Crystallinity and Accessibility of Fibrous Carboxymethylcellulose by Pad-Roll Technology

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SYNOPSIS

Statistically designed experiments have been made on partially carboxymethylated cotton fabric. The effect of the reaction parameters (concentration of sodium hydroxide and monochloroacetic acid and period of time) on the crystallinity (measured by x-ray diffraction), on the iodine sorption and on the disorder of amorphous fraction (calculated from iodine sorption capacity) are presented by polynomial models. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The products of chemical modification generally enhance the usefulness of cellulose because more desirable properties are incorporated. Recently, many cellulose derivatives have been developed to meet certain areas of applications.[1] Carboxymethylcellulose is one of the classical cellulose ethers; its preparation, using monochloroacetic acid and sodium hydroxide, has already been patented in 1921,[2] but since that time only water or alkali soluble carboxymethylcellulose of high degree of substitution have found widespread application in diverse industries.

Cotton cellulose having only 5–10 carboxymethyl groups on its 100 monomer units has fibrous character, while its properties differ from that of the original fiber. Both the ionic character and the supermolecular structure of the cotton celluloses vary in very wide ranges, depending on the reaction parameters. The high accessibility is the most promising property of the modified fiber. Preparation, properties and application of fibrous carboxymethylcellulose have been reviewed elsewhere.[3] Systematic studies in this area constitute the promise for greater understanding of the effects of modification.

Crystallinity, accessibility, and the nature of microstructural feature of cellulose holds the key to understanding the course of chemical reactions that occur in different industries.[4–6]

During carboxymethylation at high reagent concentrations—similar to the mercerization conversion—of the crystallites in the native fiber, the form from the cellulose I to the cellulose II occurs. The cellulose II crystalline form is originated from the molecular chains in the amorphous form rather than from cellulose I.[7]

Beside the cellulose I → II conversion, the degree of disorder increases during mercerization. According to Warwicker et al.,[8] absolute value cannot be given for the increase in disorder because estimates of disorder vary with the technique used. The average estimates of disorder in cotton before mercerization determined by x-ray diffraction, moisture regain, and acid hydrolysis are 29, 38, and 10%, respectively, and after mercerization 49, 57, and 20%, respectively.[8] Sometimes, however, a subsequent increase of crystallinity was observed[9–12] due to recrystallization. Increase of crystallinity during carboxymethylation, explained by the dissolution of the highly substituted part of the most accessible areas, was also reported.[13]

The amorphous region of cellulose is not completely disordered and has no homogenous structure. Rowland and Hawley[14] found that even the amorphous regions of cotton fiber possessed some ordering due to hydrogen bonding. Using a technique called chemical microstructural analysis, they determined that even in the most disordered regions, 8% of the C^3 OHs and 41% of the C^6 OHs were hydrogen bonded. Hatakeyama et al.[15] investigated the properties of amorphous fraction having various water content. The density data, heat capacity, and x-ray diffraction data suggested that a part of amorphous region of cellulose transferred to a high degree

of parallel chain orientation in the molecular conformation of individual molecules. They found that the amorphous region of natural cellulose was more ordered in the presence of water.

The highly ordered structures of amorphous regions of cellulose I and II are different from each other. Horii et al.,[16] using crosspolarization/magic angle spinning ^{13}C-NMR, suggested that the conformation of a noncrystalline component was rather hindered for cellulose I, whereas in cellulose II it was relatively relaxed. Hatakeyama et al.[17] found that the structural difference between the amorphous region of cellulose I and that of II could be emphasized in the presence of water.

Both x-ray diffraction and iodine sorption measurement are common methods for determination of crystallinity and accessibility, respectively.

Schwertassek et al.[18] investigated the iodine sorption capacity of 100% crystalline and 100% amorphous cellulose. It was found that the cellulose crystallites sorbed 18 mg iodine/g cellulose, while sorption of the amorphous region varied by its disorder. In contrast, other authors[19,20] found that iodine sorption capacity of amorphous fraction to be constant. Hessler and Power[19] used iodine sorption capacity to determine the crystallinity of cellulose. They found the sorption capacity of crystalline regions negligible while the amorphous fraction capacity was 412 mg/g. Pandey et al.[20] found 0.893 correlation between the crystallinity measured by iodine sorption capacity and by IR spectroscopy.

Bredereck[21] found a linear correlation between iodine sorption (S_I) and specific area (SA) being accessible for water.

$$SA[m^2/g] = 1.72S_I[mg/g] + 130$$

This equation was established from data measured between 42 and 199 mg iodine/g cellulose interval.

