

Carbodiimide Catalysis in Cross-Linking of Cotton Cellulose with 1,2,3,4-Butanetetracarboxylic Acid

HYUNG-MIN CHOI,^{1,*} TARIQ MAHMOOD,² JIANG DONG LI,¹ and JOHN SCHLUP²

¹Department of Clothing, Textiles and Interior Design, and ²Department of Chemical Engineering, Kansas State University, Manhattan, Kansas 66506-1405

SYNOPSIS

This study examined carbodiimide catalysis (cyanamide, dicyandiamide, disodium cyanamide) in the cross-linking of cotton cellulose with 1,2,3,4-butanetetracarboxylic acid (BTCA). Considerable improvement in the smooth drying appearance of the treated cotton substantiated the fact that cellulose cross-linking has been achieved by BTCA in the presence of carbodiimide. Bath pH was a very important factor in determining the performance properties of the treated cotton. Two possible reaction mechanisms were proposed: direct esterification and anhydride intermediate formation. Both pathways involved the formation of urea. Semiquantitative analyses of the spectra obtained by Fourier transform infrared spectroscopy revealed that the cyanamide was somewhat less effective than were dicyandiamide and sodium hypophosphite in esterification efficiency. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In searching for nonformaldehyde cross-linking agents for cellulosic fibers, various polycarboxylic acids (PCAs) were recently investigated.¹⁻⁴ These PCAs include tri- or tetracarboxylic acids, such as citric acid, 1,2,3-propanetricarboxylic acid, 1,2,3,4-butanetetracarboxylic acid (BTCA), and 1,2,3,4-cyclopentanetetracarboxylic acid.^{1,2} An *in situ* copolymer-cross-linking system of dicarboxylic acids such as maleic acid and itaconic acid was also proposed.^{3,4} Results showed that the treatment of cotton cellulose by these PCAs produced fabric with a very smooth appearance after drying with good retention of mechanical properties.

Each proposed PCA system showed some advantages and disadvantages in cross-linking efficiency, durability, whiteness, cost, and safety. BTCA was the most extensively studied compound due to its high cross-linking efficiency, its ability in maintaining fabric whiteness, and its durability during repeated home launderings.¹

In the BTCA treatment of cotton, sodium hypophosphite has been mainly applied as a highly efficient catalyst.¹⁻⁴ Unlike a conventional catalyst such as sulfuric acid, sodium hypophosphite and other similar phosphorus-containing catalysts minimize cellulose degradation during curing at elevated temperature. They enhance formation of an anhydride intermediate, which is a precursor for the esterification reaction between cellulose and PCA. (This mechanism was further substantiated by Fourier transform infrared spectroscopic,⁵ thermoanalytical, and mass spectrometric evidence^{6,7}). However, these phosphorus compounds cause a detrimental effect to the environment, i.e., eutrophication of rivers, lakes, and other water sources.⁸ In addition, sodium hypophosphite results in considerable shade changes to fabrics dyed with sulfur and some reactive dyes, due to its reductive nature.⁸⁻¹⁰

Carbodiimide compounds have been used for chemical fixation of phosphonated and carboxylated reactive dyes¹¹⁻¹³ and phosphoric acid^{14,15} into cellulose molecules. Although the same mechanism could be applied to the esterification reaction between cellulose and PCAs, very little study has been carried out to investigate the role of carbodiimide catalysis in such a reaction.

Therefore, as a continued effort to search for optimal catalysts, our current research investigated the

* To whom correspondence should be addressed at Kimberly-Clark Corp., Neenah, WI 54957.

effects of carbodiimide compounds such as cyanamide, disodium cyanamide, and dicyandiamide on the esterification reaction between cotton cellulose and PCA, specifically BTCA.

EXPERIMENTAL

Cotton print cloth (100%), weighing 107 g/m², was desized, scoured, and bleached by a supplier (Test Fabrics #400). Catalysts such as cyanamide (50% solution in water), disodium cyanamide (95% purity), dicyandiamide, and sodium hypophosphite hydrate (NaH₂PO₂·xH₂O) were purchased from Aldrich Chemicals. 1,2,3,4-Butanetetracarboxylic acid (BTCA, Tokyo Kasei Chemicals) was used as the PCA cross-linking agent. Triton X-100 (Aldrich) and Cyanalube TSI (American Cyanamide) were used as the wetting agent and softener, respectively. All chemicals were reagent grade and used without further purification.

Cotton cellulose was impregnated in an aqueous bath containing BTCA and the carbodiimide catalyst, wetting agent, and softener and was then treated with a conventional pad-dry-cure process (two dips and nips) by using a Werner-Mathis AG finishing machine. The fabric was mounted in a pin frame, dried at 85°C for 5 min, and cured at 180°C for 2 min in the laboratory oven, unless otherwise specified. After the treatment, the fabric was washed for 5 min in running tap water (process-washing) to remove unreacted acids and catalysts, and finally dried again in the laboratory oven at 85°C for 5 min.

