IONIC CROSSLINKING OF COTTON

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Abstract

Cellulose crosslinking is a very important textile chemical process, and is the basis for a vast array of durable press- and crease-resistant finished textile products. N-methylol crosslinkers containing formaldehyde give fabrics desirable properties of mechanical stability (e.g. crease resistance, anti-curl, shrinkage resistance, durable press), but also impart strength loss and the potential to release formaldehyde, a known human carcinogen. Other systems, e.g. polycarboxylic acids, have been tested with varying degrees of success. We have developed methods of forming ionic crosslinks that provide outstanding crease-angle recovery performance, as well as complete strength retention in treated goods, without the potential for releasing any low-molecular weight reactive materials, such as formaldehyde. Our work is based on reactions of cellulose with materials that impart an ionic character to the cellulose, e.g. chloroacetic acid for negative charges or 3-chloro-2-hydroxypropyl trimethyl ammonium chloride for positive charges. These reactions produce ionic celluloses that can then sorb a polyionic material of opposite charge to form crosslinks. Cellulose treated with cationized chitosan after carboxymethylation showed significant increases in crease recovery angles without strength loss.

Keywords

cellulose crosslinking, ionic crosslinking, durable press, wrinkle resistance

Introduction

The crosslinking of cellulose is a crucial textile chemical process, and provides the textile manufacturer a multitude of commercially important textile products. The most commonly used crosslinking systems are based on N-methylol chemistry. These crosslinkers give fabrics many desirable mechanical stability properties (*e.g.* crease resistance, anti-curl, shrinkage resistance, durable-press), but also impart strength loss and the potential to release formaldehyde, a known human carcinogen. [4] Other chemical systems that do not contain formaldehyde, *e.g.* polycarboxylic acids, have been explored with varying degrees of success.[9,10] In this work we report on methods of forming ionic crosslinks, rather than the typical covalent crosslinks, to provide crease-angle recovery performance without formaldehyde release.

Ionic cellulose can be produced with a variety of reagents. Figure 1 provides examples of obtaining anionic cellulose by reacting chloroacetate with cellulose and cationic cellulose by a similar reaction with 3-chloro-2-hydroxypropyl trimethyl ammonium. These reactions produce ionic celluloses that can then sorb a polyelectrolyte of opposite charge to form crosslinks.

There are numerous strategies for producing ionic crosslinks. In this work, we will discuss the use of cationized chitosan to crosslink cotton which has been made anionic with chloroacetate.

The reaction of chitosan with 3-chloro-2-hydroxypropyl trimethyl ammonium leads to a cationized polymer that maintains its cationic character regardless of pH (Figure 3).

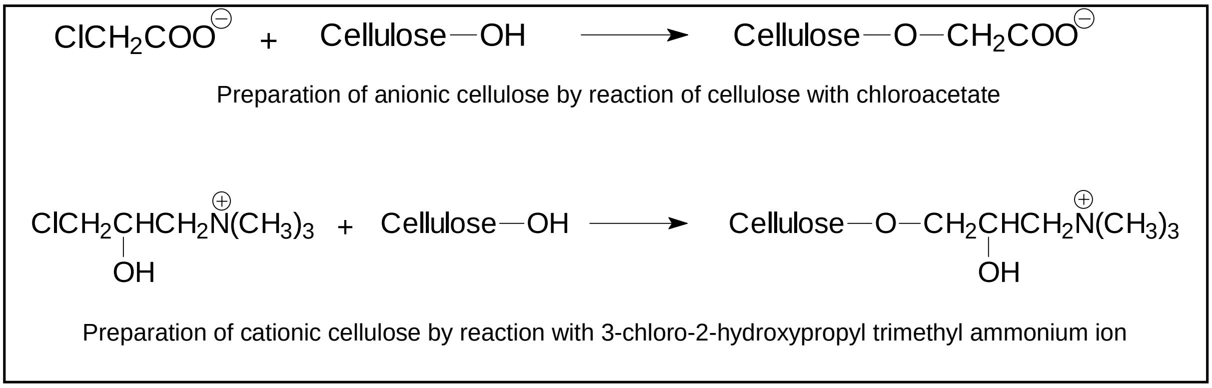

Figure 1. Preparation of ionic cellulose

Chitosan is obtained by alkaline hydrolysis of the naturally occurring polysaccharide chitin (Figure 2).

