Introduction

Cotton combines high wearing comfort with excellent dyeability and high alkali-resistance, thus becoming the most valuable and the most commonly used fiber for clothing. In spite of fast growth of synthetic fibers since the Second World War, cotton textiles still dominate the apparel market today. Cotton's inherent low resiliency and the necessity for pressing cotton garments following each laundering cycle constitute its major disadvantage. This shortcoming can be overcome by crosslinking cotton cellulose using chemical reagents with multiple functional groups reactive to cellulosic hydroxyl groups.

The most important traditional durable press (DP) finishing agent for cotton is \( N,N' \)-dimethylol-4, 5-dihydroxyethyleneurea (DMDHEU), which is a reaction product of urea, formaldehyde and glyoxal (1). DMDHEU and its modified "low-formaldehyde" versions are the most commonly used DP finishing agents by the industry. Those crosslinking systems are formaldehyde-based— formaldehyde vapor is continually released from DP finished cotton fabrics and garments during finishing, processing, storage, and consumer uses. In 1979, a study of the effect of formaldehyde on rats by the Chemical Industry Institute of Toxicology indicated that cancer occurred on rats as a result of exposure to 15 ppm formaldehyde (2). Scientists of the US federal government concluded that formaldehyde induced both gene mutations and chromosomal aberrations in rats under laboratory conditions in 1980 (3).
The impact of formaldehyde on human health has gained contentious increasing worldwide attention. In 1987, the US Environmental Protection Agency classified formaldehyde as “a suspected carcinogen” (4). More recently, a working group of the World Health Organization (WHO) International Agency for Research on Cancer concluded that formaldehyde was “carcinogenic to humans” based on sufficient evidence in nasopharyngeal cancer in humans and nasal cancer in animals in 2004 (5). The risk of formaldehyde was upgraded from "Group 2A" (probably carcinogenic to human) to "Group 1" (carcinogenic to human) (6). Studies conducted on textile industrial workers by the National Cancer Institute and National Institute of Occupational Safety and Health have shown that formaldehyde exposure caused lymphohematopoietic malignancies, particularly myeloid leukemia (7-11). Other studies also demonstrated that exposure to formaldehyde increased the risk of lung cancer (12-13).

The common approach by the industry to reduce formaldehyde concentration on DP finished cotton fabrics was to incorporate diethylene glycol in DMDHEU systems to form glycolated products, usually called ultra-low formaldehyde DMDHEU (14). However, such “low formaldehyde” versions of DMDHEU still relied solely on formaldehyde for its crosslinking reactions. It reduced free formaldehyde levels on the treated cotton fabrics, but the total formaldehyde concentration on treated cotton fabrics was not changed. The etherified DMDHEU gradually transformed to free formaldehyde and caused damage to human health and the environmental chronically at the same magnitude as traditional DMDHEU. Moreover, incorporating ethylene glycol in a DMDHEU system not only significantly increased the cost, but also reduced the effectiveness of DMDHEU as a crosslinking agent for cotton. The "low formaldehyde" DMDHEU approach was clearly not a route to solve the formaldehyde problem facing the textile industry.
Since the late 1980s, extensive efforts have been made to find alternative formaldehyde-free crosslinking agents for cotton (15). 1,3-dimethyl-4,5-dihydroxy-2-imidazolidinone (DMDHI), the addition product of glyoxal to N, N'-dimethyl urea, was an important glyoxyl derivative used as a nonformaldehyde DP finishing agent with commercial availability. But DMDHI only achieved moderate success. DMDHI had a reactivity lower than that of DMDHEU as a crosslinking agent for cotton (16). It was more expensive and it also required a much higher quantity for DP finishing processes. Zinc fluoroborate was identified as the most effective catalyst in the original patent (17), but the catalyst was not considered to be environment friendly and it also had disposal problems (15). We also found that DMDHI's applications as a DP finishing agent also had other disadvantages, such as an unpleasant odor during the finishing process.