The durable press (DP) rating (AATCC 124-1992), percent dimensional change (% DC) (AATCC 135-1992), and conditioned wrinkle re-

covery angle (WRA) measurements (AATCC 66-1990) were carried out after one home laundering to estimate the resilience of the treated fabrics.¹⁶ Mechanical properties of the treated fabrics were determined by the Elmendorf tearing test (ASTM D-1424-82), strip breaking strength (ASTM-1682-64), and Stoll flex abrasion resistance (ASTM-1175-55T).¹⁷ All tests were carried out in the warp direction with the exception of WRA and % DC. After process-washing, the whiteness index was measured by a Hunter Ultrascan Sphere Spectrocolorimeter according to ASTM E313-67.¹⁷

A Cygnus 100 Fourier transform infrared spectroscope (Matton, Inc.) containing an MTEC Model 200 photoacoustic cell attachment (Photoacoustics, Inc.) was used to analyze the treated cotton cellulose. To eliminate potential interference from moisture in the cellulose, the sample was mounted above the desiccant (CaSO₄). Carbon black (lampblack carbon, Fisher Scientific) was used as a reference material. A total of 64 scans were carried out for each sample and these spectra were averaged to obtain one spectrum.

RESULTS AND DISCUSSION

Performance Properties

Table I and Figures 1 and 2(a) show the performance properties of cotton fabrics treated by 8% owb (on the weight of bath) BTCA in the presence of three different carbodiimides: cyanamide (CY), disodium cyanamide (DSC), and dicyandiamide (DCY):

Table I Performance Properties of Cotton Treated with 8% BTCA and Carbodiimide Catalysts^a

Catalyst (Mol Ratio vs. BTCA)	% Add-on	DP Rating	Dimensional Change (%)		WRA ^b ° (w + f)	Ret. T.S. ^b (%)	Ret. B.L. ^b (%)	Ret. S.F.A. ^b (%)	Wh. Ind. ^b	pH
			Warp	Fill						
Control	0.0	1.3	-5.21	-4.69	169	100.0	100.0	100.0	80.9	—
SHP 1 : 1	5.5	3.8	-0.13	0.0	288	63.2	52.1	14.3	74.3	2.3
CY 1 : 1 ^c	5.3	3.3	0.0	0.0	275	80.9	56.4	52.7	67.1	1.9
CY 1 : 1	4.9	3.0	0.0	-0.83	275	82.4	53.6	53.5	59.9	1.9
DCY 1 : 1 ^c	7.7	3.5	0.0	0.0	278	82.4	52.9	33.0	64.2	1.9
DCY 1 : 1	7.2	3.5	0.0	0.0	289	85.3	53.6	39.2	62.9	1.9

^a All treating baths contained 1% softener and 0.1% Triton X-100. The fabric was dried at 85°C for 5 min and cured at 180°C for 2 min, unless otherwise noted.

^b Wrinkle recovery angle, retention of tearing strength, breaking load, Stoll flex abrasion resistance, and whiteness index.

^c Cured at 170°C for 2 min.

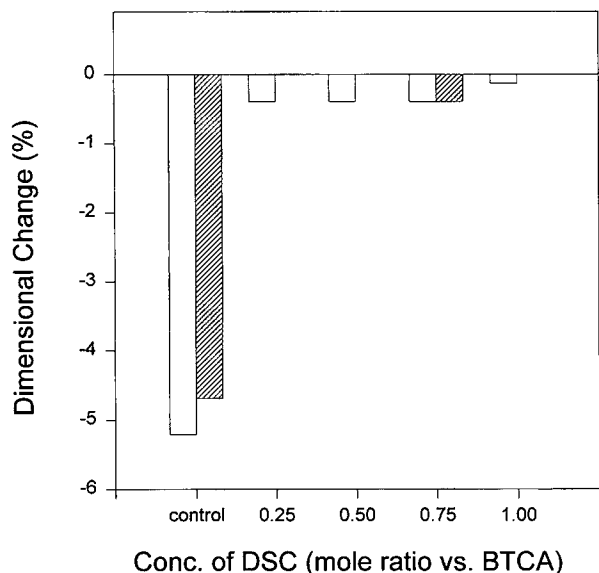
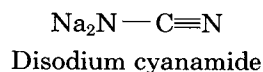
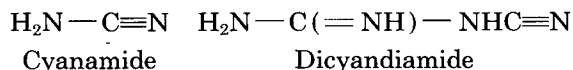


Figure 1 Dimensional change of cotton treated by 8% BTCA in the presence of different concentrations of disodium cyanamide: (□) warp; (▨) weft.



