# Formation of Five-Membered Cyclic Anhydride Intermediates by Polycarboxylic Acids: Thermal Analysis and Fourier Transform Infrared Spectroscopy

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ABSTRACT: Butanetetracarboxylic acid (BTCA) has been used as the most effective nonformaldehyde crosslinking agent for cotton and wood pulp cellulose. Our previous research has indicated that a polycarboxylic acid esterifies cellulose in two steps: the formation of a five-membered cyclic anhydride intermediate by the dehydration of two adjacent carboxyl groups, and the reaction between cellulose and the anhydride intermediate to form an ester linkage. In this research, we investigated the formation of carboxylic anhydrides by BTCA and other polycarboxylic acids in powder forms, and as finishes applied to cotton fabric using thermal gravimetry, differential scanning calorimetry, and Fourier transform infrared spectroscopy. We found that BTCA and other polycarboxylic acids in powder forms start to form five-membered cyclic carboxylic anhydrides when the temperature reaches the vicinity of their melting points. The formation of carboxylic anhydride is accelerated above the melting points. We also found that BTCA forms anhydrides at lower temperatures when it is applied to cotton fabric as a finish. An increase in temperature increases both the amount of anhydride and the amount of ester formed on the cotton fabric. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2711-2718, 1998

**Key words:** anhydride; butanetetracarboxylic acid; cellulose; cotton; crosslinking; infrared spectroscopy; intermediate; polycarboxylic acids; textile finishing; thermal analysis

### **INTRODUCTION**

Since the identification of formaldehyde as a possible human carcinogen, extensive efforts have been made to find formaldehyde-free durable press finishes to replace the traditional formaldehyde-based *N*-methylol compounds.<sup>1–3</sup> In 1988, Welch<sup>4</sup> reported that tetracarboxylic acids, with 1,2,3,4-butanetetracarboxylic acid (BTCA) in particular, are able to form effective crosslinkages in

Correspondence to: C. Q. Yang (cyang@fsc.uga.edu). Journal of Applied Polymer Science, Vol. 70, 2711-2718 (1998) cotton fabrics when salts of certain phosphoruscontaining acids were used as catalysts.<sup>5</sup> Polycarboxylic acids have been the most promising formaldehyde-free crosslinking agents for cotton cellulose among the various new reagents investigated.<sup>2–6</sup> Polycarboxylic acids were also used as crosslinking agents for wood pulp cellulose to improve wet strength and dimensional stability of paper.<sup>7–9</sup> BTCA has been the most effective crosslinking agent for cotton and wood cellulose.

We studied the mechanism of esterification of cellulose by polycarboxylic acids using Fourier transform infrared (FT-IR) spectroscopy.<sup>10–14</sup> We used two stereoisomers of 1,2-ethylenedicarboxylic acid [i.e., maleic acid (the *cis*-isomer) and fumaric acid (the *trans*-isomer)] to treat cotton fab

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Figure 1 DSC curve of BTCA powder.

ric and found that only the *cis*-isomer is able to esterify cotton cellulose.<sup>10</sup> We identified the fivemembered cyclic anhydride intermediates formed on the cotton fabric treated with various polycarboxylic acids and concluded that a polycarboxylic acid esterifies cellulose through the formation of a cyclic anhydride intermediate.<sup>11–13</sup>

In this research, we used FT-IR spectroscopy in combination with thermal gravimetry (TG) and differential scanning calorimetry (DSC) to study the formation of five-membered cyclic anhydride intermediates by BTCA and other polycarboxylic acids in powder forms and as finishes on cotton fabric.

# **EXPERIMENTAL**

#### FT-IR Spectroscopy, TG, and DSC Instrumentation

A Nicolet 510 FT-IR spectrometer with a Specac "selector" diffuse reflectance accessory was used to collect the infrared spectra. All the spectra of BTCA and other carboxylic acids samples, including the residues after the TG isothermal heating, were collected as transmission spectra using solutions and a ZnSe window. All the spectra of cotton fabric samples were collected with the diffuse reflectance accessory and presented in absorbance mode  $(-\log R/R_0)$ . Potassium bromide powder was used as a reference material to produce a background diffuse reflectance spectrum. Resolution for all the infrared spectra was 4  $cm^{-1}$ . No smoothing function or baseline correction was used. The ester carbonyl band intensities in the infrared spectra of the cotton fabric treated with BTCA was normalized against the 1317  $cm^{-1}$ band associated with the C-H bending mode of cellulose.

