

ANIONICALLY-MODIFIED COTTON AND SURFACE LAYER FORMATION WITH POLYELECTROLYTES

Amira El-Shafei¹, Dierk Knittel, E. Schollmeyer

German Textile Research Centre North-West e.V. (DTNW), D-47798 Krefeld, Germany

¹National Research Centre, Textile Research Division, Dokki, Cairo, Egypt

Phone: (+202) 3357807; Fax: (+202) 3363261, E.mail: mayamira2001@yahoo.com

Abstract

Carboxymethyl cellulose (CMC) is a water-soluble cellulose derivative widely used in textile preparations, especially for the application of sizes, which are removed shortly after the weaving process. In this paper, a strategy is given for using CMC as an anionical polymeric modifier of cotton surfaces with permanent character-imparting stable properties, such as after cationic dyeing, durable press properties and polyelectrolyte layer formation, without the use of dangerous chemicals like chloroacetic acid or salts. Thus CMC was fixed onto cotton by using CMC and Na-hydroxydichlorotriazine as an anchoring chemical. The fabric samples before and after finishing were monitored for polyelectrolyte titration values, wet and dry crease recovery angle, and K/S values after fixation of cationic dyestuff.

Key words:

carboxymethyl cellulose, anionic cotton, polyelectrolyte titration, textile finishing, crease recovery

Introduction

Demand has been increasing for active agents which can be imparted to textile materials (fabric and nonwovens) by chemical means in order to create additional properties (functional textiles) [1,2,3]. Biopolymers or their derivatives as surface modifiers can offer special properties such as giving an anionic character to cotton fabric through their reaction with suitable anchoring chemicals. As an example, carboxymethylcellulose (CMC) can be used for the permanent fixation of anionic properties as a widely available polymer with a natural base. This anionic character was previously imparted by carboxymethylation of the cellulose cotton fabric using monochloroacetic acid and sodium hydroxide [6,11].

Carboxymethyl cellulose (CMC) is a water-soluble cellulose derivative widely used in textile finishing. As in sizing processes, attaching it to textile fabrics -mainly involves hydrogen bonding. CMC is therefore considered as a temporary finish, which has to be removed during washing processes, thus causing alteration in the weight and handle of the fabrics, and also increasing the pollution load of waste water. Because of this we suggested permanently affixing CMC onto cotton fabric by using bifunctional crosslinking agents which are expected from the formation of covalent bonds with hydroxyl groups of cellulose and CMC [9,11]. As the bifunctional material, sodium hydroxy 2,6 dichloro-1,3,5-triazine (Na-HDCT) is used.

The reaction of cellulose with crosslinking agents has been studied extensively [4]. The compounds have generally been polyfunctional compounds, often bifunctionals which are capable of forming a covalent bond with the hydroxyl groups of cellulose, and yielding a crosslinked structure in a single step.

A scheme for their anchoring reaction is represented as given in Scheme 1:



Scheme 1. Reaction of bifunctional reactant X-R-X with hydroxyl group of cellulose cotton fabric and groups of carboxymethyl cellulose (CMC)

The introduction of a crosslinking reaction within the fibre is accompanied by profound changes in the physical properties of finished cotton fabric, which are often highly desirable.

Experimental

Materials

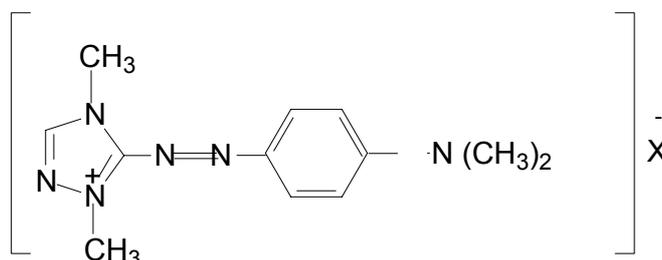
Mill scoured and bleached cotton fabric (Testex) plain weave, 102 g/m²;
 Carboxymethyl cellulose (CMC) (mean Mw 90 kDa, DS 0.7 Aldrich),
 Sodium hydroxy-2,6-dichloro triazine (Na-HDCT) (7% aqueous solution, Degussa),
 Basic dye (Astrazone® Basic Red 22), Marlipal® 13/80 (non-ionic wetting agent) (Hüls-Degussa). All other chemicals are laboratory-grade.