Data are also presented for the untreated control and for cotton fabrics treated with BTCA and sodium hypophosphite (SHP).

The BTCA and carbodiimide treatment of cotton produced cross-linked cellulose molecules as indicated by considerable increases in DP rating, % DC, and conditioned WRA of the treated fabric. Among the three different methods for resilience (or smooth-drying appearance) measurement, carbodiimide-treated fabrics tended to show slightly low DP ratings and WRA compared with those of the SHP-treated. However, % DC values (in both warp and weft) were practically identical for all types of catalysts. Untreated control samples resulted in negative values representing severe fabric shrinkage after home laundering.

Little difference was observed in the smoothness after drying of the treated fabrics at the different curing temperatures of 170 and 180°C (Table I). Whiteness indices of the fabrics treated with carbodiimides were lower than for the SHP-treated sample, probably due to residual nitric acid in BTCA. The yellowing problem was eliminated by utilizing BTCA from another supplier, as observed in a previous study.⁸ On the other hand, the cross-

linking of cotton cellulose using BTCA and carbodiimide resulted in considerably higher strength retention in tearing and Stoll flex abrasion resistance, compared with the SHP-treated sample, while retention of the breaking load was almost identical (Table I).

The cotton samples were also treated with 8% BTCA in the presence of different concentrations of DSC. As shown in Figure 1, % DC was relatively constant with a varying disodium cyanamide level. Conversely, WRAs continuously decreased with increase in DSC concentration, which also caused a continuous increase in bath pH [Fig. 2(a)]. At the same time, retention of the Stoll flex abrasion resistance was increased up to a 0.75 mol ratio of DSC vs. BTCA, whereas other mechanical properties showed small deviations by varying the DSC concentration [Fig. 2(b)]. Since DSC was a stronger base than were CY and DCY, it was expected that a low concentration of DSC would be needed to obtain a similar degree of cross-linking.

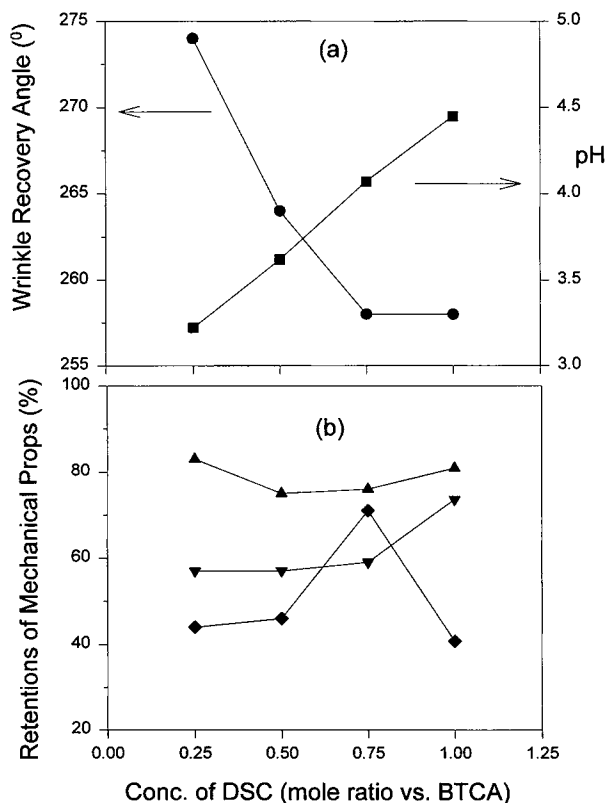


Figure 2 Performance characteristics of cotton treated by 8% BTCA in the presence of different concentrations of disodium cyanamide: (a) (●) wrinkle recovery angle; (■) bath pH. (b) (▲) retention of tearing strength; (▼) retention of breaking load; (◆) retention of Stoll flex abrasion resistance.

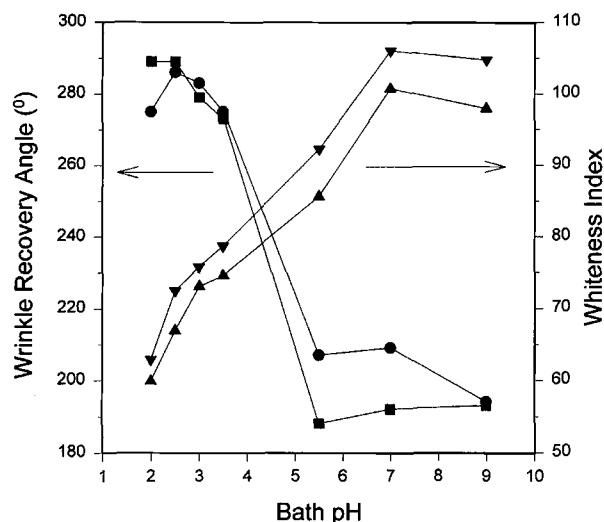


Figure 3 Effects of bath pH on wrinkle recovery angle (WRA) and whiteness index (WI) of the cotton treated by cyanamide (CY) and dicyandiamide (DCY): (●) BTCA + CY (WRA); (■) BTCA + DCY (WRA); (▲) BTCA + CY (WI); (▼) BTCA + DCY (WI).

