

IR Spectroscopy Study of Cyclic Anhydride as Intermediate for Ester Crosslinking of Cotton Cellulose by Polycarboxylic Acids. V. Comparison of 1,2,4-Butanetricarboxylic Acid and 1,2,3-Propanetricarboxylic Acid

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ABSTRACT: In recent years extensive efforts have been made to use multifunctional carboxylic acids as formaldehyde-free crosslinking agents for cotton to replace the traditional formaldehyde-based *N*-methylol reagents. In our previous research we found that a polycarboxylic acid esterifies cellulose through the formation of a five-membered cyclic anhydride intermediate by dehydration of two adjacent carboxyl groups. In this research we used Fourier transform IR (FTIR) spectroscopy to study the formation of cyclic anhydride intermediates and crosslinking of cotton by 1,2,4-butanetricarboxylic acid (BTA) and 1,2,3-propanetricarboxylic acid (PCA). BTA and PCA form five-membered cyclic anhydrides in the same temperature range. Both acids form the anhydrides at lower temperatures when a catalyst is present. When an acid molecule is bonded to cotton through an ester linkage, only PCA is able to form a second anhydride intermediate. We found that PCA is a more effective crosslinking agent, and it imparts higher levels of wrinkle resistance to the cotton fabric than BTA. Therefore, the formation of a five-membered cyclic anhydride by a polycarboxylic acid accelerates the esterification of cotton by the acid. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2142–2150, 2001

Key words: cellulose; cotton; esterification; crosslinking; FTIR spectroscopy; polycarboxylic acid; wrinkle-resistant cotton

INTRODUCTION

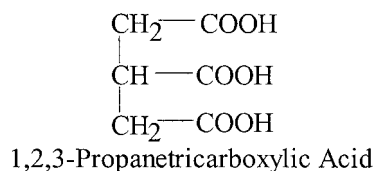
N-Methylol reagents, such as dimethyloldihydroxyethyleneurea (DMDHEU), have long been used as crosslinking agents to produce wrinkle-resistant cotton fabrics in the textile industry. In recent years, however, extensive efforts have been made to use polycarboxylic acids to replace the traditional DMDHEU due to increasing concern with the toxicity of formaldehyde.¹ Polycar-

boxylic acids are among the most promising non-formaldehyde durable press finishes for cotton with sodium hypophosphite (NaH_2PO_2) and monobasic sodium phosphate (NaH_2PO_4) as catalysts.^{2–6} Polycarboxylic acids were also used as crosslinking agents for wood pulp cellulose to improve the wet strength of paper.^{7–13}

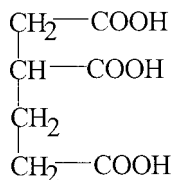
In our previous research we used FTIR spectroscopy to study the mechanism of ester crosslinking of cellulose by polycarboxylic acids and found that a polycarboxylic acid esterifies cellulose through the formation of a five-membered cyclic anhydride intermediate by dehydration of the carboxylic groups.^{14–19} We identified

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(PCA)



1,2,4-Butanetricarboxylic Acid

(BTA)

Scheme 1 The molecular structures of PCA and BTA.

cyclic anhydride intermediates formed on cotton by various multifunctional carboxylic acids.

In this research we used FTIR spectroscopy to investigate the formation of cyclic anhydrides by 1,2,4-butanetricarboxylic acid (BTA) and 1,2,3-propanetricarboxylic acid (PCA), two trifunctional acids with similar molecular structures (Scheme 1).

We compared the effectiveness of BTA and PCA for crosslinking cotton cellulose so that we could further elucidate the relationship between the formation of anhydride intermediates and the esterification of cellulose by a polycarboxylic acid.

EXPERIMENTAL

Materials

The PCA (Aldrich, Milwaukee, WI), BTA (Nippon Kasei Chemical Co.), NaH_2PO_2 (Aeros Organics, Pittsburgh, PA), and NaH_2PO_4 (J. T. Baker, Phillipsburg, NJ) were reagent grade chemicals. The cotton fabric was a sized and bleached plain weave 100% cotton print cloth weighing 100 g/m^2 (Testfabrics style 400).

Cotton Fabric Treatment

A cotton fabric sample was impregnated with a solution containing a polycarboxylic acid with or without a catalyst. The impregnated fabric was passed through a two-roll laboratory padder (Rapid Labortex) with two dips and two nips to reach an average wet pick-up of 100–105%. It was

then dried at 85°C for 3 min and cured at a specified temperature for 2 min in a Mathis curing oven. All the concentrations were presented as weight percentage of the bath (% w/w).

Evaluation of Fabric Performance

The wrinkle recovery angle (WRA) was measured according to AATCC 66-1990 test method. All the fabric samples were tested after one washing cycle without a detergent.

