# Grafting onto Cotton Fiber with Acrylamidomethylated β-Cyclodextrin and Its Application

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**ABSTRACT:** To chemically attach β-cyclodextrin (CD) molecules to cotton cellulose, *N*-methylol-acrylamide (NMA) was used to synthesize a CD containing monomer, which was then grafted onto cellulose fibers. Initiation of the cotton cellulose backbone with ceric ion before the addition of acrylamidomethyl cyclodextrin (CD-NMA) monomer was shown to be beneficial for grafting onto cotton cellulose by studying the reactions of ceric ion with CD, CD-NMA, or cotton cellulose. The amount of chemically attached CD was determined by fluorescence measurements and compared with graft yields. The possibility of textile finishing of CD containing cotton fibers was investigated using benzoic acid as an antibacterial finishing agent or vanillin as an aroma finishing agent. Antibacterial activity of benzoic acid-treated samples were retained even after 10 laundering cycles and the vanillin fragrance lasted much longer compared with the control sample, suggesting that utilization of CD in functional textile finishing is indeed possible. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1986–1991, 2000

**Key words:** cyclodextrin; cotton fiber; grafting; antimicrobial finish; aroma finish

## INTRODUCTION

A distinct feature of cyclodextrin (CD) is its ability to form inclusion compounds, where inclusion formation is mainly affected by the geometric shape of the molecule rather than chemical interactions. The hydrophobic portion of the guest molecule is positioned such that maximum contact with the nonpolar cavity is possible while the hydrophilic portion is located on the outer surface of the inclusion complex such that it is near the proximity of the hydroxyl groups of the host and solvent. Molecules that are much larger or longer than the cavity may also form inclusion complexes through the entrapment of a specific group or side chain in the cavity. For example, a 2:1 complex between CD and the guest molecule may be formed, as in the case of vitamin D. The inclusion occurs through the displacement of water molecules from the hydrated hydrophobic cavity by the less polar guest molecules and is thermodynamically favored by the interaction between the relatively nonpolar guest molecule and the hydrophobic cavity.

Attempts to utilize CD in textile applications started in the late 1980s.[1–6] This was brought about by the recognition that the inclusion complex formation capability of CD can be applied to the deodorant, aroma, antimicrobial, insect repellent, and mite repellent finishes that have recently become popular, and in treating effluents. The major drawback in the utilization of CD was

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the high price, but commercial production of CD started in the late 1970s and it is now produced relatively inexpensively. Since then research and development of CD applications have become active, and the possibilities of using CD in textile finishing are being explored recently in the textile industry. With the trend in the textile industry demanding high quality and new properties, the range of application of CD is expected to expand along with its application in the environment industry.

In this study, chemical bonding of CD onto cellulose was attempted instead of the physical attachment normally used in the past. Acrylamidomethyl CD (CD-NMA), a vinyl monomer synthesized by reacting *N*-methylolacrylamide (NMA) in the presence of an acid catalyst, was grafted onto cellulose. The chemical bonding of CD onto cellulose was confirmed by the determination of the CD content of purified samples, from which all homopolymers, unreacted CD-NMA, methylolacrylamide, and CD had been removed by extraction. The amount of chemically bound CD was determined from fluorescence measurements of solid samples. The possibilities of utilizing CD in textile finishing was studied by entrapping benzoic acid as antimicrobial finishing agent and vanillin as an aroma finishing agent.

## EXPERIMENTAL

### Materials and Reagents

Scoured and bleached cotton fibers were used. β-CD (Nihon Shokuhin Kako Co., Tokyo, Japan) was recrystallized in water three times and dried at 110°C for ca. 4 h and kept in a desiccator. The 2-*p*-toluidinyl-naphthalene-6-sulfonic acid (potassium salt; TNS) (Sigma Chemical Co., Missouri, USA) used in the measurement of CD content was recrystallized twice, vacuum dried, and stored in a refrigerator. NMA (extra pure grade; Tokyo Kasei Kogyo Co., Tokyo, Japan), 35% hydrochloric acid (extra pure grade; Junsei Chemical Co., Tokyo, Japan), 85% formic acid (extra pure grade; Junsei Chemical Co.), and ceric ammonium nitrate (CAN) (guaranteed grade; Kanto Chemical Co., Tokyo, Japan) were used as received without further purification. Other extra pure grade and guaranteed grade chemicals were also used as received and distilled deionized water was used.