The effects of pH, in the reaction of BTCA and cellulose molecules in the presence of carbodiimide, were further evaluated by treating cotton cellulose with BTCA and CY or DCY at different pH levels. Fifty percent NaOH was used as a buffer solution to control bath pH. Results substantiated the fact that the bath pH was an important factor in deter-

mining WRA and strength retention of the fabric treated by BTCA and carbodiimides (Figs. 3 and 4). Considerable variations were also shown in whiteness indices at different pH levels (Fig. 3). To achieve over 60% strength retention and a high level of smoothness after drying, along with good whiteness, the bath pH should be maintained around 3–3.5.

We also examined mixed catalyst systems containing carbodiimide and SHP. As seen in Figure 5, the cotton cellulose samples were treated with 6.5% BTCA in the presence of different amounts of SHP and CY. Results indicated that increasing the SHP concentration within the mixed system resulted in increases of DP rating and WRA, but in decreases in retention of mechanical properties. Specifically, the decrease in the Stoll flex abrasion resistance of the treated fabric, as SHP increased, was substantial.

Although the effectiveness of the three carbodiimide catalysts was only slightly different, their optimal concentration and bath pH must be carefully controlled. Since cyanamide is a primary skin irritant and has low stability during storage, DCY and DSC are preferable for practical applications.

Potential Mechanism

The presence of tautomeric carbodiimides could facilitate the esterification reaction of polycarboxylic acid and cellulose in two ways: Both reactions in-

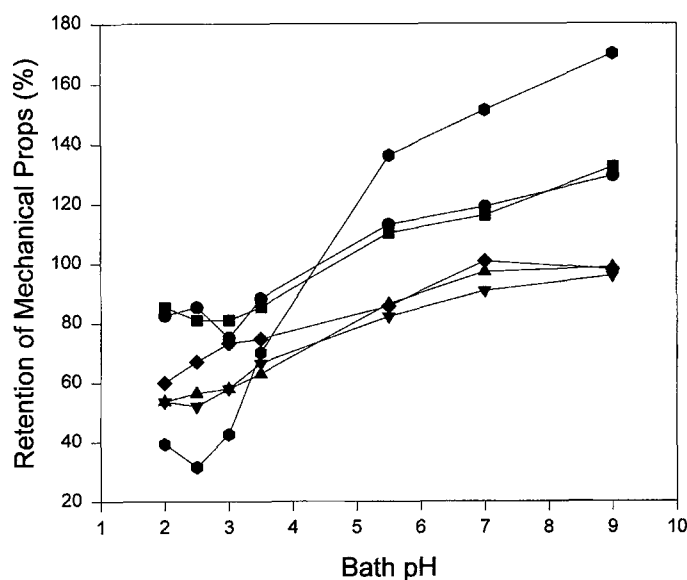


Figure 4 Effects of bath pH on retention of tearing strength (TS), breaking load (BL), and Stoll flex abrasion resistance (SFA) of cotton treated by CY and DCY: (●) TS-CY; (■) TS-DCY; (▲) BL-CY; (▼) BL-DCY; (◆) SFA-DCY; (●) SFA-CY.