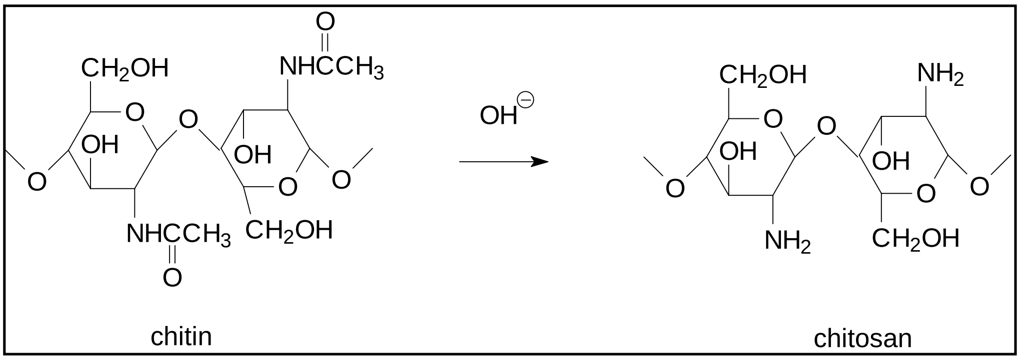

Figure 2. Preparation of chitosan from chitin

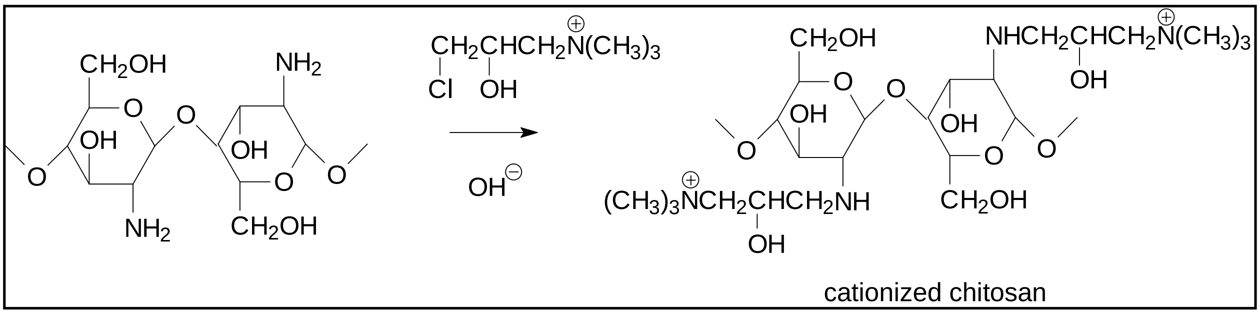

Figure 3. Preparation of cationized chitosan

Experimental

Anionic cellulose was produced with various carboxymethyl content (up to 125 mmol per 100 g fabric) by a method similar to those previously reported [1, 2, 5, 6, 7, 8]. Bleached cellulosic fabric was impregnated with 20% aqueous NaOH for 10 minutes at room temperature, followed by padding to a wet pickup of 100%. Samples were dried at 60^{o}C. These alkali-treated samples were then steeped for 5 minutes at room temperature in aqueous solutions of chloroacetic acid that had been neutralized with sodium carbonate at various concentrations (0 to 3.0 M). These samples were then squeezed to 100% wet pickup, sealed in plastic bags and heated at 70^{o}C for 1 hour. The samples were then washed and dried at room temperature. Blanks were included. This produced 7 different levels of carboxymethylation, *i.e.* 6.15, 30.2, 60.7, 87.1, 97.3, 114.5, and 123.7 mmols of carboxymethyl groups per 100 grams of fabric, as determined by titration.