Among the nonformaldehyde crosslinking agents reported in the literature since the 1980s, multifunctional carboxylic acids have been the most promising nonformaldehyde crosslinking agents when sodium hypophosphite (NaH₂PO₂) was used as the catalyst (15). 1,2,3,4-butanetetracarboxylic acid (BTCA) was the most effective one. Only those polycarboxylic acids with relative small molecular sizes, such as BTCA, have greater accessibility to the internal amorphous regions of cotton and therefore are more effective crosslinking agents for cotton (18). The cotton fabrics and garments finished by such polycarboxylic acids demonstrated high levels of wrinkle-resistance, smooth drying properties, good laundering durability, and fabric strength retention much greater than that of cotton treated with DMDHEU. The overall performance of polycarboxylic acids as a class of DP finishing agents was modestly better than the low formaldehyde DMDHEU, but
polycarboxylic acids the required a curing temperature higher than that used for DMDHEU. The cost of the BTCA system, including both the acid and catalyst, is also higher.

Since 1989, we studied and developed the following alternative cotton DP finishing systems based on maleic acid (MA), a much more cost-effective polycarboxylic acid:

(1) The synergistic combination of citric acid (CA) and poly(maleic acid) (PMA) (18-22);

(2) The oligomers of MA (23-28);

(3) The combination of MA and sodium hypophosphite (NaH₂PO₂) (29-31).

We investigated the esterification mechanism of polycarboxylic acids on cotton (32-40), the catalysis mechanism of hypophosphite for esterification of polycarboxylic acids on cotton (41-43), and the mechanism of cotton fabric strength loss caused by the use of polycarboxylic acids as DP agents (44-49). We also developed acid-base titration and infrared spectroscopy as quantitative and semiquantitative analytical methods for cotton fabrics treated with various polycarboxylic acids (50-55).

Since cotton is one of the most flammable textile fibers, flame retardant finishing of cotton was another most important area in textile functional finishing. N-methylol dimethylphospho-propionamide, exemplified by Pyrovatex CP and Pyrovatex CP New (Huntsman), and tetrakis(hydroxymethyl)phosphonium chloride, commercially known as THPC, were developed in the 1970s (56,57). They are still the major durable flame retardants for cotton.
used by the industry today. Those flame retarding systems contain formaldehyde. Recently, we developed a nonformaldehyde flame retardant finishing system for a Nomex/cotton blend based on a hydroxyl-functional organophosphorus oligomer (HFPO) as the flame retardant and BTCA as the crosslinking agent between cotton and the flame retardant (58).

We also discovered that polycarboxylic acids were effective in reducing peak heat release rate (PHRR) of cotton. Treating cotton fleece with different polycarboxylic acids was successful in reducing the fabric flammability of the cotton fleece from "Class 3" to "Class 1" (16 CFR 1610) (59-63). Polycarboxylic acids have not been used as flame retardants for cotton. Our research showed that a polycarboxylic acid, once esterified on cotton, was able to function as a condensed phase flame retardant for cotton by reducing PHRR and increasing char formation of cotton cellulose.

**Mechanism of Cotton Ester Crosslinking and Its Catalysis**

BTCA was first disclosed, together with NaH2PO2 (catalyst), as an effective DP finishing system for cotton in 1988 (64). Welch proposed the formation an anhydride intermediate before the esterification of a polycarboxylic acid with cotton cellulose, but provided no experimental data (64). We applied FT-IR spectroscopy as an analytical tool in the investigation of the reaction mechanism because the carboxylic acid, ester, and anhydride—the reactant, product, and intermediate of the reaction respectively—all had strong and characteristic carbonyl bands in their IR spectra. We first examined the ester formed on the cotton treated with the two isomers of 1,2-ethylenedicarboxylic acids, i.e., MA (the cis-isomer) and fumaric acid (FA, the trans-isomer), as shown in Scheme 1. We observed that MA esterified cotton whereas FA did not. Since MA was a cis-isomer, it was able to form a
5-membered cyclic anhydride, whereas FA was a trans-isomer and therefore was not able to form a cyclic anhydride. Thus, the data supported the proposed reaction mechanism (32). In addition, we observed that the amount of ester on the BTCA-treated cotton increased as the curing temperature increased, whereas that on the MA-treated cotton remained constant. Because BTCA had four carboxylic acid groups, it was able to form the 2nd and 3rd anhydride, therefore, it formed more esters per each molecule as the curing temperature increased. On the other hand, MA could only form one cyclic anhydride and was unable to form the 2nd one when it had one ester-linkage with cotton. Thus, the MA-treated cotton always had 1:1 ester/carboxy molar ratio regardless of curing temperature. Therefore, all the data supported the mechanism of the formation of a cyclic anhydride as the reactive intermediate for esterification of a polycarboxylic acid on cotton (32).

