

# Durable Press Finish of Cotton/Polyester Fabrics with 1,2,3,4-Butanetetracarboxylic Acid and Sodium Propionate

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**ABSTRACT:** Sodium hypophosphite (SHP) is widely used as an effective catalyst for the esterification reaction of cellulose with 1,2,3,4-butanetetracarboxylic acid (BTCA). However, catalysts containing phosphorus cause significant shade changes in dyed fabrics because of their reductive nature, and the effluents containing phosphorus cause eutrophication in rivers and lakes. Hence, their commercial application as catalysts in textile processing is limited. In this study sodium propionate and its catalytic activities as a nonphosphorous catalyst were investigated. The evidence for esterification and crosslinking of cellulose with BTCA in the presence of sodium propionate was shown by an improved wrinkle recovery angle and durable press rating of treated fabrics. The presence of ester groups in the treated fabrics was confirmed by FTIR analysis. The performance of sodium propionate as a catalyst for BTCA was comparable to that of SHP. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 654–661, 2001

**Key words:** butanetetracarboxylic acid; sodium hypophosphite; sodium propionate; ester linkage

## INTRODUCTION

Cellulose to which crosslinking has been introduced has improved elastic recovery due to the inhibition of slippage between the molecules when forces are applied. However, crosslinked fabrics show increased wrinkle recovery while their strength is significantly decreased. One of the reasons for the strength loss is that the forces applied to the crosslinked fabrics tend to concentrate on a certain area. Dimethyloldihydroxyethylene urea, which forms an ester linkage with the hydroxyl group of cellulose, is widely used as a crosslinking agent for improving the wrinkle recovery of cellulose fabrics.<sup>1</sup> However, because of the problem of formaldehyde release, active in-

vestigations on nonformaldehyde crosslinking agents were carried out. One of the results of these studies was polycarboxylic acids that form an ester linkage with cellulose. The research for polycarboxylic acids began in 1960, and active investigations on them, such as reaction mechanisms, started in 1991.<sup>2–6</sup> Welch<sup>3</sup> and Yang<sup>4</sup> reported that a cis-type maleic acid, which can produce an anhydride, formed an ester linkage with cellulose at lower temperature than a trans-type fumaric acid. Two studies<sup>6,7</sup> found that 1,2,3,4-butanetetracarboxylic acid (BTCA) containing four carboxyl groups bonded to the adjacent carbons of its molecular backbone was the most effective crosslinking agent of polycarboxylic acids.

The esterification reaction of BTCA with cellulose proceeds through several steps.<sup>2–6,8</sup> When BTCA is heated at high temperature, a five-membered cyclic anhydride intermediate forms; this intermediate reacts with the hydroxyl group of cellulose to form an ester linkage through a nu-

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cleophilic substitution reaction. The formation of an intermediate anhydride proceeds in the presence of weak alkaline catalysts, and sodium carboxylate promotes the formation of this anhydride.<sup>2,8,9-12</sup> Sodium hypophosphite (SHP) was widely used as the most effective catalyst for the formation of an anhydride intermediate of BTCA because excellent wrinkle recovery and almost no yellowing of the treated fabrics were obtained.<sup>7</sup> However, its disadvantages were that it can cause a shade change of fabrics dyed with certain sulfur or reactive dyes and it brings about eutrophication in rivers and lakes because of the phosphorus in it. Therefore, an investigation<sup>13</sup> was carried out on a nonphosphorous catalyst for BTCA that could substitute for the SHP.

This study is on the effect of the curing temperature and pH of the treating solution on the formation of an anhydride intermediate in the esterification reaction of BTCA with cellulose. A new substitute catalyst that did not contain phosphorus and that was comparable to SHP in performance was also investigated.

## EXPERIMENTAL

### Fabrics

Cotton and polyester (60/40%) blended fabrics, which had been scoured and bleached, were used. The yarn count was Ne 51 for the warp and weft, and the fabric density was 110 ends/in. and 92 picks/in.

### Chemicals

The BTCA was purchased from Aldrich Chemical Co., the SHP catalyst was procured from Shinyo Chemical Co., and the sodium propionate was also from Aldrich. Triton X-100 was used as the wetting agent (Shinyo Chemical Co.), and Avivan 7066 was used as the softening agent (Ciba-Geigy).

