

# Absorbent Properties of Carboxymethylated Fiber, Hydroentangled Nonwoven and Regenerated Cellulose: A Comparative Study

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## ABSTRACT

Commercially-available, bleached cotton fibers, rayon, and their hydroentangled counterparts were carboxymethylated to produce cellulosic products with increased absorbency. These cellulose materials were tested for absorbance, spectroscopic properties, degree of substitution and carding ability. Carboxymethylated fibers and hydroentangled webs exhibited increased water retention as the degree of substitution increased before losing fiber integrity and carding ability.

## INTRODUCTION

The cotton industry is increasing under pressure for market share from wood pulp regenerated cellulose for absorbent product applications [1]. Rayon fibers manufactured from wood pulp cellulose are more absorbent than bleached cotton fibers [2], and this has led manufacturers to favor wood-sourced cellulose for absorbent applications such as feminine hygiene, adult incontinence and diaper products. Due to regenerated cellulose's superior moisture absorbent properties, less material is required in the manufacturing of absorbent products, thus reducing material costs.

Increased absorbance of cellulose can be achieved through chemical modification via esterification or etherification using readily available commercial reagents including monochloroacetic acid [3]-[8], acetic anhydride [9], and acrylates among others [10],[11]. As the concentration of reagent increases, the degree of substitution (DS) of the hydroxyl groups on the cellulose increases, resulting in a more absorbent material [6],[7],[12]. The highest possible DS is 3.0 for fully substituted cellulose at the three hydroxyl positions in each monomeric unit. As the DS approaches 1.0 significant structural changes may occur, making the substrate gelatinous, or in some cases, completely water-soluble [7],[13]. In addition

to increased absorbency at higher DS values, the material loses tensile strength and becomes sticky and unmanageable to further processing [14],[15].

In an effort to counter the inherent absorbent advantage of wood pulp sourced cellulose, the research reported herein focused on increasing the absorbance of cotton fiber cellulose through chemical modification using commercially available monochloroacetic acid. The objective was to examine the processing limits of carboxymethylation in carding applications and to compare the absorbent properties of carboxymethylated fibers, hydroentangled nonwovens and regenerated wood pulp cellulose. Water retention values (WRV), degree of substitution, spectroscopic properties, and processability through conventional carding equipment were measured among six sources of cotton fibers, rayon fibers, and their hydroentangled equivalents. To the best of our knowledge, there are no previously published comparative studies on the processability of carboxymethylated cellulose sources. The experimental results of this study are reported and discussed herein.

## MATERIALS

Bleached, non-mercerized cotton fibers (High Q Ultra™) were supplied by Barnhardt Inc. Rayon fibers were supplied by Cotton Inc. Regenerated wood pulp fibers (Galaxy Trilobal™ and Viloft™) were provided by Kelheim Fibers GmbH. Hereafter, High Q Ultra™ fibers will be referred to as bleached cotton or hydroentangled (H.E.) bleached cotton; Galaxy Trilobal™ will be referred to as Trilobal; Viloft™ will be referred to a Crenellated; Rayon and H. E. Rayon are not trade names and will be referred to by their common names. All material samples were conditioned for a minimum of 24 hours in a textile testing laboratory maintained at standard

textile testing conditions of  $21 \pm 1^\circ\text{C}$  and  $65 \pm 2\%$  relative humidity in accordance with ASTM D1776. Sodium hydroxide, monochloroacetic acid, glacial acetic acid and isopropanol were purchased from Sigma Aldrich and used without further purification.