In some cases the adsorption of iodine was found to take place on patches of sites in the cellulose–water gel.[22] X-ray studies of the iodine-containing celluloses suggested that iodine penetrated the crystalline regions when the adsorption exceeded 11–12%.[23] For these reasons iodine sorption was critized by Wadsworth et al.,[6] but this method remains essentially one that provides an index of the accessibility.[5]

EXPERIMENTAL

Carboxymethylation

Bleached cotton fabric of 108 g/m² from Goldberger Textile Printing Factory (Hungary) was soaked in

a 10 cm³ cc CH_3COOH/dm^3 acetic acid solution at 50°C for 5 min, then was washed with tap water and neutralized with distilled water. The fabric was then dried at room temperature.

Solutions of sodium hydroxide and monochloroacetic acid were mixed and cooled. This solution was used 20 min after mixing.

Cotton fabric was padded by mixed solution with two dips (each for 1 min, liquor ratio 1 : 40) at room temperature. Fabric sealed in a polyethylene foil was put into an oven thermostated at 70°C, which is the optimum temperature of the reaction[24-26] for different time periods. The cloth was washed by tap water, soaked with 8 cm³ cc HCl/dm^3 hydrochloride acid solution for 60 min, neutralized by distilled water, and air dried at room temperature.

Three factors (concentrations of reagents and period of time) were varied while temperature of reaction, dipping, washing, and drying conditions were held constant. Concentration range of sodium hydroxide solution was 3–5 mol/kg chosen according to region of its sorption maximum.[27] Molar ratio of sodium hydroxide and monochloroacetic acid was between 1.5 and 7.6.

A 5 × 5 Latin square with one replicate was used as an experimental design (5^{3-1} = 25 factor level combinations for the three factors). The experimental conditions are shown in Table I. In order to estimate the variance of the replication we repeated the center point of design six times. For comparison sample padded by 5 mol/kg NaOH solution was manufactured. Further treatment of this fabric was the same as that of carboxymethylated ones.

The effects of the reaction parameters on the degree of substitution (DS) were presented elsewhere (see Fig. 1).[28]

X-Ray Diffraction

Crystallinity of the samples were measured by x-ray diffraction method (Müller Mikro 111, Cu K_α radiation, 2Θ = 5–35°). The diffractograms were analyzed using DuPont Curve Resolver.

Iodine Sorption

The iodine sorption was measured according to Schwertassek[29] and Nelson[30] with three repetitions.

RESULTS AND DISCUSSION

Crystallinity

Using the Stepwise Variable Selection procedure of Statgraphics,[31] a functional dependence was estab-

Table I   Experimental Conditions for Factoral Design

No.	Independent Variables	Coded	Level					Interval of Variation	Dimension
			−2	−1	0	1	2		
1	Concentration of monochloroacetic acid	C_{MCAA}	0.66	1.00	1.33	1.66	2.00	0.33	mol/kg
2	Concentration of sodium hydroxyd	C_{NaOH}	3.0	3.5	4.0	4.5	5.0	0.5	mol/kg
3	Period of time	t	20	40	60	80	100	20	min

lished between the ratios of crystallites (Cell I. and II.), of amorphous material (A) and the independent variables (C_{MCAA}, C_{NaOH} and t) from x-ray diffraction data.

