Ionic crosslinking of cellulose

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Cellulosic fabric has been treated with anionic (chloroacetic acid) and cationic (3-chloro-2 hydroxypropyl trimethylammonium chloride) materials followed by the application of a polycation (cationized glycerin) and a polyanion (1,2,3,4-butanetetra carboxylic acid) to improve the fabric durable press performance. It is observed that the ionic crosslinks stabilize the cellulose using ionic materials which do not release hazardous reactive chemicals but at the same time provide improved wrinkle recovery angle as well as complete strength retention in treated goods. The polyelectrolyte, the ionic content of the fabrics, and various features of the application procedure have been varied to optimize the results and to develop an in-depth fundamental physical and chemical understanding of the stabilization mechanism.

Keywords: Cellulose, Ionic crosslinking, Wrinkle recovery

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1 Introduction

The textile market has shown an interest in easy care, wrinkle-resistant cellulosic fabrics over the years. Untreated cellulose has poor recovery, because cotton is stabilized by hydrogen bonds within and between cellulose chains. Moisture between the polymer chains can invade the cellulose structure and temporarily release the stabilizing hydrogen bonds which experience frequent breaking and reforming when extended. The newly formed hydrogen bonds tend to hold cellulose chain segments in new positions when external stress is released. Preventing wrinkle retention of cellulose can be accomplished by the crosslinking of polymer chains, thus making intermolecular bonds between chains, so that water cannot release. In a typical durable press (DP) treatment, some hydrogen bonds are replaced with covalent bonds between the finishing agent and the fibre elements. As the covalent bonds are much stronger than the hydrogen bonds, they can resist higher external stress and disruption by water. Hence, treated cellulose has a higher initial modulus and better elastic recovery. After the external force is released, the energy stored in the strained covalent bonds provides the driving force to return chain segments back to their original positions.

Formaldehyde-based cellulose crosslinking was a very important textile chemical breakthrough of the 1930s and it is still the basis for a vast array of modern finished cellulose products today. N-methylol crosslinkers have the biggest use in durable press finishing. They give fabrics crease resistance, shrinkage control, anti-curl, and durable press, but they also impart strength loss and release formaldehyde, a known human carcinogen. Today’s textile industry has, for a long time, been searching for durable press finishes that can give same results as formaldehyde-based finishes, but cause less strength loss and no formaldehyde release. For example, polycarboxylic acids and citric acid have been used with varying degree of success. The performance of crosslinkers can be measured by dry and wet wrinkle recovery angle (WRA). Dry WRA is important for outerwear clothing to help resist dry wrinkling during wearing and wet WRA is more important for bedding which is almost never ironed and must resist wrinkling during laundering. In our earlier work, the simultaneous enhancement of both wet and dry WRA has been studied. In addition, ionic crosslinks may have other important advantages, such as antimicrobial activity and enhanced dyeability. The development of multiple methods of forming ionic crosslinks to give non-wrinkle effects to cellulosic fabric has already been reported.

These include (i) treatment of cellulose with an anionic material followed by reaction with a polycation, (ii) treatment