FTIR Spectroscopy

A Nicolet Magna 760 FTIR spectrometer was used to collect the transmission spectra of all the powder samples. The IR spectra of the powders were collected using KBr pellets immediately after the powders of polycarboxylic acids were heated at a specified temperature for 2 min. The IR spectra of the treated cotton fabric samples were diffuse reflectance spectra collected with a Specac diffuse reflectance accessory, and they were presented in absorbance mode ($-\log R/R_o$). The resolution for the IR spectra was 4 cm^{-1} and there were 120 scans for each spectrum. Potassium bromide powder was used as a reference material to produce a background spectrum for the diffuse reflectance spectra. No smoothing functions and baseline correction were used. To measure the intensity of the ester carbonyl band, the treated fabric was first washed in deionized water to remove the unreacted acid and catalyst, then treated with a $0.1M$ NaOH solution at room temperature for 4 min to convert the free carboxylic acid on the fabric to a carboxylate anion so that the ester carbonyl band could be separated from that of the overlapping carboxylic acid carbonyl. The sample was then dried and ground in a Willey mill to form a powder before spectroscopy analysis. The ester carbonyl band intensity in the IR spectra of the treated cotton fabric was normalized against the 1318 cm^{-1} band associated with the C—H bending mode of cellulose.

Thermal Analysis

A Mettler TG50 thermobalance was used for thermal analysis. The samples were heated from room temperature (25°C) to a specified temperature at a rate of $10^\circ\text{C}/\text{min}$ with a continuous nitrogen flow rate of $10 \text{ mL}/\text{min}$. The sample size for the thermogravimetric (TG) experiments was approximately 9 mg.

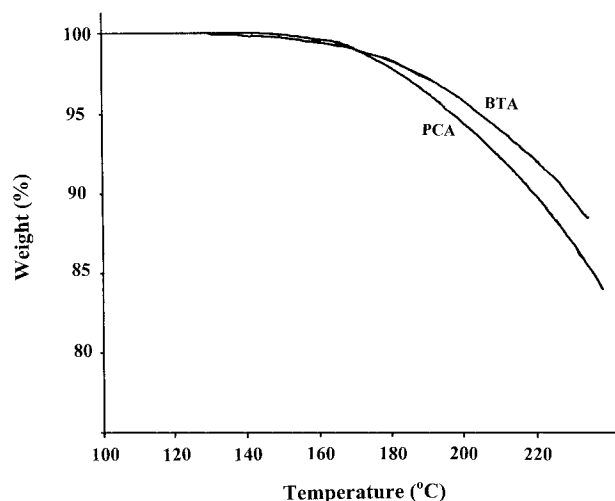


Figure 1 The TG curves of BTA and PCA.

RESULTS AND DISCUSSION

Figure 1 presents the TG analysis (TGA) curves of BTA and PCA. The BTA lost weight when the temperature was increased to 160°C and beyond. The TG data indicated that BTA started to dehydrate above 160°C, and it lost 4.5% of its original weight at 200°C.

The IR spectra of BTA heated at temperatures ranging from 120 to 200°C are shown in Figure 2. The two carbonyl stretching bands at 1736 and 1703 cm^{-1} in the spectrum of BTA below its melting point (122–123°C) were due to the free and hydrogen-bonded carboxylic acid (Fig. 2, spectrum A). The band at 906 cm^{-1} in spectrum A in Figure 2 was associated with the OH \cdots O out of plane deformation of the carboxylic acid dimer. When the temperature was increased to 150°C, the free carboxylic acid carbonyl band significantly reduced its intensity whereas the hydrogen-bonded carboxylic acid carbonyl became predominant in the spectrum (Fig. 2, spectrum B), indicating the conversion of a free carboxylic acid group to a hydrogen-bonded one. A weak band at 1780 cm^{-1} due to a five-membered cyclic anhydride emerged in the spectrum when the temperature reached 160°C (Fig. 2, spectrum C). This showed that BTA started to dehydrate to form a cyclic anhydride at 160°C. The bands at 1853 and 1780 cm^{-1} , which were due to the symmetric and asymmetric stretching of a five-membered cyclic anhydride, respectively, increased their intensity as the temperature was increased to 200°C (Fig. 2, spectra C–E). The three explicit bands at 1087, 1048, and 926 cm^{-1} were attributed to the

C—O—C stretching modes of the five-membered cyclic anhydride.^{20,21}

As shown in the TGA curve of PCA in Figure 1, the melting point of PCA was 162–163°C. The PCA started to lose weight above 160°C, and it lost 5.5% of its original weight at 200°C.

The IR spectra of PCA heated at different temperatures are presented in Figure 3. The two bands at 1854 and 1782 cm^{-1} due to the symmetric and asymmetric stretching modes of a five-membered cyclic anhydride emerged when the temperature reached 160°C (Fig. 3, spectrum C). When the temperature was increased to 180°C and beyond, the two anhydride carbonyl bands became predominant and four explicit bands appeared at 1082, 1004, 959, and 905 cm^{-1} (Fig. 3, spectra D and E). The bands at 1082/1004 and 959/905 cm^{-1} (both as doublets) were attributed to the C—O—C stretching modes of the five-membered cyclic anhydride of PCA.^{20,21} The TGA and FTIR data showed that formation of five-membered cyclic anhydride intermediates by BTA and PCA take place in the same temperature region.