A Mettler TG50 thermobalance and Mettler DSC20 differential scanning calorimeter were used for thermal analysis. All the samples were heated from room temperature (25°C) to a specified temperature at a rate of 10°C min<sup>-1</sup> with a continuous nitrogen flow rate of 10 mL min<sup>-1</sup>. The sample size for the DSC and TG experiments was ~ 9 mg.

## **Materials**

BTCA and citric acid were reagent-grade chemicals supplied by Aldrich Chemical Co. (Milwaukee, WI). All-*cis*-1,2,3,4-cyclopentanetetracarboxylic acid was supplied by Pfaltz & Bauer (Stamford, CT). The cotton fabric used was a desized and bleached print cloth (Testfabrics Style 400).

#### **Fabric Treatment**

The cotton fabric was impregnated with a solution containing BTCA. The impregnated fabric was passed through the squeeze rolls of a Cromtax 3-Roll laboratory padder to give a wet pickup of 100-105%, based on the original weight of the fabric. The treated fabric was dried at 85°C for 10 min before TG isothermal heating. The cotton fabric samples after TG isothermal heating were also treated in a 0.1M NaOH solution for 2 min at room temperature to convert the free carboxylic acid to the carboxylate salt, and dried at 85°C for 10 min before FT-IR spectroscopy analysis.

## **RESULTS AND DISCUSSION**

Presented in Figures 1 and 2 are the DSC and TG curves of the BTCA powder, respectively. No heat



**Figure 2** TG and differential thermal gravimetry (DTG) curves of BTCA powder.

absorption and weight loss were observed when the BTCA powder is heated from room temperature to 180°C. Above 180°C, BTCA starts to absorb heat and to lose weight simultaneously, as shown in Figures 1 and 2, respectively. The heat absorption reached its maximum ~ 200°C, whereas the differential TG curve (dM/dT)showed a peak at 196°C, indicating the maximum rate of weight loss at that temperature. The BTCA sample loses ~ 12% of its weight when the temperature reaches 250°C (Fig. 2).

The melting point of BTCA is 196°C. The heat absorption observed in the DSC curve of BTCA in the 180–220°C region (Fig. 1) is obviously not entirely due to melting, because of the weight loss observed in the TG curves in the same temperature region (Fig. 2). To determine the nature of the heat absorption and weight loss in this temperature region, we applied FT-IR spectroscopy to analyze the residue of the BTCA powder after a 2-min TG isothermal heating procedure at different temperatures, ranging from 160 to 250°C.

The infrared spectra of BTCA before heat treatment is presented in Figure 3(A), in which the band at 1710 cm<sup>-1</sup> is due to the stretching mode of the carboxylic acid carbonyl. No changes are observed in the spectrum of the BTCA sample after 2-min isothermal heating at 160°C [Fig. 3(B)]. Two weak shoulders in the 1850–1780 cm<sup>-1</sup> region emerge in the spectrum of the BTCA after the 2-min isothermal heating at 180°C [Fig. 3(C)]. Those observations are consistent with the TG and DSC data discussed previously that little change takes place in the BTCA powder below 180°C.

Two distinct bands at 1853 and 1781 cm<sup>-1</sup> appeared in the spectrum after BTCA was isothermally heated at 190°C [Fig. 3(D)]. Those two bands become more intense, with the isothermal heating at 200°C [Fig. 3(E)]. The two strong bands at 1853 and 1781 cm<sup>-1</sup> observed in Figure 3(D,E) are due to the symmetric and asymmetric stretching modes of a five-membered cyclic anhydride carbonyl.<sup>15</sup> The symmetric stretching band at high frequency is stron-



**Figure 3** Transmission infrared spectra of (A) BTCA, and (B–F) BTCA with 2-min TG isothermal heating at different temperatures (°C): 160, 180, 190, 200, and 250 (from top to bottom).-



