Distribution of Carboxyl Groups in Carboxymethylated Cotton Fibers

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ABSTRACT: Cotton cellulose was partially carboxymethylated by a one-bath method using monochloroacetic acid and sodium hydroxide. A method was developed to study the extent of the carboxymethylation of cellulose within the cotton fibers using scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX). Uranyl nitrate was used as a stain. Scanning electron photomicrographs revealed that the carboxymethylation of cellulose occurred throughout the cotton fiber cross section. However, the X-ray microanalysis data indicated a variation in the extent of the reaction among the morphological regions that have different chemical accessibility. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 203–207, 1999

Key words: cotton; carboxymethylation; distribution in cross section; Kassenbeck's structure; scanning electron microscopy; energy-dispersive X-ray analysis

INTRODUCTION

The highly accessible structure of carboxymethylated cotton fiber can be advantageous in various areas of textile finishing. Results of the research, begun by Reid and Daul,[1] have been very promising but unfortunately have not reached industrial applications. One possible reason for this lack of industrial use might be that the substitution of the carboxymethyl groups are thought to affect subsequent finishing reactions. For example, detrimental effects of the carboxymethylation were sometimes observed in later finishing with crosslinking agents. These were explained by the decrease in the number of available reactive hydroxyl groups in the crosslinking reaction that followed the carboxymethylation.[2,3]

The degree of substitution (DS) is an important factor but not the only one influencing the properties of the modified fiber. The accessibility of cellulose, for example, swelling and hydrophilicity, is increased by carboxymethylation. While accessibility is related to the DS, there is not a direct correlation. In studying chemical accessibility, researchers have found that fibers having nearly the same DS had different accessibility depending upon the reaction parameters.[4] Rácz et al.[5] observed that the disorder of the amorphous fraction, an important factor in determining fiber properties, did not depend solely on the carboxyl content. The disorder of the structure, often used as an indicator of the extent of the modification, does not increase monotonously with higher values of important reaction parameters such as the concentration of chemicals and the period of time. The reason for this phenomenon has been shown

to be the dissolution and removal of the mostly substituted, highly accessible fractions.[5]

Carboxymethylation of cellulose fiber proceeds initially at accessible hydroxyl groups and subsequently with slow penetration into the ordered regions. The measurements of the DS represent average values for the carboxyl content (mmol/mol cellulose), while the local concentrations of the carboxymethyl groups are hypothesized to differ within various morphological regions of the cotton fiber. This inhomogeneity is believed to be larger at the beginning of the reaction than during the later time period. It is not surprising that in the narrow range of the DS, 0.03–0.1, the macroscopic fiber properties are not always in strong correlation with the DS. The aim of this work was to study the location of the carboxylmethyl groups within cotton fibers having a similar DS but carboxymethylated for different times, in order to obtain more information about the chemical accessibility and the time course of the reaction.

EXPERIMENTAL

Carboxymethylated Cotton Fiber

The cotton fibers were taken from fabrics carboxymethylated with a mixture of monochloroacetic acid and sodium hydroxide solutions for selected time periods of up to 120 min.[4] The carboxyl content, as a measure of the DS, was obtained by a procedure based on the sodium ion-sorption method of Neale and Stringfellow[4,6−8]; carboxyl groups were back-titrated with a hydrochloric acid solution in the presence of an excess of sodium hydroxide using phenolphthalein as an indicator.

A fabric specimen between 0.3 and 0.6 g, weighed with an accuracy of 0.1 mg, was placed in an Erlenmeyer flask. Solutions of 25 cm^3 of 0.02M NaOH and 25 cm^3 of 0.86M NaCl were added. After 48 h, the fabric was filtered and then rinsed with distilled water until neutrality was achieved. The filtrate was collected (100 cm^3), and an aliquot of 50 cm^3 of this liquor was titrated with 0.01M of the HCl solution using phenolphthalein as an indicator. The same volume of the original mixture of NaOH and NaCl solutions was used as a control. The moisture content of the samples was taken into consideration during the calculation of the carboxyl content of the fabric specimen. A fabric specimen of about 0.5 g was weighed then dried at 105ºC for 5 h and weighed

Table I   Carboxyl Content (c_c) and Iodine-Sorption Capacity (S_I) of Carboxymethylated Fabrics as a Function of the Reaction Time (t_{cm})[4]

t_{cm} (min)	c_c (mmol/mol cellulose)	S_I (mg/g cellulose)
0[a]	8.5	38
10[a]	45	69
30	60	73
60	75	80
90	67	112
120[a]	55	79

[a] Samples used in the microscopical analysis.

again to determine the moisture content. Three repetitions were used for the measurement of both the carboxyl content and the moisture content. The adsorption of the untreated (blank) sample was subtracted from the carboxyl content of each of the treated samples and the results expressed in mol/mol of cellulose, which is the DS.

