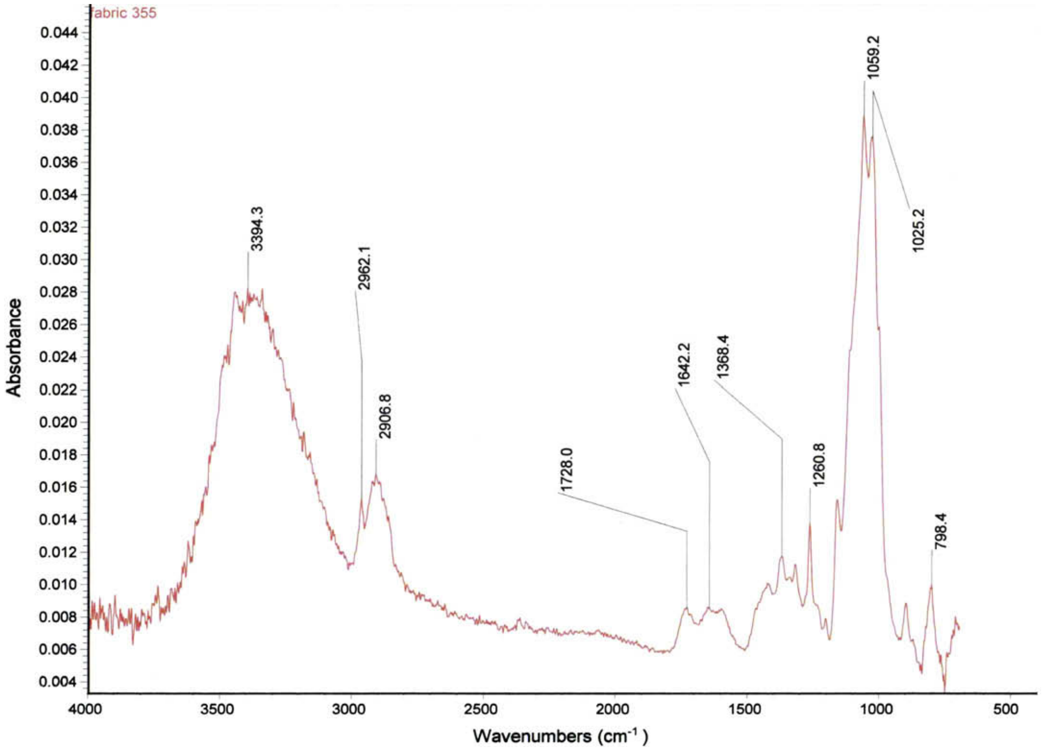


Fig. 11. FTIR of CMC treated with 30 g/L SME.

Table 7
Effect of finishing regime and treatment sequence on the surface topography of treated samples.

Figure no.	Substrates	Changes topographical
12	Blank (untreated cotton)	Smooth ridges, concave grooves, protruding fibrils and harsh surface
13	Cotton fabric treated with SiE	Smooth ridges, concave grooves, smooth surface, SiE homo-polymer formed on the fabric surface and between interfibers
14	CMC fabric	Swelled fibres, flat ridges, concave grooves protruding fibrils and harsh fibre surface
15	CMC fabric post treated with SiE	Swelled fibres, flat ridges, very smooth fibre surface
16	Cationized CMC fabric (Ionic crosslinked)	Swelled fibres, flat ridges, concaves grooves and wrinkled fibre surface
17	(Ionic crosslinked) cationized CMC fabric post treated with SiE	Swelled fibres, flat ridges, very smooth fibre surface

SiE, silicone elastomer; CMC, Carboxymethylated cotton.

due to the nitrogen added to the cotton during cationization. This was observed whether the fabric was treated with SiE or not but with certainty that the value was higher for those fabric post treated with SiE.

(vi) Tensile strength of CMC fabric or ionic crosslinked cotton fabric samples were still higher even after treatment with SiE compared with the untreated fabric.