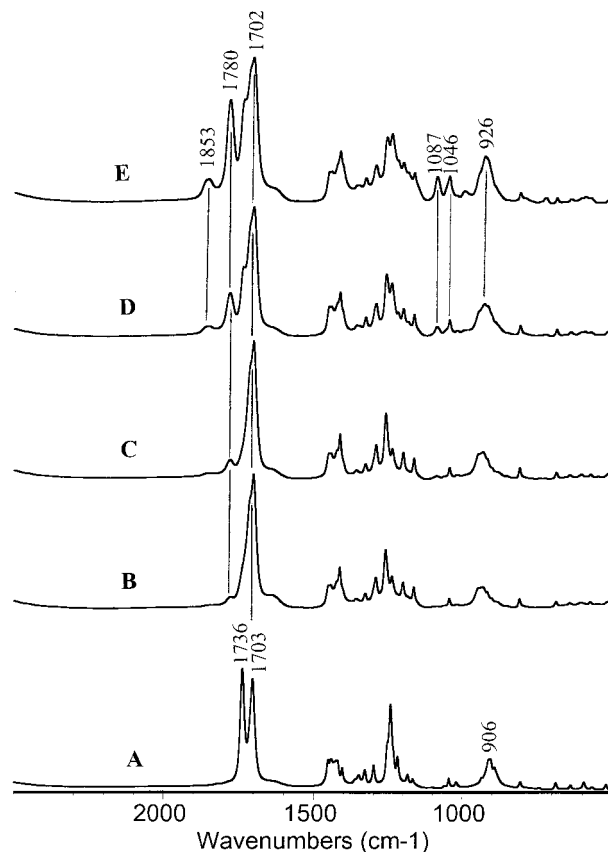


Figure 2 Transmission IR spectra of BTA heated at (A) 120, (B) 150, (C) 160, (D) 180, and (E) 200 °C for 2 min.

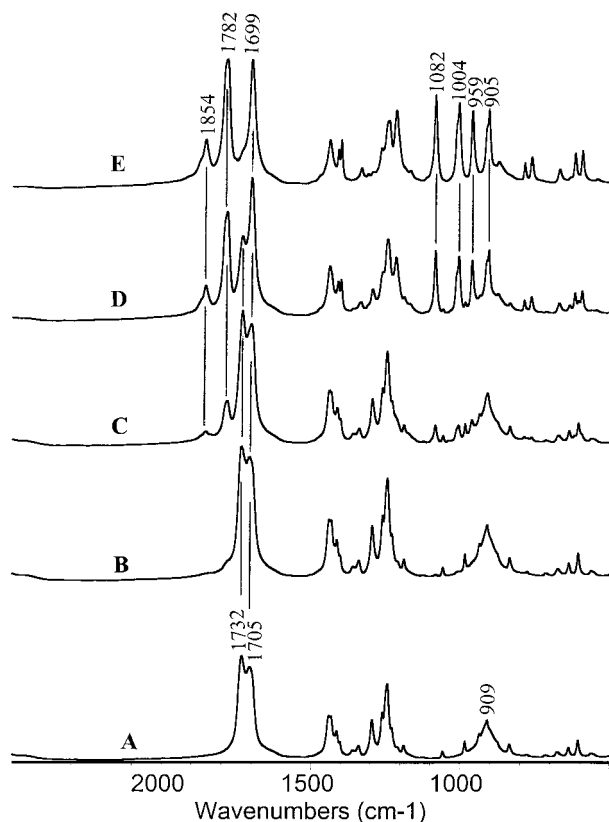


Figure 3 Transmission IR spectra of PCA heated at (A) 140, (B) 150, (C) 160, (D) 180, and (E) 200 °C for 2 min.

Cotton fabric was treated with 6% PCA and 6.5% BTA and then cured at temperatures ranging from 140 to 200 °C for 2 min. The BTA and PCA solutions had equal carboxylic acid molar concentration. The ester carbonyl band intensity of the cotton fabric thus treated is presented as a function of the curing temperature in Figure 4. The amount of ester formed on the treated cotton fabric increased as the curing temperature was increased. The amount of ester formed on the PCA-treated fabric was significantly larger than that on the BTA-treated fabric (Fig. 4), showing that PCA was more effective than BTA for esterifying cotton.

The WRA of the treated cotton fabric is plotted against the curing temperature in Figure 5. As the curing temperature was increased from 150 to 200 °C, the WRA of the PCA-treated fabric increased from 188 to 240° whereas the BTA-treated fabric increased from 192 to 219°. Because the wrinkle resistance of the treated cotton was a direct result of the crosslinking of cellulose molecules, the significantly higher WRA for the PCA-treated fabric (Fig. 5) clearly indicated that PCA was a more effective crosslinking agent for cotton.