Cell I. $= 55.78 - 6.28x_2 - 2.03x_1x_2$

standard deviation   9.8

degree of freedom   22
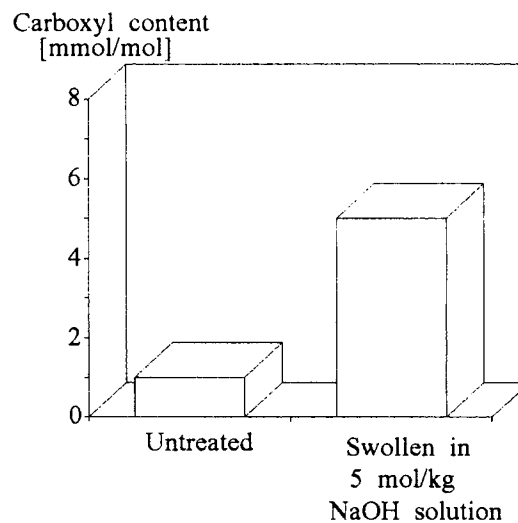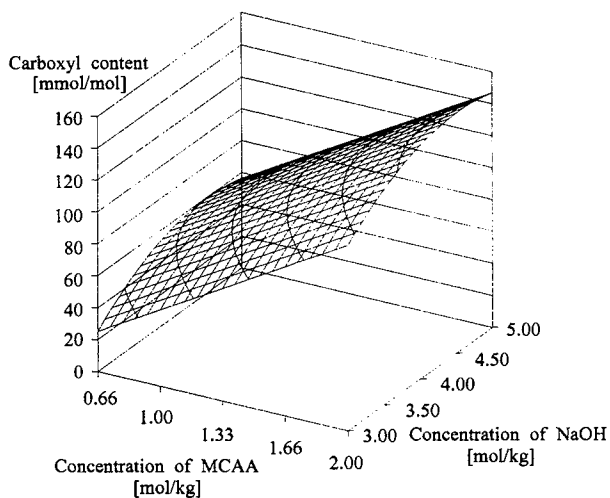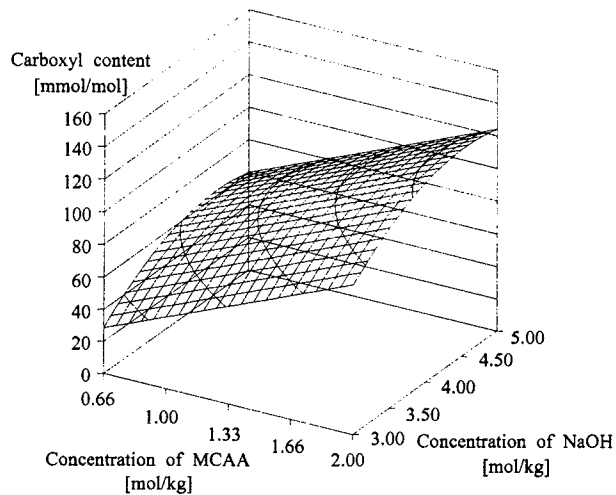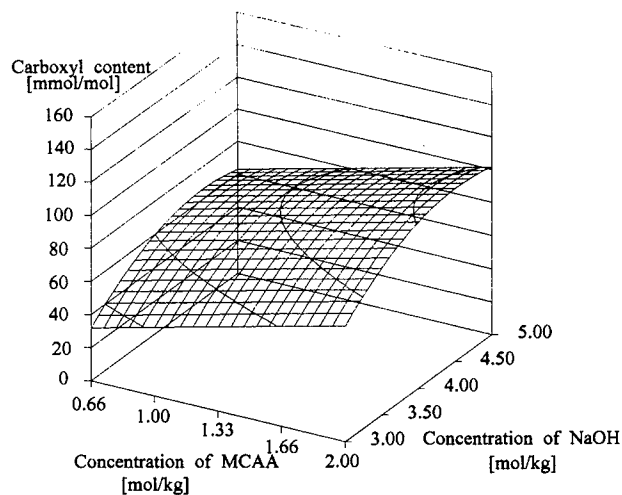
Figure 1   Carboxyl content of carboxymethylated cotton as a function of reagent concentrations and period of time (carboxymethylated for 20, 60, and 100 min, respectively).[35]

Table II   Statistical Data of Polynomial Regression for Cellulose I, Cellulose II, and Amorphous Content

	Cell. I		Cell. II		A	
	t-Value	Significance Level	t-Value	Significance Level	t-Value	Significance Level
Constant	45.2323	0	7.0398	0	22.2049	0
x_1	2.3494	0.0282	-3.1144	0.0051	—	—
x_2	-6.0816	0	5.9735	0	—	—
x_1x_2	—	—	—	—	3.9443	0.0006