### Treatment of Fabrics

The fabrics were treated by the pad-dry-cure process. The aqueous padding solution consisted of crosslinking agent, catalyst, wetting agent, and softening agent (0.1%). The fabrics were padded with the 2 dip-2 nip method, and the wet pickup was 80%. The dry temperature and time were 85°C and 3 min, respectively. The cure temperature was 140–190°C, and the cure time was 1–5

min. The fabrics were thoroughly washed with frequent stirring in 50°C water for 30 min and then dried. All the samples were conditioned under a 20°C, 65% relative humidity atmosphere.

### Tests and Analysis

The wrinkle recovery angle was AATCC 66-1978, and the DP rating was tested according to AATCC 124 (normal cycle,  $41 \pm 3^\circ\text{C}$ , tumble dry). The tensile strength was tested according to ASTM D 1682-64 (1-in. raveled strip), the tearing strength was tested according to ASTM D 1424-83 (Elmendorf), and the abrasion resistance was tested according to ASTM D 3885-80 (flex abrasion). The IR spectra were analyzed by FTIR with a Nicolet 520. The aqueous BTCA/catalyst solution was thoroughly dried at 100°C and cured. The pellet for analysis of the intermediate anhydride was prepared by mixing it with KBr powder. The IR spectra of the treated fabrics were also analyzed with a KBr pellet.

## RESULTS AND DISCUSSION

### Reaction of BTCA to Cellulose in Presence of Sodium Carboxylate Catalysts

Cyclic anhydride can be formed by heating. However, it can be formed more effectively even at low temperature in the presence of a sodium carboxylate catalyst.<sup>14</sup> Trask-Morrell et al.<sup>12</sup> reported on the basis of thermal analysis that the reaction time and reaction energy for anhydride formation both decreased in the presence of a catalyst. Figure 1 shows the process of the esterification reaction of BTCA with cellulose in the presence of sodium carboxylate. The BTCA was transformed to a carboxylate anion by sodium carboxylate, and the carboxylate anion was converted to anhydride by heat that formed an ester linkage with cellulose through the nucleophilic substitution reaction.<sup>3</sup> A basic investigation on anhydride formation was necessary because the esterification reaction between BTCA and cellulose occurred through intermediate anhydride.

### Effect of Temperature on Anhydride Formation

Figure 2 shows the IR spectra of anhydride formation that depended on the cure temperatures. The anhydride carbonyl peaks around 1840 and 1780  $\text{cm}^{-1}$  grew higher as the curing tempera-