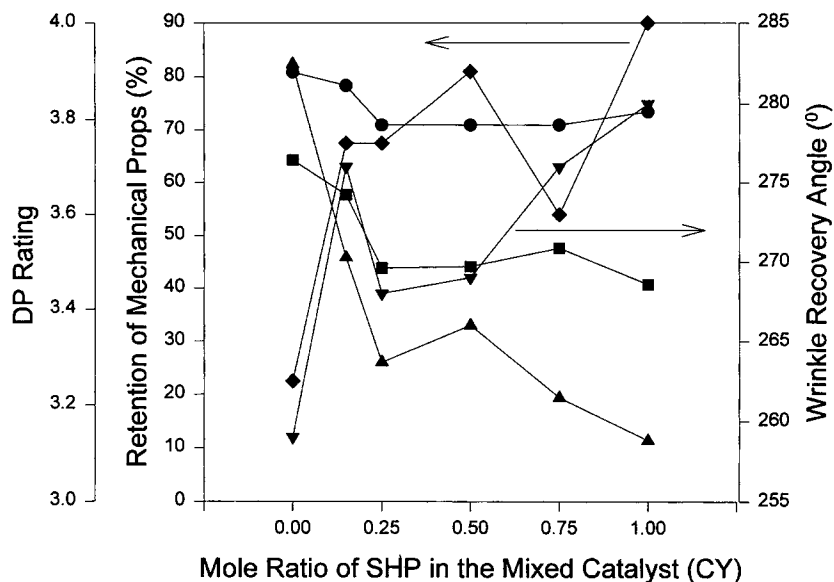


Figure 5 Effects of sodium hypophosphite concentration in the mixed catalyst system with CY on performance properties of cotton treated by 6.5% BTCA: (●) TS; (■) BL; (▲) SFA; (▼) WRA; (◆) DP rating.

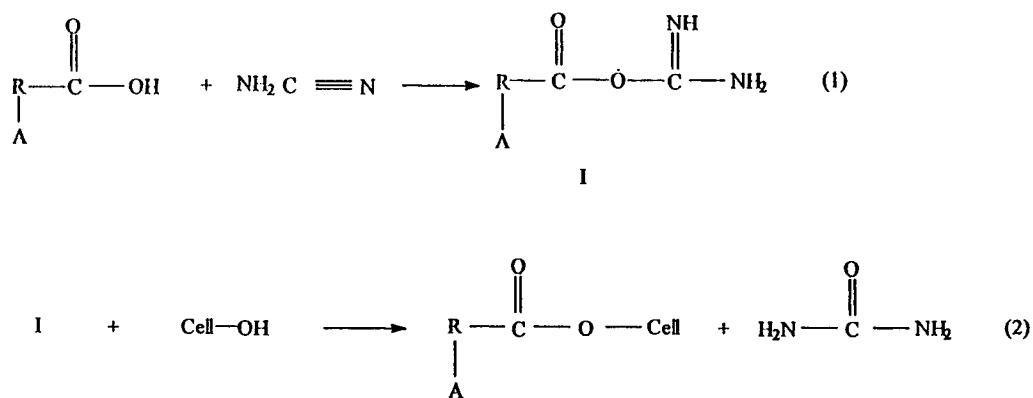
volve the formation of urea as shown in Schemes 1 and 2, where *A* is the moiety of BTCA. Similar mechanisms have been previously proposed for phosphorylation and dyes containing carboxyl groups.¹⁸ In eqs. (1) and (2) in Scheme 1, carbodiimide facilitated a direct esterification reaction between cellulose and BTCA. Contrarily, in Scheme 2, the carbodiimide enhanced the formation of an anhydride intermediate that was a precursor for the esterification reaction between PCA and cellulose molecules. The anhydride intermediate for the reaction between PCA and cellulose was confirmed in a previous study.⁵

However, formation of urea by hydrolysis of carbodiimide can easily occur at elevated temperature

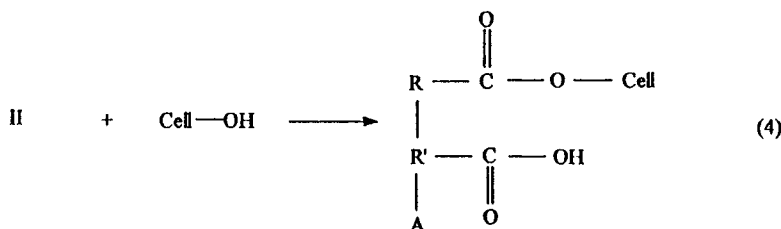
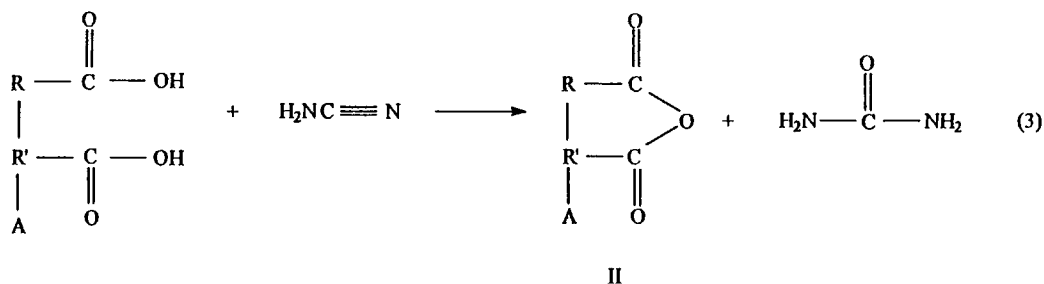
and under acidic conditions, as in the finishing conditions used in the present study (Scheme 3).¹⁹ Different catalytic activity of the three carbodiimides (CY, DCY, DSC) in the esterification of cellulose and BTCA could be related to the hydrolysis rate of the individual compounds.