## EXPERIMENTAL

### Carboxymethylation

The carboxymethylation procedure for fibers and hydroentangled fabrics was modified from U.S. Patent 3,589,364 [16]. Cellulose fibers or H.E. fabrics (1.0 g) were immersed in a solution (100 mL) of isopropanol/deionized water (9:1) and heated to  $40^\circ\text{C}$  while stirring under nitrogen. An 8% aqueous NaOH solution (13.2 mL, 1.7 M) was added dropwise and the reaction was heated to  $60^\circ\text{C}$  for 30 min. Monochloroacetic acid (0.2 g, 2.12 mmol) in 3 mL of isopropanol was added dropwise to the reaction while rapidly stirring and the temperature was raised to  $70^\circ\text{C}$  and stirred for 4 hrs. After this time the reaction was cooled to room temperature and neutralized with glacial acetic acid. The derivatized product was removed from the reaction mixture, placed on a Buchner funnel, rinsed under reduced pressure with deionized water (100 mL), washed with a 4:1 MeOH/deionized water solution (100 mL), followed by 100% MeOH (100 mL). After the product had air dried, it was placed in a vacuum oven and dried at  $100^\circ\text{C}$  for 20 min.

### Water Retention Value (WRV)

A sample of derivatized cellulose material was immersed in a beaker of deionized water for two hours and then removed. The excess water was allowed to drain from the sample before being placed into a specially designed centrifuge tube and spun for 20 min at 4200 rpm. The sample was immediately removed from the centrifuge tube and weighed, with the weight recorded as the "wet weight". The sample was then dried in a preheated ( $110^\circ\text{C}$ ) vacuum oven for 20 minutes, removed, and immediately reweighed, with the weight recorded as the "dry weight". The equation for determining WRV is as follows:  $\text{wt} = \text{weight}$

$$\text{WRV} = [(\text{wet wt} - \text{dry wt})/(\text{dry wt})] \times 100 \quad (1)$$

### Degree of Substitution (DS)

The degree of substitution of each cellulose material was determined using the standard method, ASTM D1439-15 [17]. In this process, sodium carboxymethylcellulose is converted to the free acid form then treated with a known amount of aqueous NaOH (0.3-0.5 N) to provide the sodium carboxylate.

The excess NaOH is then back titrated with a known HCl (0.3-0.5 N) solution allowing for the calculation of the DS. The determination of the DS,  $G$ , was calculated using the following equations:

$$A = (BC - DE)/F \quad (2)$$

$$G = 0.162A / (1 - 0.0584A) \quad (3)$$

A = milliequivalents of acid consumed per gram of substrate

B = NaOH solution added, mL

C = normality of NaOH solution

D = HCl required for titration of excess NaOH, mL

E = normality of HCl

F = acid carboxymethylcellulose used, g

162 = gram molecular mass of anhydroglucose unit of cellulose

58 = net increase in molecular mass of anhydroglucose unit for each carboxymethyl group substituted.

### Infrared Spectroscopy (ATR/FT-IR)

All sample measurements were performed directly on the cellulose materials in the solid state. For the (ATR/FT-IR) measurements, a Bruker Vertex 70 bench top instrument was employed. Cellulose samples were exposed to air for less than a minute before analysis. The samples were placed on the germanium ATR crystal and then secured using a high pressure clamp to ensure intimate contact of the sample with the crystal during surface analysis. There were 32 interferograms collected for each sample before the average spectrum was generated. The resolution was maintained at  $8 \text{ cm}^{-1}$ . All spectral measurements were done at room temperature over the spectral region of  $650\text{-}4500 \text{ cm}^{-1}$  using a DTGS detector and KBr beam splitter. Data were processed using Bruker OPUS version 6.5 software.

## RESULTS AND DISCUSSION

Monochloroacetic acid carboxymethylation of cellulose has been investigated extensively as a means to increase the absorbent property of wood pulp and cotton celluloses [18]-[21]. Monochloroacetic acid was chosen for its low cost, convenience, safe handling ability and solubility in polar solvents including isopropanol and water. This research sought to determine the limitations of carboxymethylation between various cellulose fiber types and hydroentangled nonwovens in order to improve absorbency while maintaining carding processability.