General procedure

Anionic cellulose was produced by padding cellulose cotton fabric in a solution of different concentrations of carboxymethyl cellulose (CMC) (2-8%) and Na-HDCT (2% to 12%, depending on the solution) and a wetting agent (0.1%) to a wet pick up of 80-120% (owing weight of fabric (owf), drying in air to a residual humidity of 20-40% and fixed at 140°C for 10 min. Washing was done in Linitest at 40°C for 15 min.

Dyeing the treated fabric

The treated cotton was dyed with CMC without the addition of salt using the basic dye Astrazone red, whose structure is illustrated below (Scheme 2). The dyeing bath concentration was 500 mg/l, and the material to liquor ratio was 1:50. The aqueous solution of the dye containing the sample was put in a shaking water bath, and the temperature was raised to 80°C and maintained for 60 min. At the end of the dyeing process, the sample was washed several times with boiling water and 0.1% Marlipal, finally washed with cold water and then dried at ambient conditions and conditioned to standard humidity.



Scheme 2. Chemical structure of Astrazone Basic Red 22 C.I. 11055

Testing and analysis

Polyelectrolyte titration was performed according to the process outlined in Horn [5] and Knittel [8].

Color measurement was done using the K/S apparatus (Datamaster DC 3880, Datacolor AG), Droptest (wettability) according to TEGEWA [2],

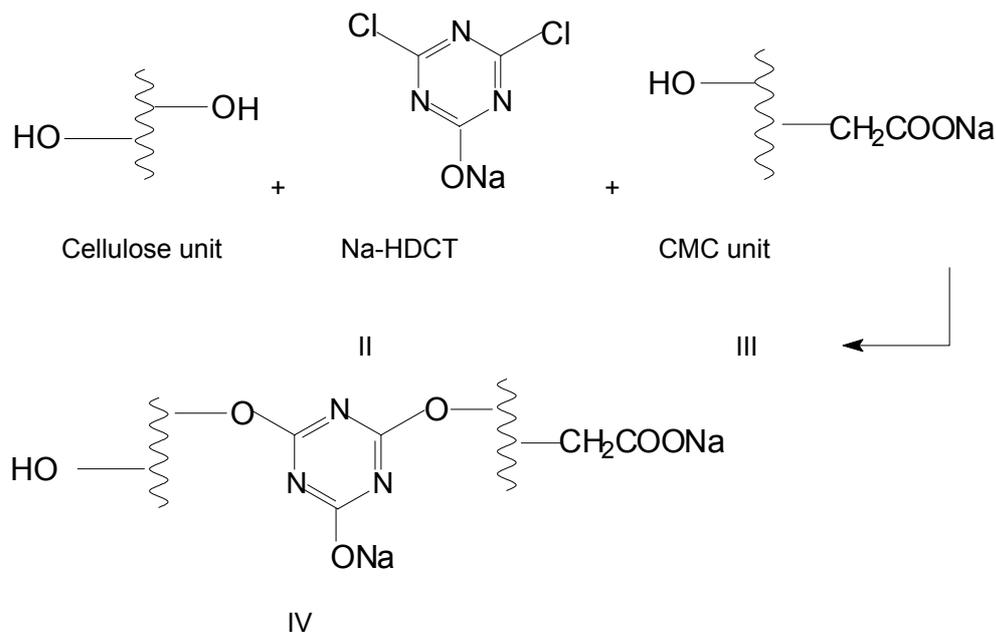
Crease recovery angles were measured according to DIN 53 890.

FT-IR spectra were taken with a Biorad FTS-45 spectrometer in diffuse reflexion mode.