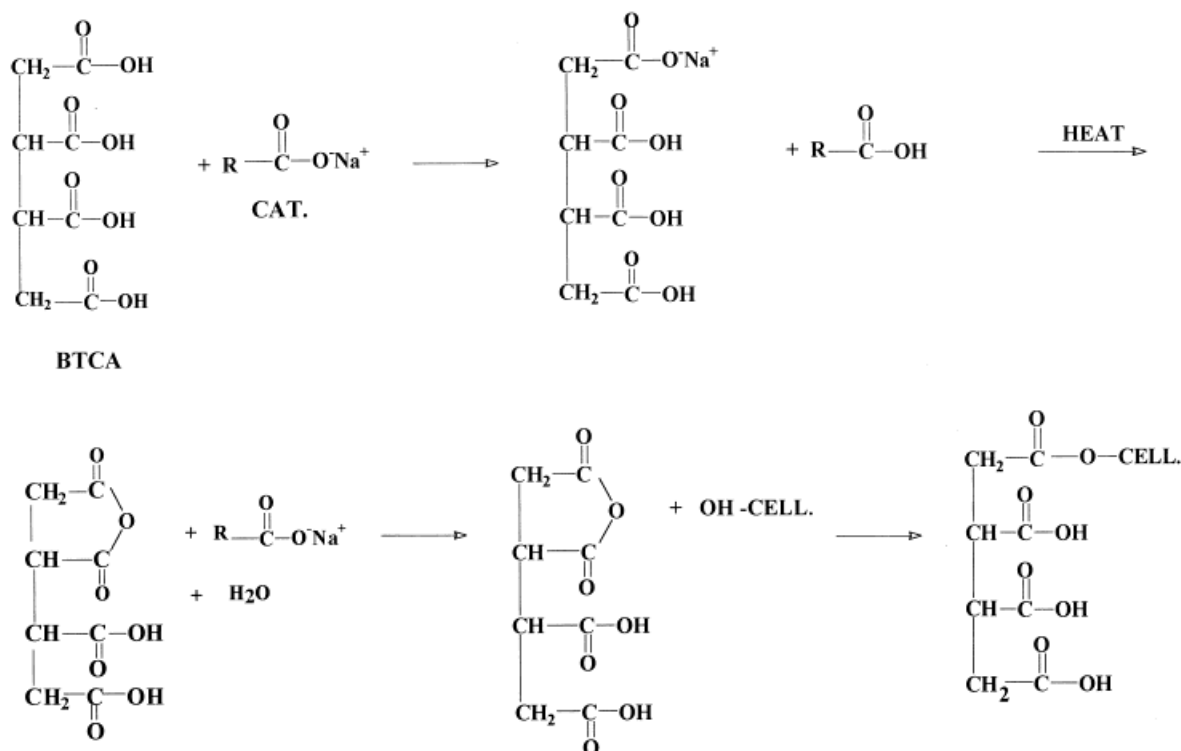


Figure 1 The mechanism of catalysis in the reaction of BTCA with cellulose.

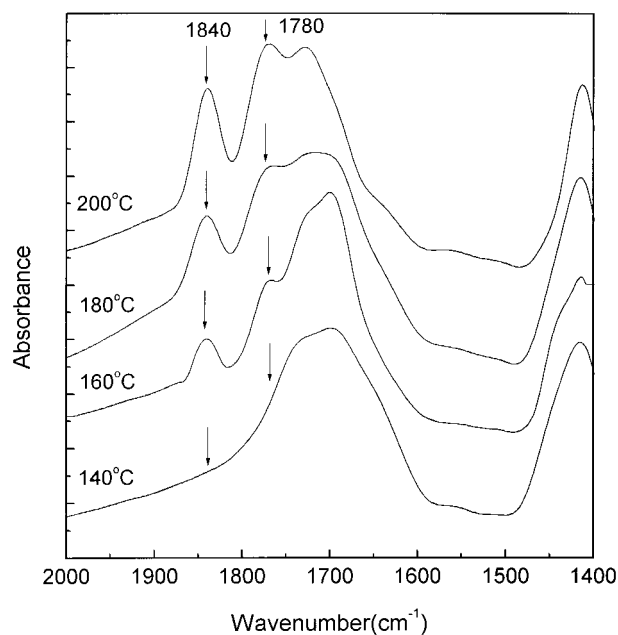


Figure 2 IR spectra of aqueous BTCA/SHP (1 : 0.3 mole ratio) solution cured at different temperatures for 10 min after being thoroughly dried. (8% owb BTCA).