Indeed, results summarized in this report represent a break through in textile finishing, especially easy care finishing of cotton fabrics and deserve mill trials.

3.5. FTIR analysis

FTIR analysis was carried out onto bleached cotton fabric (blank) and all other modified or treated with SiE as listed below:

The summary of band position and their assignments [39,40] for each spectrum are set out in Tables 5 and 6.

It is seen from Figs. 8 and 9 and Table 5 that the common bands differences between CMC and cotton fabric which can be summarized as follows:

- A broad strong peak at 3382 cm^{-1} is attributed to stretching vibration of carboxylic –OH groups. This peak was not observed in spectrum of cotton fabrics.
- In CMC spectrum, there is a medium peak at 1731 cm^{-1} assigned for $-C{=}O$ stretching vibration of carboxylic groups. This peak also not observed in FTIR spectra of cotton fabrics.
- In spectrum of CMC, sharp strong peak at 1059 cm^{-1} and small peak at 707 cm^{-1} are assigned for carboxylate anion symmetric stretching bending respectively. These two bands are not observed in spectrum of cotton fabric.

The above findings indicate the formation of carboxymethyl cotton cellulose.

Figs. 10 and 11 show the FTIR of SiE at pH 4 and CMC fabric treated with SME. Summary of bands position and their assignments are given in Table 6. Salient features abstracted from Figs. 9 and 10 and Table 6 were:

- Strong and sharp absorption beak observed at 3380 cm^{-1} assigned for –NH and $-^{\oplus}NH_3$ stretching.
- It is further noted that, the medium peaks at 1642 cm^{-1} assigned for $-C-N^{+}-$ stretching vibration.
- Two weak peaks observed at 1261 and 1094 cm^{-1} assign for Si–CH_3 in silanes –CH_3 symmetric deformation and Si–O–Si in siloxanes Si–O–Si antisym. stretch respectively. These two peaks are also found in spectra of CMC treated with SME (Fig. 4). Indicating the formation of Si–O–Si–cellulose complex.

3.6. Scanning electron micrograph (SEM)

In this study, we investigated the effects of SiE treatments on cotton fabrics by comparing the micrographs of cotton, CMC or ionic crosslinked cotton before and after treatment with the same concentration of SiE. To facilitate discussions, the surface characteristics of the samples are listed in Table 7.

Examination of bleached cotton fabric micrograph (Fig. 12) shows typical fibers with twisted, wrinkled and harsh surfaces that are produced when fibers from the boll dehydrate upon boll opening (Li & Hardin, 1998). It is also seen characteristic parallel ridges fibril with smooth ridges, concave grooves spiralling around the fiber at an acute angle to its axis and protruding fibrils.

Fig. 13 shows scanning electron micrograph of cotton fabric treated with SiE. It is evident that the fibers shows smooth ridges and smooth surface characteristic whereas concave grooves are still appear. It is evidence that SiE form a continuous polymer film around the fibres and there are some SiE homo-polymer formed on the fabric surface and between the fibers (pointed by arrows). It