The carboxymethylation of bleached cotton fibers was initially investigated utilizing a typical two step carboxymethylation procedure [16]. In the first step alkali cellulose is generated by treatment with aqueous sodium hydroxide, followed by the subsequent addition of monochloroacetic acid in isopropanol. Although not initially a component of the investigation, reaction optimization became necessary as the ratio of isopropanol to deionized (DI) water proved to have a significant impact on the water retention value (WRV). An isopropanol to DI water ratio of 5:1 resulted in a WRV of 0.7 g/g (Table I, entry 1). Increasing the ratio to 9:1 (iPrOH:DI H<sub>2</sub>O) further improved the WRV to 1.1 g/g (Table I, entry 2). Performing the reaction in 100% isopropanol resulted in an even greater WRV of 1.7 g/g (Table I, entry 3). Under these reaction conditions, it was important to note that water was still present via the aqueous sodium hydroxide solution. However, when a subsequent reaction was performed with a sodium hydroxide solution prepared in isopropanol, with 100% isopropanol as the solvent, the WRV decreased tremendously (Table I, entry 4). From these experiments it was concluded that the presence of water was essential to achieving a higher WRV and therefore, a higher degree of substitution [4]. The volume of solvent present in the reaction was also determined to influence the WRV. As shown in entries 5 and 6 in Table I, increasing the solvent volume from 150 mL to 200 mL resulted in an increased WRV from 1.5 g/g to 1.7 g/g, respectively.

TABLE I. Effect of solvent composition and volume on WRV of bleached cotton fibers.

Entry	iPrOH: H <sub>2</sub> O	solvent volume (mL)	chloroacetic acid (mg)	WRV (g/g)
1	5:1	100	200	0.7
2	9:1	100	200	1.1
3	only iPrOH <sup>a</sup>	100	200	1.7
4	only iPrOH <sup>b</sup>	100	200	0.4
5	9:1	150	200	1.5
6	9:1	200	200	1.7

<sup>a</sup>NaOH 1.7 M in DI water

<sup>b</sup>NaOH 0.15 M in iPrOH

To further investigate the effect of carboxymethylation on WRV, the bleached cotton fibers were treated with an increasing amount of monochloroacetic acid (Table II). For the following sequence of carboxymethylations, 100 mL of 9:1

isopropanol to DI water were used per gram of substrate. The WRV increased from 0.7 to 2.9 g/g as the amount of monochloroacetic acid was increased from 100 mg (1.06 mmol) to 400 mg (4.23 mmol). However, cellulose fibers treated with 500 mg (5.29 mmol) monochloroacetic acid became too difficult to handle while trying to obtain the WRV, due to increased fiber swelling. Hydroentangled (H.E.) bleached cotton fabrics treated under identical reaction conditions yielded similar results as those obtained with the bleached cotton fibers. However, in a few instances the hydroentangled fabrics were able to retain slightly more water than their free fiber counterparts. Specifically, at 100 mg (1.06 mmol) and 300 mg (3.18 mmol) monochloroacetic acid, the WRVs were 0.9 g/g compared to 0.7 g/g and 1.8 g/g compared to 1.6 g/g, respectively.

A comparative carboxymethylation study of WRVs between two bleached cotton sources and four regenerated cellulose sources, treated with identical reaction conditions and with varied amounts of monochloroacetic acid, was performed (Table II). All cellulosic substrates were treated with 100 mg (1.06 mmol) to 300 mg (3.18 mmol) monochloroacetic acid. Both bleached cotton sources were treated with up to 400 mg (4.23 mmol) monochloroacetic acid and rayon was treated with up to 500 mg (5.29 mmol). Not all cellulosic substrates were treated at higher concentrations of monochloroacetic acid due to the formation of a gelatinous substance that made further analyses impossible. Rayon fibers carboxymethylated with 500 mg (5.29 mmol) monochloroacetic acid resulted in a WRV of 9.0 g/g before losing fiber integrity. Similarly to the hydroentangled bleached cotton fabric, the hydroentangled rayon fabric outperformed its free fiber counterpart, resulting in higher WRVs across the entire series. The various rayon fibers reacted similarly, with the only exception occurring at 300 mg (3.18 mmol) monochloroacetic acid. The WRVs at this concentration proved more favorable to Trilobal than Crenellated, yielding a WRV of 7.2 g/g over 4.6 g/g, respectively. These fibers display different cross-sectional shapes (y-shaped cross-section versus flat cross-section with crenellated surface) which presumably account for the difference in WRVs at higher concentrations of monochloroacetic acid.