Cell II. $= 7.16 - 2.12x_1 + 4.04x_2$ $A = 33.44 + 2.97x_1x_2$

standard deviation   5.5   standard deviation   7.5

degree of freedom   22   degree of freedom   23
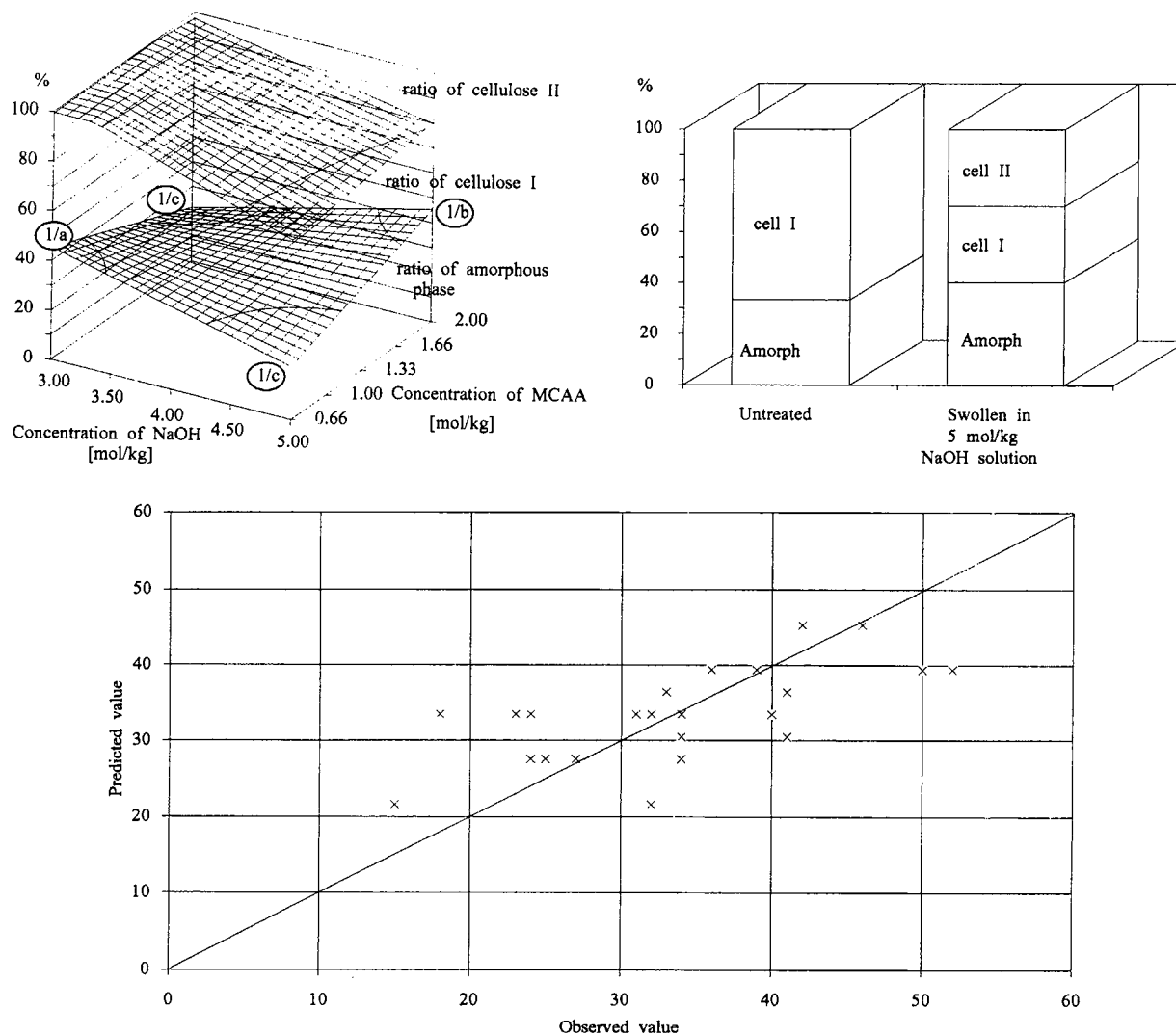
Figure 2   Crystal structure of carboxymethylated