Cationic chitosan was produced by the reaction of 85% N-deacetylated chitin with 3-chloro-2-hydroxypropyl trimethyl ammonium chloride using a method that differed somewhat from the method previously reported by Kim *et al*. [3]. 161 grams of 85% N-deacetylated chitin was slurried in 1156 grams of 69% w/w solution of 3-chloro-2-hydroxypropyl trimethyl ammonium chloride. NaOH (50% w/w) was added dropwise to maintain pH of 10 to 11. The slurry was stirred overnight; then the temperature was raised to 95^{o}C for 4 hours, cooled to room temperature and adjusted to pH 7 with acetic acid. The resulting reaction product was soluble in the reaction mixture. When recovered by drying, the resulting product was easily re-dissolved in room-temperature water at pH 7.

To accomplish the ionic crosslinking, cationized chitosan was applied to the anionic cellulosic fabrics by padding through solutions of cationized chitosan in water at 100% wet pickup, then drying at 105^{o}C. Various concentrations of cationic chitosan were used in the padding bath, *i.e.* 0, 0.5, 2, 4, and 6% solution concentration.

Materials

The materials used are presented in Table I.

Table I. Materials

Material	Supplier
Chloroacetic acid	reagent grade, Fisher Scientific
3-chloro-2-hydroxypropyl trimethyl ammonium chloride	CR2000 cationic reagent, 69% solution, Dow Chemical,
Chitosan	85% N-deacetylated chitin, Vanson Chemicals
Cotton fabric	scoured and bleached plain weave, 114 g/m^2 ,Testfabrics

All chemicals were used as received.

Methods of Analysis

Nitrogen analysis was provided by Dow Chemical Company using a Leuco HCN Analyzer.

Carboxymethyl content of cellulosic fabrics was determined as follows. Samples were steeped overnight in 0.1% HCl solution at room temperature. These were then washed with distilled water until the wash water showed no presence of chloride by an $AgNO_3$ drop test. Samples were dried at 105^{o}C, then brought to standard conditions. Exactly 0.3 grams of each sample was carefully weighed and combined with 100 mL distilled water and 20 mL of 0.05N NaOH in a beaker. This mixture was titrated with standardized HCl solution to a phenolphthalein end point. The carboxymethyl content was calculated as follows.

$$\textit{mmols carboxymethyl content per 100 grams} = 100 * (V_o - V) * (N_{HCl}) / (0.3)$$

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

Crease angle measurements were made by AATCC Standard Test Method 66, Wrinkle Recovery of Fabrics: Recovery Angle Method. The presented results are the sum of the recovery angle of the tested fabric in the warp and weft directions. Breaking strength was determined with an Instron tensile tester using ASTM test method D1682.

Results and Discussion

The nitrogen content of the treated fabrics are shown in Table II. As expected, the nitrogen content increases as the application level of cationized chitosan increases. Laundering the treated fabrics did not decrease the nitrogen content, indicating that a durable finish was obtained.

Table II. Nitrogen Content for Treated Fabrics (% Nitrogen)

COO^- content, mmoles/100g	Cationized chitosan concentration in pad bath				
	0% blank	0.5%	2%	4%	6%
6.2	0%	0.015%	0.021%	0.072%	0.19%
30.2	0%	0.07%	0.21%	0.26%	0.31%
60.7	0%	0.16%	0.30%	0.38%	0.42%
87.1	0%	0.25%	0.31%	0.38%	0.47%
97.3	0%	0.33%	0.39%	0.48%	0.49%
114.5	0%	0.33%	0.39%	0.49%	0.51%
123.7	0%	0.36%	0.41%	0.49%	0.52%

The dry and wet wrinkle recovery angles measured for the treated fabrics are given in Table III and Figures 4 and 5. As can be seen, both recovery angles increase as the carboxymethyl content and the cationized chitosan application level increase. The wet recovery angles in particular show remarkable increases.