Polyelectrolyte Titration (PELT) on the treated fabric was carried out with a particle charge detector (Zetasizer PCD 03pH, Müttek) and immersing the treated fabric in cationic solution (Polydiallyldimethyldiammonium chloride) and back titration of the unbounded cationic with anionic solution (Sodium poly-ethenesulphate).

Results and discussion

Cotton cellulose reacts with carboxymethyl cellulose in the presence of Na-HDCT as a crosslinking agent with chemical bond formation. The tentative mechanism is suggested as follows in Scheme 3.



Scheme 3. Assumed structure of CMC-finished cotton

FTIR analysis of treated cotton

For pure CMC, the IR spectra show a broad band at 3444 cm^{-1} due to the stretching frequency of the -OH group [1]. The band at 2922 cm^{-1} is due to C-H stretching vibration. The presence of a strong band at 1614 cm^{-1} confirms the presence of the COO- group. The bands around 1422 and 1335 cm^{-1} are assigned to CH_2 -scissoring and OH -bending vibration respectively. The band at 1061 cm^{-1} is due to $>\text{CH-O-CH}_2$ stretching. Most of these bands are too similar to the cotton base signals as shown in Figure 1, so only minor changes can be interpreted in the IR spectra of the treated fabric.

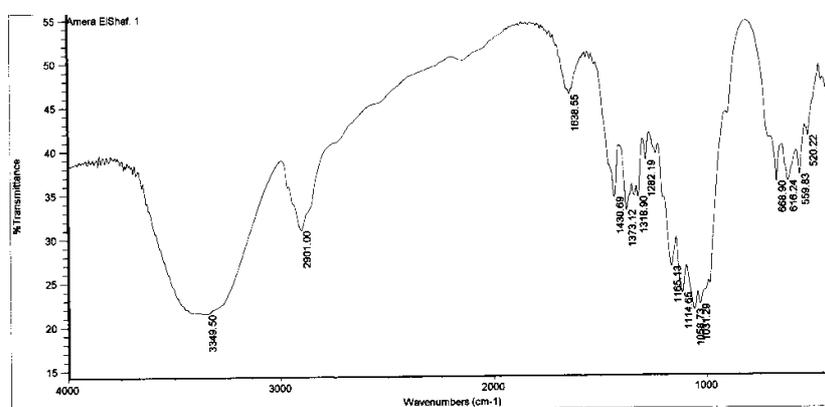


Figure 1. FTIR of blank cotton

As shown in Figure 2, the appearance of broad peaks at 1700 cm^{-1} and the increase in intensity of the peak at 1600 cm^{-1} which are attributed to the carboxylate anion (-COO-) [are ***] than that of untreated cotton; the peak at 1060 cm^{-1} , which is attributed to C-O-C saturated ether stretching, is the decisive signal for successful anchoring.

The cotton fabrics treated with CMC have different carboxyl content according to the concentration of both the CMC and Na-HDCT-solution. The properties of the cotton fabrics thus modified were monitored for crease recovery angle (CRA, wet and dry), wettability, K/S-values after cationic dyeing, and polyelectrolyte titration.

The anionic character of the surface has been proven by cationic dyeing as a tool for analysis, which can be used for quantification of the CMC anchored in future and by polyelectrolyte titration (PELT),

the principle of polyelectrolyte titration. In the case of negative charge, polycations are used for incubation, and the excessive amount of polycations is back-titrated with suitable polyanions.