TABLE II. WRVs of carboxymethylated cellulose fibers and fabrics.

chloroacetic acid (mg/1G cellulose)	Bleached Cotton WRV (g/g)	H-E Bleached Cotton WRV (g/g)	Rayon WRV (g/g)	H-E Rayon WRV (g/g)	Crenellated WRV (g/g)	Trilobal WRV (g/g)
0 (0.00 mmol)	0.4	0.4	0.4	0.9	0.8	0.9
100 (1.06 mmol)	0.7	0.9	0.9	1.4	1.4	1.4
200 (2.12 mmol)	1.1	1.1	1.5	2.1	2.2	2.3
300 (3.18 mmol)	1.6	1.8	2.3	4.5	4.6	7.2
400 (4.23 mmol)	2.9	2.8	3.0	N/A	N/A	N/A
500 (5.29 mmol)	N/A	N/A	9.0	N/A	N/A	N/A

To confirm the presence of carboxymethyl groups in the treated cellulosic substrates, IR and  $^{13}\text{C}$  CP-MAS NMR spectra were obtained for the six untreated and treated cellulose fibers and hydroentangled fabrics. *Figure 1* shows the IR spectrum of a series of hydroentangled bleached cotton fibers, including the untreated fiber and fibers treated with up to 400 mg (4.23 mmol) of monochloroacetic acid. Evident from the IR spectrum are the broad absorption bands at  $3334\text{ cm}^{-1}$  due to the  $-\text{OH}$  stretching frequency, the absorption band at  $2894\text{ cm}^{-1}$  due to the C-H stretching vibration, and the most significant absorption band at  $1589\text{ cm}^{-1}$  due to the C=O stretching of the  $\text{COO}^-$  group [22]-[26]. The carbonyl peak at  $1589\text{ cm}^{-1}$  was observed in each sample of carboxymethylated cellulose. Not only is IR significant in characterizing the carboxymethylation of fibers, it can also be used as a tool for determining the relative value of the degree of substitution. Similarly,  $^{13}\text{C}$  CP-MAS NMR confirmed the presence of carboxymethyl groups on each of the cellulosic substrates with the emergence of a carbonyl peak at 178 ppm. *Figure 2* shows the  $^{13}\text{C}$  CP-MAS NMR spectra of the untreated and carboxymethylated bleached cotton fibers. The carbonyl peak at 178 ppm in *Figure 2* increases in proportion to the increasing amount of monochloroacetic acid used. As with FTIR,  $^{13}\text{C}$  CP-MAS NMR has recently become a valuable tool for determining the average DS of carboxymethylcellulose [27].

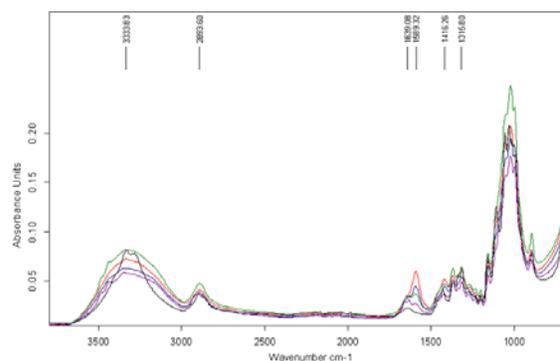


FIGURE 1. IR Spectra of hydroentangled bleached cotton fabric, untreated up to 400 mg (4.23 mmol) monochloroacetic acid. Black = untreated. Purple = 100 mg (1.06 mmol) monochloroacetic acid. Green = 200 mg ( 2.12 mmol) monochloroacetic acid. Blue = 300 mg (3.18 mmol) monochloroacetic acid. Red = 400 mg (4.23 mmol) monochloroacetic acid.