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of cellulose with a cationic material followed by application of a polyanion, and (iii) treatment of cellulose with a precondensate of an ionic reactive material and a polyelectrolyte of the opposite charge. Methods (i) and (ii), which have been used in this study, involve a pretreatment step for the cellulosic fabric, but the third method is very similar to commercial DP applications. Cellulose can react with several materials which impart an anionic character to it, for example chloroacetic acid (CAA), chlorosulfonic acid\footnote{5} and sodium 4-(6,13,3,5-triazinylamino)-benzenesulphonate\footnote{7} or a cationic character, for example 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHTAC)\footnote{6}, 1,1-dimethyl-3-hydroxy-azetidinium chloride and 1,1-diethyl-3-hydroxy-azetidinium chloride.\footnote{5} Our work is based on Methods (i) and (ii), the first method consisting of the reaction of cellulose with CAA, which produces partially carboxymethylated cellulose followed by a treatment with a polycation, for instance cationized chitosan, cationized glycerin, cationized ethylene glycol, cationized dextrose, cationized D-cellulose, and cationized β-cyclodextrin.\footnote{9} WRA improvements with divalent cations such as Ca\textsuperscript{++} and Mg\textsuperscript{++} have been observed. Method (ii) consists of the reaction of cotton with CHTAC to produce cationic cellulose followed by the application of a polyanion, namely polyacrylic acids, 1,2,3,4-butaneetetracarboxylic acid (BTCA), ethylenediamine tetraacetic acid, nitrilotriacetic acid, trisodium salt, monohydrate, ethylenediamine di(o-hydroxyphenylacetic acid, oxalic acid, citric acid and maleic acid. In this work, the treatment of cellulosic fabric with cationic (CHTAC) and anionic (CAA) materials followed by the application of polyanion (BTCA) and polycation (cationized glycerin) has been studied. Both the methods show promising results with excellent washing durability. Polyelectrolytes are strongly bound and thus do not desorb during washing.\footnote{5}

2 Materials and Methods

2.1 Materials

Scoured, desized, and bleached plain woven cellulosic fabric, procured from Testfabrics, Inc. and having the specifications style # 400; weight 102 g/m\textsuperscript{2}; width 44-45 inches; 78 ends x 76 picks; ISO 105/F02, was used for the study. Aqueous sodium hydroxide (20% weight) solution and glycerin were obtained from Fisher Chemicals; CAA (99%) was purchased from Aldrich Chemical Company Inc.; and sodium salt of CAA was prepared with sodium carbonate.

2.2 Ionic Cellulosic Fabric Production

The fabric was treated with anionic and cationic materials to produce ionic cellulose, giving the opportunity of forming ionic crosslinks, following the Methods (i) and (ii), as described above.\footnote{5,8}

2.2.1 Reaction of Cellulose with CAA

The optimum conditions for carboxymethylation of cellulose using CAA and the determination of carboxyl content were extracted from the previous work.\footnote{5} Cellulosic fabric samples were soaked in 20% NaOH aqueous solution for 10 min at room temperature (RT) and then squeezed to a wet pick-up (wpu) of approximately 100%. The samples were dried at 60°C for 10 min. The alkali-treated samples were steeped in aqueous solutions of sodium salt of CAA with different concentrations (0, 0.5, 1, 1.5, 2.5 M) for 5 min and then squeezed to approximately 100% wpu. After the samples were packed in polyethylene bags and kept at 70°C for 1 h, they were washed several times with water (hot and cold), acidified with 0.2 M acetic acid and again washed with distilled water to adjust the pH at 7. Finally, the samples were dried at room temperature for 24 h.

The carboxylic acid group contents of the partially carboxymethylated fabrics were determined as per the following procedure. The fabrics were cut into small pieces and then steeped in 100 mL of 0.5% aqueous HCl for 16 h. The samples were then filtered off and washed several times with distilled water until free from HCl, maintaining a pH of ~7. Silver nitrate drop test was performed which showed no presence of chloride. The samples were dried at 105°C for 3 h. Accurate weight of samples (exactly 0.2 g each) was soaked in 25 mL of 0.05 N aqueous NaOH solutions at RT for 4 h. First, a blank solution (solution without any sample) was titrated with 0.05N aqueous HCl solution using phenolphthalein pH indicator. The volume of HCl solution (mL) spent was recorded for the blank. Each of the solutions with different carboxymethylated samples was titrated similarly. The carboxyl contents of samples were calculated using the following relationship:

\[
\text{Carboxymethyl contents (mmols)/100 g} = 100 \times \frac{(V_{\text{blank}} - V_{\text{sample}})_{\text{HCl}} \times N_{\text{HCl}}}{0.2}
\]
where \( V_{\text{blank}} \) is the volume of HCl used for the titration of blank solution; \( V_{\text{sample}} \), the volume of HCl used for the titration of sample solution; and \( N_{\text{HCl}} \), the normality of HCl titrant. Finally, five different carboxymethylations, namely 6.2, 30.2, 60.7, 87.1 and 114.5 mmol carboxymethyl groups/100 g of fabric, were obtained.