PCA and BTA are both trifunctional carboxylic acids with very similar molecular structures. Both acids form a five-membered cyclic anhydride in the same temperature region. The only differ-

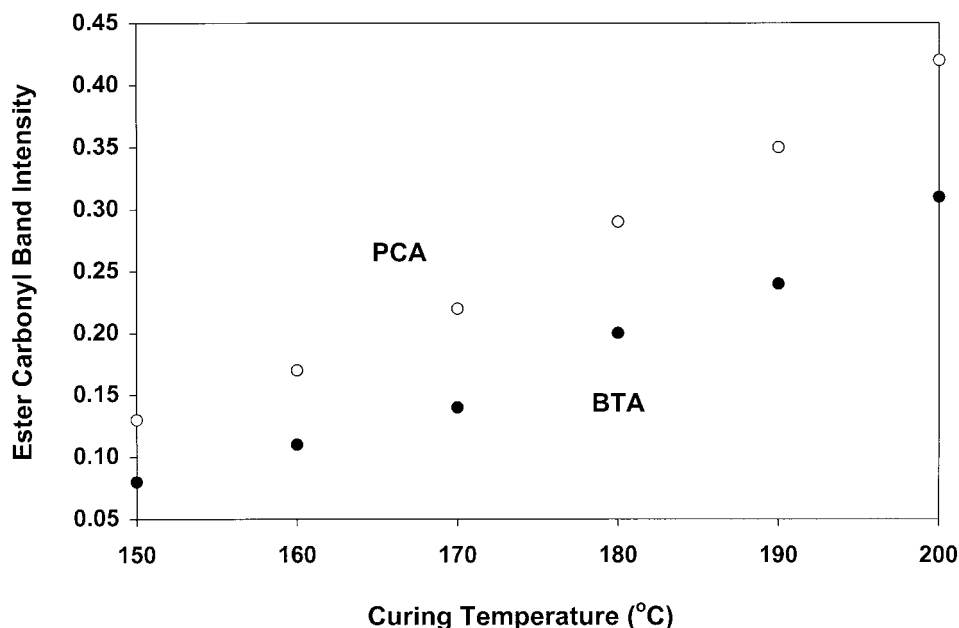


Figure 4 The ester carbonyl band intensity of the cotton fabric treated with 6% PCA and that treated with 6.5% BTA versus the curing temperature.

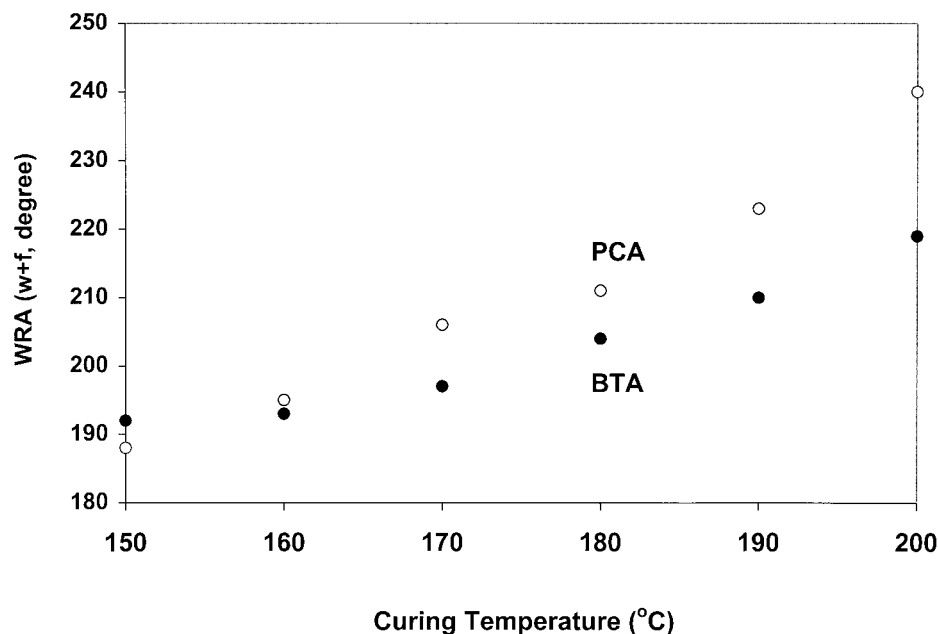
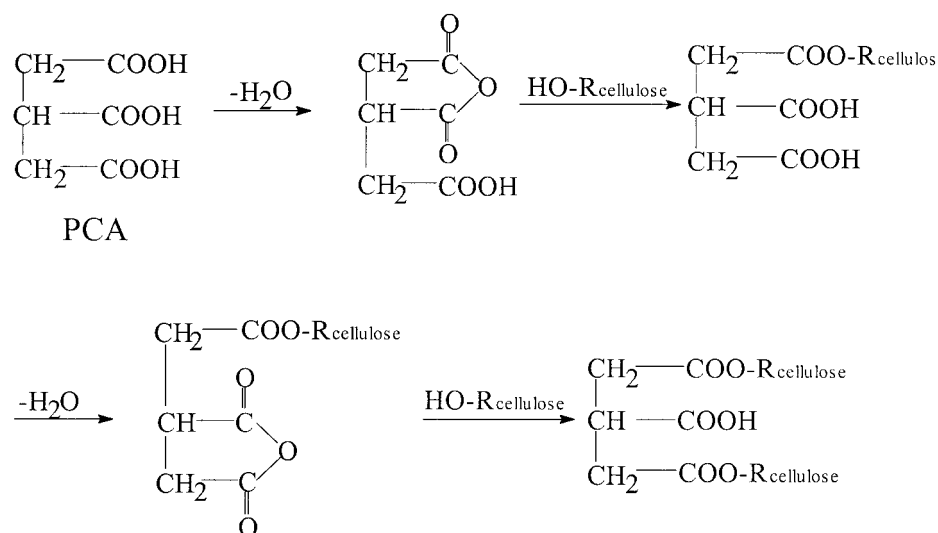