### Synthesis of CD-NMA Grafted Cotton Fibers

#### *Synthesis of CD-NMA*

Purified CD, NMA, and formic acid (catalyst) were added to 50 mL of water in a three-necked reactor equipped with a mechanical stirrer, thermometer, and a condenser. The reaction was performed at 80°C for 30 min. Upon completion of reaction, 300 mL of acetone was added and the mixture was stored at 5°C to allow complete precipitation of the products. The precipitates were filtered, washed several times in 200 mL of acetone, dried at 30°C in a vacuum drying oven for 12 h, and then stored in a refrigerator.

#### *Grafting*

Grafting was performed in a three-necked reactor equipped with a stirrer, condenser, and a nitrogen inlet tube. Approximately 0.5 g of cotton fibers and CAN initiator solution in 1% nitric acid[7] were added to water to make the solids' content 1%. After stirring the mixture for 20 min with nitrogen purge, 10 g of CD-NMA or its inclusion complex was added and reacted at 40°C for 20, 40, 60, 90, or 120 min. On completion of the reaction, the product was washed sufficiently with running water to remove unreacted monomers and homopolymers, neutralized with 1% sodium carbonate, washed again with running water, then washed in boiling water for 30 min, and dried at 110°C for 1 h. The graft yield was calculated from the initial weight of cellulose and the measured weight of the product from which residual monomers and homopolymers had been removed by the above procedure.

#### *Antimicrobial and Aroma Finishing of Cellulose Fibers with CD Inclusion Complexes*

CD-NMA and the guest molecule, benzoic acid, were added to 100 mL of distilled water and mixed in a homogenizer for 30 min at 7500 rpm. The inclusion complex thus formed was precipitated with 300 mL of acetone, filtered, and vacuum dried. The inclusion complex was then grafted onto cellulose fibers to prepared antimicrobial fibers. To prepare aroma finished cotton fibers, 10 mL of a 10% ethanol solution containing approximately 0.05 g vanillin was added to 0.8 g of CD-NMA grafted cotton fibers in which graft yield was 50% and shook for 24 h at room temperature to form inclusion complexes on the graft chains. The product was washed with hot water to remove any free vanillin and dried.

### Analysis

#### *Double Bond Content*

The double bond content of CD-NMA was determined according to the method of Kamel et al.[8]

Approximately 1 g of CD-NMA was added to 10 mL of water in a glass bottle, then 10 mL of 3% mercaptoethanol and 2 mL of 2*N* sodium hydroxide were added and stirred at room temperature for 60 min to carry out the addition of the mercaptoethanol to double bonds. The amount of residual mercaptoethanol was determined by oxidative titration with 0.1*N* iodine solution using 0.5% starch solution as indicator after adding 5 mL of 1*N* hydrochloric acid. The double bond content was calculated using the following equation:

$$\text{Double bond content (mmol/gCD-NMA)} = \frac{(V_B - V_S) \times 0.1 \times f}{W}$$

where $W$ is the weight of sample (g); $V_B$ is the amount of iodine solution used in blank titration (mL); $V_S$ is the amount of iodine solution used in sample titration (mL); and $f$ equals the factor of 0.1*N* iodine solution.

### *Ceric Ion Content*[9,10]

Approximately 13 mL of 0.01*N* ferrous ammonium sulfate solution was added to 5 mL of reaction medium to convert the Ce IV to Ce III, then the excess ferrous ammonium sulfate was titrated with 0.01*N* ceric sulfate using 1.5% *o*-phenanthroline solution as indicator.

