

Durable Press Finishing of Cotton with Polycarboxylic Acids. II. Ester Crosslinking of Cotton with Dithiosuccinic Acid Derivative of *s*-Triazine

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Received 16 August 1996; accepted 26 March 1997

ABSTRACT: The preparation of an alternative polycarboxylic acid to replace the most promising but expensive crosslinking reagent butanetetracarboxylic acid (BTCA) was reported in Part I.¹ Part II studies the efficiency of the crosslinking of cotton with the dithiosuccinic acid derivative of *s*-triazine (HDTST). Diffuse Reflectance infrared (DR FTIR) spectroscopy in combination with wrinkle recovery angle measurements (WRA) were used to analyse the efficiency of cotton cellulose crosslinking. Energy Dispersive X-ray analysis (EDX) of the polycarboxylic acid-finished cotton fabric was performed to study sulphur distribution. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 171–177, 1997

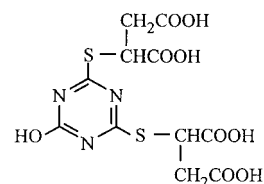
Key words: polycarboxylic acid; thiosuccinyl-*s*-triazine derivative; formaldehyde-free durable press finishing; diffuse reflectance infrared spectroscopy; energy dispersive X-ray analysis

INTRODUCTION

Crosslinking of cotton cellulose with polycarboxylic acids has provided an alternative route to formaldehyde-free durable press cotton fabric.² Polycarboxylic acids containing more than three carboxylic groups react with hydroxyl groups in cotton cellulose and crosslink cotton through stable ester bonds. Esterification can occur at elevated temperature with heat alone or can be accelerated by the presence of salts of weak acids.^{2–4} Welch⁵ and Andrews⁶ proved that the most effective

catalyst for durable press finishing with polycarboxylic acids such as BTCA was sodium hypophosphite (SHPI).

Part I of this series¹ described the preparation of 2-hydroxy-4,6-di-thiosuccinyl-*s*-triazine (HDTST); its constitution is shown below:



HDTST

It was expected that this polycarboxylic acid would esterify cotton in the following manner:

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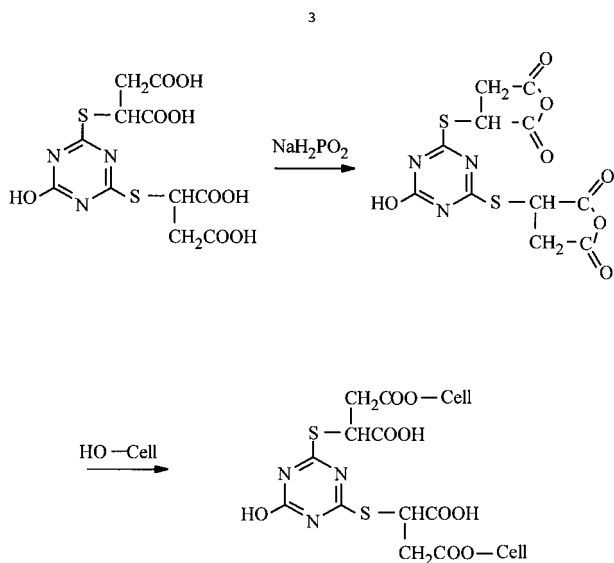
Contract grant sponsor: Commission of the European Communities (Program TEMPUS).

Contract grant sponsor: Slovenian Ministry of Science and Technology.

Journal of Applied Polymer Science, Vol. 66, 171–177 (1997)

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CCC 0021-8995/97/010171-07



This study investigates the optimum conditions for effective crosslinking of cotton fabric with HDTST in the presence of SHPI. To analyze the efficiency of crosslinking, Diffuse Reflectance infrared (DR FTIR) spectroscopy analysis of treated cotton fabrics was used, in combination with WRA measurements. Yang^{7,8} developed a method that permits the characterization of ester crosslinks in cotton fabrics by infrared spectroscopy. In polycarboxylic acid-finished cotton fabrics the carbonyls retained exist in three forms: ester, carboxylic acid, and carboxylate anion. In the case of cotton cellulose esterified with a polycarboxylic acid containing three or more carboxylic groups, all three forms of carbonyls could be present. In infrared spectra the band due to an ester carbonyl group appears around 1735 to 1715 cm^{-1} , and the band due to a carboxylic acid carbonyl group appears in the same region. Treatment of polycarboxylic acid-finished cotton fabric with a sodium hydrox-

Table I Concentration of HDTST and SHPI in the Finishing Baths and Temperature of Curing

Treatment*	% HDTST	% SHPI	Curing Temperature (°C)
T1	4.0	6.5	190
T2	8.0	6.5	190
T3	8.0	3.2	190
T4	8.0	9.8	190
T5	8.0	13.0	190
T6	8.0	6.5	180
T7	8.0	6.5	160

* pH of the finishing baths were 2.7 (without adjustment).

ide solution converts the acid to the carboxylate anion. The overlapping of bands for carboxylic acid groups and ester groups is thus avoided.