cotton as a function of reagent concentrations and the plot of observed and predicted values for amorphous, cellulose I, and cellulose II content, respectively.
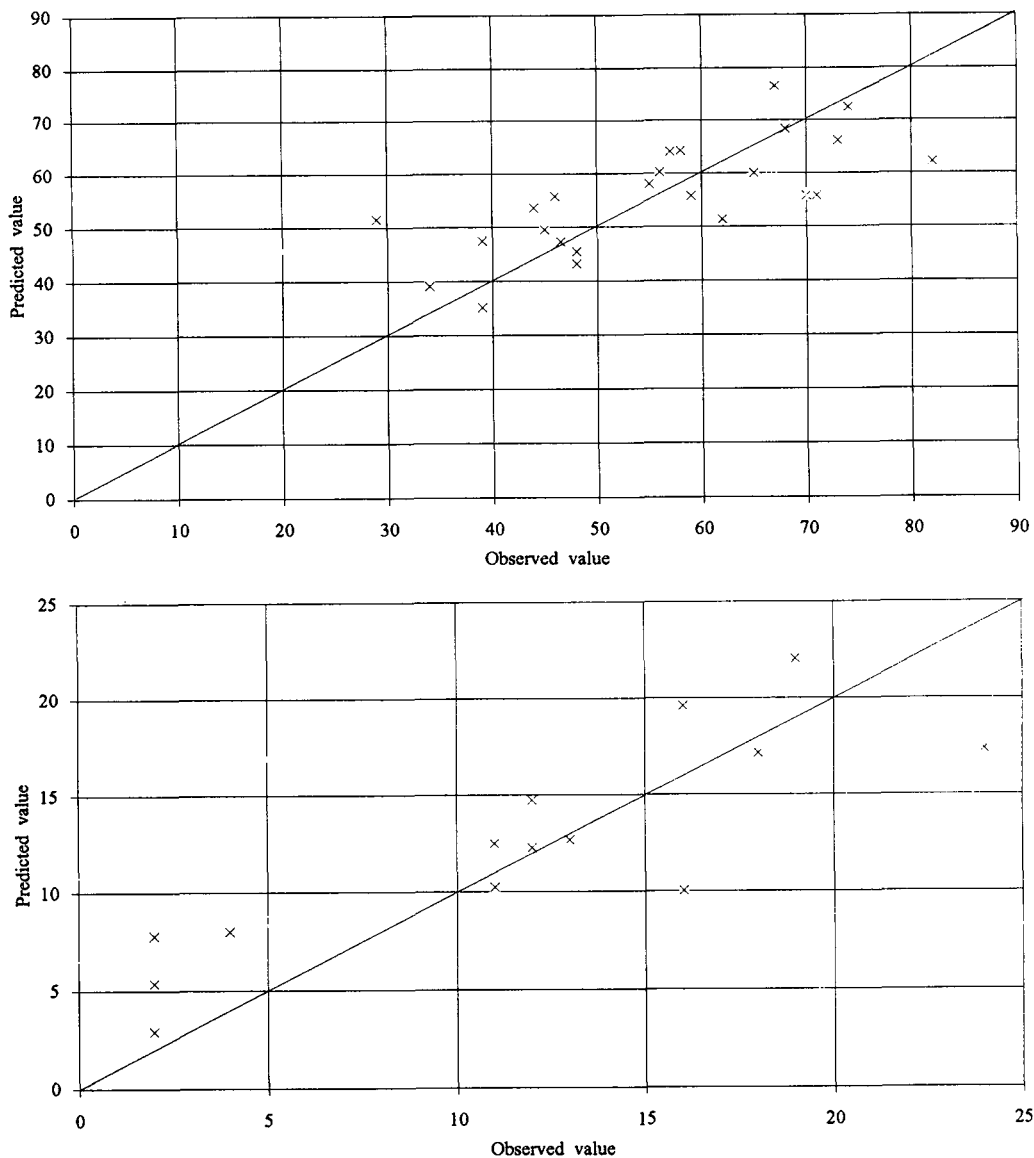
Figure 2 (*Continued from the previous page*)