FTIR Analyses

The untreated and treated cotton fabrics with BTCA and CY, DCY, or SHP were immersed in 0.1*N* acetic acid for 5 min at room temperature and air-dried to ensure the absence of carboxylate groups. These samples were regarded as acid-rinsed samples. One-half of each sample was again washed with 0.1*N*



Scheme 1



Scheme 2

NaOH solution for 5 min at room temperature to convert free carboxyl groups into carboxylate groups and then air-dried. These samples are termed base-rinsed samples.

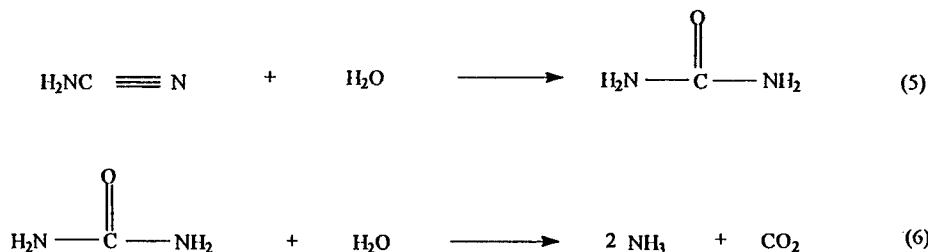
Figure 6 shows the FTIR spectra of the untreated control and acid-rinsed samples. The Y-axis of the spectra is an arbitrary scale for photoacoustic response. These acid-rinsed samples show strong carbonyl peaks for ester linkages and free carboxyl acids at 1720 cm^{-1} (Peak 1). Unlike the samples treated with BTCA and SHP, the samples treated with BTCA and CY or DCY, in Figure 6(C) and (D), showed an additional peak at 1597 cm^{-1} (Peak 2). This peak was considerably more prominent in the DCY-treated sample. The presence of this additional peak can be properly attributed to two possibilities: First, it can be due to the $-\text{C}\equiv\text{N}$ absorption, indicating attachment of CY or DCY to the fabric, or second, it may be due to the carbonyl peak caused by absorption of residual urea.

Kjeldahl nitrogen analyses were carried out to confirm the presence of nitrogen within the fabric

(Table II). The samples treated by BTCA and DCY contained significant amounts of nitrogen in both washed and unwashed samples. No process-washing was carried out for either sample. After one home laundering, the level of nitrogen in the washed sample dropped, indicating removal of unreacted DCY from the surface.

Once the fabrics were washed by NaOH, unesterified free carboxyl groups were converted to carboxylate ($-\text{COO}^-\text{Na}^+$). This conversion was indicated by the peaks for both ester carbonyl at 1720 cm^{-1} (peak 1) and carboxylate carbonyl at 1570 cm^{-1} (peak 2), as shown in Figure 7. By the NaOH rinse, the additional peak shown at 1597 cm^{-1} in the CY or DCY-treated samples in Figure 6 disappeared or overlapped with carboxylate carbonyl peak (peak 2) in Figure 7.

To confirm CY peaks in the spectrum, two drops of 50% CY solution was applied on the base-rinsed sample treated by BTCA and CY (Fig. 8). Cyanamide exhibits an intense, poorly resolved doublet at $2225\text{--}2260\text{ cm}^{-1}$, as shown in peak 1 in Figure 8,



Scheme 3

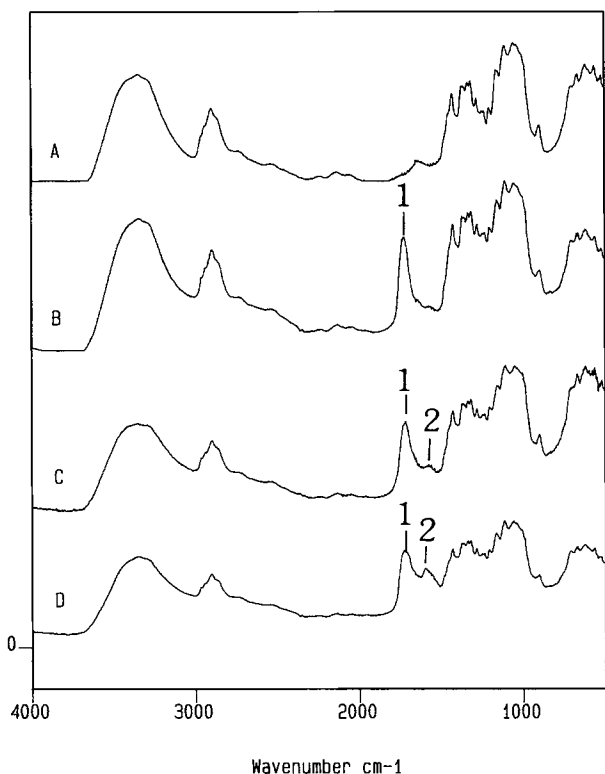


Figure 6 FTIR spectra of the untreated control and acid-rinsed cotton samples (peak 1: 1720 cm^{-1} ; peak 2: 1597 cm^{-1}): (A) control; (B) BTCA + SHP; (C) BTCA + CY; (D) BTCA + DCY.