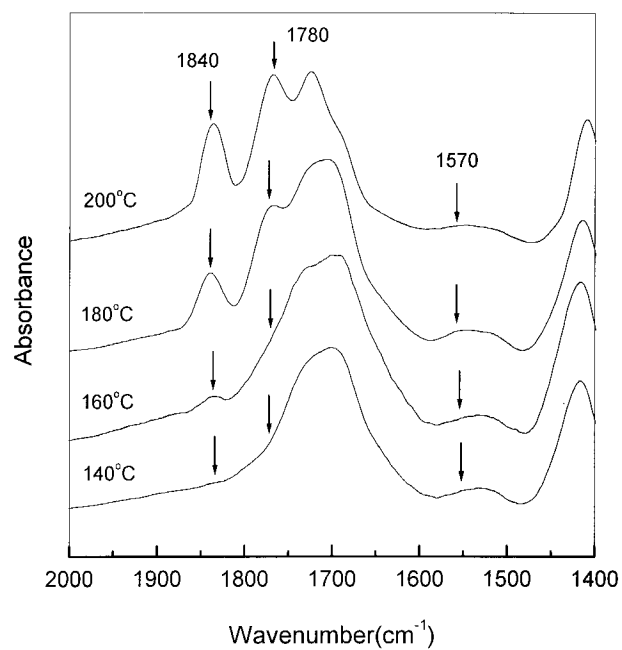
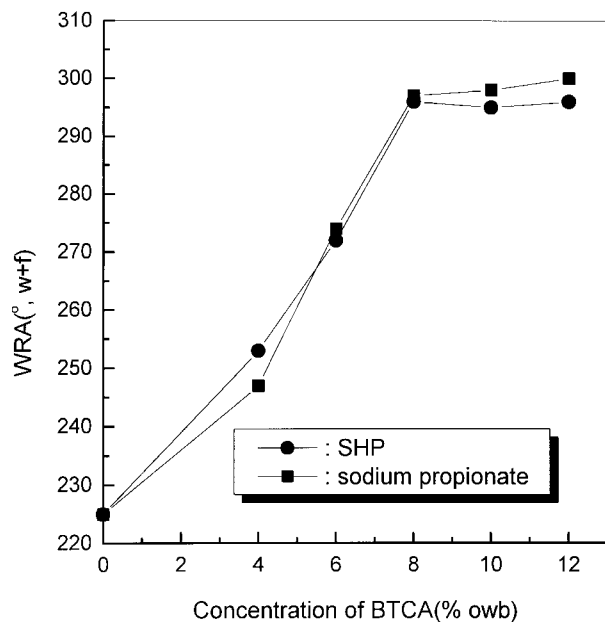
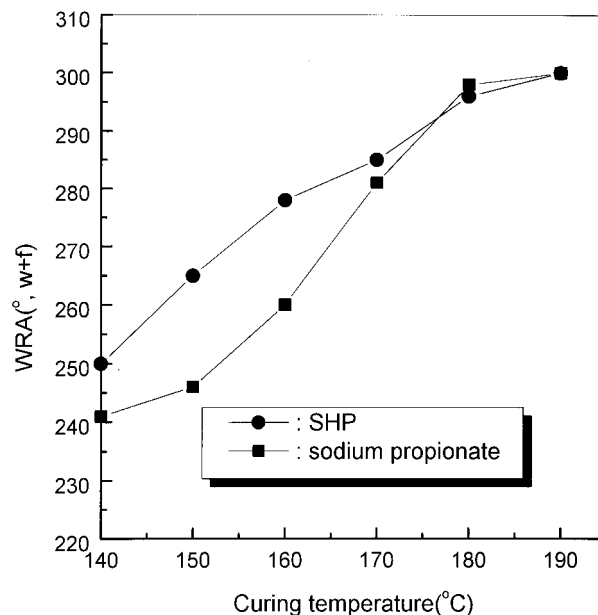


Figure 3 IR spectra of aqueous BTCA/sodium propionate (1 : 0.3 mole ratio) solution cured at different temperatures for 10 min after being thoroughly dried. (8% owb BTCA).



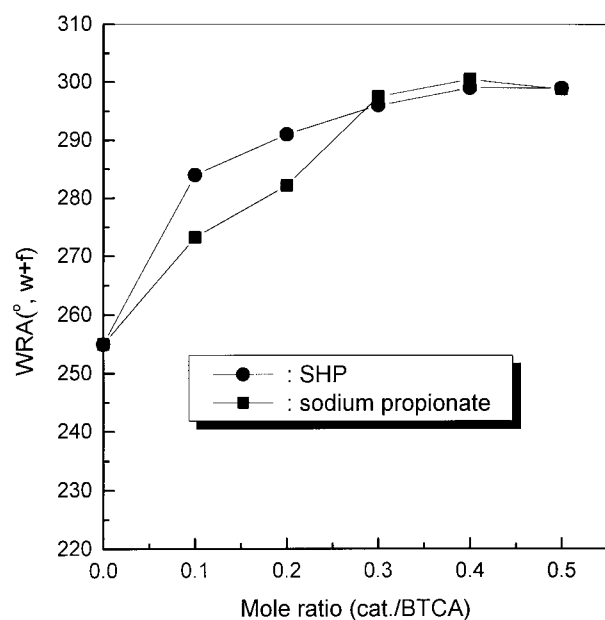
**Figure 4** The effect of the BTCA concentration on the wrinkle recovery angle of treated fabrics. Curing conditions: BTCA/catalyst = 1 : 0.3 (mole ratio); 180°C; 3 min.