were considered, where

$$x_1 \to C_{MCAA}$$

$$x_2 \to C_{NaOH}$$

$$x_3 \to t$$ are the coded level of factors.

The t values and the significance levels of the polynomial equations are shown in Table II.

The standard deviation calculated from the repetition of center point of design for cellulose I, for cellulose II, and for amorphous fraction were 12.2, 5.5, and 5.9, respectively, with 5 degrees of freedom.

The surfaces describing the data of the carboxymethylated samples and the bars of untreated and alkali swollen samples are shown in Figure 2.

The figures suggest that:

1. Concentrations:
   a. Samples carboxymethylated at the lowest concentrations and swollen in 5 mol/kg NaOH solution, respectively, have nearly the same degree of disorder (circled 1/a on Fig. 2).
   b. Unexpectedly, only the same disorder is obtained at highest concentrations of reagents (circled 1/b on Fig. 2).
   c. In certain regions of the investigated interval the disorder is decreasing by increasing reagent concentrations, and its value is becoming lower than the disorder of the untreated cellulose.
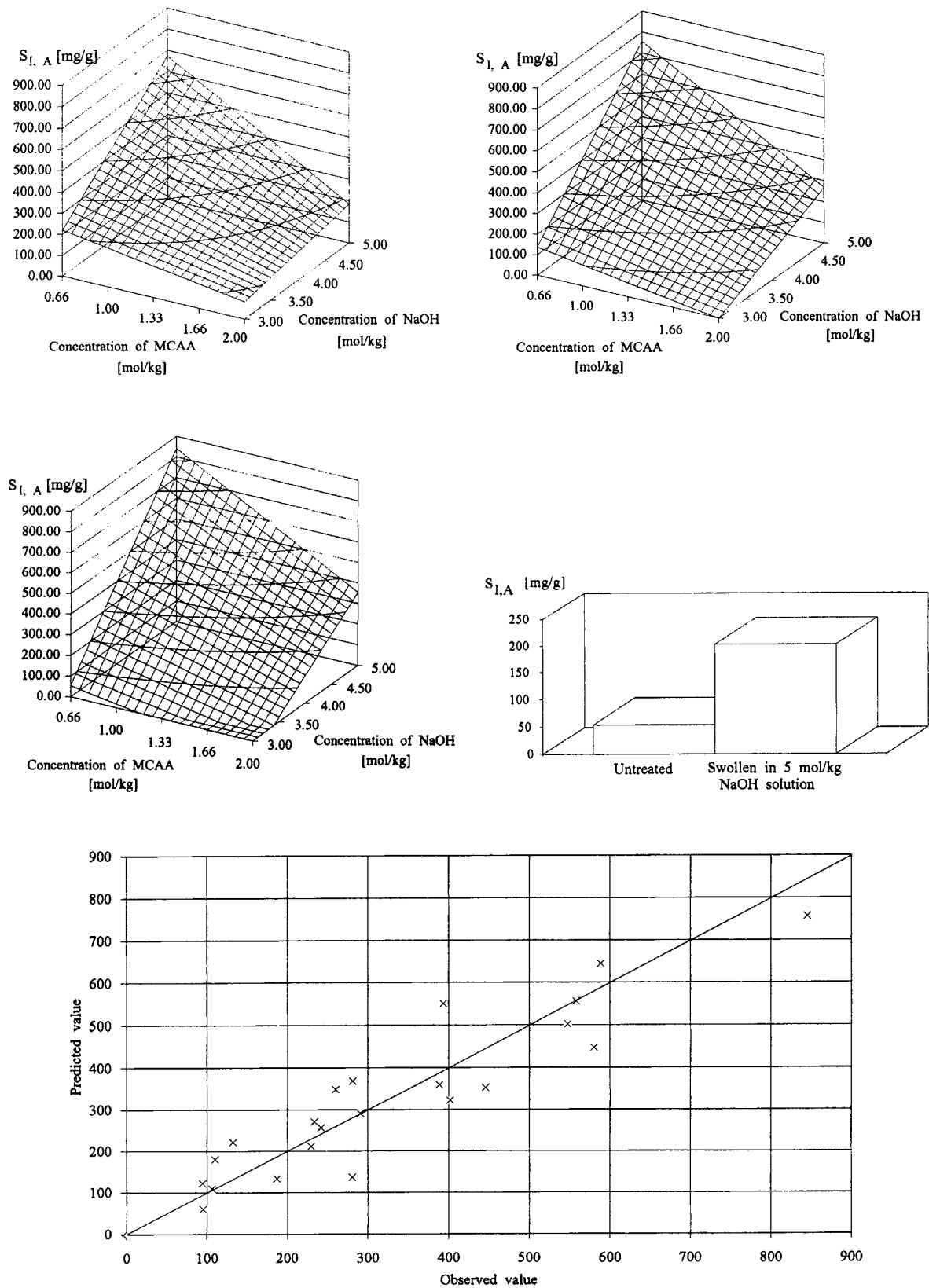
Figure 3 Disorder of the amorphous fraction (carboxymethylated for 20, 60, and 100 min, respectively) and the plot of observed and predicted values.

Table III   Statistical Data of Polynomial Regression for Iodine Sorption of Amorphous Fraction

	$S_{I,A}$	
	t-Value	Significance Level
Constant	16.8496	0
x_2	−6.4337	0
x_2	9.1477	0
$x_1 x_2$	−2.4163	0.0254
$x_2 x_3$	2.3362	0.03

Such a large crystallinity cannot be caused by recrystallization; thus (circled 1/c on Fig. 2), it is a proof for dissolution of highly substituted, most accessible fractions. All data of disorders should be considered as results of two coexisting processes, namely, chemical reaction and dissolution.

   d. The crystal lattice change from cellulose I to cellulose II depends almost only on the alkali concentration.

2. Time: The ratios of cellulose I, cellulose II, and amorphous phase do not depend on the reaction time in the investigated interval.

3. Degree of Substitution: No direct correlation between crystallinity (Fig. 2) and DS (Fig. 1) can be postulated.

Disorder of Amorphous Fraction

X-ray and iodine sorption data were used to determine the disorder of amorphous fraction of the samples.

Iodine sorption of cellulose is a sum of sorptions on amorphous material and crystallites. The maximum value of the latter one, according to Schwertassek,[18] is 18 mg/g. Sorption on amorphous fraction can be calculated from the equation:

$$S_I = \frac{C}{100} S_{I,C} + \frac{A}{100} S_{I,A}$$

where

S_I iodine sorption measured on the sample [mg/g]

C ratio of crystallites measured by x-ray diffraction [mass %]

A ratio of amorphous material measured by x-ray diffraction [mass %]

$S_{I,C}$ iodine sorption on crystallites, 18 mg/g

$S_{I,A}$ iodine sorption on amorphous material—to be calculated [mg/g]

By statistical treatment of data the following functional dependence was established between the iodine sorption on amorphous material ($S_{I,A}$) and the independent variables (C_{MCAA}, C_{NaOH} and t) (see Fig. 3).

$$S_{I,A} = 290.1256 - 78.332x_1 + 111.3758x_2$$
$$- 21.8072x_1 x_2 + 21.0837x_2 x_3$$

standard deviation   86.1
degree of freedom   20

The t values and the significance levels of the polynomial equations are shown in Table III.

The standard deviation calculated from the repetition of center point of design was 42.7 with 5 degree of freedom. For calculation, the constant value of absolute error was supposed.