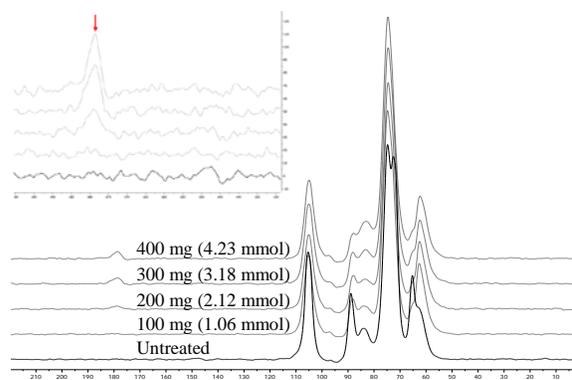


FIGURE 2.  $^{13}\text{C}$  CP-MAS NMR spectra of untreated and carboxymethylated bleached cotton.

The degree of substitution for each carboxymethylated fiber and H.E. fabric was determined using the classical back titration method (ASTM D1439-03)[17]. The DS results for each cellulosic substrate treated with 200 mg (2.12 mmol) monochloroacetic acid are tabulated in *Table III*. The titration method produced the absolute value of the DS, whereas the FTIR and <sup>13</sup>C CP-MAS NMR methods result in the relative value of the DS. The average DS can be calculated from the spectra of <sup>13</sup>C CP-MAS NMR based on the ratio of integration of the carbonyl peak to the C-1 signal peak [27]. From *Figure 2*, the average DS of the cellulosic fibers treated with 200 (2.12 mmol), 300 (3.18 mmol), and 400 mg (4.23 mmol) monochloroacetic acid were calculated to be 0.18, 0.21, and 0.24, respectively. It is important to note, grinding of the whole fibers to 40 mesh with a Wiley Mill did not significantly alter the reactivity of the fibers and resulted in a similar DS, as confirmed thru the titration analysis method.

TABLE III. Degree of Substitution of different fiber sources at 200 mg (2.12 mmol) monochloroacetic acid.

Fiber Source	DS @ 200 mg (2.12 mmol)
Rayon	0.089
Bleached Cotton	0.090
H.E. Bleached Cotton	0.103
Crenellated	0.121
H.E. Rayon	0.133
Trilobal	0.159

The relative DS can be calculated from the FTIR spectra by taking the ratio between the absorption bands at 1589 cm<sup>-1</sup> and 2894 cm<sup>-1</sup> [26]. The absorption at 1589 cm<sup>-1</sup> is assigned to the stretching vibration of the carbonyl group and that at 2894 cm<sup>-1</sup> is the stretching vibration of C-H. This ratio provides an estimate of the relative number of carbonyl groups found in the substrate,  $R_{rel} = A_{1589}/A_{2894}$ . Using the equation,  $DS_{rel} = R_{rel} - N$ , the numerical constant was determined,  $N$ , by setting  $DS_{rel}$  equal to zero for the original cellulose sample [28]. Once the constant had been determined for each of the different fiber

sources, the DS could be calculated following the formula. *Figure 3* shows the relationship between the relative DS of each fiber and the increasing concentration of monochloroacetic acid. As previously mentioned, all cellulosic substrates were treated with up to 300 mg (3.18 mmol) monochloroacetic acid, however, only three cellulose sources were treated with 400 mg (4.23 mmol) and only one with 500 mg (5.29 mmol). Above 300 mg (3.18 mmol) monochloroacetic acid, the substrates became gelatinous and difficult to handle while trying to obtain WRVs and DS. At 300 mg (3.18 mmol) monochloroacetic acid, H. E. rayon has the highest relative DS of 0.768.

In some cases, in order for cotton fibers to be processed for commercial absorbent commodities they must first undergo a carding procedure. During the carding process the cotton fibers are disentangled, cleaned, mixed and oriented in direction, resulting in a continuous matt of fibers. Therefore, in order for derivatized cotton fibers to be relevant in absorbent commodities they must possess carding ability. To examine the carding ability of the carboxymethylated cotton fibers, the reaction of cellulosic fibers was scaled up to 10 grams of substrate and then tested on a minicard. At this larger scale a few adjustments were necessary to achieve optimized reaction conditions. Firstly, increasing the volume from 1.0 L to 1.5 L per 10 grams of substrate allowed for more efficient stirring. Secondly, decreasing the mole fraction of monochloroacetic acid from 2 g (21.2 mmol) to 1 g (10.6 mmol) greatly improved the carding ability of the carboxymethylated fibers. Using 2 g monochloroacetic acid resulted in a higher WRV (1.6 g/g compared to 0.7 g/g for 1 g), however, the higher degree of carboxymethylation caused the fibers to become too matted for carding. Therefore, it was determined that carboxymethylated cotton fibers with WRVs between 0.7 g/g and 1.6 g/g can be efficiently processed for manufacturing of absorbent commodities.