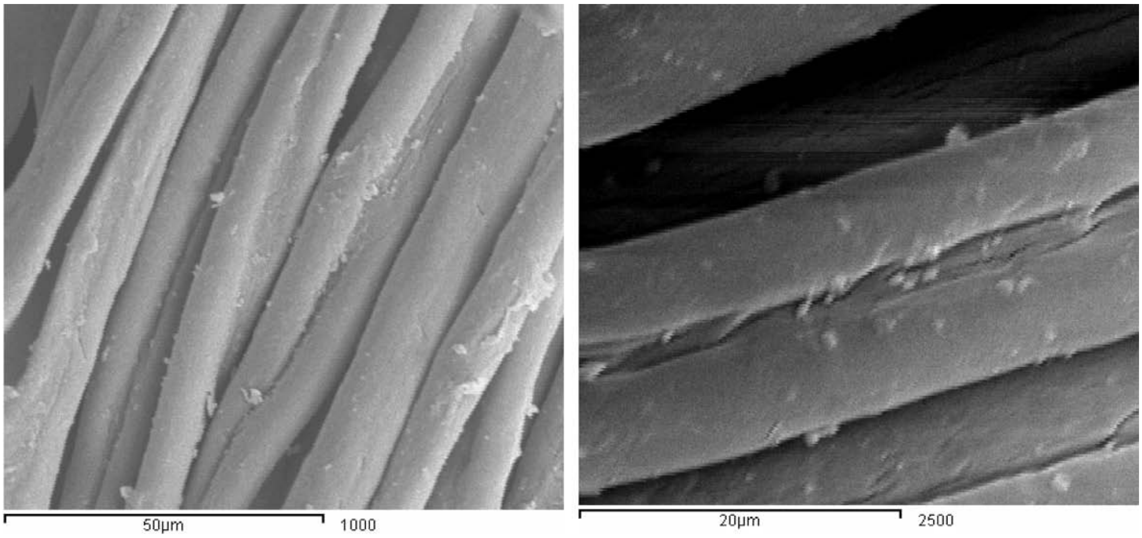


Fig. 12. Scanning electron micrograph (SEM) of blank (untreated cotton).

seems, however, that the decrement in fabric roughness (increasing in smoothness) is due to the film-forming property of SiE.

Fig. 14 shows scanning electron micrograph of CMC. It is evident for micrograph that the fibers are swelled and show flat ridges, concave grooves, few protruding fibrils and harsh fibre surface. From CMC micrograph (Fig. 14), we can see that the change in the structure of fibers surface is comparatively notable. After carboxymethylation treatment the surface of cellulose fibers become rough, loose and striated. The external fibrillation of modified cellulose fibers was also exfoliated partially. In addition, the surface of cellulose fibers shows some helical ditches orientated along the direction of micro-fibril (pointed by arrows). Fibre swelling is due to the higher sodium hydroxide concentration used during the carboxymethylation reaction.

Fig. 15 shows SEM of CMC fabric after treatment with SiE. It is evident that, the surfaces of CMC fibers treated with SiE had swelled and circulated fibres ridges, very smooth fibre surface, no concave grooves or protruding fibrils are observed. Although carboxymethylation reaction reduces the fibre smoothness and increase the surface ditches (as seen in Fig. 14), subsequent treatment of CMC fabric with SiE highly improved the surface roughness and homogenously covered all ditches and grooves. This may be attributed to the increased surface negativity after carboxymethylation reaction which results in an increase adhesion of SiE to the fibres. Similar results were obtained when the ionically crosslinked cotton fabric (Fig. 16) was treated with SiE (Fig. 17).

It could be concluded that, post-treatment with SiE results in a remarkable changes in surface properties regardless of the used substrate i.e., cotton, CMC or ionic crosslinked cotton, as confirmed by SEM. The extent of surface modification, expressed as smoothness, coating of loose fibers, as well as disappearing of ditches and grooves, was determined by the type of post-treated substrate and, location, extent of distribution as well as degree of fixation of SiE onto and/or within this substrate.