Figure 1 shows the production of anionic cellulose in two steps. The crosslinks are found to be bonded to cellulose through a very stable ether linkage.

### 2.2.2 Reaction of Cellulose with CHTAC

Cationic cellulose fabric was produced by cold pad-batch treatment of fabrics with mixtures of different mole ratios of CHTAC, cationization reagent and NaOH. Four different mole ratios, such as 0.23/0.475, 0.46/0.95, 1.28/1.53 and 1.83/2.2 respectively were used. Aqueous solutions of each reagent were prepared separately as per the following procedure. A known amount of NaOH was charged into a 1 L glass beaker and filled with distilled water to 500 mL and cooled to room temperature. In the same way, a known amount of CHTAC solution was charged into another beaker and filled with distilled water to 500 mL. These two solutions were mixed in a 1000 mL beaker, cooled to RT in ice and immediately applied onto cellulose fabric using the following procedure. Fabrics were padded through the CHTAC/NaOH solutions, squeezed to a wpu of approximately 100% and rolled on to a beam. The fabrics were then covered with plastic to prevent air interaction and kept overnight at RT. Finally, the fabrics were washed with a nonionic wetting agent at boiling temperature for 10 min, centrifuged and dried at RT for 24 h. Application with the last mole ratio (1.83/2.2) was repeated multiple times in order to accomplish higher degree of cationization. The level of nitrogen fixed (%N) for each treatment was determined by nitrogen analysis using a Leuco CHN analyzer. Cellulosic fabrics having 4 different levels of fixed %N, such as 0%(untreated) 0.19%, 0.28%, 0.46%, and 0.57% respectively were produced. The possible reaction mechanism is shown in Fig. 2. The crosslinks are found to be bonded to cellulose through a very stable ether linkage as stated previously.

### 2.3 Reaction of CHTAC with Glycerin

The optimum condition for quaternization of glycerin was extracted from the study by Hashem et al. CHTAC (1156 g) was charged into a 2L beaker and 228mL of 50% NaOH solution was added dropwise to adjust the pH of CHTAC at 10-11 followed by the addition of 46.05 g glycerin. The glycerin to CHTAC mole ratio was kept at 1:10. The mixture was stirred for 10 min at RT, transferred into a preheated water bath and stirred at 60°C for another 20 h. A viscous and yellowish mixture was collected at the end. The resulting reaction product was cooled off to room temperature, filtered and pH adjusted to 7 with acetic acid. The resulting reaction mixture was recovered by drying; the product had a high degree of cationization and was easily redissolved in water at room temperature.

### 2.4 Traditional Durable Press Application

To compare the WRA performance of ionic crosslinked fabrics and traditional N-methylol treated cellullosic fabric, a resin treated sample was also produced. The chemicals used in the reaction mixture and their concentrations were as follows: Freez® 900 Reactant (modified ethylene urea resin), 250 g/L; Freecat® 9 Accelerator (MgCl₂ and AlCl₃ catalyst), 62.5 g/L; Renex® 36 (wetting agent), 1 g/L; and Mykon® HD (polyethylene softener), 3% on the weight of bath. The application process was pad-dry-cure. The fabric was first padded through the mixture with approximately 100% wet pick-up and then dried at 105°C for 5 min followed by curing at 177°C for 2 min. Finally, the fabric was washed with a nonionic wetting agent at boiling temperature for 10 min and dried at room temperature for 24 h.