Table III. Dry and wet wrinkle recovery angles for treated fabrics (dry/wet)

COO^- content, mmoles/100g	Cationized chitosan concentration in pad bath				
	0% blank	0.5%	2%	4%	6%
6.2	140/130	145/200	180/250	156/200	140/260
30.2	145/135	156/208	188/206	172/250	164/264
60.7	140/144	154/204	162/200	190/252	160/274
87.1	142/150	162/200	172/200	166/250	180/295
97.3	145/148	158/200	162/230	174/272	180/295
114.5	145/140	154/226	160/256	178/284	184/320
123.7	148/130	156/224	166/286	180/298	192/326

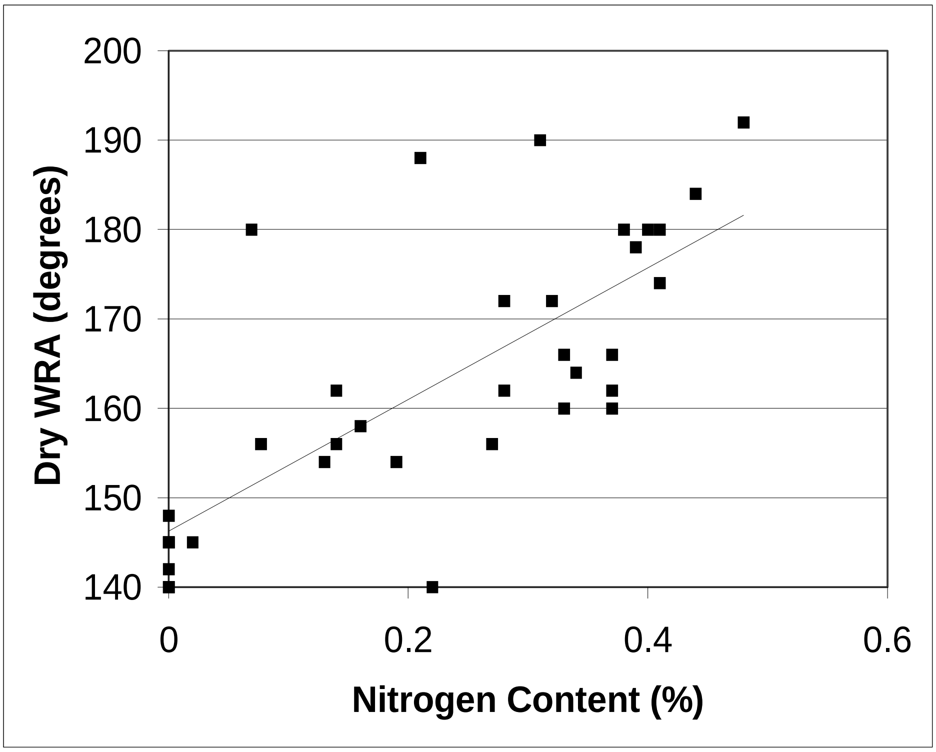

Figure 4. Effect of treatment on dry wrinkle recovery angle

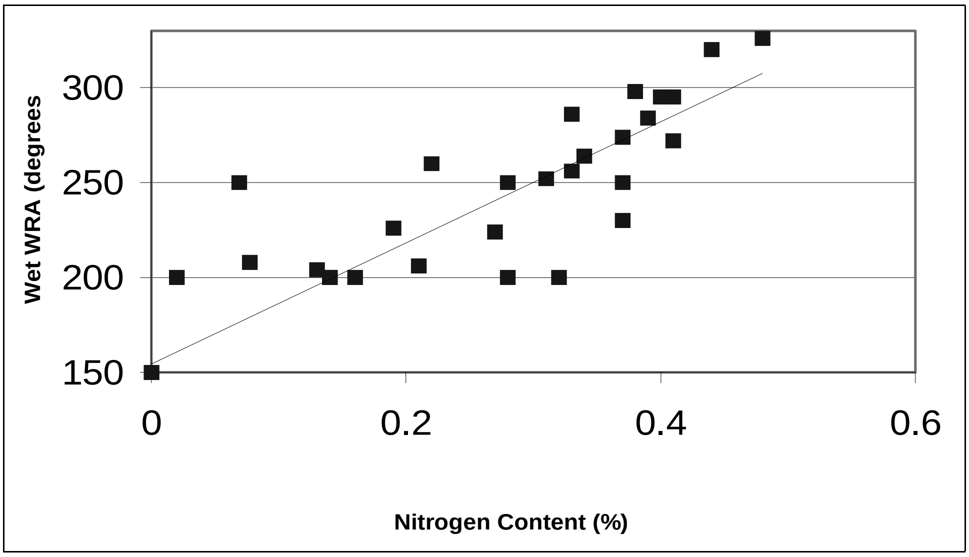

Figure 5. Effect of treatment on wet wrinkle recovery angle

The breaking strengths of the treated fabrics are given in Table IV and Figure 6. Unlike other crosslinking systems, this ionic system not only does not adversely effect the fabric breaking strength, but also the strength actually increases as the treatment level is increased.