For semiquantitative measurements,⁷ the ester carbonyl band intensities (the 1724 cm^{-1} band in infrared spectra of HDTST/SHPI finished and NaOH solution-treated cotton fabrics) were normalized against the 1313 cm^{-1} band intensity. The 1724 cm^{-1} band intensity is a measure of the total quantity of ester groups present in the finished cotton fabrics, which includes both the ester groups between the cotton cellulose and singly bonded acid molecules and the HDTST ester groups, which crosslink the cellulose molecules. Therefore, the 1724 cm^{-1} band intensity alone can not be used as a measure of the degree of HDTST ester crosslinking in the cotton fabrics. The carbonyl band intensity ratio (1724/1585 cm^{-1}) can be used as another parameter to compare the different degrees of ester crosslinking in fabrics. A molecule of HDTST can form an intermolecular crosslinkage only when it forms more than one ester group with cellulose molecules. The more carboxylic groups esterified per HDTST molecule, the more intermolecular ester crosslinkages are

Table II The Influence of HDTST and SHPI Concentration in the Finishing Bath on the Ester Carbonyl Band Intensity, on the Carbonyl Band Intensity Ratio and WRA Values of HDTST/SHPI Finished Cotton Fabrics

Treatment	% HDTST	% SHPI	Ester Carbonyl Band Intensity	Carbonyl Band Intensity Ratio	WRA (°)
T1	4.0	6.5	0.61	0.49	217
T2	8.0	6.5	0.80	0.55	224
T3	8.0	3.2	0.80	0.53	222
T4	8.0	9.8	0.70	0.50	221
T5	8.0	13.0	0.65	0.50	208

Table III The Ester Carbonyl Band Intensity, Carbonyl Band Intensity Ratio and WRA Values for Cotton Fabrics Cured at Different Temperatures

Treatment	Curing Temperature (°)	Ester Carbonyl Band Intensity	Carbonyl Band Intensity Ratio	WRA (°)
T2	190	0.80	0.55	224
T6	180	0.64	0.52	220
T7	160	0.58	0.51	214

formed between cellulose molecules for the same quantity of the ester groups in the cotton fabrics. With such crosslinking, fewer carboxylate anions or carboxylic acid groups remain free.⁸

HDTST crosslinked cotton fabrics contains two atoms of sulphur per crosslinked molecule. This permits the use of EDX to collect elemental information of crosslinked cotton fabrics.

EXPERIMENTAL

Fabric Treatment

Desized, scoured, bleached, and mercerized cotton fabric was immersed in the aqueous treating solu-

tion containing different concentrations of polycarboxylic acids HDTST and curing catalyst—sodium hypophosphite (SHPI). Table I shows the concentration of HDTST and SHPI in the finishing baths.

The fabric was padded to give a wet pickup of 95 to 105%; wet pickup is defined as the percentage increase in fabric weight on impregnation. The fabric was suspended in a forced draught oven and predried at 90°C for 5 min. After curing in the Werner Matthis thermofixation equipment for 3 min (temperature of curing is shown in Table I), the cloth was rinsed in running water for 10 min. After drying, the cloth was pressed flat.