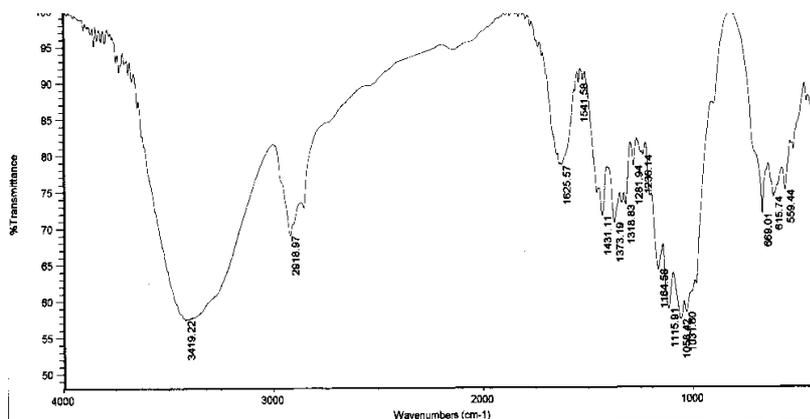


Figure 2. FTIR of modified cotton with CMC and Na-HDCT

Figures 3-5 measure the colour strength (K/S-values) by using a cationic dye and polyelectrolyte titration (which measures anionic properties at the surface).

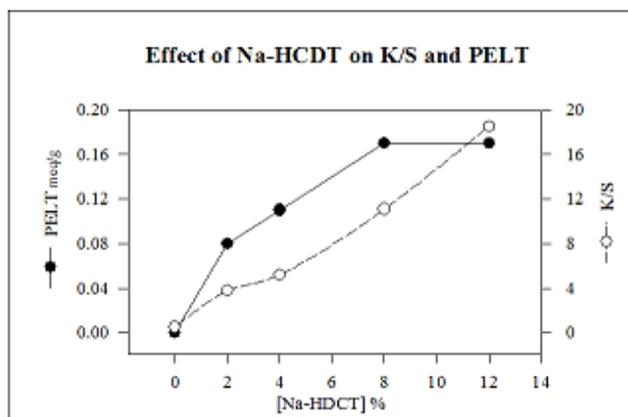


Figure 3. Effect of Na-HDCT concentration on cationic dyeing (K/S) and on accessible polyelectrolyte charges (PELT)

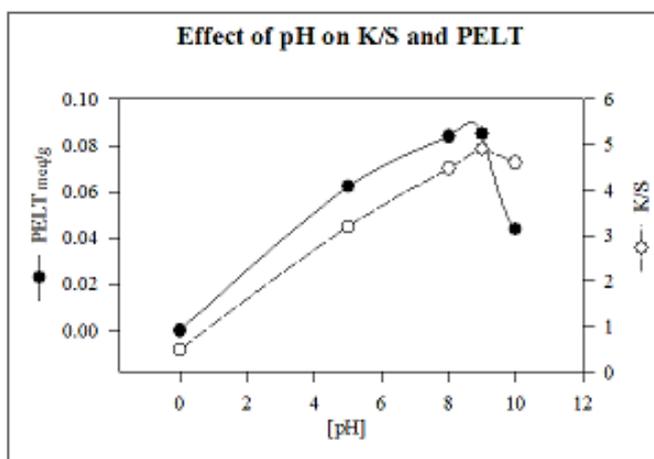


Figure 4. Effect of pH-value on cationic dyeing (K/S) and on accessible polyelectrolyte charges (PELT).

It is seen that for a given CMC- and Na-HDCT concentration at pH=9, enhanced K/S values for the dyed sample and PELT values are obtained. By pH >9, significant decrements in the obtained K/S and PELT results occur, which might be attributed to some instability of the anchoring chemical. The

increase in the anchoring Na-HDCT concentration from 1% to 12% is accompanied by a distinct increase in the anionic properties of treated cotton, as indicated by PELT and also proved by a high K/S-value in cationic dyeing.

An optimum for CMC-fixation is found between pH 8 and 9, but may be used under slightly acidic conditions, resulting in reasonable anionic values of the cotton treated.