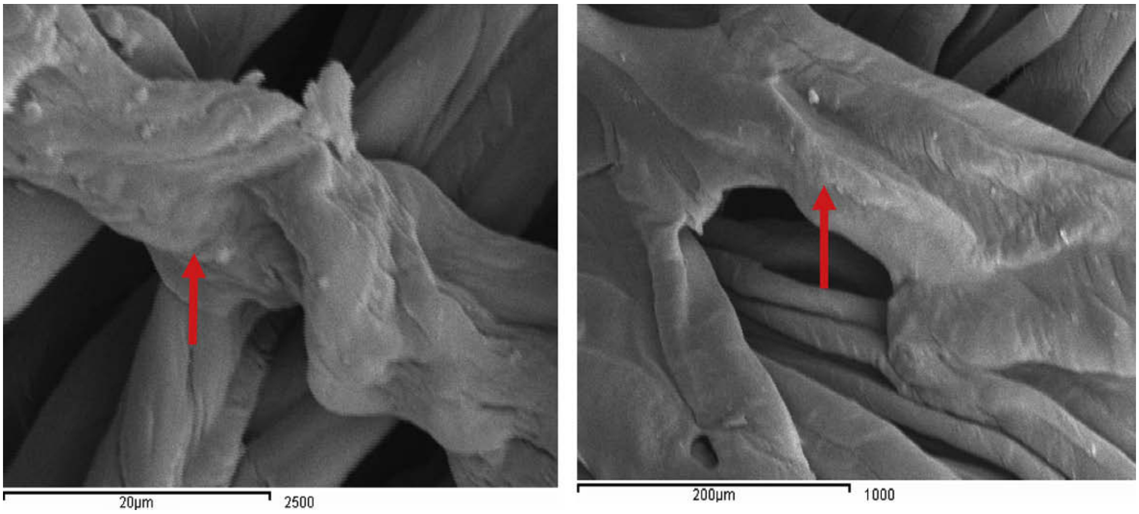


Fig. 13. SEM of cotton fabric treated with SiE.

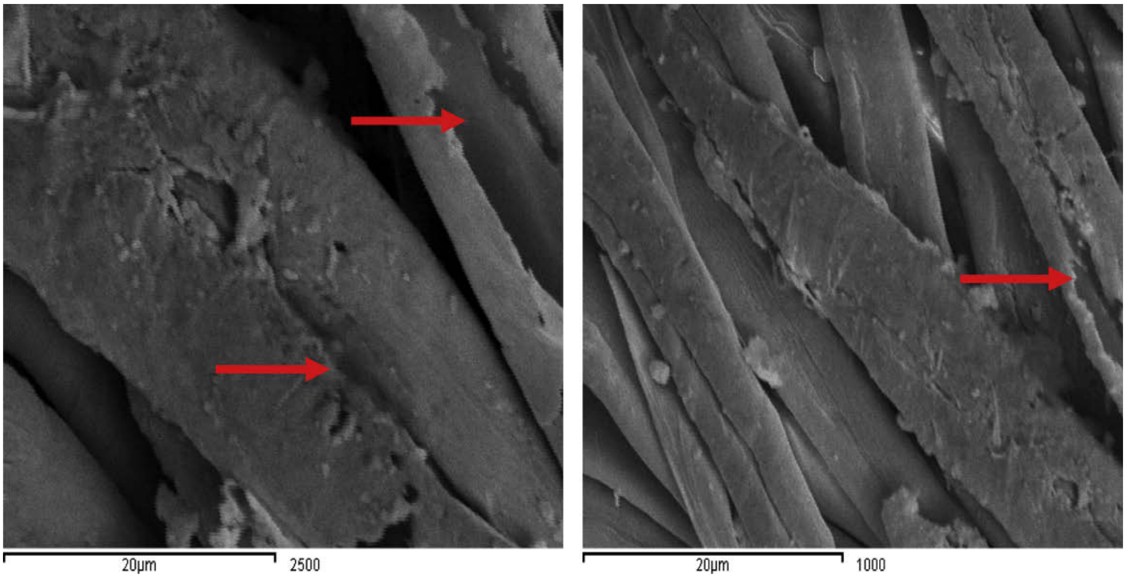


Fig. 14. SEM of CMC fabric (–COOH content = 61.5 meq/100 g fabric).