**Figure 4** Percentage weight loss of BTCA powder with 2-min TG isothermal heating at different temperatures.

ger than the asymmetric stretching band at low frequency for a noncyclic anhydride carbonyl, whereas the opposite is true for a cyclic anhydride.<sup>15–17</sup> The band at 933 cm<sup>-1</sup> in Figure 3(D,E) is due to the stretching mode of C—O—C bonds of a cyclic anhydride.<sup>16</sup> Therefore, we can conclude that the anhydride detected by FT-IR spectroscopy in Figure 3 is a five-membered cyclic anhydride formed by the dehydration of two adjacent carboxyl groups in a BTCA molecule shown as follows:



The two anhydride carbonyl bands become predominant in the spectrum, whereas the intensity of the 1710 cm<sup>-1</sup> band due to the carboxylic acid carbonyl is drastically reduced when the BTCA sample is isothermally heated at 250°C [Fig. 3(F)], indicating that the majority of the carboxylic acid groups in the BTCA molecules are converted to anhydrides. A band at 966 cm<sup>-1</sup> emerging in the spectrum [Fig. 3(F)] is probably due to the second anhydride group formed in a BTCA molecule.

The percentage weight loss of BTCA with 2-min isothermal heating at different final tem-

peratures is presented in Figure 4. Data show that significant weight loss takes place only when the temperature reached >180°C. BTCA loses  $\sim 13\%$  of its original weight in the TG experiment when the final temperature reaches 250°C, which represents the dehydration of  $\sim 85\%$  of the carboxylic acid groups in BTCA.

Because the band at 1781  $\text{cm}^{-1}$  in Figure 3 is due to the carbonyl of the five-membered cyclic anhydride, whereas the band at  $1710 \text{ cm}^{-1}$  is associated with carboxylic acid carbonyl, we used the carbonyl band intensity ratio (1781/1710  $cm^{-1}$ ) to measure the amount of anhydride formed relative to that of the carboxylic acid group of BTCA. The carbonyl band intensity ratio  $(1781/1710 \text{ cm}^{-1})$  at different isothermal temperatures is shown in Figure 5. It can be seen that the carboxylic acid groups are dehydrated to form anhydrides at temperatures >180°C. One also observes that the increase in the carbonyl band intensity ratio  $(1781/1710 \text{ cm}^{-1})$  in Figure 5 follows the same pattern as the increase in percentage weight loss of BTCA in Figure 4 as the isothermal temperature is raised.

BTCA is also isothermally heated at 190°C for different times. The TG and DTG curves indicate that weight loss is accelerated after isothermal heating starts at 190°C, and it reaches the maximum at 2 min (as shown in Fig. 6). The BTCA sample loses  $\sim 9\%$  of its original weight after isothermal heating for 12 min, which represents  $\sim 60\%$  conversion of carboxylic acid to anhydride in the BTCA molecules.

Presented in Figure 7 are the infrared spectra of the BTCA powder isothermally heated at 190°C



**Figure 5** Carbonyl band intensity ratio  $(1781/1710 \text{ cm}^{-1})$  in the spectra of BTCA powder with 2-min isothermal heating at different temperatures.



Figure 6 TG and DTG curves of BTCA powder with isothermal heating at 190°C.

for different times. The bands at 1853, 1781, and  $933 \text{ cm}^{-1}$  due to the cyclic anhydride appear in the spectrum after 1 min of isothermal heating, and their intensities increase as the isothermal heating time increases (Fig. 7). After 3-min heating, the intensity of the 1781 cm<sup>-1</sup> band surpasses that of the band at 1710 cm<sup>-1</sup> due to carboxylic acid carbonyl. One distinct band at 966 cm<sup>-1</sup> emerges in the spectrum after 8-min heating [Fig. 7(F)].

The percentage weight loss and the carbonyl band intensity ratio  $(1781/1710 \text{ cm}^{-1})$  of BTCA at 190°C with different isothermal heating times are shown in Figures 8 and 9, respectively. One observes that the percentage weight loss and the carbonyl band intensity ratio increase with the same pattern as the isothermal heating temperature increases (Figures 8 and 9). All the TG and



**Figure 7** (A–E) Transmission infrared spectra of BTCA at 190°C with different TG isothermal heating times (min): 0, 1, 2, 3, 4, 8, and 12 (from top to bottom).