### *CD Content*

Fluorescence of TNS entrapped in the CD group on the graft chain was evaluated to determine the amount of chemically bound CD. Fluorescence measurements were performed with KBr pellets made with a hand press from 50 mg of KBr and 0.5 mg of the cellulosic inclusion complex of TNS using a Spectrofluorophotometer RF 5000 (Shimadzu, Japan) at room temperature (25°C). An incident beam of wavelength 362 nm through a 1.5-nm slit was used to measure the fluorescence at wavelength 433 nm through a 5-nm slit. The calibration curve for the determination of CD content was made with inclusion complexes of CD with TNS. The inclusion complexes were prepared by sonication of a mixture of 0.01 $\sim$ 0.05 mL 1% CD solution ($8.8 \times 10^{-8} \sim 4.4 \times 10^{-7}$ mol) and 10 mL of a $5 \times 10^{-5}M$ acetate buffered TNS solution (pH 5.3) for 24 h at 50°C in a ultrasonic bath.[11]

### *Evaluation of Antimicrobial and Aroma Activity*

Quantitative determination of the antimicrobial activity was evaluated according to AATCC test method 100 using *Staphylococcus aureus* as the test bacterium and the aroma activity was evaluated by sensory test.

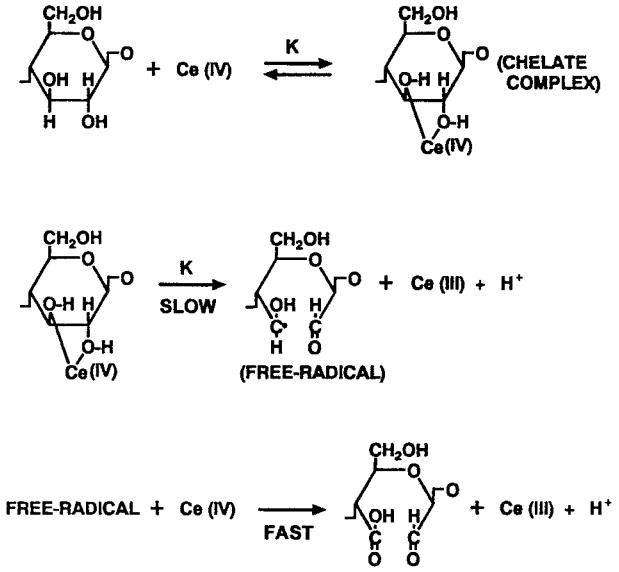
## RESULTS AND DISCUSSION

### Grafting onto Cellulose Fibers

CD-NMA differs from other vinyl monomers such as acrylonitrile or methylmethacrylate in that it contains a $\beta$-CD group which was used as a model compound in the study on the oxidation of glucose and cellulose by Ce IV. That is, the CD-NMA group itself may be oxidized just as cellulose to produce a free radical at the C-3 position, and being a cyclic compound consisting of seven glucose units, it is much larger than other vinyl monomers such that penetration into the amorphous region of cellulose is less feasible. Thus, it was predicted that the consumption of Ce IV and the initiation reaction would show different behavior from other grafting reactions and that the grafting would occur mainly on the surface of the cellulose fibers.

The mechanism of the oxidation of CD by Ce IV suggested by Pottenger and Johnson[12] shown in Scheme 1 is identical to the oxidation of cellulose by Ce IV except that the oxidation of the hemiacetal group at the chain ends as in the case of cellulose cannot occur because it does not have a reducing end group. Although the equilibrium complex formation constant of CD with Ce IV is 10.3, which is lower than that of cellulose which is 39.4, the initial Ce IV consumption rate of CD is much higher than cellulose and that of CD-NMA is even higher. Therefore, CD in CD-NMA may also be initiated in addition to cellulose, and CD-NMA may function as the initiation site as well as functioning as the monomer being grafted. Thus the grafting of CD-NMA was expected to exhibit a different behavior from grafting with other vinyl monomers.

To study the behavior of CD and Ce IV, the rate of consumption of Ce IV was evaluated by measuring the residual ceric ion concentration in the medium. Extensive complexation of Ce IV with CD occurred within 20 min (Fig. 1, curve A), whereas the consumption of Ce IV by cellulose fibers (Fig. 1, curve B) was much slower despite the more severe reaction condition compared with that of CD. The rate of consumption of Ce IV by CD-NMA (Fig. 1, curve C) shows that it is faster in the case of CD-NMA compared with pure CD with most Ce IV being depleted from the solution




**Scheme 1** Mechanism of oxidation of cyclodextrin by cerium (IV).

in 5 min. This is believed to be due to the additional consumption of Ce IV in the oxidation of the double bond. Thus, formation of radicals on the cellulose backbone, before the addition of CD-NMA to the reaction mixture, was thought to be advantageous for grafting.