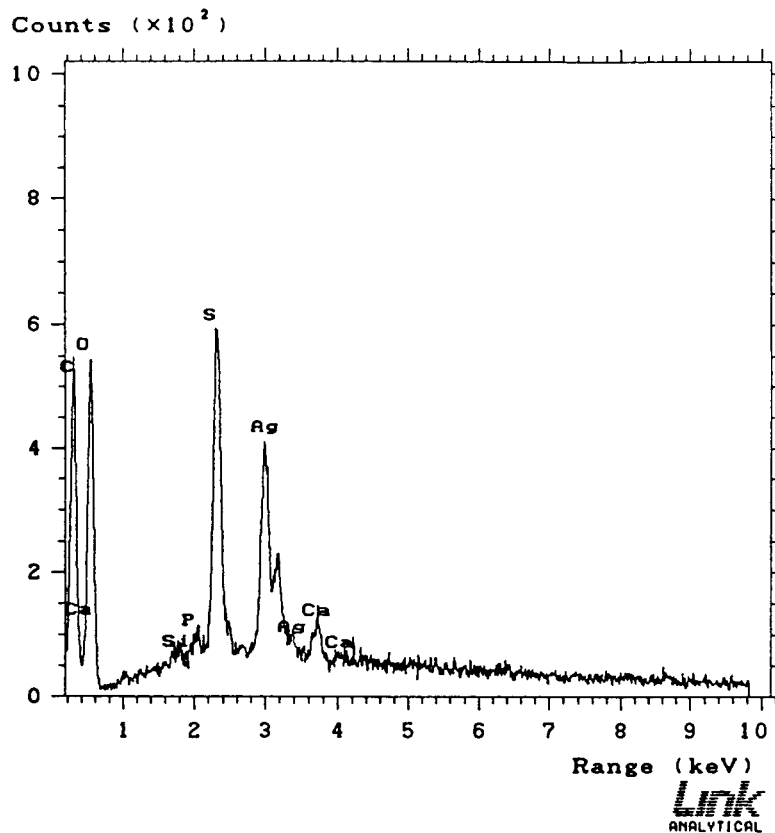


Figure 1 Concentration of C, O, and S in HDTST finished cotton fabric.

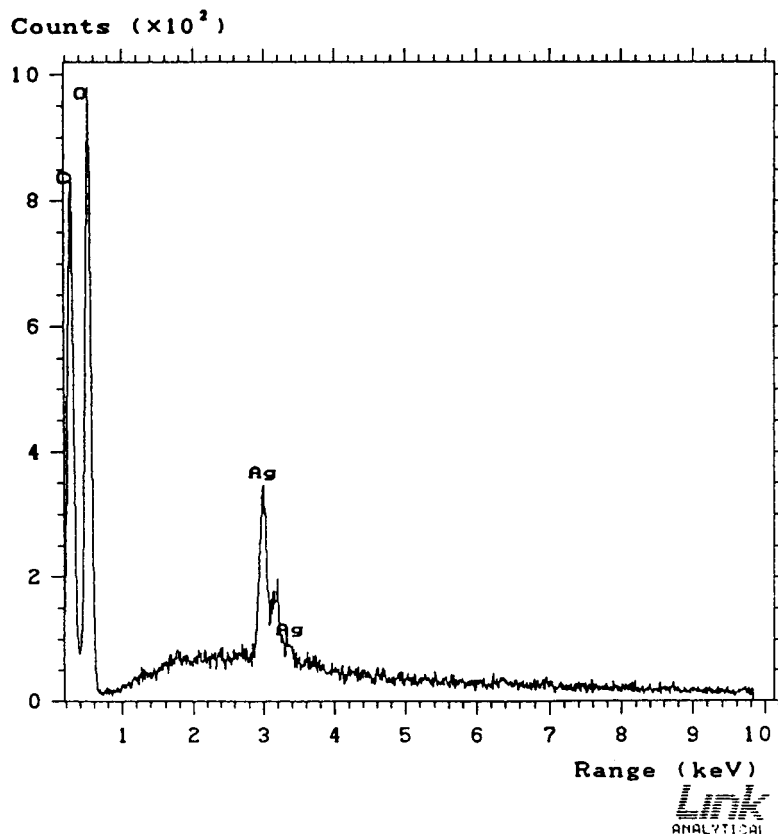


Figure 2 EDX spectrum of blank-treated cotton fabric.

Further Treatment of HDTST/SHPI-Finished Cotton Fabric

To study the esterification of cotton fabrics by infrared spectroscopy, further treatment of the finished cotton was necessary. After curing and washing, the cotton fabrics were treated in 0.1M NaOH solution for 2 min at room temperature and dried again.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DR FTIR) Analysis of Treated Fabric

IR analysis of cotton fabric was carried out with the Perkin-Elmer 1740 Fourier Transform Spectrophotometer using the Perkin-Elmer diffuse reflectance accessory. The spectrophotometer was coupled to a PC-486 with a Perkin-Elmer Data Manager system for data handling. The resolution of all spectra was 4 cm^{-1} and 100 scans were collected.

The cotton samples were cut into circles to fit the sample cup filled with potassium bromide. The height of the sample cup was adjusted to ob-

tain spectra with the best resolution. Potassium bromide powder was used as a reference material to produce a background spectrum.

Wrinkle Recovery Angle (WRA) Measurements

The standard test method for wrinkle recovery of woven textile fabrics using the vertical strip apparatus has been used to measure the conditioned wrinkle recovery angle (ASTM D1295-67).⁹

Energy Dispersive X-Ray Analysis (EDX) of Treated Fabrics

To collect elemental information from the finished cotton fabrics, energy dispersive X-ray analysis (EDX) was used. Analyzed fabrics were coated with a 300 Å thick layer of conductor using the Bio-Rad diode sputter coater. The usual conductor for these purposes is gold. However, in some EDX spectra, gold would overlap with analyzed sulphur, so silver was used instead.