![MA and FA](image)

Scheme 1. MA and FA

We further applied the technique of FT-IR spectra subtraction to identify the 5-membered cyclic anhydride on the cotton treated by different polycarboxylic acids (34). Shown in Figs. 1A and 1B are the FT-IR spectra of the BTCA-treated cotton before and after curing at 160°C for 2 min, respectively. The two distinct peaks at 1852 and 1782 cm\(^{-1}\) appearing in the difference spectra (Fig. 1C) were associated with the symmetric and asymmetric stretching modes, respectively, of a 5-membered cyclic anhydride of BTCA. The two bands at 1722 and
1580 cm⁻¹ in Fig. 1D are due to the stretching of ester and free carboxylate carbonyl, respectively. We observed that the intensity of the ester carbonyl band at 1722 cm⁻¹ increased as that of the anhydride carbonyl band at 1778 cm⁻¹ was increased in Fig. 2. We also identified the formation of cyclic anhydrides on cotton and measured the ester carbonyl band intensity of 16 multifunctional carboxylic acids, including MA, itaconic acid, succinic acid (SUA), 1,2,3-propanetricarboxylic acid (PCA), CA, 1,2,3,4-cyclobutanetetracarboxylic acid, all-cis-1,2,3,4-pentantetrahydroxycarboxylic acid, all-cis-1,2,3,4,5,6-cyclohexacarboxylic acid, PMA, and a number of other unsaturated and aromatic polycarboxylic acids (34). All the experimental data provided further evidence to prove the mechanism of cotton esterification by a polycarboxylic acid having two of its carboxylic acid groups bound to the adjacent carbons as shown in Scheme 2.

![Graph showing IR spectra and absorbance](image)

Fig. 1. The IR spectra of the cotton fabric treated with 6% BTCA: (a) dried; (b) dried and cured at 160°C for 2 min; (c) b-a; (d) dried, cured and rinsed with 0.1 M NaOH.

Fig. 2. The absorbance of the anhydride and ester carbonyl bands in the spectra of the cotton fabric treated with 6% BTCA and cured at 160°C for 2 min.
Scheme 2. Mechanism of esterification of cotton by a polycarboxylic acid through the formation of the 5-membered cyclic anhydride intermediate

We were able to use the difference FT-IR spectroscopy to identify different anhydrides formed on the cotton treated with PCA as shown in Scheme 3 (36). When PCA was applied to cotton, it first formed the first 5-membered cyclic anhydride intermediate, which esterified cotton. Since PCA had its three carboxylic acid groups bound to the adjacent carbons of the molecular backbone, it was able to form a 2nd anhydride intermediate as shown in Scheme 4. To prove this hypothesis, we identified the two anhydrides formed on the cotton fabric treated with PCA under two different conditions. Cotton fabric was treated with 8% PCA and cured at 180°C for 2 min. The infrared spectra of the PCA-treated fabric before and after curing are presented in Figs. 3A and 3B respectively. Two explicit bands at 1852 and 1783 cm⁻¹ due to the symmetric and asymmetric
stretching modes of the 5-membered cyclic anhydride appeared in the difference spectrum (Fig. 3C), thus indicating the formation of an anhydride intermediate by PCA on the cotton fabric under that curing condition. We also observed that the band frequencies of the anhydride formed on the PCA-treated cotton fabric (1852/1783) in Fig. 3C were very close to those of BTCA anhydride (1852/1782) in Fig. 1C. This was because PCA and BTCA had similar molecular structures.