due to photoacoustic response from its $\text{—C}\equiv\text{N}$ group.¹⁹ In addition, a photoacoustic response at $2160\text{--}2200\text{ cm}^{-1}$ (peak 2) was also observed, presumably due to the isocyanide structure ($\text{—N}^+=\text{C—}$), representing adduct formation of some portion of applied cyanamide with BTCA. Furthermore, at 1650 cm^{-1} , a photoacoustic response of the $\text{—C}=\text{N—}$ group was also observed as peak 3 due to its tautomeric structure.

The ratio of ester carbonyl (peak 1 in Fig. 7) and carboxylate carbonyl (peak 2 in Fig. 7) groups has been semiquantitatively used to determine the level of esterification within the treated sample.⁵ The results of the FTIR analytical spectra summarized in Table III show that the efficiency of cross-linking was somewhat lower with the CY-treated fabric than

Table II Kjeldahl Nitrogen Analyses (8% BTCA)

Samples	% Nitrogen
Control	0.028
BTCA + DCY (washed)	1.33
BTCA + DCY (unwashed)	1.88

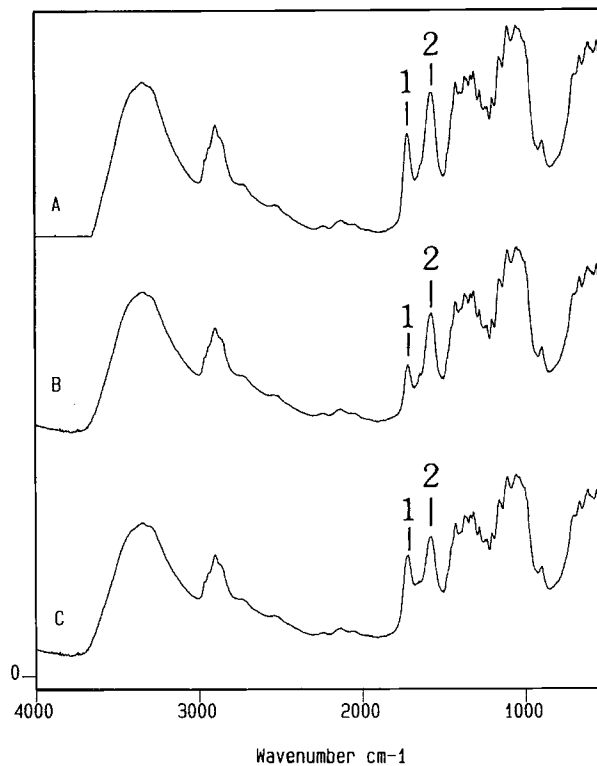


Figure 7 FTIR spectra of the base-rinsed cotton samples (peak 1: 1720 cm^{-1} ; peak 2: 1570 cm^{-1}): (A) BTCA + SHP; (B) BTCA + CY; (C) BTCA + DCY.

with the SHP- or DCY-treated samples. These results coincide with the performance characteristic data discussed in the previous section.

CONCLUSIONS

To produce nonformaldehyde–nonphosphorus durable press finished systems of cotton cellulose, we examined three different carbodiimide catalysts: cyanamide, dicyandiamide, and disodium cyanamide. The treatment with BTCA in the presence of car-

Table III FTIR Analysis of the Treated Fabrics (8% BTCA)

Catalyst	Add-on (%)	Peak Height at 1720 cm^{-1} Base-rinsed	Peak Height at 1570 cm^{-1} Base-rinsed	A ^a
SHP	5.5	170.6	218.5	0.78
CY	4.9	120.7	197.8	0.61
DCY	7.2	184.2	207.2	0.89

^a Ratio A = (peak height 1720 cm^{-1} , base-rinsed/peak height at 1570 cm^{-1} , base-rinsed).