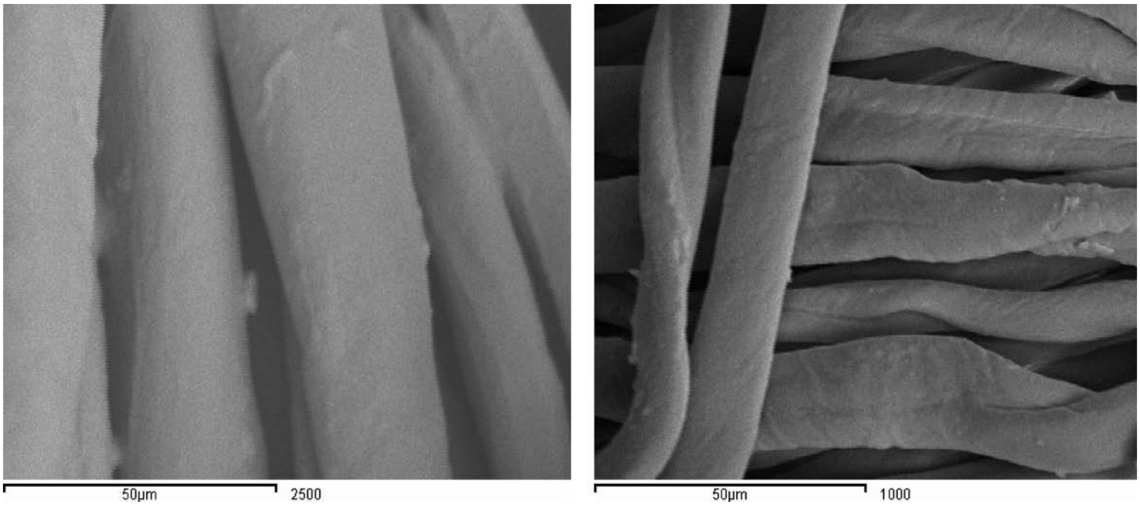


Fig. 15. SEM of CMC fabric (–COOH content = 61.5 meq/100 g fabric) treated with SiE.

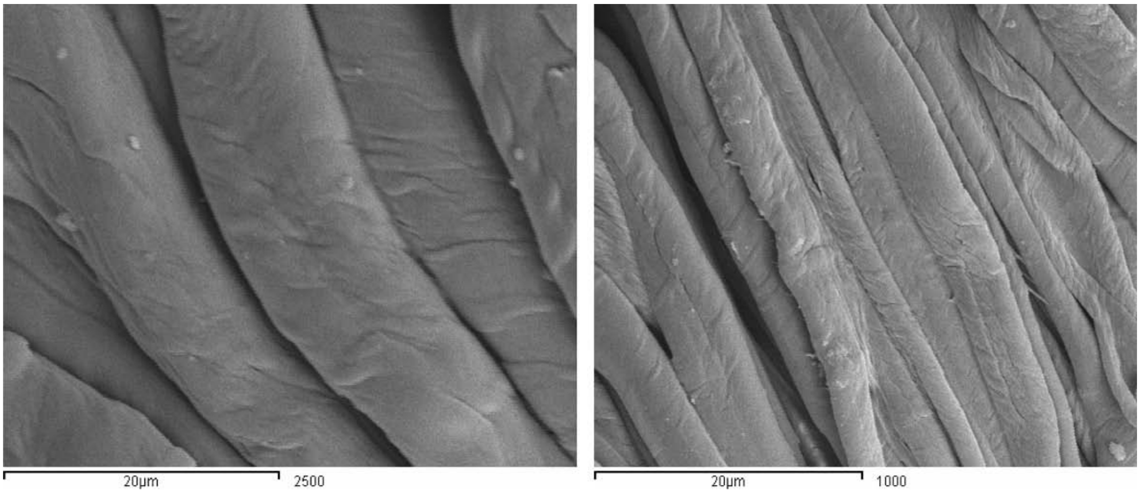


Fig. 16. SEM of CMC fabric followed by cationization (ionic crosslinked).