The figures suggest that:

1. Concentrations: The degree of disorder characterized by iodine sorption capacity of amorphous fraction varies in a very wide interval. Its values can be significantly higher or lower than that of the sample swollen in 5 mol/kg NaOH solution. The maximum value of iodine sorbed by the amorphous fraction is more than twice as big as the amount (412 mg/g) measured by Hessler[19] on cellulose considered a standard for amorphous fraction for calculation of crystallinity. Crystallinity data calculated from the iodine sorption values (S_I) by Hessler's method had no correlation with the x-ray crystallinity data.

Both the most disordered (circled 1/a on Fig. 3) and the less disordered (circled 1/b on Fig. 3) amorphous fractions are at those parts of the investigated concentration interval where the dissolution of highly accessible molecules is dominating (circled 1/c on Fig. 2). High concentration of alkali makes less ordered amorphous material (circled 1/a on Fig. 3). Amorphous phases of cellulose carboxymethylated at high acid and low alkali concentrations are less disordered than that of the untreated cotton (circled 1/b on Fig. 3). These facts represent the crucial importance of carboxymethylation technology.

2. Time: The difference between the maximum and minimum values of disorder increases as a function of time.
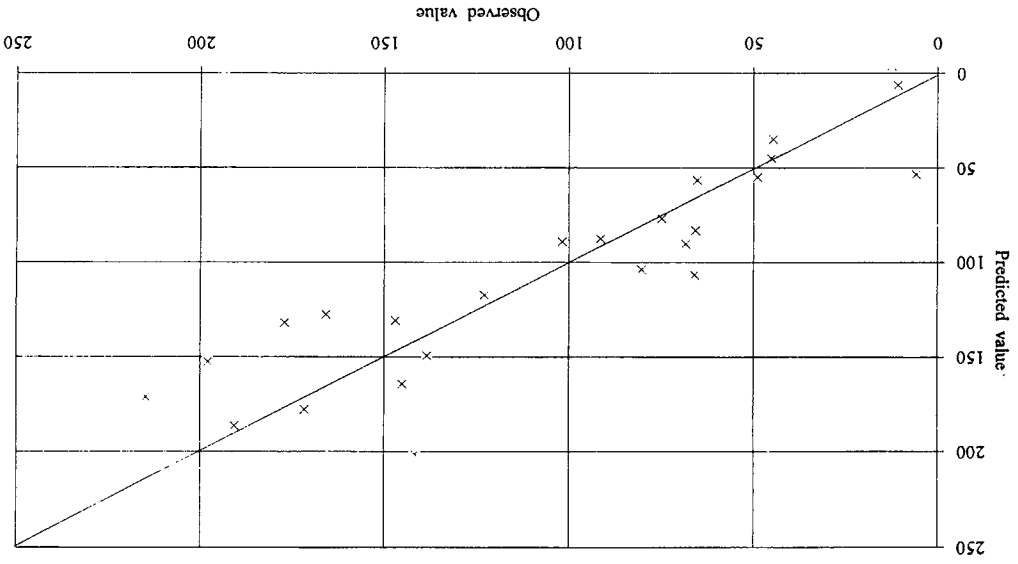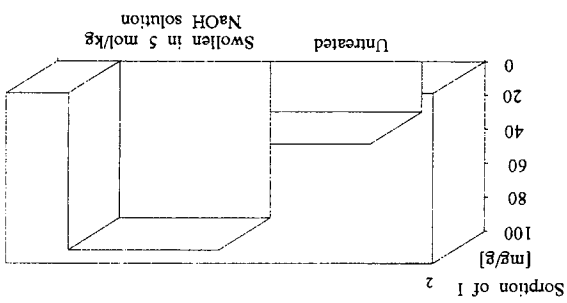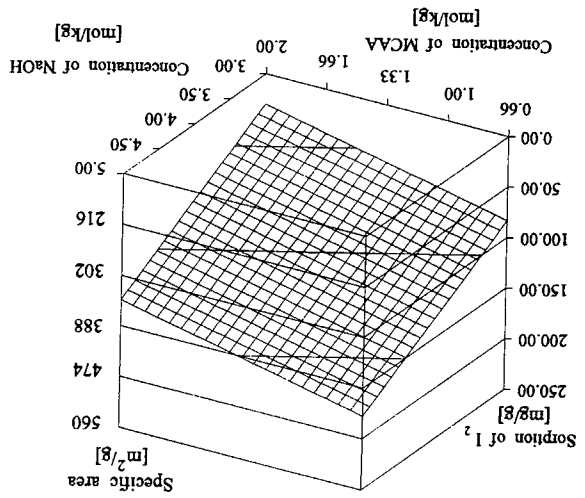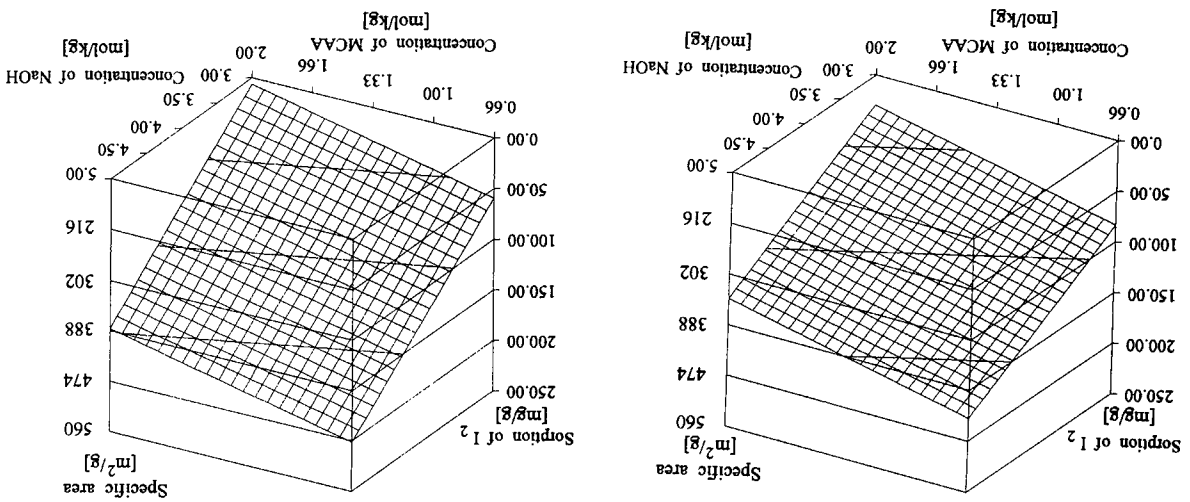
Table IV Statistical Data of Polynomial Regression for Iodine Sorption Capacity