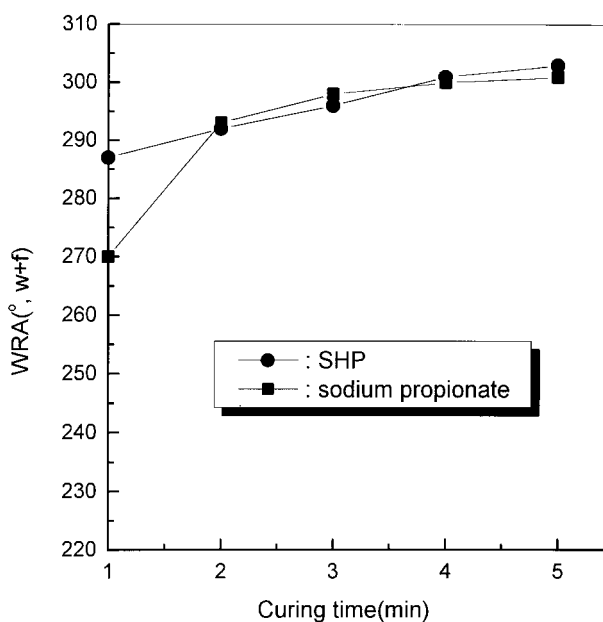
**Figure 6** The effect of curing temperatures on the wrinkle recovery angle of treated fabrics. Curing conditions: 8% owb BTCA; BTCA/catalyst = 1 : 0.3 (mole ratio); 3 min.

tures increased. Figure 3 shows the formation of the anhydride carbonyl peaks when sodium propionate was used as a catalyst instead of SHP. As in Figure 2, the anhydride carbonyl peak also

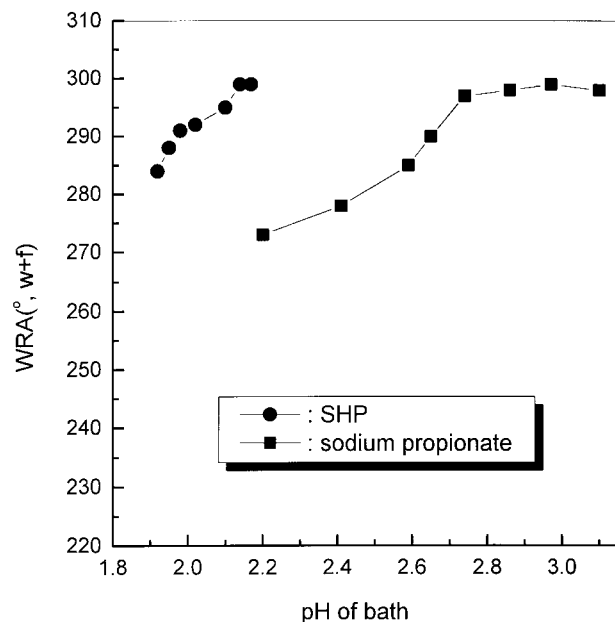
grew higher as the curing temperatures increased. However, in Figure 3 the small carboxylate carbonyl peak appears at around  $1570\text{ cm}^{-1}$ ; the reason for this was that the pH of sodium



**Figure 5** The effect of the catalyst concentration on the wrinkle recovery angle of treated fabrics. Curing conditions: 8% owb BTCA; 180°C; 3 min.

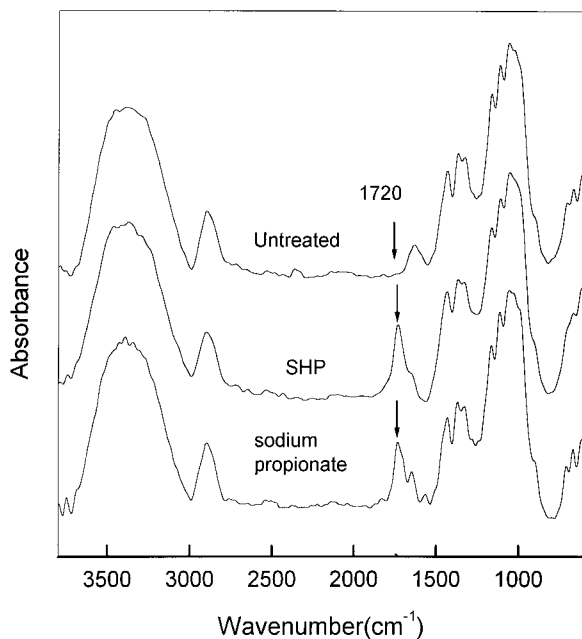


**Figure 7** The effect of curing time on the wrinkle recovery angle of treated fabrics. Curing conditions: 8% owb BTCA; BTCA/catalyst = 1 : 0.3 (mole ratio); 180°C.