Table IV. Breaking strengths of treated fabrics (N)

COO^- content, mmoles/100g	Cationized chitosan concentration in pad bath				
	0% blank	0.5%	2%	4%	6%
6.2	143	145	147	156	156
30.2	143	148	151	159	166
60.7	147	136	115	144	166
87.1	141	149	155	164	168
97.3	136	137	148	154	169
114.5	134	138	148	155	170
123.7	123	130	153	158	174

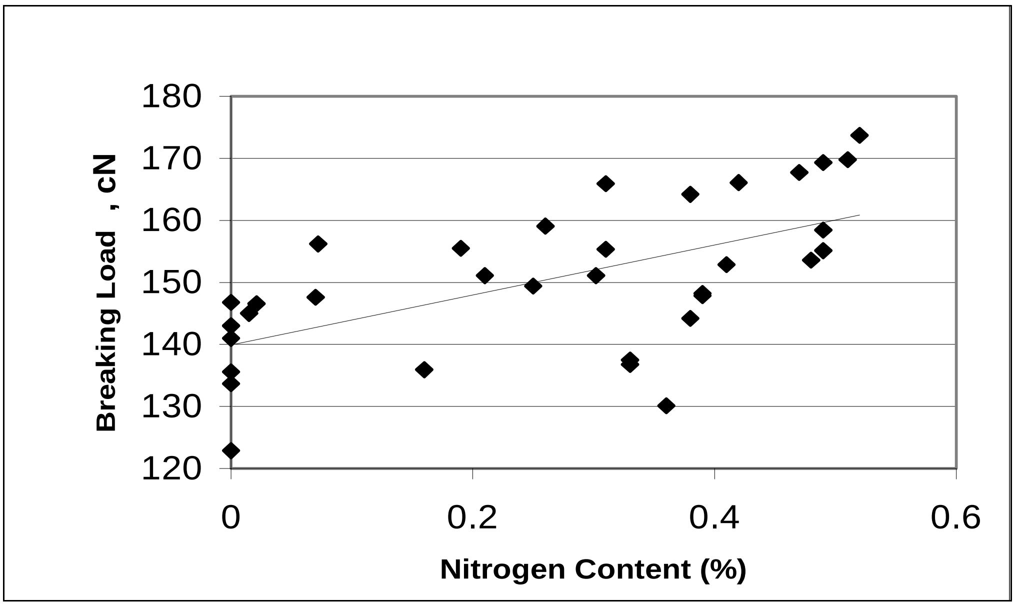

Figure 6. Effect of treatment on strength

Conclusions

Wrinkle resistance in cellulosic fabrics can be achieved with ionic crosslinks. Carboxymethylated woven cotton fabric treated with cationized chitosan showed significant increases in wrinkle angle recovery without strength loss. This process allows for enhanced wrinkle resistance without the chance of formaldehyde release.

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