Because the consumption of ceric ion by CD-NMA is much faster than that by cotton cellulose, it was thought that formation of radicals on the cotton cellulose backbone would be less probable

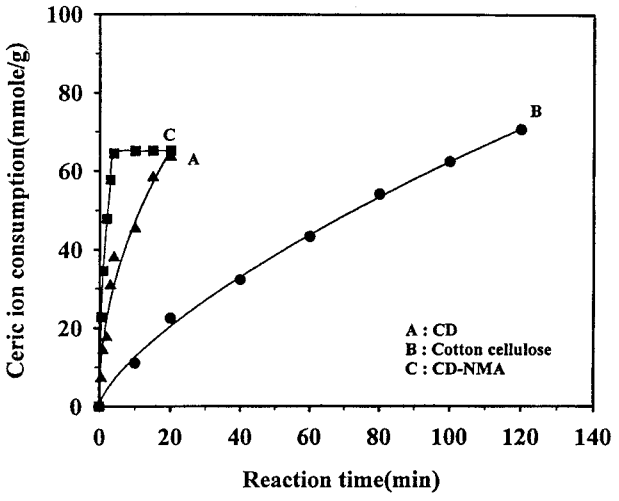



**Figure 1** Ceric ion consumption rate profile of CD, CD-NMA, and cotton cellulose at 40°C. Reaction conditions: 1. A and C: 10 g CD (or CD-NMA), 50 mL of 0.012*M* CAN in 1% $HNO_3$; 2. B: 2 g cotton fiber, 200 mL of 0.012*M* CAN in 1% $HNO_3$.

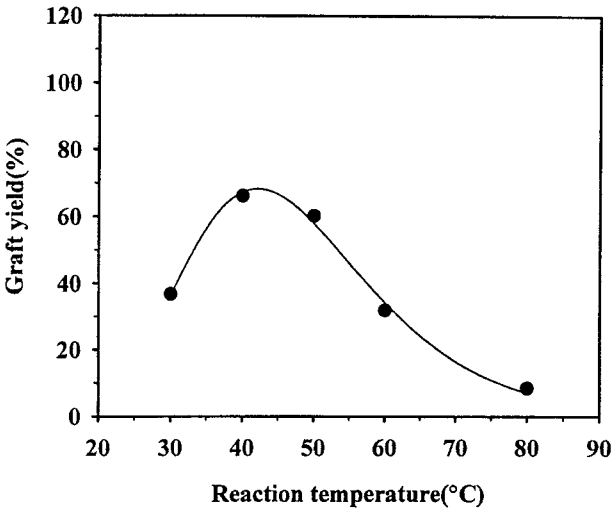



**Figure 2** Effect of reaction temperature on the graft yield. Grafting conditions: cotton fiber, 0.5 g; CD-NMA, 10 g; CAN (0.012*M* in 1% $HNO_3$), 50 mL; time, 60 min.

if CD-NMA and CAN are added simultaneously. Therefore, preliminary experiments were performed and it was found that grafting was more effective when CD-NMA was added after allowing cotton cellulose and CAN to react. Approximately 20 min proved to be sufficient to ensure efficient grafting, thus all experiments for investigating optimum graft conditions were performed by adding CD-NMA 20 min after the addition of initiator.

Figure 2 shows the effect of the grafting temperature on the graft yield. It suggests that 40°C is the optimum temperature and above this temperature the graft yield decreases drastically. Higher termination rates and the acid hydrolysis of CD-NMA at higher temperatures appear to have been a more significant factor.