The carboxyl content as measured by sodium ion sorption and the chemical accessibility characterized by the iodine-sorption capacity of the fabrics[4] are shown in Table I. The values of the carboxyl content and the iodine-sorption capacity changed over the course of the reaction time with an observed maximum value for each. The two maxima for carboxyl content (DS) and iodine sorption (chemical accessibility) occurred at different reaction times, 60 and 90 min, respectively. This illustrates that the accessibility is not solely correlated with the DS. Two reaction times (10 and 120 min) that resulted in somewhat similar carboxyl contents, that is, the DS (0.0365 and 0.0465), were selected for microscopical analysis.

Electron-Beam X-ray Microanalysis

Untreated and carboxymethylated yarns were tagged, embedded, microtomed, and studied with a scanning electron microscope combined with an X-ray analyzer. The microscopical investigation was conducted for untreated fabric and fabric treated for 10 and 120 min.

Uranium Tagging

To study the location of the carboxyl groups within the cotton fiber by X-ray microanalysis, the carboxyl groups were tagged with a heavy element: uranium. This method is based on the

previous work of Durso[9] that utilized the reaction with uranyl nitrate to measure carboxymethyl ether groups. Fabric samples were immersed in a 5% (w/v) solution of uranyl nitrate in an aqueous ethanolic mixture (4 : 1 ethanol and water) for 24 h. Following the reaction, the specimens were rinsed repeatedly in water and finally in ethanol.

Yarn Embedding

In preparation for X-ray microanalysis and microscopy, yarns were embedded and sectioned by a microtome. Each uranium-tagged yarn was embedded in Spurr's low viscosity resin using a plastic embedding capsule. Cross sections of the embedded yarns were cut with glass knives using a DuPont Sorvall MT2 ultramicrotome. Sections with a thickness of 3–5 μm were cut and mounted on carbon stubs with double-stick tape. The edges of the tape were sealed with carbon paint. Microscopy specimens were coated with carbon in a Veeco VE400 high-vacuum evaporator.

Microscopical Analysis

Microscopy data were gathered using a JEOL JSM35 scanning electron microscope equipped with a Tracor Northern 2000 energy-dispersive X-ray analyzer in the Material Science Center at Cornell University. Secondary electron images and back-scattered electron images of the yarn cross sections were taken at an accelerating voltage of 10 kV, a working distance of 15 mm, and a beam current of 15 nA. For X-ray intensities at selected locations and area maps, a working distance of 39 mm was used.

The X-ray emission counts were accumulated for the range of 1–10 keV for 20 s. The region of interest for the uranium signal was set for the range of 3.1–3.5 keV. The net count intensity for the uranium signal was obtained by subtracting the integral of the background signal within the same limits from the integral of the uranium peak. X-ray data were collected by placing the 1 μm spot probe at selected morphological locations within the cross sections of a single cotton fiber (Fig. 1). These locations were identified based on Kassenbeck's model[10] that defined three zones differing in their fine structure and accessibility to enzymatic hydrolysis. Three replicates of each location within a morphological zone were analyzed and averaged.

Figure 1 Morphological location (A, B, L) within the cotton fiber used for the X-ray spot probe analyses.

RESULTS AND DISCUSSION

All cotton fibers in the cross section of a yarn appeared bright in the back-scattered electron images of the carboxymethylated and uranium stained yarns, indicating the presence of uranium and, thus, carboxylmethyl groups. The carboxymethylation reaction was shown to occur in fibers throughout the yarn structure. Upon examination at high magnification, individual cotton fibers exhibited the presence of carboxylmethyl groups across the entire fiber cross section (Fig. 2).

The X-ray intensities across the fiber cross sections showed a high concentration of the carboxymethyl groups. However, the various morphological regions were observed to differ in intensity, indicating differing concentrations of carboxymethyl groups (Table II). In the untreated fiber, the highest concentration of carboxyl groups was found in the lumen (L). We believe this is due to the reaction of uranyl nitrate with proteinaceous and waxy materials known to be present in the cotton lumen.[11] Observation of the lowest concentration in zone A fits with Kassenbeck's model,[10] where zone A had the lowest chemical accessibility to enzymatic hydrolysis.

For the concave part of the cross section of the cotton fiber in Kassenbeck's structure, the data that we obtained were not statistically different from that of the convex part. (Note that the terms concave and convex are relative to the plane of the page in Fig. 1.) Therefore, we averaged the data together and labeled it zone B (Fig. 1). This morphological region of the cotton fiber (B) had higher X-ray intensities than did zone A (Table II). The orders of intensities within the morphological re-

(a)

(b)

Figure 2 (a) Back-scattered electron image of the cross section of a carboxymethylated and uranium-tagged cotton fiber; (b) X-ray map of the same fiber.

gions were the same for specimens treated for different lengths of time, representing different stages of carboxymethylation finishing. The location within the cotton fiber that had a lower concentration of carboxymethyl groups was the

highly curved extremes of the bean-shaped cross section of the cotton fiber: zone A in Figure 1.