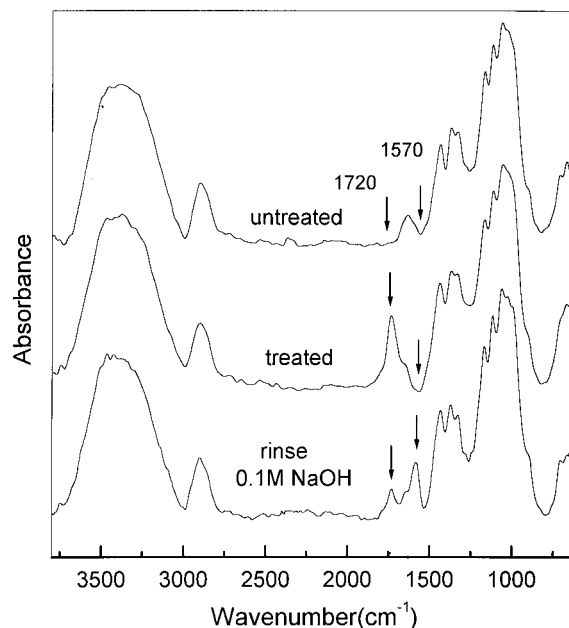


**Figure 8** The effect of the bath pH on the wrinkle recovery angle of treated fabrics. Curing conditions: 8% owb BTCA; 180°C; 3 min.

propionate was higher than that of SHP, and therefore the former produced carboxylates easier than the latter.



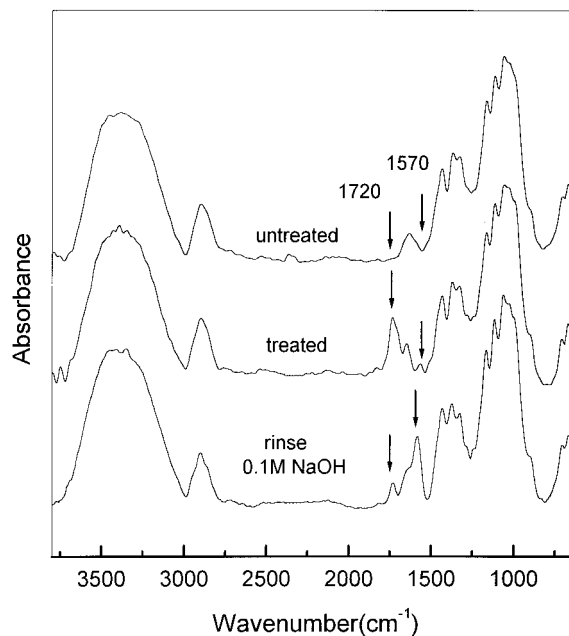
**Figure 9** IR spectra of cotton fabrics treated with BTCA and different catalysts. Curing conditions: 8% owb BTCA; BTCA/catalyst = 1 : 0.3 (mole ratio); 180°C; 3 min.



**Figure 10** IR spectra of cotton fabrics treated with BTCA/SHP or BTCA/SHP followed by rinsing in 0.1M NaOH solution. Curing conditions: 8% owb BTCA; 180°C; 3 min; BTCA/catalyst = 1 : 0.3 (mole ratio).

#### Effect of Processing Parameters on Crosslinking

The wrinkle recovery angle of the treated fabrics was measured to investigate the effect of various



**Figure 11** IR spectra of cotton fabrics treated with BTCA/sodium propionate or BTCA/sodium propionate followed by rinsing in 0.1M NaOH solution. Curing conditions: 8% owb BTCA; 180°C; 3 min; BTCA/sodium propionate = 1 : 0.3 (mole ratio).