The concentration of the CAN was varied from 0.006 to 0.024*M* to study the effect of initiator concentration on the graft yield. In Figure 3 the graft yield shows a maximum at 0.012*M* CAN. To observe the influence of grafting time, the graft yields of samples grafted for different periods at 40°C were determined. In Figure 4, the graft yield shows a maximum of 65% at 1 h then decreases slightly.

The variation of the graft yield with the double bond content of CD-NMA monomer was investigated. When the double bond content was 0.9 mmol/g CD-NMA, the graft yield was very low. This appears to be due to the acid hydrolysis of the acrylamidomethyl group of CD-NMA capable of undergoing graft reaction. The graft yield was highest when a monomer in which double bond

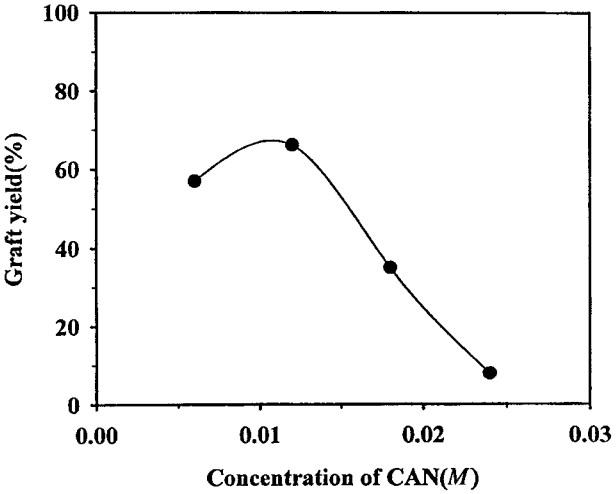



**Figure 3** Dependence of graft yield on the CAN concentration. Grafting conditions: cotton fiber, 0.5 g; CD-NMA, 10 g; CAN (0.012*M* in 1% $HNO_3$), 50 mL; temperature, 40°C; time, 60 min.

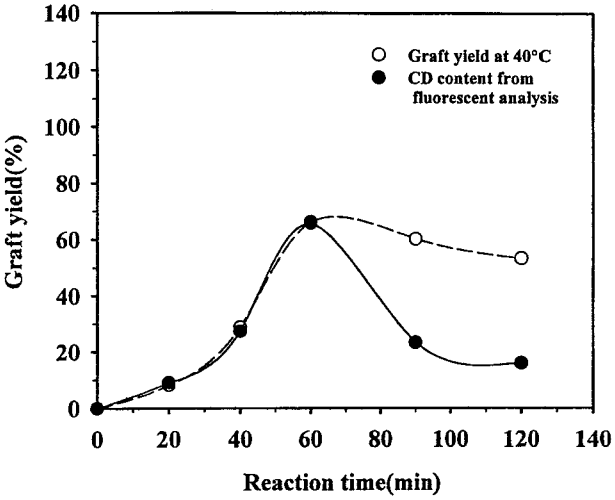



**Figure 5** Comparison of graft yield from weight analysis and from fluorescent analysis of CD content.

content was 1.8 mmol/g CD-NMA was used and decreased slightly when the double bond content was 2.6 mmol/g CD-NMA, which is believed to be due to the higher probability of forming homopolymers.

The TNS fluorescence probe was utilized in the analysis of the CD content of the grafted polymer in which CD is chemically bonded to cellulose. The graft yield calculated from the fluorescence analysis of the CD content of samples grafted at 40°C are shown in Figure 5. The graft yields from weight and fluorescence analysis are similar up to approximately 1 h but differ at longer reaction times. This appears to be a result of various factors, but among them, the grafting of NMA produced by the acid hydrolysis or degradation of CD-NMA may have resulted in an overestimation of the graft yield calculated from weight analysis. Another explanation may be that complexation of TNS may be hindered by the presence of the grafted chains when the graft yields are high.