FT-IR spectroscopy data presented herein indicate that the weight loss observed in the TG experiments was a result of the formation of anhydride by the dehydration of the carboxylic acid groups in BTCA.

We studied the formation of five-membered cyclic anhydride from 1,2,3,4-cyclopentanetetracarboxylic acid (CPTA) and citric acid (CA) using



**Figure 8** Percentage weight loss of BTCA powder at 190°C with different TG isothermal heating times.



Figure 9 Carbonyl band intensity ratio (1781/1710  $cm^{-1}$ ) in the spectra of BTCA powder at 190°C with different TG isothermal heating times.

DSC, TG, and FT-IR spectroscopy (Table I). CPTA starts to absorb heat and to lose weight when the temperature reaches 180°C. The two anhydride carbonyl bands at 1784 and 1863  $cm^{-1}$  emerge in the infrared spectrum after 2-min isothermal heating at 180°C (Table I). Data also show that CA forms anhydride at 160°C, which is above its melting point (155°C).

We also investigated the formation of the cyclic anhydride by polycarboxylic acids on cotton fabric using TG and FT-IR spectroscopy. The cotton fabric treated with 12% BTCA is first heated with isothermal heating at 100°C for 10 min to remove the adsorbed  $H_2O$ , then continuously heated in the thermal balance at a  $10^{\circ}$ C min<sup>-1</sup> rate from 100 to 190°C. The TG curve of the treated cotton fabric (100–190°C) is presented in Figure 11. Unlike the TG data of BTCA powder that showed little weight loss under 180°C (Fig. 2), the BTCAtreated cotton fabric gradually loses  $\sim 1.6\%$  of its weight in the entire temperature region from 100 to 190°C (Fig. 10).

The cotton fabric treated with 6% BTCA is exposed to 2-min isothermal heating at different final temperatures that range from 130 to 190°C. The infrared spectra of the BTCA-treated cotton fabric after 2-min isothermal heating are shown in Figure 11. One observes that the two bands at 1783 and 1852  $\text{cm}^{-1}$  due to the five-membered cyclic anhydride carbonyl appear in the spectrum when the BTCA-treated fabric is isothermally heated at 130°C (Fig. 11), indicating the formation of the anhydride on the fabric at that temperature. The intensity of the anhydride carbonyl Table I The Name, Structure, Melting Point, Temperature of Anhydride Formation, and the Anhydride Carbonyl Band Frequency

of the Poly	ycarboxylic Acids Investigated with TG and	d FT-IR Spectro	scopy		
Name	Structure	Melting Point (°C)	Temperature of Anhydride Formation (°C) <sup>a</sup>	Anhydride Carbonyl Band Frequency (cm <sup>-1</sup> , powder)	Anhydride Carbonyl Band Frequency (cm <sup>-1</sup> , on cotton)
	HOOC COOH				
BTCA	H00С—СН <sub>2</sub> —СН—СН—СН <sub>2</sub> —СООН	196	≥190	1781/1853	1783/1852
CPTA	HOOC	195	≥180	1784/1863	1783/1861
	COOH				
CA	H00C-CH <sub>2</sub> -CH-CH <sub>2</sub> -C00H	153	≥160	1788/1869	Weak and overlapped
	HO				
<sup>a</sup> Temper	ature at which the formation of anhydride was observe	ed during TG experi	ments described in this art	icle.	



**Figure 10** TG curve of the cotton fabric treated with 12% BTCA.

band (ratioed against the  $1730 \text{ cm}^{-1}$  band) increases as the isothermal heating temperature increases (Fig. 12). Both the TG data and the FT-IR spectra presented herein indicated that BTCA forms anhydride at temperatures much lower than its melting point when it is applied to the cotton fabric as a finish.

When BTCA is applied to the cotton fabric as a solution, its molecules are absorbed by the fiber and its carboxylic acid groups hydrogen-bond (Hbond) with the cellulosic hydroxyl groups. When



Figure 11 Diffuse reflectance infrared spectra of BTCA-treated cotton fabric with 2-min isothermal heating at different temperatures (°C): before isothermal heating, 130, 140, 150, 160, 180, and 190 (from bottom to top).