Figure 5 The WRA of the cotton fabric treated with 6% PCA and that treated with 6.5% BTA versus the curing temperature.

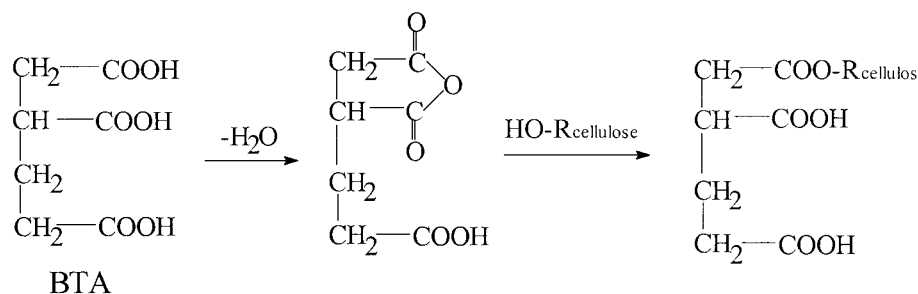
ence is that PCA has all of its three carboxylic acid groups bonded to the adjacent carbons whereas BTA has an extra methylene group in its molecular backbone. When PCA is bonded to cotton cellulose through the esterification of an anhydride intermediate, it is able to form a second five-membered cyclic anhydride intermediate,

which can further esterify cotton to form a crosslink (Scheme 2).

The BTA was not able to form a second five-membered cyclic anhydride once it was bonded to cotton through the esterification of its first anhydride intermediate (Scheme 3). BTA can only crosslink cotton through the reaction of its C-4



Scheme 2 The bonding of PCA to cotton cellulose through the esterification of an anhydride intermediate and the forming of a second five-membered cyclic anhydride intermediate.



Scheme 3 The bonding of BTA to cotton through the esterification of its first anhydride intermediate.

carboxylic acid group or the formation of a six-membered cyclic anhydride intermediate followed by its esterification. We previously found that those polycarboxylic acids having their carboxyl groups bonded to the adjacent carbons of their molecular backbones and capable of forming five-membered cyclic anhydrides are more effective for esterifying cellulose than those polycarboxylic acids having their carboxyl groups bonded to the alternative carbons.¹⁶ The formation of the second ester linkage by a BTA molecule must have a lower reaction rate than that by PCA. As a result, BTA becomes less effective in esterifying and crosslinking cotton than PCA.

To test this hypothesis, we studied the anhydride formed on the cotton fabric treated with PCA. The cotton fabric was treated with 8% PCA and cured at 180°C for 2 min. The IR spectra of the PCA-treated fabric before and after curing are presented in spectra A and B, respectively, in Figure 6. Two explicit bands at 1852 and 1783 cm^{-1} due to the symmetric and asymmetric stretching modes of a five-membered cyclic anhydride appear in the difference spectrum (Fig. 6, spectrum C), thus indicating the formation of an anhydride intermediate by PCA on the cotton fabric under that curing condition. Observe that the band frequencies of the anhydride formed on the PCA-treated cotton fabric (1852/1783) in spectrum C in Figure 6 are very close to those of the PCA anhydride (1854/1782) in spectra D and E in Figure 3.

Cotton fabric was treated with 12% PCA in combination with 4% NaH_2PO_2 as a catalyst, dried at 80°C for 3 min, and cured at 150°C for 2 min. With such a high concentration and a low curing temperature, the overwhelming majority of PCA reacting with cotton was singly bonded PCA molecules.²² The cured fabric was washed to remove the unreacted PCA and NaH_2PO_2 , rinsed with 0.1M HCl to convert any carboxylate anion

bound to the cotton to carboxylic acid, dried, and finally recured at 180°C for 2 min. Two bands at 1843 and 1775 cm^{-1} attributed to the symmetric