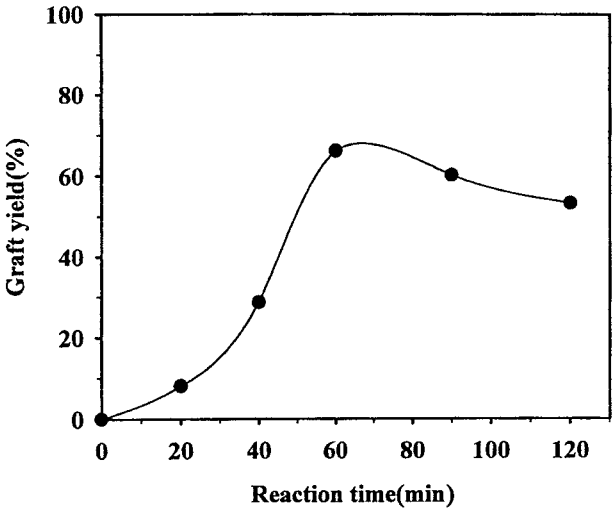



**Figure 4** Variation of graft yield with grafting time. Grafting conditions: cotton fiber, 0.5 g; CD-NMA, 10 g; CAN (0.012*M* in 1% $HNO_3$), 50 mL; temperature, 40°C.

### Antimicrobial and Aroma Finishing of Cellulose Fibers with CD Inclusion Complexes

The cotton fibers grafted with the inclusion complex of CD-NMA and benzoic acid, which is an antiseptic compound, was ground to powders. When the samples were tested with *Staphylococcus aureus* and *Escherichia coli*, which can be found in human or animal intestines, the reduction of bacteria (%) of samples of different graft yields was 75% at 25% graft yield and 99.5% above 40% graft yield. This suggests that CD-NMA and benzoic acid inclusion complexes may be utilized to obtain excellent antimicrobial properties.

To determine the durability of the finish to laundering, the reduction of bacteria (%) after laundering 5 and 10 times according to JIS L 0217 was measured and the finished sample was durable to laundering, retaining a 100% reduction of bacteria even after 10 laundering cycles.

Table I shows the sensory test results of CD-NMA grafted samples treated with vanillin along with a control sample. In the case of the control cotton sample, the fragrance disappeared after 2

**Table I Results of Sensory Test of Vanillin Fragrance**

| | Time (day) | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 1[a] | 2[a] | 3[a] | 4[a] | 5[a] | 6[a] | 7[a] |
| Sample | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| Control | ○ | ○ | × | × | × | × | × | × | × | × | × | × | × | × |

[a] Stored at 80°C after storing at room temperature for 7 days.
○, fragrance detected; ×, no fragrance.

days when stored at room temperature, whereas in the case of the CD-NMA grafted cotton, fragrance was retained even after prolonged storing, initially at room temperature for 7 days then at 80°C for 7 days. The formation of inclusion complex resulted in controlled release of the vanillin fragrance and a much longer lifetime of the fragrance.

## CONCLUSION

To chemically attach CD molecules to cellulose, NMA was used to synthesize a CD containing monomer, which was then grafted onto cellulose fibers. The possibility of textile finishing of CD containing cotton fibers was investigated using benzoic acid as an antibacterial finishing agent or vanillin as an aroma finishing agent. The following conclusions were drawn from a study on the reaction conditions and the application of the CD attached cotton in textile finishing:

1. The consumption of Ce IV by CD-NMA was much faster than that by cellulose. Therefore, the initiator must be added before the addition of the monomer to ensure formation of sufficient graft sites.
2. CD attached cotton fibers can be obtained by grafting with CD-NMA using Ce IV initiator and graft yield was maximum when grafted at 40°C for 1 h with 0.012*M* CAN solution. But considering the structure and molecular weight of CD-NMA, it is believed that the grafting occurred mainly at the surface of cellulose.
3. Antimicrobial properties were obtained by grafting cotton fibers with an inclusion complex of CD-NMA and benzoic acid, which is an antiseptic compound. The grafted fibers exhibited above 99.5% reduction in bacteria at graft yields higher than 40%. The durability of the antimicrobial property to laundering was excellent, showing no change in the percent reduction of bacteria even after 10 laundering cycles.
4. CD-NMA grafted cellulose fibers can be utilized in the aroma finishing of cotton. The fragrance of CD-NMA grafted cellulose fibers treated with vanillin was retained even after prolonged storing, initially at room temperature for 7 days then at 80°C for 7 days.

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