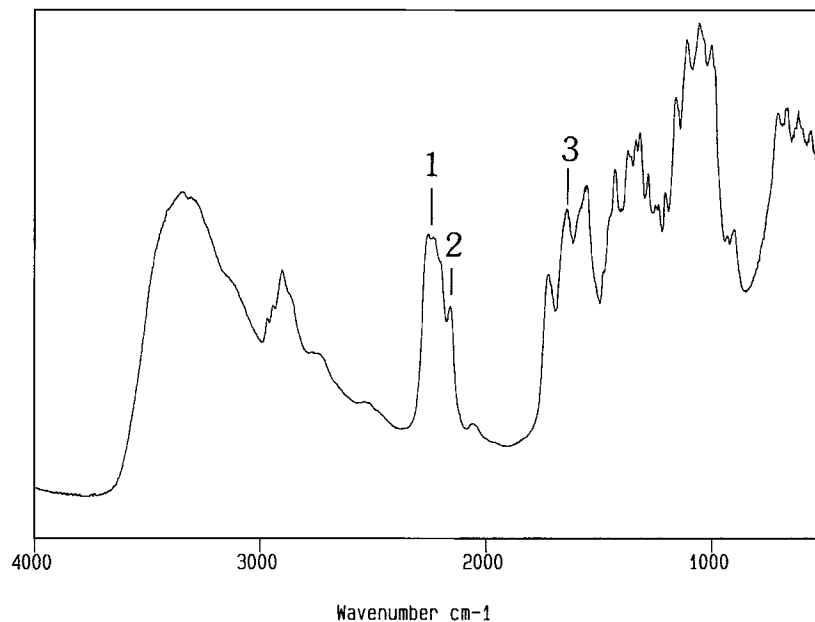


Figure 8 FTIR spectra of cyanamide applied on the base-rinsed cotton sample (peak 1: 2225–2260 cm^{-1} ; peak 2: 2160–2200 cm^{-1} ; peak 3: 1650 cm^{-1}).

bodiimides results in considerable increases in DP rating, % DC (both warp and weft directions), and conditional WRA. The bath pH was an important factor in determining WRA and strength retention as well as whiteness of the treated cotton. In the mixed systems, an increase in SHP concentration increased the DP rating and WRA and decreased the retention of mechanical properties considerably.

The proposed mechanisms indicate that the carbodiimides can enhance the reaction between BTCA and cellulose in two ways: direct esterification and formation of an anhydride intermediate. Both reactions formed urea molecules.

FTIR was used to confirm the esterification of cellulose with BTCA and carbodiimides. Semiquantitative analyses suggested that CY was slightly less effective than was DCY or SHP.

This project has been supported by Cotton, Inc., and the Kansas Agricultural Experiment Station.

REFERENCES

1. C. M. Welch, *Text. Res. J.*, **58**(8), 480–486 (1988).
2. C. M. Welch and B. A. K. Andrews, *Text. Chem. Color.*, **21**(2), 213–217 (1989).
3. H. Choi, *Text. Res. J.*, **62**(10), 614–618 (1992).
4. H. Choi, and C. M. Welch, in *Book of Papers*, International Conference & Exhibition, AATCC, October 4–7, 1992, p. 287.
5. C. Q. Yang, *Text. Res. J.*, **61**(8), 433–440 (1991).
6. B. J. Trask-Morrell, B. A. K. Andrews, and E. E. Graves, *J. Appl. Polym. Sci.*, **43**, 1717–1726 (1991).
7. B. J. Trask-Morrell and H. Choi, *J. Appl. Polym. Sci.*, **51**, 769–779 (1994).
8. H. Choi, C. M. Welch, and N. M. Morris, *Text. Res. J.*, **63**(11), 650–657 (1993).
9. H. Choi, J. D. Li, R. D. Goodin, and T. D. Pratt, *Am. Dyestuff Rep.*, **83**(2), 38–43, 51 (1994).
10. C. M. Welch and J. G. Peters, *Text. Chem. Color.*, **25**(10), 25–29 (1993).
11. P. O. Nkeonye, *J. Soc. Dye. Color.*, **102**(12), 384–391 (1986).
12. P. O. Nkeonye, and I. D. Rattee, *Text. Res. J.*, **58**(1), 57–59 (1988).
13. G. Alberghina, M. E. Amato, and S. Fisichella, *Dyes Pigments*, **7**, 33–44 (1986).
14. Jpn. Kokai Tokkyo Koho JP 8,247,973, (1982) (to American Cyanamide Co.).
15. Jpn. Kokai Tokkyo Koho JP 8,247,974, (1982) (to American Cyanamide Co.).
16. *AATCC Technical Manual*, American Association of Textile Chemists and Colorists, Research Triangle Park, NC, 1993.
17. *Annual Book of ASTM Standards*, American Association of Testing and Materials, Philadelphia, PA, 1992.
18. H. G. Khorana, *Chem. Rev.*, **53**, 145–165 (1953).
19. D. R. May, in *Kirk-Othmer Encyclopedia of Chemical Technology*, H. Mark, et. al., Eds., Wiley, New York, 1979, Vol. 7, pp. 291–306.

Received May 16, 1994

Accepted July 19, 1994