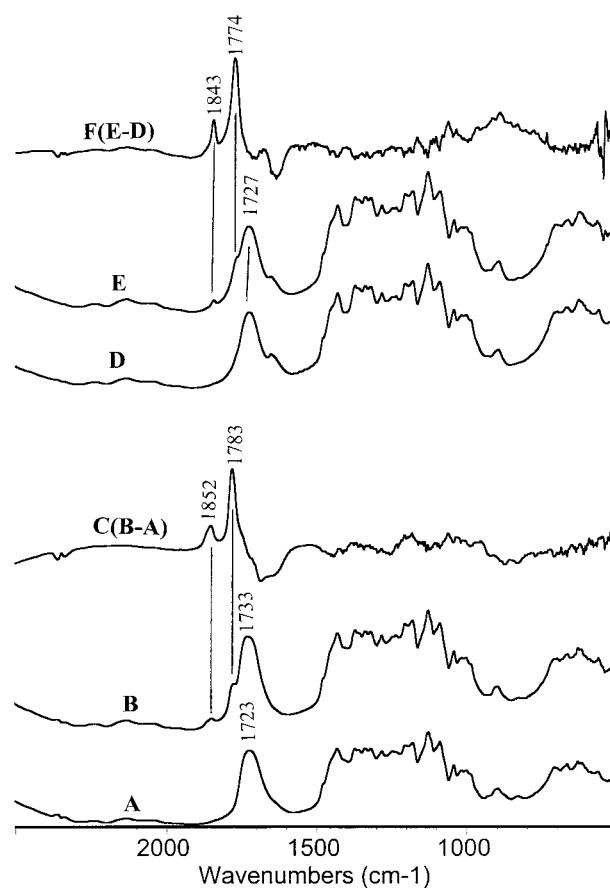


Figure 6 IR spectra of the cotton fabric treated with 8% PCA (spectrum A); the cotton fabric thus treated and cured at 180°C for 2 min (spectrum B); the difference spectrum of B - A (spectrum C); the cotton fabric treated with 12% PCA and 4% NaH_2PO_2 , cured at 150°C for 2 min, and then washed with 0.1M HCl (spectrum D); the cotton fabric thus treated and then cured at 180°C for 2 min (spectrum E); and difference spectrum of E - D (spectrum F).

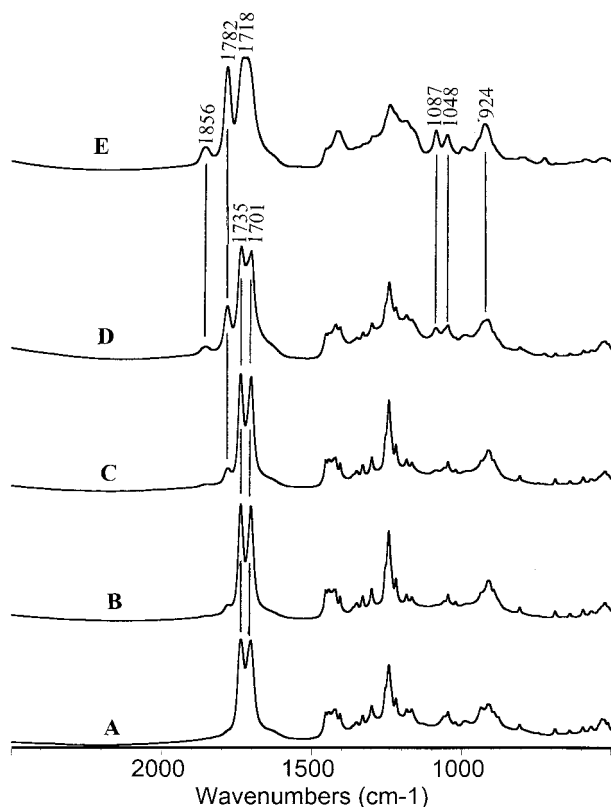


Figure 7 Transmission IR spectra of BTA/NaH₂PO₄ (2:1, w/w) heated at (A) 120, (B) 140, (C) 150, (D) 160, and (E) 180 °C for 2 min.

and asymmetric stretching mode of a five-membered cyclic anhydride emerged in the difference spectrum (Fig. 6, spectrum F). The frequencies of the two anhydride bands (1843/1774) in spectrum F in Figure 6 are approximately 10 cm⁻¹ lower than those of PCA anhydride (1852/1783) in spectrum C in Figure 6 and the shape of the band at 1843 cm⁻¹ in spectrum F in Figure 6 also appears to be sharper, thus indicating that the anhydride formed on the recured cotton was the second cyclic anhydride of PCA as shown in Scheme 2. We applied the same experimental procedure and could not identify the formation of either a five- or six-membered cyclic anhydride on the BTA-treated cotton fabric.