	S_I	
	t-Value	Significance Level
Constant	17.8241	0
x_1	−3.2475	0.0039
x_2	8.5941	0
x_2x_3	2.0254	0.0557

Specific Area

Iodine sorption data are studied by Bredereck;[21] surface area of cellulose samples were calculated from this equation. Values of iodine sorption [mg/g] are well-known numbers for textile chemists; that is why these data are plotted in Figure 4.

By statistical treatment of data the following functional dependence was established between the iodine sorption and the independent variables (C_{MCAA}, C_{NaOH} and t).

$$S_I = 103.7876 - 13.37108x_1$$
$$+ 35.3852x_2 + 5.89674x_2x_3$$

standard deviation   29.1
degree of freedom   21

The t values and the significance levels of the polynomial equations are shown in Table IV.

The standard deviation calculated from the repetition of the center point of the design was 39.8 with 5 degree of freedom.

The figures suggest that:

1. Concentration: Specific area of carboxymethylated samples vary in a very wide interval. Its values can also be significantly lower or higher than that of sample swollen in 5 mol/kg NaOH solution.
   a. Analogously to the disorder data, iodine sorption capacity is increased by carboxymethylation, even at the lowest reagent concentrations, nearly the same extent as by swelling in 5 mol/kg NaOH solution (circled 1/a on Fig. 4).
   b. The minimum values of iodine sorption are at the high acid and low alkali concentrations where the disorder measured by x-ray diffraction is also very small (circled 1/b on Fig. 4).
   c. In spite of low value of disorder in this

concentration interval, the largest specific area was obtained at the highest alkali and lowest acid concentrations (circled 1/c on Fig. 4). Amorphous fraction in this part of the investigated interval is very disordered, its accessibility is extremely high, as mentioned before.

2. Time: Reaction time has no significant effect on the iodine sorption.

CONCLUSION

It has generally been believed that disorder is increased by carboxymethylation. Systematic investigation of the effect of reaction parameters on this character suggested that the type of change depends on the technology, and even decrease of disorder and of accessibility can be obtained. Some adverse effects of carboxymethylation, which had been interpreted as occupation of highly accessible hydroxyl groups,[32,33] can be generated by reduction of disorder and accessibility.

Accessibility of amorphous fraction was found to be very different, depending on the reaction parameters. Calculation of crystallinity from iodine sorption[19] and hydroxyl reactivity determined by crystallinity[34] might be valid only for celluloses containing amorphous fractions of nearly the same accessibility.

Large accessibility of modified cellulose might be advantageous in some textile finishing processes. Cellulose of high sorption capacity can be a more effective reservoir in controlled release systems, for example in pesticide formulations, than the unmodified one.

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