**Figure 12** Anhydride carbonyl band intensity and the ester carbonyl band intensity in the spectra of BTCA-treated cotton fabric with 2-min isothermal heating at different temperatures.

BTCA is in a powder form, its carboxylic acid groups form H-bonds with each other. The Hbonds between carboxylic acid groups is stronger than that between a carboxylic acid group and a cellulosic hydroxyl group, and therefore requires higher temperatures to be dissociated to form an anhydride. This may explain the different temperatures at which BTCA forms cyclic anhydride as a powder and as a finish on cotton fabric.

When esterification takes place on a cotton fabric sample treated with a polycarboxylic acid, the carbonyl on the fabric exist in two forms: the ester and the free carboxylic acid. The ester and the carboxyl carbonyl bands overlap  $\sim 1730~{\rm cm^{-1}}$  in an infrared spectra.<sup>18–20</sup> The ester carbonyl band can be separated from the overlapping carboxyl band by treating the fabric sample in a dilute NaOH solution to convert the free carboxylic acid to a carboxylate anion.<sup>18-20</sup> The BTCA-treated cotton fabric after 2-min isothermal heating at different final temperatures were rinsed with 0.1*M* NaOH. The ester carbonyl band intensity of the fabric samples thus treated is shown in Figure 12. One observes that both the anhydride carbonyl band and the ester carbonyl band increase their intensities when the isothermal heating temperature increases from 130 to 200°C (Fig. 12). Thus, data support the reaction mechanism that a polycarboxylic acid esterifies cotton cellulose through the formation of a five-member cyclic anhydride intermediate by the dehydration of its two carboxyl groups.

# **CONCLUSIONS**

BTCA and other polycarboxylic acids in powder forms start to form five-member cyclic carboxylic anhydrides when the temperature reaches the vicinity of their melting points. The formation of carboxylic anhydride is accelerated above the melting points. When BTCA is applied to cotton fabric as a finishing agent, it forms anhydride as a reactive intermediate on the fabric at lower temperatures. The combination of TG, DSC, and FT-IR spectroscopy residue analysis proves to be a useful technique for the study of esterification and crosslinking of cellulose by polycarboxylic acids.

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#### REFERENCES

- C. D. McKerron and L. A. Rich, Chem. Week, 140, 15 (1981).
- 2. C. M. Welch, Rev. Prog. Color., 22, 32 (1992).
- 3. D. Laemermann, Melliand Textilberichte, 3, 274 (1992).
- 4. C. M. Welch, Textile Res. J., 58, 480 (1988).
- C. M. Welch and B. A. Kottes Andrews, *Textile Chem. Color.*, **21**, 13 (1989).

- B. A. Kottes Andrews, *Textile Chem. Color.*, 22, 65 (1990).
- Y. J. Zhou, P. Luner, P. Caluwe, and B. Tekin, Products of Papermaking, 2, 1045 (1993).
- 8. D. F. Caulifield, TAPPI J., 77, 205 (1994).
- D. Horie and C. J. Biermann, *TAPPI J.*, 77, 135 (1994).
- 10. C. Q. Yang, Textile Res. J., 61, 433 (1991).
- C. Q. Yang, J. Polym. Sci. Polym. Chem. Ed., 31, 1187 (1993).
- C. Q. Yang and X. Wang, J. Polym. Sci. Polym. Chem. Ed., 34, 1573 (1996).
- C. Q. Yang and X. Wang, *Textile Res. J.*, 66, 595 (1996).
- C. Q. Yang and X. Wang, J. Polym. Sci. Polym. Chem. Ed., 35, 557 (1997).
- L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 3rd ed., Chapman and Hall, London, 1975, p. 144.
- N. B. Clothup, L. H. Daly, and S. E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Academic Press, San Diego, CA, 1990, p. 310, Chap. 9.
- G. Socrates, Infrared Characteristic Group Frequencies, Wiley, Chichester, England, 1994, p. 93.
- 18. C. Q. Yang, Textile Res. J., 61, 298 (1991).
- C. Q. Yang and B. A. K. Andrews, J. Appl. Polym. Sci., 43, 1609 (1991).
- C. Q. Yang and G. Bakshi, *Textile Res. J.*, 66, 377 (1996).