Figure 7 presents the IR spectra of the mixture of BTA and NaH₂PO₄ heated at different temperatures. The two carbonyl bands at 1735 and 1701 cm⁻¹ in spectrum A in Figure 7 are associated with the free and hydrogen-bonded carboxylic acid group. Without the presence of NaH₂PO₄, the free carboxylic acid group was converted to a hydrogen-bonded one when the temperature was increased beyond the BTA melting point (Fig. 2,

spectrum B). In the presence of NaH₂PO₄, however, the band at 1735 cm⁻¹ did not collapse at 150 °C (Fig. 7, spectrum C), thus indicating that NaH₂PO₄ preserved the free carboxylic acid group of BTA above its melting point. The two bands at 1856 and 1782 cm⁻¹ from the symmetric and asymmetric stretching modes of the cyclic anhydride appeared at 150 °C (Fig. 7, spectrum C), which was 10 °C lower than without NaH₂PO₄ (Fig. 2, spectrum C). The intensities of these two bands at 180 °C (Fig. 7, spectrum E) were similar to those at 200 °C without NaH₂PO₄ (Fig. 2, spectrum E). The IR spectra of the mixture of PCA and NaH₂PO₄ heated at different temperatures are presented in Figure 8. The two anhydride bands appeared in the spectrum at 150 °C (Fig. 8, spectrum B). These two bands became predominant in the spectrum at 180 °C (Fig. 8, spectrum E). The IR spectroscopy data showed that NaH₂PO₄ accelerated the formation of the cyclic anhydrides by BTA and PCA.

Cotton fabric was treated with 6.5% BTA/4% NaH₂PO₄ and 6% PCA/4% NaH₂PO₄ and cured at

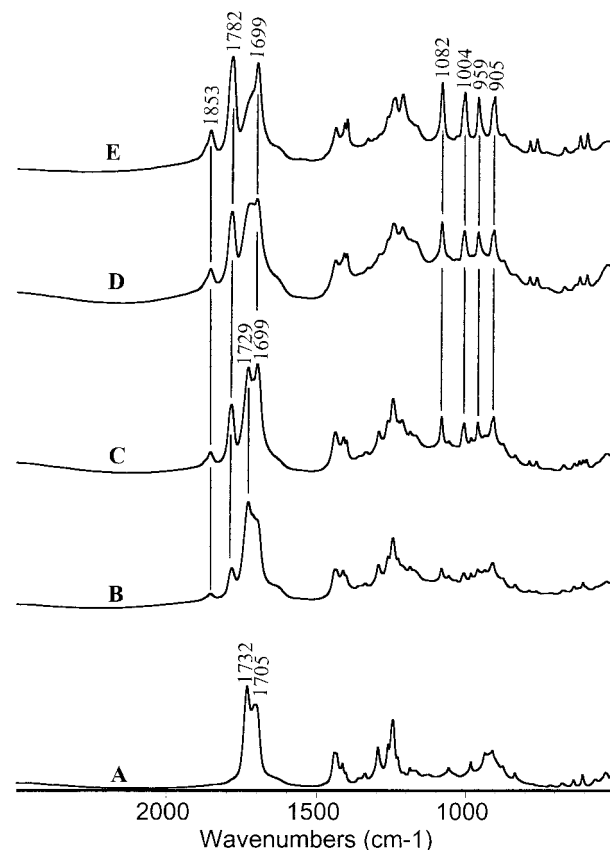


Figure 8 Transmission IR spectra of PCA/NaH₂PO₄ (2:1, w/w) heated at (A) 140, (B) 150, (C) 160, (D) 170, and (E) 180 °C for 2 min.

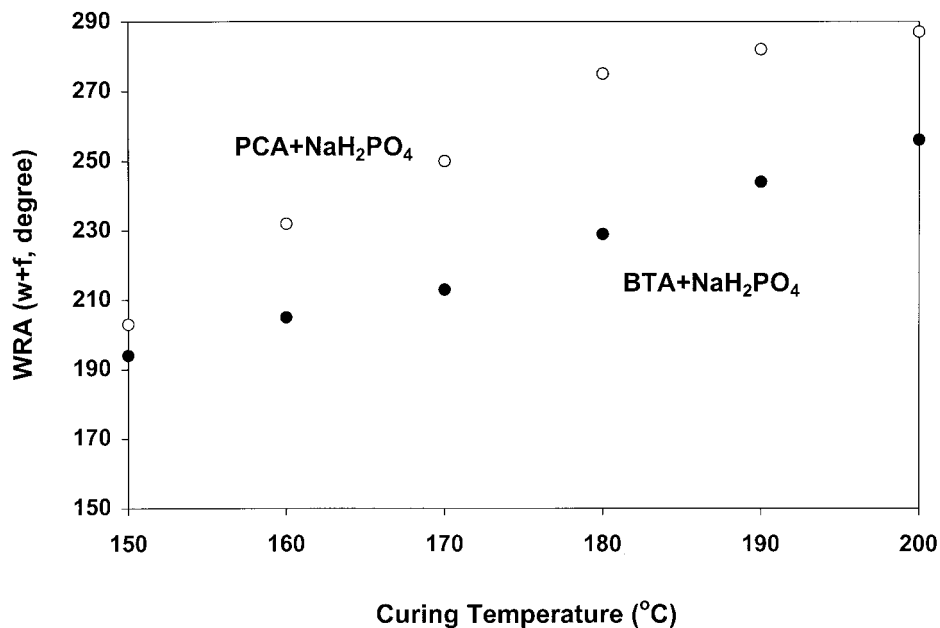


Figure 9 The WRA of the cotton fabric treated with 6% PCA/4% NaH₂PO₄ and that treated with 6.5% BTA/4% NaH₂PO₄ versus the curing temperature.