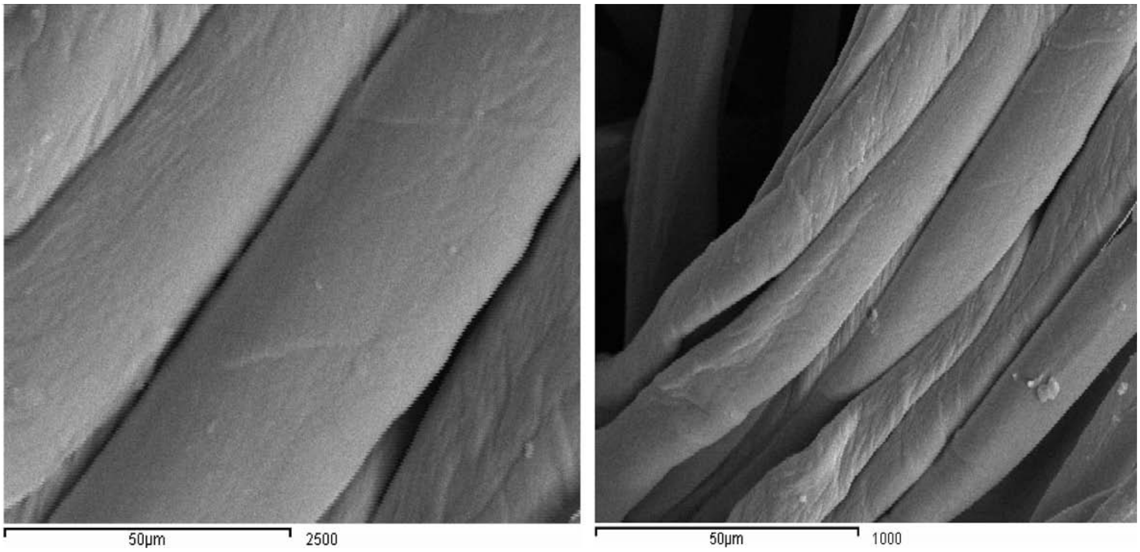


Fig. 17. SEM of CMC fabric followed by cationization (ionic crosslinked) then treated with siE.

4. Conclusion

This research work has shown that: (i) the optimum condition for fixation of SiE onto the fabric involve treatment of the fabric with an aqueous solution containing 30 g/L SiE at pH 4 then squeezed to a wet pick up of 100%, dried at 100 °C for 5 min then cured at 170 °C for 3 min, (ii) the performance properties of the treated cotton fabric depend largely on the fabric carboxyl content and SiE concentration, (iii) the concentration of SiE required to achieve maximum properties was 30 g/L and the fabric carboxyl content should not increased above 65 meq/100 g fabric, (iv) maximum DRA and WRA were obtained with those fabric pre-ionic crosslinked then treated with SiE, then come the CMC fabric, followed by the untreated ionic crosslinked fabric acquired DRA equal 225°, (v) the surface roughness of the fabric was greatly improved after SiE treatment, the improvement was pronounced with CMC fabric or ionic crosslinked fabric, (vi) The fabric wettability decreased after SiE treatment and the extent of decrease is determined by the type of substrate, (vii) the tensile strength of CMC fabric or ionic crosslinked cotton fabrics were very high even after treatment with SiE compared with the untreated fabric, (vii) The FTIR analysis proved the formation of Si–O–Si-cellulose complex. Scanning electron micrograph show that, post-treatment with SiE results in remarkable changes in surface properties regardless of the used substrate i.e., cotton, CMC or ionic crosslinked cotton. The extent of surface modification, expressed as smoothness, coating of loose fibers, as well as disappearing of ditches and grooves, was determined by the type of post-treated substrate and extent of distribution as well as degree of fixation of SiE onto and/or within this substrate.

Indeed, results summarized in this report represent a break through in textile finishing, especially easy care finishing of cotton fabrics and deserve mill trials.

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