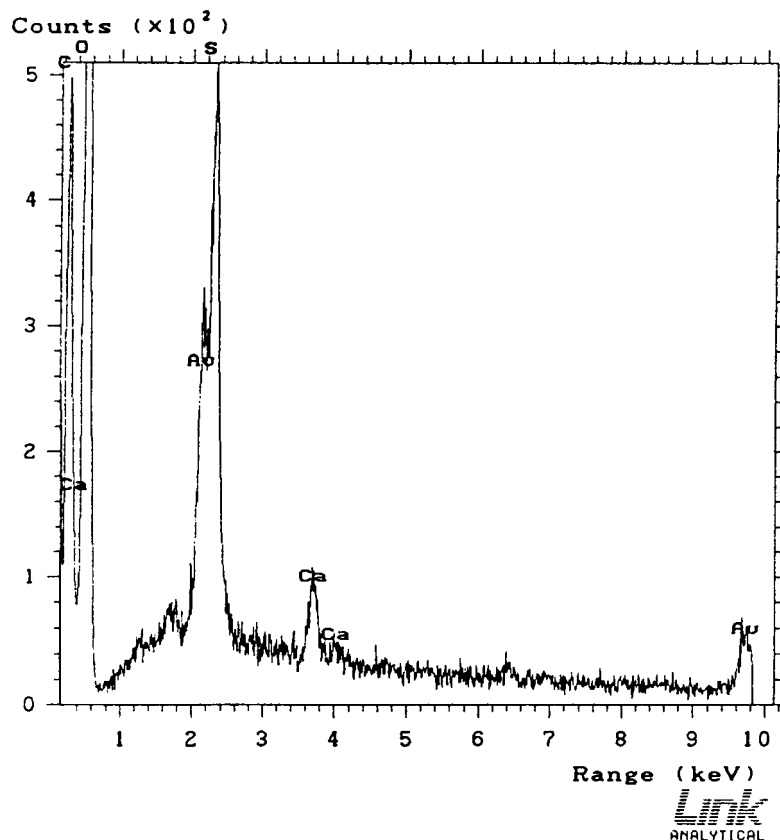


Figure 3 The concentrations of C, O, and S from an EDX cross-section microanalysis of a cotton fiber finished with 8% HDTST and 6% SHPI.

RESULTS AND DISCUSSION

DR FTIR Analysis and WRA Measurements of HDTST/SHPI Finished Cotton Fabrics

The influence of HDTST and SHPI concentration in the finishing baths and curing temperature was studied by DR FTIR spectroscopy and WRA measurements.

The ester carbonyl band intensity and the carbonyl band intensity ratio data obtained from the infrared spectra of cotton fabrics finished with two different HDTST and four different SHPI concentrations are collected in Table II.

Data in Table II show that with increasing HDTST concentration the effectiveness of crosslinking increases. This is shown by higher values for the carbonyl band intensity, the carbonyl band intensity ratio, and the WRA for cotton fabrics finished in baths containing 8% HDTST (T2) compared to data obtained for cotton fabrics finished in baths containing 4% of HDTST (T1).

HDTST/SHPI finishing baths of different SHPI concentrations (Table I) were prepared. The effi-

ciency of esterification was analyzed by DR FTIR spectroscopy and WRA measurements. The influence of SHPI concentration on the total quantity of ester groups present in the fiber and their effectiveness in crosslinking cotton cellulose is summarized in Table II. Data from DR FTIR spectroscopy are supported by WRA measurements (Table II) and show that the optimum SHPI concentration is around 6%. Increasing the SHPI concentration in the finishing bath from 3.2 to 6.5% increases the efficiency of crosslinking, but increasing SHPI concentration above 6.5% decreases the quantity of ester linkages and the crosslinking effectiveness of the bonded HDTST molecules. A possible explanation is that excessive concentrations of small highly mobile molecules of SHPI hinder the absorption of bulky HDTST molecules by the fiber.