The X-ray microanalysis and total carboxyl content data were also used to study the time course of the reaction. Ratios of X-ray intensities and of carboxyl contents for the whole fiber (DS) were calculated between 10- and 120-min reaction times (Table II). The ratio of the carboxyl content for the whole fiber is higher (0.78) than the ratios observed for the X-ray intensities of the morphological regions, the L, B, and A zones (0.43–0.57). This suggests that the initial reaction occurred on the surface rather than deeper inside the secondary wall of the fiber where the X-ray microanalysis data were collected.

The relative intensities of the various zones in the cotton fiber over the time course of the reaction were compared. The increase in the carboxymethyl content with reaction time was highest for zone A of the secondary wall, indicating that a longer reaction time is needed to penetrate the less chemically accessible region of the cotton fiber (120 min). The consequence of this phenomenon is observed in an analysis of the increases in the X-ray intensities at the various morphological locations in the cotton fiber at different reaction intervals (10, 120–10 min) that are presented in Table II. The intensities for the various morphological regions were more similar across the fiber cross section for the period of 10–120 min, that is, at the end of the reaction, than for the initial reaction period of 10 min. As expected, the distribution of the carboxyl groups became more uniform as the reaction proceeded and the reaction penetrated further into the cotton structure over the reaction time of 120 min.

In summary, although the order of the decreasing concentration of carboxyl groups within the morphological regions of the cotton fiber remained the same during the reaction (L, B, A), the

Table II   X-ray Intensities for Uranium at Selected Morphological Locations on Carboxymethylated Cotton Fibers

Time of Treatment	Untreated (Blank)	10 min[a]	120 min[a]	10/120 min[a]	120–10 min[a]
Lumen L	1981 (391)	1645 (482)	2870 (718)	0.57	1225
Secondary wall B	643 (127)	1023 (212)	2235 (685)	0.45	1212
Secondary wall A	341 (52)	776 (146)	1787 (489)	0.43	1011
Carboxyl content (DS, mol/mol cellulose)	0.0085	0.0365	0.0465	0.78	0.010

[a] Untreated (blank) has been subtracted.

absolute and relative X-ray microanalysis data indicate that the difference in the carboxymethyl group concentration among the zones decreased over the time of the reaction. This means that in a given time all of the morphological regions of the cotton fiber are accessible to the small monochloroacetic acid molecule. This may differ somewhat from that of relatively huge molecular-size reagents, such as cellulolytic enzymes used in Kassenbeck's experiment.[10]

Since monochloroacetic acid successfully penetrates the less accessible zone of the cotton fiber, carboxymethylation has potential application as a pretreatment prior to further chemical modifications. Leza et al.[12] used this approach in the grafting of previously carboxymethylated cotton. Carboxymethylation also influences soil removal and decontamination of cotton fabrics. Pesticides[13] and body oils,[14] such as triglycerides, have been observed in the lumen and secondary wall of the contaminated cotton fibers. With increase in the number of negatively charged groups upon carboxymethylation, the improved hydrophilicity of the secondary wall and the lumen of the cotton fiber is advantageous for enhanced soil removal in the laundry process.[15,16]

REFERENCES

1. Reid, J. D.; Daul, G. C. Text Res J 1947, 17, 554.
2. Ateya, K. Text Res J 1971, 41, 258.
3. Hebeish, A.; Kantouch, A.; Soliman, F. K. Cell Chem Technol 1978, 12, 301.
4. Kálmán, F.; Borsa, J.; Madarász, R.; Rusznák, I. Colloid Polym Sci 1989, 267, 349.
5. Rácz, I.; Borsa, J.; Bodor, G. J Appl Polym Sci 1996, 62, 2015.
6. Neale, S. M.; Stringfellow, W. Trans Faraday Soc 1937, 33, 881.
7. Pak, S.; Ando, Y.; Koshikawa, J.; Iijima, T. J Macromol Sci Phys B 1984, 23, 85.
8. Pak, S.; Borsa, J.; Iijima, T. Angew Makromol Chem 1993, 208, 87.
9. Durso, D. F. In Methods in Carbohydrate Chemistry; Whistler, R. L.; BeMiller, J. N., Eds.; Academic: New York, 1980; Vol. VIII, p 127.
10. Kassenbeck, P. Text Res J 1970, 40, 330.
11. Catlett, M. S.; Giuffria, R.; Moore, A.; Rollins, M. L. Text Res J 1951, 21, 880.
12. Leza, M. L.; Casinos, I.; Guzman, G. M. J Macromol Sci Chem A 1990, 27, 42.
13. Obendorf, S. K.; Sagan Kasunick, R.; Ravichandran, V.; Borsa, J.; Coffman, C. W. Arch Environ Contam Toxicol 1991, 21, 10.
14. Obendorf, S. K. Text Chem Color 1988, 20(5), 11.
15. Rácz, I.; Obendorf, S. K.; Borsa, J. Text Res J 1998, 68, 69.
16. Csiszár, E.; Borsa, J.; Rácz, I.; Obendorf, S. K. Arch Environ Contam Toxicol 1998, 35,129.