

Preparation of *O*-Carboxymethyl Chitosans and Their Effect on Color Yield of Acid Dyes on Silk

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ABSTRACT: *O*-Carboxymethyl chitosans with a low degree of substitution (DS) and a high degree of deacetylation (DD) were prepared directly from chitin and characterized by using ¹H-NMR, ¹³C-NMR, and elemental analysis methods. In our study, *O*-carboxymethyl chitosans could increase the color yield of Acid Red 44 and Acid Green 25 on silk

fabrics without lowering the corresponding washing fastness property. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2500–2502, 2003

Key words: biomaterials; polysaccharides; renewable resources

INTRODUCTION

Chitosan is a polysaccharide obtained by deacetylating chitin. The amino group of the glucosamine unit of chitosan exhibits cationic character in acidic environments and this property is useful in the dyeing of protein fibers such as wool and silk in acidic media as the ionic interactions between the chitosan-treated fiber and acid dyes are increased.

Kako and coworkers^{1–4} have studied the effect of chitosan on the physicochemical and dyeing properties of tussah silk fabrics with various dyes. They found that the dye uptake of acid dyes was increased as the amount of chitosan on silk was increased. It is likely that the chemical derivatives of chitosan can also improve the color yield of acid dyes on silk. We studied the effect of *O*-carboxymethyl chitosan on the color yield of acid dyes on silk and summarized the results in this article.

EXPERIMENTAL

Preparation and characterization of *O*-carboxymethyl chitosans

Chitin (Sigma, St. Louis, MO; practical grade) was purified as reported.⁵ The purification included deproteinization, demineralization, and decoloration. The purified chitin (1 g) was mixed under nitrogen with freshly prepared aqueous NaOH solution (40 g/100 mL) and isopropanol (Aldrich, Milwaukee, WI; 0.5 g) at 90°C.

Finely powdered chloroacetic acid of a specific amount was then added and the reactants were stirred for 24 h. The reaction was stopped at pH 7 with the addition of concentrated HCl solution in an ice bath. The mixture was then dialyzed in running water for 3 days. The water was then evaporated at 50°C under reduced pressure. The solid collected was dried overnight in a vacuum oven at 60°C. The reaction was repeated with different amounts of chloroacetic acid (Aldrich) and chitin as summarized in Table I.

The ¹H-NMR spectra were obtained at 80°C by using deuterated formic acid (1 g/100 mL) as solvent with a Bruker (DPX400) NMR spectrometer. The ¹³C-NMR spectra were obtained at 80°C with an Inova Varian (AS500) NMR spectrometer. The C% and N% of these samples were measured with an Elementar (Vario EL) analyzer.

O-carboxymethyl chitosans on silk fabrics

O-carboxymethyl chitosans (1 g/100 mL) were applied on bleached woven silk fabrics (weight: 76.5 g/m²) by padding at 100% pick-up. The fabrics were then dried and cured at 150°C. The fabrics were then

TABLE I
Mole Ratio of Reactants and the Reaction Yield of *O*-Carboxymethyl Chitosans

Sample name	Molar ratio of chloroacetic acid to chitin monomer unit	Appearance	Yield (g)
OCMCH0	0	Pale brown	0.811
OCMCH1	0.1	Pale brown	0.815
OCMCH2	0.3	Pale brown	0.820
OCMCH3	0.5	Pale brown	0.831

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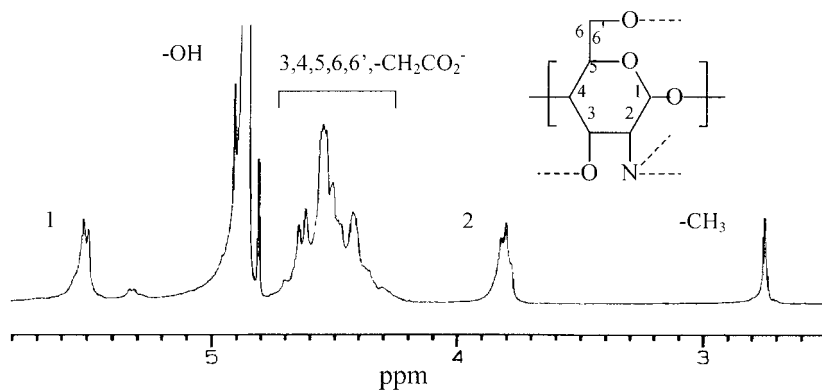


Figure 1 ¹H-NMR spectrum of OCMCH3.