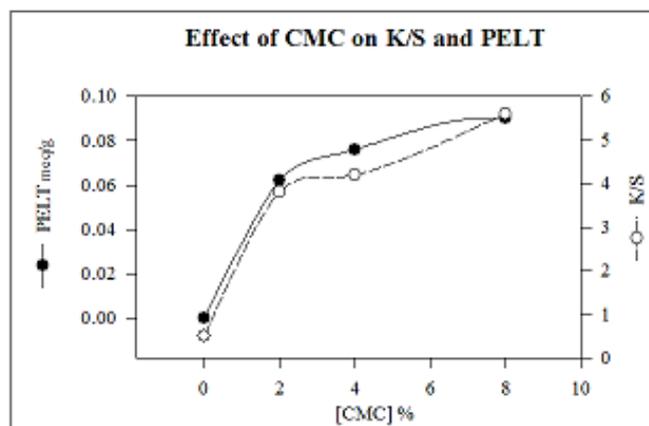


Figure 5. Effect of CMC-concentration on cationic dyeing (K/S) and on accessible polyelectrolyte charges (PELT)

The data of Figure 5 confirm that about 2% of CMC in the treating bath is sufficient for obtaining good anionic character. This means that highly viscous baths can be avoided.

Polyelectrolyte measurements on finished fabric may be used to assess the availability of ionic charges on the fabric surface, which give information on the (statistical) sites of the crosslinker and on the possible chain segment mobility of polymer on fibre [7]. Chain mobility may determine any functionality envisaged.

The results of polyelectrolyte titration on CMC-treated cotton (Figures 3-5) are an example of how, in contrast to the current use of the crosslinking (mainly cyanauric chloride derivatives), only one-third of the potential charge equivalents of the base CMC-polymer remain accessible after fixation onto the textile. It can be shown that by varying the amount of crosslinking used, a higher charge accessibility can be reached with a resulting lower add-on. The charge accessibility related to the amount of permanent add-on can be increased considerably by using less of the crosslinking chemicals, but with the risk of only low coverage and thus a lower total binding capacity of the treated fabric.

Wrinkle-resistant cottons come under regulatory scrutiny because of the need for chemical treatments to improve resiliency. To understand why cotton is not resilient, one has to consider how the basic building blocks, cellulose chains, fit into the fibre structure, or morphology. Unlike synthesis, cellulose chains in cotton have no natural bridges, or crosslinks, between them. Once deformed by laundering or wrinkling, the cellulose chains do not return to their original position. For this reason, cotton and other cellulosic must be chemically treated to impart smooth drying properties and dimensional stability[10].

By use of the treatment outlined, we obtain an improvement in textile properties such as wet and dry wrinkle resistance of cotton, wettability and the anionic properties of cotton fabric.

Tables 1-3 show the values of CRA and wettability depending on the reaction conditions of Na-HDCT, and the concentration of CMC and pH-value respectively in the treating bath used.

It is seen in Table 3 that by increasing the pH from 5-9 in padding liquor, there is an increase in the crease recovery angle and a distinct increase in the absorbency of the cotton fabric, because the hydrophilic properties of cotton fabric are increased due to the presence of carboxyl groups in the anchored CMC even with a low add-on. The treated cotton also exhibit a higher dry CRA (209°) at pH 9 compared with blank cotton (120°), and also an increase in wet CRA from (120°) for blank cotton to (230°) for treated fabric at pH 9. A further increase in pH is accompanied by a decrease in the crease recovery angle and absorbency; this is a tendency which reflects the results on dyeing and polyelectrolyte titration.

Table 1 shows the effect of raising the concentration of Na-HCDDT in the treatment bath from 2-4%. It is accompanied by an increase in the dry and wet crease recovery angles, from 215° in dry CRA at [Na-HCDDT], 4% compared with blank cotton (120°), and also an increase in wet CRA, from 120° for blank cotton to (230°). A further increase in [Na-HCDDT] decreases the wet and dry crease recovery angle. This could be associated with the favourable increase in [Na-HCDDT], which is accompanied in the increase in CMC add-on as illustrated in Table 1, which in turns makes the fabric more rigid and decreases the dry and wet CRA.