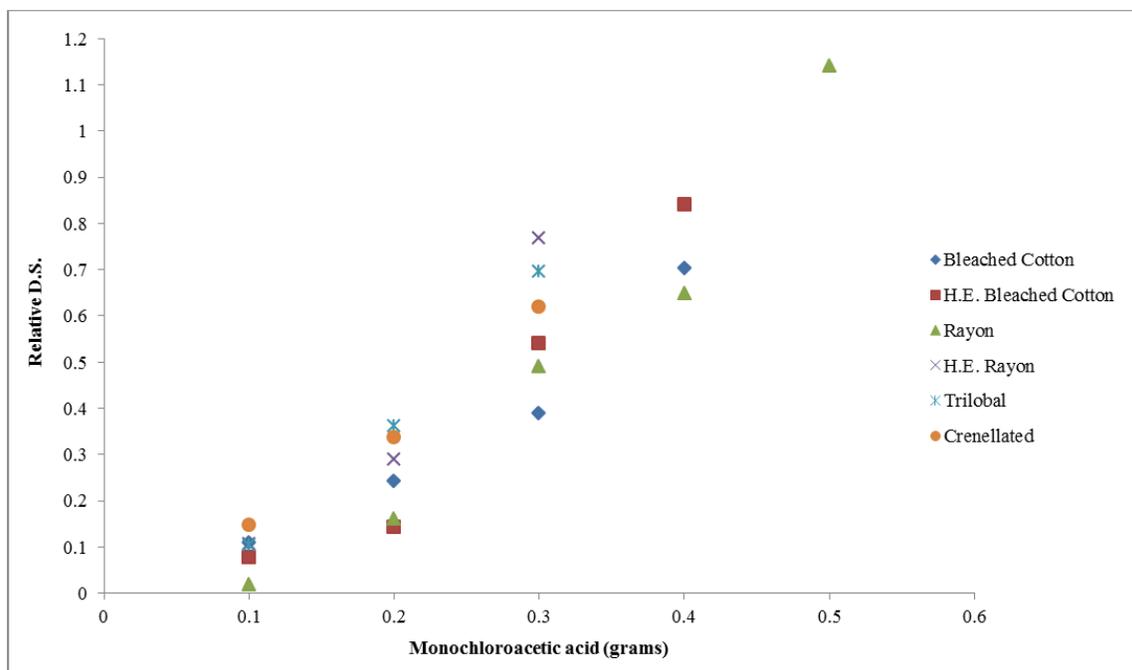


FIGURE 3. Relative DS of different cellulose substrates with varying concentrations of monochloroacetic acid using FTIR analysis.

In order to better understand the “window of cardable fibers” with WRVs between 0.7 g/g and 1.6 g/g, *Table IV* and *Figure 4* display the relationship between relative DS and WRV for all cellulosic substrates studied. *Table IV* tabulates the relative DS and WRVs (g/g and %) for each cellulose source at each concentration of monochloroacetic acid. The shaded area represents those cellulosic fibers that fall within the window of processability based on their WRV. *Figure 4* allows for a more visual representation of the data. The window of processability is in fact very small in comparison to the number of experiments conducted. Although many of the cellulosic substrates perform well with greater concentrations of monochloroacetic acid, in terms of WRV and DS, these fibers fall outside of the window of processability and therefore cannot be efficiently carded and used in the manufacturing of absorbent products.