different temperatures for 2 min. The WRA of the treated cotton fabric at different curing temperatures is presented in Figure 9. The WRA of cotton fabrics treated with BTA or PCA was significantly increased when NaH₂PO₄ was present. The data showed that NaH₂PO₄ accelerated ester cross-

linking of cotton by BTA and PCA, probably through its catalytic effects for the formation of an anhydride intermediate. The WRA of the cotton fabric treated with PCA/NaH₂PO₄ was 30–45° higher than that treated with BTA/NaH₂PO₄ when the temperature was above 160°C. The re-

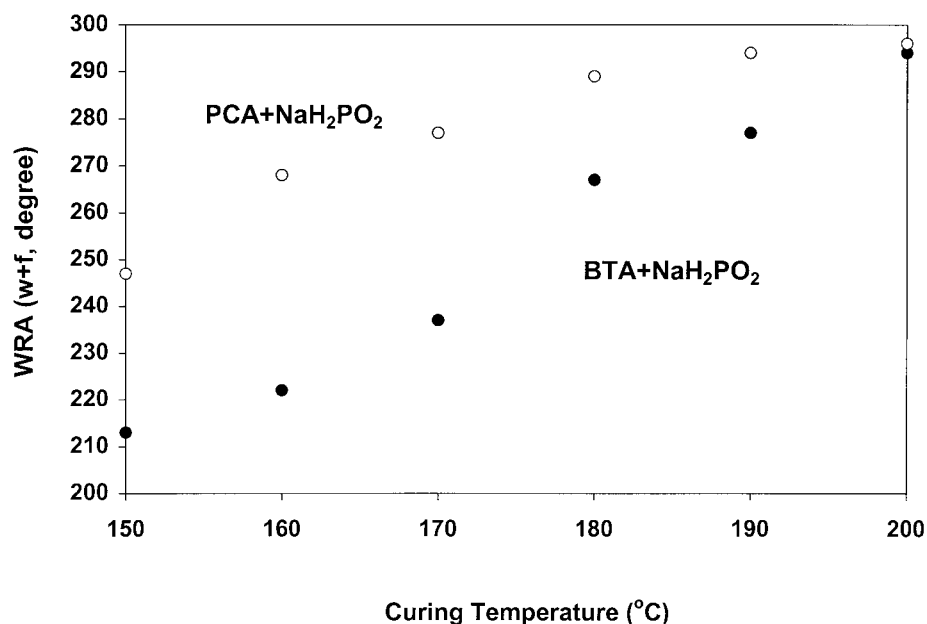


Figure 10 The WRA of the cotton fabric treated with 6% PCA/4% NaH₂PO₂ and that treated with 6.5% BTA/4% NaH₂PO₂ versus the curing temperature.

sults demonstrated that PCA is a far more effective crosslinking agent for cotton cellulose in the presence of NaH_2PO_4 as a catalyst.

Cotton fabric was also treated with 6% PCA/4% NaH_2PO_2 and 6.5% BTA/4% NaH_2PO_2 and cured at different temperatures for 2 min. Figure 10 shows the WRA of the treated cotton fabric as a function of curing temperature. The NaH_2PO_2 is a more effective catalyst than NaH_2PO_4 for esterification of cotton by a polycarboxylic acid. The WRA was further increased for both BTA- and PCA-treated cotton fabrics when NaH_2PO_2 was present. The WRA of the cotton fabric treated with PCA/ NaH_2PO_2 was significantly higher than that treated with BTA/ NaH_2PO_2 when the curing temperature was below 190°C (Fig. 10). At 180°C the fabric treated with PCA/ NaH_2PO_2 was 20° higher than that treated with BTA/ NaH_2PO_2 . The difference in the WRA between those two treated fabrics became smaller as the curing temperature increased, and the WRA of the cotton fabric treated with the two acids was almost identical at 200°C (Fig. 10). This was probably because NaH_2PO_2 catalyzed the esterification of the C-4 carboxylic acid group of BTA at higher temperatures, thus making BTA a more effective crosslinking agent as the curing temperature increased. The catalytic effect of NaH_2PO_2 for esterification of cotton by a polycarboxylic acid will be discussed in a future article.

CONCLUSION

BTA and PCA form five-membered cyclic anhydrides in the same temperature region. When an acid molecule is bonded to cotton through an ester linkage, only PCA can form a second anhydride intermediate. PCA is a more effective crosslinking agent, thus imparting higher levels of wrinkle resistance to the cotton fabric than BTA with or without the presence of a catalyst. These results strongly suggest that formation of a five-mem-

bered cyclic anhydride by a polycarboxylic acid accelerates the esterification of cotton by the acid.

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