Table 1. Effect of Na-HDCT concentration in treating bath on crease recovery angle (CRA) and wettability; condition used: [CMC] 4%; pH 9

[Na-HCDDT] [%]	Add-on [wt.-%]	CRA [°]		Drop ingress ion time [s]
		Dry	Wet	
2	0.5	209	224	2
4	1.2	215	230	2
8	2.83	190	210	~1
12	5.92	175	200	2
Blank		120	120	14

Table 2. Effect CMC-concentration on crease recovery angle and on wettability: condition used: [Na-HDCT] 2%; pH, 9.

[CMC] [%]	CRA [°]		Drop ingress ion time [s]
	Dry	Wet	
2	198	218	2
4	200	230	2
8	210	235	~1
Blank	120	120	14

Table 3. Effect of pH on crease recovery angle and on wettability; conditions used: [CMC] 4%; [Na-HDCT] 2%.

pH value	CRA [°]		Drop ingress ion time [s]
	Dry	Wet	
5	197	230	3
9	209	230	2
10	198	207	2
Blank	120	120	14

Conclusion

The anionic properties of cellulosic fabric can be easily and permanently enhanced by using carboxymethylcellulose and Na-HDCT as the anchoring chemical. No hazardous chemicals like chloroacetic acid or sodium chloroacetate need be used. This treatment provides a polymeric anionic layer on the cotton surface, which can even form a basis for introducing further layers of the opposite charge. There is also an improvement in textile properties, such as for example the crease recovery angle (wet and dry), and the wettability and K/S values of cationic dyeing.

Acknowledgement

We wish to thank the Ministry for Science and Research of the North-Rhine-Westphalia region of the Federal Republic of Germany for their financial support. This support was granted as part of the project 'DTNW/Support for attainment of further funds'.

Financial support for the research work by the Deutsche Forschungsgemeinschaft (DFG) is greatly appreciated (file no.445AGY-112/37/04).

The authors express their gratitude to Degussa AG for supplying the research chemicals.

References:

1. Biswal, D.B., Singh, R.P.: *Carbohydrate Polymer*, **57**, 379-387 (2004).
2. Beichter Stalter, P.; Wurster, G. Schmidt et al, *Der TEGEWA-Tropftest*, *Melliand Textil Ber.* **68**, 581-583 (1987).
3. Charles Tomasino: *Chemistry & Technology of Fabric Preparation*, Department of Textile Eng. Chemistry and Science College of Textile, NCSU, Raleigh, North Carolina 97-108 (1992).
4. Hebeish, A.; Rafei, R.: *Synthesis and Application of Reactive Carbohydrate Part VIII, Carboxymethyl cellulose containing pendant double Bonds*, *Amer. Dyestuff Rep.* **6**, 37-45 (1991).
5. Horn, D.; Euk, C-C.: *Charge Determination of proteins with polyelectrolyte titration*, *J. Biochem.* **258**, 1665-1670 (1983).
6. Hauser, P.J.; Smith, C.B.; Hashem, M.M.: *Ionic Crosslinking of Cotton*, *AUTEX Research Journal* **4**, 2, 2004.
7. Knittel, D.; Schollmeyer, E.: *Chitosan and its derivatives for textile finishing, part 4: Permanent finishing of cotton with ionic carbohydrate and analysis of thin layers obtained*. *Melliand Textilber.* **83** (2002) E15-E16.
8. Knittel, D.; Schollmeyer, E.: *Permanente Oberflächenmodifizierung von Textilien mit gebildenden Biopolymeren*, *DTNW-Mitt.* **35** (2001) ISSN 1430-1594.
9. Knittel, D.; Schollmeyer, E.: *unpublished results*.
10. Kotes Andrews B.A., (*Wrinkle resistance cotton and formaldehyde release*) *Colourage* 87-93 (1995).
11. Racz, I.; Borsa, J.: *Carboxymethyl cotton fabric for pesticide protective work clothing*, *Text. Res. J.* **68**, 1, 9, 1996
12. Tresoro, G.C.: *Crosslinking of cellulose*, *Hand book of fibre science and technology, vol II: Chemical processing of fibre and fabrics functional finishes, part A*, Marcel Dekker New York (1983) 1-46.

▽△