**Table I Effect of BTCA Concentration on Breaking Strength, Tearing Strength, and Abrasion Resistance of Treated Fabrics**

Retention of	BTCA Concentration (owb %)					
	0	4	6	8	10	12
Breaking strength (%)						
SHP	100	60.8	57.2	56.5	52.9	49.2
Sodium propionate	100	69.7	66.3	60	58.5	58.5
Tearing strength (%)						
SHP	100	51.2	49.7	49.3	48.1	47.8
Sodium propionate	100	59.8	56.7	56	53.4	53.2
Abrasion resistance (%)						
SHP	100	29.2	24.1	23	19.1	18.3
Sodium propionate	100	35.4	25.8	25.1	21.7	20

The fabrics were treated at 180°C for 3 min, and the BTCA/catalyst mole ratio was 1 : 0.3.

factors such as the concentration of the crosslinking agent BTCA, the mole ratio of a catalyst to BTCA, the curing temperatures, the curing time, and the pH of the padding solution on the crosslinking. Figure 4 shows the wrinkle recovery angles of the treated fabrics as a function of the BTCA concentration. The wrinkle recovery angle obtained by SHP was slightly higher than that by sodium propionate at 4% BTCA, and the performance of the two catalysts was similar at 8% BTCA or above. There was no significant increase in the wrinkle recovery angle above 8% BTCA. Figure 5 shows the wrinkle recovery angle of the treated fabrics as a function of the mole ratio of the catalyst to BTCA. The wrinkle recovery increased significantly as the amount of a catalyst increased until the mole ratio of the catalyst to BTCA was 0.3. The SHP showed slightly better performance than sodium propionate at a lower mole ratio than 0.3, but with the mole ratio of 0.3 two catalysts showed similar performance. Figure 6 shows the wrinkle recovery angle of the treated fabrics as a function of curing temperatures ranging from 140 to 190°C. The wrinkle recovery in-

creased significantly as the curing temperature increased to 180°C. The SHP showed better performance at temperatures lower than 180°C, but above 180°C both were similar. The color of the treated fabric was altered at 190°C. Figure 7 shows the wrinkle recovery angle of the treated fabrics as a function of the curing time. At a curing time of not less than 2 min both catalysts showed almost the same wrinkle recovery angle, and the wrinkle recovery angle did not increase much even if the curing time was increased to over 3 min. Figure 8 shows the effect of the pH of the aqueous padding solution on the wrinkle recovery angle of the treated fabrics. With the SHP catalyst the wrinkle recovery angle increased continuously when the pH increased from 1.9 to 2.1, while in sodium propionate catalyst it increased significantly until pH 2.7 and very little afterward. Figure 9 presents the FTIR spectra of the fabrics treated by the optimum process conditions. It shows that the carbonyl peak appeared at around 1720 cm<sup>-1</sup>, which did not appear on the untreated fabrics. Three types of carbonyl groups existed when the esterification reaction occurred

**Table II Effect of Softener Concentration on Wrinkle Recovery Angle (WRA) of Treated Fabrics**

WRA ( <i>w + f</i> )	Softener Concentration (owb %)					
	0	0.5	1	1.5	2	2.5
SHP	296	296	298	296	296	295
Sodium propionate	298	298	298	297	297	298

The BTCA concentration was 8% owb. The fabrics were treated at 180°C for 3 min, and the BTCA/catalyst mole ratio was 1 : 0.3.

**Table III Effect of Softener Concentration on Breaking Strength, Tearing Strength, and Abrasion Resistance of Treated Fabrics**

Retention of	BTCA Concentration (owb %)					
	0	0.5	1	1.5	2	2.5
Breaking strength (%)						
SHP	56.5	56.6	56.1	57.2	56.5	55.6
Sodium propionate	60	59.1	59.9	59.1	59.1	58.7
Tearing strength (%)						
SHP	49.3	65.4	75	77.7	81.2	84.3
Sodium propionate	56	74.3	83.2	86.3	92.4	92.4
Abrasion resistance (%)						
SHP	23	52	118	111.8	76	72
Sodium propionate	25.1	65.6	106	108	100	98

The BTCA concentration was 8% owb. The fabrics were treated at 180°C for 3 min, and the BTCA/catalyst mole ratio was 1 : 0.3.