For example, rayon was the only cellulose source to be treated with 500 mg (5.29 mmol) monochloroacetic acid and resulted in a relative DS of 1.141 and a WRV of 9.0 g/g or 896.3%. In spite of its superior WRV, it cannot be carded. Similarly, after reaction with 300 mg (3.18 mmol) monochloroacetic acid, the substrate with the greatest WRV was Trilobal with a WRV of 7.2 g/g or 720.5%, and the substrate with the largest relative DS was H.E. Rayon with a relative DS of 0.768.

However, despite the superior absorbent properties of these substrates compared to the other cellulosic fibers, they cannot be carded.

From the inserted region of *Figure 4*, the window of processability, it is evident that one cellulose source outperforms the others in both WRV and relative DS. Falling just within the determined limits of the window of processable fibers is bleached cotton treated with 300 mg (3.18 mmol) monochloroacetic acid, resulting in a WRV of 1.6 g/g and a relative DS of 0.389. Rayon treated with 200 mg (2.12 mmol) monochloroacetic acid also falls within the window with a WRV of 1.5 g/g, however, it has a lower relative DS of 0.161. A number of cellulosic substrates produced a comparable WRV, with values of 1.4 g/g or 1.1 g/g, however, these substrates also resulted in a much lower relative DS. From the data many of the cellulosic substrates produced large WRVs and relative DS with increasing amounts of monochloroacetic acid, however, only a few fell within the determined window for processable fibers to be used in the manufacturing of absorbent products.

TABLE IV. Relative DS and WRVs (g/g and percentages) of all fiber types. Shaded region represents the window of process ability.

	Mole Fraction of Monochloroacetic Acid					
	0 mg (0 mmol)	100 mg (1.06 mmol)	200 mg (2.12 mmol)	300 mg (3.18 mmol)	400 mg (4.23 mmol)	500 mg (5.29 mmol)
Fiber Source	Degree of Substitution (DS), Water Retention Value (WRV) (g/g, %)					
Bleached Cotton	0.000/0.4 g/g 36.1%	0.109/0.7 g/g, 71.2%	0.243/1.1 g/g, 109.7%	0.389/1.6 g/g, 162.8%	0.702/2.9 g/g, 291.0%	n/a
H.E. Bleached Cotton	0.000/0.4 g/g 41.7%	0.078/0.9 g/g, 92.2%	0.143/1.1 g/g, 111.3%	0.541/1.8 g/g, 179.3%	0.841/2.8 g/g, 280.7%	n/a
Rayon	0.000/0.4 g/g 43.1%	0.02/0.9 g/g, 94.1%	0.161/1.5 g/g, 148.2%	0.49/2.3 g/g, 226.6%	0.65/3.0 g/g, 296.5%	1.141/9.0 g/g, 896.3%
H.E. Rayon	0.000/0.9g/g 88.0%	0.106/1.4 g/g, 141.4%	0.289/2.1 g/g, 206.0%	0.768/4.5 g/g, 447.4%	n/a	n/a
Trilobal	0.000/0.9 g/g 85.3%	0.105/1.4 g/g, 138.1%	0.362/2.3 g/g, 233.1%	0.696/7.2 g/g, 720.5%	n/a	n/a
Crenellated	0.000/0.8 g/g 84.0%	0.147/1.4 g/g, 135.0%	0.338/2.2 g/g, 222.9%	0.619/4.6 g/g, 460.0%	n/a	n/a