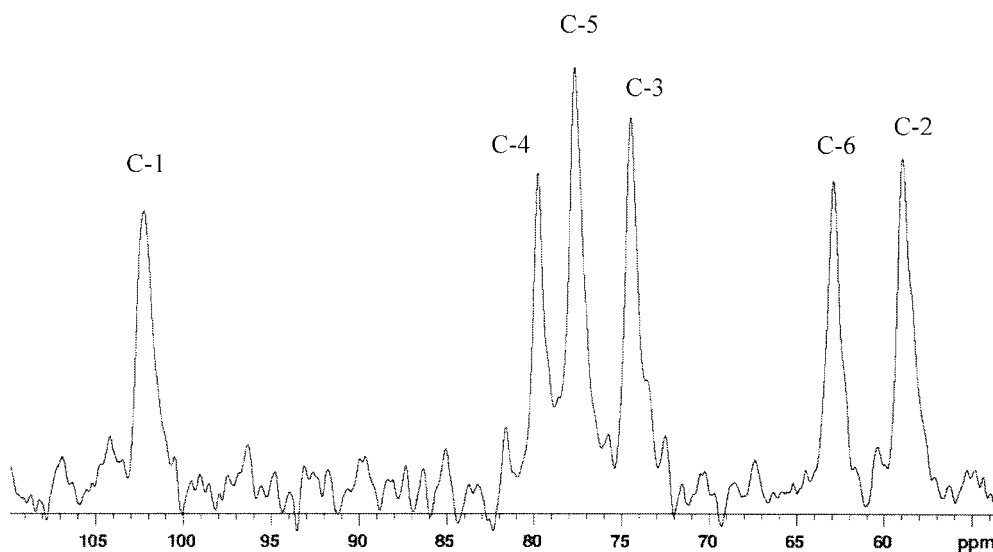


Figure 2 ¹³C-NMR spectrum of OCMCH0.

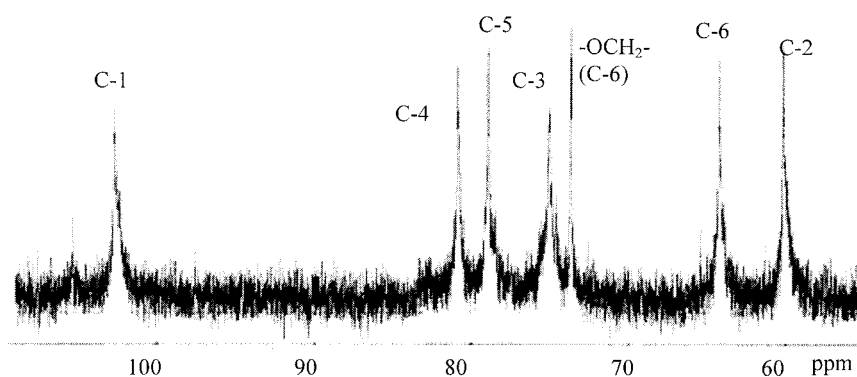


Figure 3 ¹³C-NMR spectrum of OCMCH3.

dyed with two acid dyes, namely, Acid Red 44 and Acid Green 25, at 4% depth by using standard procedures.⁶

Evaluation of the dyed fabrics

All dyed fabrics were conditioned in a standard conditioning room [at 20°C, 65% relative humidity (RH)] for 24 h before any evaluation. The color properties of the

fabrics were measured with a Datacolor Elrepho 2000 spectrophotometer. The minimum reflectance value of the fabric in the visible region was used for computation of the color yield (K/S value) by the Kubelka and Munk equation. The color difference ΔE^* (D65/10) was computed by using the CIELAB color difference equation. The color fastness to washing of the fabrics was determined with Test A1S of ISO 105-C06: 1994(E).