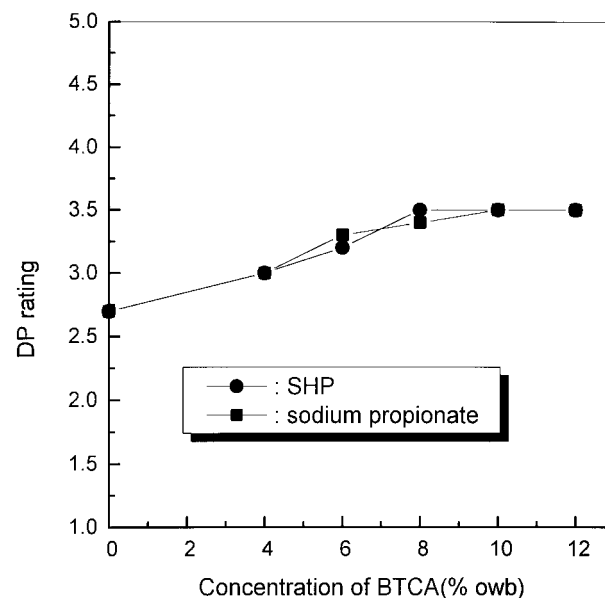
between carboxylic acid and cellulose: the carbonyl peak of the acid that formed the ester linkage with cellulose, the carbonyl peak of the acid not participating in the esterification linkage, and the carbonyl peak of the carboxylate anion.<sup>5,14</sup> The ester carbonyl peak overlapped the carboxyl carbonyl peak at around 1720  $\text{cm}^{-1}$ , and the carboxylate carbonyl peak appeared at around 1570  $\text{cm}^{-1}$  in the FTIR spectrum. Sodium hydroxide converted the carboxyl carbonyl group to the carboxylate anion. Therefore, the ester carbonyl peak could be separated from the overlapping carboxyl carbonyl peak when the cured fabrics were further treated with 0.1M NaOH solution. Figures 10 and 11 show the ester carbonyl peak separated from the overlapped peaks. This revealed the ester linkage formed on the fabrics treated in the presence of sodium propionate, as well as in the presence of SHP, as a catalyst.

#### Effect of BTCA Concentration on Strength of Treated Fabrics

Table I shows the strength retention of treated fabrics as a function of the BTCA concentration ranging from 4 to 12%. The retention of the tensile strength decreased as the BTCA concentration increased. The retention of the tearing strength and abrasion resistance also decreased as the BTCA concentration increased. Sodium propionate showed better strength retention than SHP. The pH of the padding solution containing sodium propionate was higher than that of SHP, thus deteriorating the fabrics less.

#### Effect of Softening Agent on Wrinkle Recovery and Strength of Treated Fabrics

Tables II and III show the wrinkle recovery angle and strength retention of the treated fabrics as a function of the concentration of the softening agent (0–2.5%) in the padding solution. The softening agent had no influence on the wrinkle recovery angle and tensile strength, but it significantly improved the retention of the tearing



**Figure 12** The effect of BTCA concentration on the DP rating of treated fabrics. Curing conditions: BTCA/catalyst = 1 : 0.3 (mole ratio); 1.5% owb softener; 180°C; 3 min.

strength and abrasion resistance of treated fabrics as the softening agent content increased. The retention of abrasion resistance was not lower than 100% when the concentration of the softening agent was either 1.0 or 1.5%. Figure 12 shows the durable press rating as a function of the BTCA concentration. The fabrics were treated with the padding solution containing BTCA; its concentration was 4–12%, the mole ratio of the catalyst to BTCA was 0.3, the softening agent was 1.5%, and the curing was at 180°C for 3 min. The durable press rating of the treated fabrics increased as the BTCA concentration increased up to 8%, which had a durable press rating of 3.5, but it did not improve over 8%.

## CONCLUSIONS

The optimum processing conditions for treating the cotton/polyester blended fabrics with BTCA was 8% BTCA, a 0.3 mole ratio of either SHP or sodium propionate to BTCA, and curing at 180° for 3 min. The amount of crosslinking depended on the BTCA concentration, curing conditions, catalyst, and the pH of the padding solution. Sodium propionate was superior to SHP as a catalyst for BTCA in respect to the strength retention of the treated fabrics. The addition of softening agent to the padding solution significantly improved the retention of the tearing strength and abrasion resistance of the treated fabrics. The softening agent on the treated fabrics reduced the friction of fibers and evenly distributed the stress

at the contact point of the warp and weft throughout the fabrics. The results proved that sodium propionate can be successfully used as a catalyst for BTCA in substitution for the conventional catalyst SHP.

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