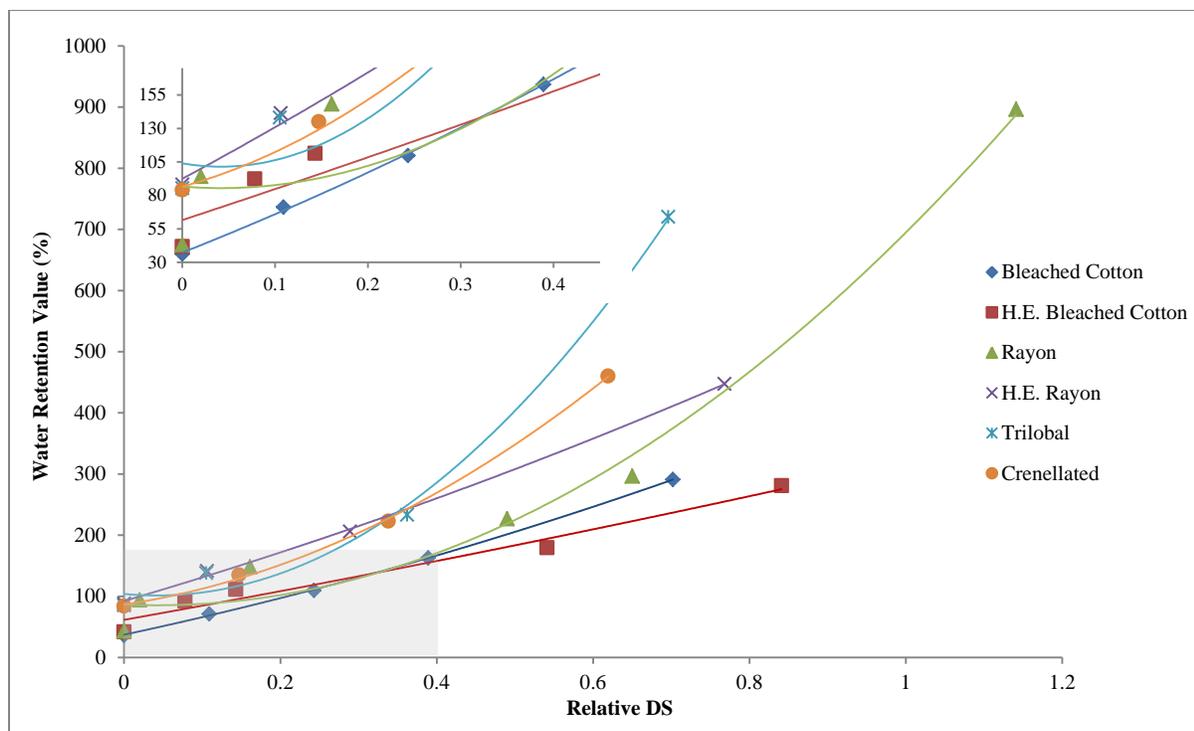


FIGURE 4. WRVs and relative DS for each fiber type. Shaded area represents the window of processability with an expanded view of the region inserted at the upper left corner.

## CONCLUSION

In this study, six fibers and hydroentangled fabrics were reacted with 100 – 500 mg (1.06 – 5.29 mmol) of monochloroacetic acid and were found to have increased absorbent properties. The optimum conditions for carboxymethylation of the cellulosic substrates were 100 mL of 9:1 isopropanol to DI water and 200 mg monochloroacetic acid per gram of substrate. As the concentration of monochloroacetic acid increased, the water retention values and the degree of substitution increased across all substrates. Bleached cotton fibers increased in WRV from 0.7 g/g to 2.9 g/g when using 100 mg to 400 mg monochloroacetic acid and retained good carding ability up to the 300 mg (3.18 mmol) level. The hydroentangled variations of fibers outperformed their free fiber counterparts, having slightly higher WRVs and degrees of substitution. The standard titration method for determining the absolute DS was utilized in conjunction with FTIR and <sup>13</sup>C CP-MAS NMR methods for determining the relative DS and the results were consistent with observations. A scaled up reaction showed the carding ability of carboxymethylated fibers containing WRVs between 0.7 g/g and 1.6 g/g can be utilized in the manufacturing of absorbent products. Bleached cotton fibers at a mole fraction of 300 mg (3.18 mmol) produced a product with increased absorbent properties that fell just within the window of processability, outperforming the other cellulose sources with a WRV of 1.6 g/g and a relative DS of 0.389. These results demonstrate a plausible use for carboxymethylated fibers in textile processes which require fiber carding and for product applications requiring absorbent materials.

## ACKNOWLEDGEMENT

The authors would like to thank Dr. Terri Von Hoven for conditioning fibers and hydroentangled fabrics.

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