### 2.5 Treatment of Anionic Cellulose with Cationized Glycerin

Carboxymethylated cellulose fabrics were treated separately with cationized chitosan, cationized glycerin, calcium chloride, magnesium chloride, cationized ethylene glycol, cationized dextrose,
cationized D-cellobiose and cationized β-cyclodextrin. All of these cationic crosslinkers gave promising results, but in this paper only the cationic glycerin treatment is reported, as it enhanced the WRA of the fabrics the best. Crosslinking with cationic glycerin was studied using pad-dry-cure, cold pad-batch and exhaustion application procedures. Treatment with exhaustion and cold pad-batch methods produced a high wet WRA but only average dry WRA. On the other hand, a higher dry and wet WRA was observed with the pad-dry-cure method. Therefore the results obtained by pad-dry-cure application were recorded. The treatment procedure used was as follows: blank and carboxymethylated (having 5 different carboxyl contents) fabrics were cut into 15 cm x 15 cm pieces and warp and weft directions were marked. The fabrics were soaked in different concentrations of aqueous cationized glycerin solutions. A blank (0%) and three different concentrations of crosslinker [1, 3, and 6% with weight (w/w)] solutions were prepared. The cationic glycerin was dissolved in deionized water at a pH of 7. The samples were squeezed to a wet pick-up of approximately 100% using a laboratory padding machine. The samples were then dried in a laboratory tenter frame oven at 85°C for 5 min and cured at 140°C for 1.5 min. Then, the fabrics were washed with a nonionic wetting agent (2 g/L) at 100°C for 10 min with a liquor ratio of 1:50. Finally, the fabrics were rinsed with cold water, centrifuged and dried at RT for 24 h.

2.6 Treatment of Cationic Cellulosic Fabrics with BTCA

This application is for Method (ii) which is the second part of our work. The approach is to form ionic crosslinks between cellulose chains by treating cationic cellulosic fabric with a polyanion. Different polyanions, namely BTCA, polycarboxylic acids, ethylenediaminetetraacetic acid, nitritotriacetic acid trisodium salt monohydrate, ethylenediamine di(o-hydroxyphenylacetic acid, oxalic acid, citric acid, and malic acid, were used as crosslinkers. All of these crosslinkers improved crease recovery angle of the fabric with varying degree of success, but the higher WRA was achieved with BTCA treatments. BTCA acts as a polyelectrolyte and forms ionic crosslinks with cationic cellulose, not as an ether-forming material. Therefore, for Method (ii) only the results of treatments with BTCA was recorded. Untreated and cationized cellulosic fabrics with varying level of fixed nitrogen were used. Aqueous solutions of BTCA with concentrations of 1, 3, and 6% (w/w) were prepared. The pH of the solutions was adjusted to 6-7 with 50% NaOH solution, as the pH of crosslinker solutions were initially < 2, which may reduce the strength of cellulose. The application procedure for treatments was the same as previously described for cationic glycerin treatment.

3 Results and Discussion

3.1 WRA of Treated Fabrics

Crease recovery angles were measured according to AATCC Standard Test Method 66 Option 2. WRA was recorded as the added total of warp and weft averages. The WRA of resin-treated, untreated, carboxymethylated and polycation-treated samples are shown in Table 1. Standard deviation of WRA measurements was between 3° and 12°. A correlation between wet WRA and carboxyl content for cationic glycerin treatment was also observed. The wet and dry WRA enhanced with an increase in carboxyl content of the treated fabric. Wet WRA was found to be higher than dry WRA due to the formation of crosslinks in the wet stage of the application. The cationized cellulosic fabrics were also treated with a polyanion, BTCA. This application is for Method (ii). The results are shown in Table 2. The BTCA treatment shows an increase in both dry and wet WRA, the wet WRA being higher than dry. A correlation between wet WRA and %N fixed was also obtained for BTCA treatment. Higher %N fixed onto cellulose produces a higher WRA.