TABLE II
Water Solubility of *O*-Carboxymethyl Chitosans at Room Temperature

Sample	DD (%)	DS (%)	Solubility in neutral water (10 g/L)	Solubility in aqueous HAC solution (10 g/L)
OCMCH0	84	0	Insoluble	Soluble
OCMCH1	84	1	Slightly soluble	Soluble
OCMCH2	83	2	Slightly soluble	Soluble
OCMCH3	83	10	Soluble	Soluble

TABLE III
Effect of *O*-Carboxymethyl Chitosans with Different DS on the Color Properties of Silk Fabrics

Treatment	DS (%)	Dyestuff (C.I.)	K/S value	ΔE^*	Color change
No		Acid Red 44	16.8	0.0	1-2
OCMCH0	0	Acid Red 44	19.0	7.4	1-2
OCMCH1	1	Acid Red 44	17.8	2.7	1-2
OCMCH2	2	Acid Red 44	18.8	2.4	1-2
OCMCH3	10	Acid Red 44	18.2	1.9	1-2
No		Acid Green 25	18.8	0.0	2-3
OCMCH0	0	Acid Green 25	20.8	4.6	2-3
OCMCH1	1	Acid Green 25	20.7	3.0	2-3
OCMCH2	2	Acid Green 25	20.7	2.3	2-3
OCMCH3	10	Acid Green 25	20.3	2.2	2-3

RESULTS AND DISCUSSION

Figure 1 shows the $^1\text{H-NMR}$ spectrum of sample OCMCH3. The peak assignments are also shown in the same figure. The degree of deacetylation (DD) of the samples was calculated on the basis of $^1\text{H-NMR}$ spectra. The $^{13}\text{C-NMR}$ spectra of OCMCH0 and OCMCH3 are shown in Figures 2 and 3, respectively.

The $^{13}\text{C-NMR}$ spectrum of OCMCH3 shows detailed information on each carbon of the carboxymethylated glucosamine unit. The $^{13}\text{C-NMR}$ spectra indicate that the derivatives obtained had carboxymethyl group substituted exclusively on the oxygen of C6-carbon of glucosamine unit, but not on the oxygen of C3-carbon or N atoms. This is reasonable as the reactivity of the hydroxyl group of C6 is higher. The DD of all samples was evaluated by using the $^1\text{H-NMR}$ integral intensities of $-\text{CH}_3$ protons (I_{CH_3}) at 2.74 ppm and C2-H (I_{H_2}) at 3.8 ppm:

$$\text{DD}\% = [1 - (I_{\text{CH}_3}/3I_{\text{H}_2})] \times 100$$

The degree of substitution (DS) of the derivatives was calculated by using the DD value, C% and N% of the sample's elemental analysis as shown below. Table II summarizes the DD and DS values of the chitosan derivatives:

$$\text{DS}\% = [7/12 \times (\text{C}\%/\text{N}\%) + \text{DD} - 4] \times 100$$

The DS and aqueous solubility of these samples increased as the amount of chloroacetic acid increased. Sample OCMCH3 with higher DS was soluble in wa-

ter. This is due to the presence of more carboxylic acid groups. The color yield (K/S value), color difference (ΔE^*), and color fastness to washing of chitosan derivatives treated silk are summarized in Table III.

CONCLUSION

O-Carboxymethyl chitosan treatment increased the final exhaustion of acid dyed silk fabrics. This can be seen from the K/S and color difference values. However, the color fastness to washing was not affected. Sample OCMCH0 improved the final exhaustion better than the others. The results show that the introduction of carboxymethyl on chitosan cannot further improve the final exhaustion, although the interaction between the acid dyes and carboxymethyl chitosans is better through the hydrogen bonding and the polar-polar interaction. It is likely that the hydrophilicity of the chitosan is increased by the addition of carboxymethyl group as indicated in Table II, decreasing the overall interaction between acid dyes and the chitosan derivative. However, the color yield of acid dyes on silk is still improved by the chitosan derivative treatment.

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