To study the effect of curing temperature on the efficiency of crosslinking, DR FTIR spectra of cotton fabrics padded with HDTST/SHPI and cured at different temperatures were obtained. Data showing the ester carbonyl band intensity,

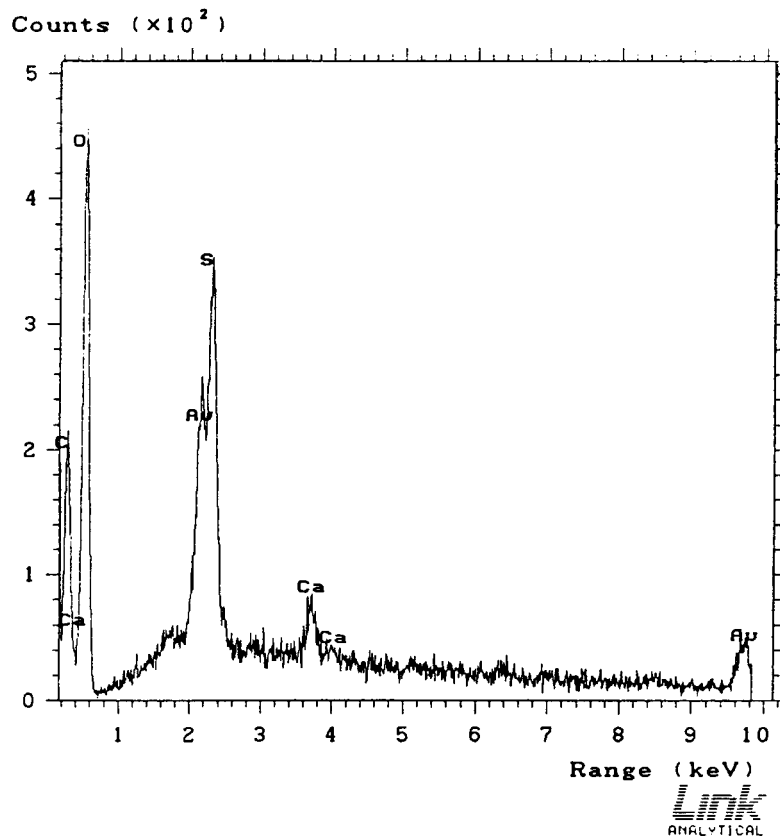


Figure 4 The concentrations of C, O, and S from an EDX cross-section microanalysis of a cotton fiber finished with 8% HDTST and 13% SHPI.

carbonyl band intensity ratio, and WRA values are collected in Table III. Data for the ester carbonyl band intensity and WRA values show that with increasing curing temperature the efficiency of crosslinking increases. The optimum curing temperature is 190°; however, at this temperature significant yellowing occurs.

EDX Analysis of HDTST/SHPI Finished Cotton Fabrics

To collect elemental information from HDTST finished cotton fabrics (8% HDTST, 6.5% SHPI, pH = 2.7, curing temperature 190°C and time of curing 3 min), energy dispersive X-ray analysis (EDX) was performed. First, the sample of HDTST finished cotton fabrics was analyzed in a flat position: The concentrations of C, O and S in the HDTST finished cotton fabric are shown in the EDX spectrum in Figure 1.

A sharp band appears for S at 2.2 keV (600 counts) and concentrations of C and O are different (550 and 545 counts) when compared to the EDX

spectra obtained for blank-treated cotton fabrics (850 and 960 counts) as shown in Figure 2. These EDX results give evidence that when the esterification occurs, sulphur is still present in the fiber.

When the influence of SHPI concentration on the efficiency of esterification was studied by DR FTIR spectroscopy, it was noted that the penetration of the polycarboxylic acid into the fiber is an important factor to obtain efficient crosslinking. Previously it was postulated that the excessive concentration of small highly mobile molecules of SHPI hinder the absorption of bulky HDTST molecules by the fiber. To study the penetration of HDTST into the fiber, EDX was carried out.

The EDX cross-section microanalysis of cotton fibers finished with 8% HDTST and 6% SHPI (Fig. 3) shows higher carbon, oxygen, and sulphur concentration than the EDX cross-section microanalysis of cotton fabric finished with the same HDTST concentration and 13% SHPI (Fig. 4). It is reasonable to conclude that with higher SHPI concentrations the amount of crosslinked HDTST on the fiber is lower.

CONCLUSIONS

The HDTST/SHPI crosslinking system was studied in detail by DR FTIR spectroscopy and WRA measurements. The best performance was obtained from cotton fabrics finished with 8.0% HDTST, 3.2–6.5% SHPI, at pH 2.7, curing temperature of 180–190°, and curing time of 3 min. The HDTST/SHPI crosslinking system was further analyzed by EDX microscopy. This method gave evidence that bound sulphur was present in the fiber after curing. EDX results support the data obtained from infrared spectroscopy and WRA measurements that show that penetration of crosslinker and catalyst into the fiber is hindered if the concentration of the latter is high.

Many thanks to the Commission of the European Communities (Program TEMPUS) and to the Slovenian

Ministry of Science and Technology for the necessary financial support.

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