The WRA of anionic cellulosic fabric treated with a polyanion seems to improve the crease recovery angle better than that of cationic cellulose treated with a polyanion. Treatment of anionic cellulose with

<table>
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<th>Table 1—Dry and wet WRA for cationized glycerin treated fabrics</th>
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<td>[Cationized glycerin treatment (pad batch method); Control</td>
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<tr>
<td>(untreated)—138/125, and Resin treatment —272/266]</td>
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<tr>
<td>COO⁻ content mmol/100 g</td>
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<td>6.2</td>
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<td>30.2</td>
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<td>60.7</td>
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<td>87.1</td>
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* Cationized glycerin concentration in per cent.
Table 2—Dry and wet WRA for BTCA treated fabrics

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<tr>
<th>Cationization content (%)</th>
<th>Wrinkle recovery angle, deg (dry/wet)</th>
<th>0°</th>
<th>1°</th>
<th>2°</th>
<th>3°</th>
<th>4°</th>
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* BTCA concentration in per cent.

cationic glycerin shows wet WRA between 240° and 280° and dry WRA between 180° and 230°. The average difference of wet WRA between blanks and treated fabrics is 120°, which is a very significant increase, while that of dry WRA is 55°. The BTCA treatment produces wet WRA between 180° and 240° and dry WRA between 160° and 190°.

3.2 Whiteness Index of Untreated and Treated Samples

CIE whiteness index of the cellulose fabrics was determined by a DataColor Spectrasmatch SF600X spectrophotometer. Four measurements were done for each sample and the average value was calculated and reported. The data for each treatment is shown in Figs 3 and 4. The whiteness index of treated fabrics seems to decrease as the concentration of crosslinker increases. It is also observed that the decrease in whiteness index is higher for BTCA treatment. The change is more significant for the treatments of fabrics having higher levels of cationic or anionic content. The whiteness index of untreated fabric dropped from 62.58 to as low as 51.77 for cationic glycerin treatments and 31.82 for BTCA treatments. The whiteness index of resin treatment fabric was measured as 51.04.

3.3 Breaking Strength of Treated Samples

The breaking strength of the fabrics was determined with a Syntech Tensile Strength Tester according to ASTM Test Method D5035. The breaking loads for untreated and treated fabrics in warp direction are shown in Figs 5 and 6. Strength testing for 150 treated samples reveals up to 58% increase in tensile strength. Only one sample shows strength loss of 7%. The standard deviation of strength tests for treated samples is found to be between 2 lb and 5 lb. On average, cationized glycerin
3.3.1 Breaking Strength and WRA

Ionic crosslinks between cellulose chains stabilize the structure and therefore, fabrics resist wrinkling. The WRA and strength data for treated fabrics prove that increasing the density of crosslinks in the polymer provides a higher WRA, especially wet WRA and strength gain. Both the improvements are significant. Figures 7 and 8 show that the wet WRA of treated samples versus strength data have correlations with the coefficients of determination ($R^2$) of 0.71 for cationic glycerin and 0.42 for BTCA treatments respectively.

4 Conclusions

Ionic crosslinking of cellulose for DP finish can be a potential solution for today’s textile industry, which is searching for DP finishes that can give the same advantages as formaldehyde-based finishes without causing strength loss and formaldehyde release. There are many alternatives to form ionic crosslinks, for example making cellulose anionic with CAA and reacting with a polycation or producing cationic cellulose with CHTAC and then reacting with a polyanion. In both procedures, the polymer chains are bound at as many sites as possible with having an excellent washing durability. These treatments produce improvements in both dry and wet WRA with significant increase in tensile strength. Up to 140° increase in WRA is obtained in wet state and up to 100° in dry state, including as high as 58% strength gain. In addition to the increase in crease recovery angle, the ionic crosslinks may have other important advantages, such as antimicrobial activity and enhanced dyeability. The chemicals used are common and inexpensive industrial reactants. Processes use existing equipment and do not need a high temperature curing. Similar processes are already widely used in the textile industry. The process appears to be economically feasible, the cost estimated to be less than formaldehyde-based finishes and there are no unusual safety or environmental issues.

References