\[
\begin{align*}
\text{PCA} & \quad \text{BTA} \\
\text{CH}_2\text{COOH} & \quad \text{CH}_2\text{COOH} \\
\text{CH}\text{COOH} & \quad \text{CH}\text{COOH} \\
\text{CH}_2\text{COOH} & \quad \text{CH}_2\text{COOH}
\end{align*}
\]

Scheme 3. PCA and BTA

\[
\begin{align*}
\text{CH}_2\text{COOH} & \quad \text{CH}_2\text{COOH} \\
\text{CH}\text{COOH} & \quad \text{CH}\text{COOH} \\
\text{CH}_2\text{COOH} & \quad \text{CH}_2\text{COOH}
\end{align*}
\]

Scheme 4. Formation of different anhydride intermediates by PCA

Cotton fabric was treated with 12% PCA and 4% NaH2PO2 and then cured at 150°C for 2 min. With such a high concentration and a relatively low curing temperature, the overwhelming majority of
PCA reacting with cotton was expected to be singly bonded to cotton. The cured fabric was then washed to remove the unreacted PCA, rinsed with 0.1 M HCl to convert any carboxylate anion to carboxylic acid, dried, and finally re-cured at 180°C for 2 min. Two bands at 1843 and 1775 cm⁻¹ due to the symmetric and asymmetric stretching mode of a 5-membered cyclic anhydride emerged in the difference spectrum (Fig. 3F). The frequencies of the two anhydride bands (1843/1774) in Fig. 3F were 9 cm⁻¹ lower than those of the first anhydride (1852/1783) in Fig. 3C and the width of the anhydride carbonyl symmetric stretching band at 1843 cm⁻¹ was obviously narrower in Fig. 3F than the same peak in Fig. 3C. Thus, the data proved that the anhydride formed on the re-cured cotton was a different cyclic anhydride of PCA as shown in Scheme 4. The 2nd cyclic anhydride of PCA had more ring strain, thus shifting the carbonyl band to lower frequencies.

We also studied the crosslinking of cotton by PCA and also by 1,2,4-butane tricarboxylic acid (BTA, Scheme 3). Cotton fabric was treated with the combination of 6% PCA and 4% NaH₂PO₂ and with the combination of 6.5% BTA and 4% NaH₂PO₂, and cured at different temperatures for 2 min. Fig. 4 shows that the wrinkle recovery angle (WRA) of the treated cotton fabric as a function of the curing temperature. The WRA of the cotton fabric treated with PCA/NaH₂PO₂ was significantly higher than that treated with BTA/NaH₂PO₂ when the curing temperature was below 190°C. At 180°C, the fabric treated with PCA/NaH₂PO₂ had a WRA 20° higher than that treated with BTA/NaH₂PO₂. The difference in WRA between those two treated fabric samples became smaller as the curing temperature increased to 190°C. The WRA of the cotton fabric treated with the two acids was almost identical at 200°C (Fig. 4).

BTA was not able to form a second 5-membered cyclic anhydride once bound to cotton through the esterification of its first anhydride intermediate (Scheme 4). BTA can only crosslink cotton through formation of a 6-membered cyclic anhydride intermediate followed by its first esterification reaction. Previously, we found that those polymeric carboxylic acids having their
carboxyl groups bonded to the adjacent carbons of their molecular backbones and capable of forming 5-membered cyclic anhydrides, such as poly(maleic acid), are more effective for esterifying cellulose than those polycarboxylic acids having their carboxyl groups bonded to the alternative carbons, such as poly(acrylic acid) (39). The formation of the second ester linkage by a BTA molecule through formation of 6-membered anhydride intermediate must have a slower reaction rate and therefore it required a significantly higher curing temperature. Thus, the data presented confirmed the esterification mechanism of polycarboxylic acid on cotton discussed previously.

Fig. 3. FT-IR spectra of (A) the cotton treated with 8% PCA; (B) the cotton treated and cured at 180°C for 2 min; (C) B-A; (D) the cotton treated with 12% PCA, cured at 150°C for 2 min and rinsed with 0.1M HCl; (E) the cotton thus treated and re-cured at 180°C for 2 min; (F) E-D.

Fig. 4. The WRA of the cotton fabric treated with 6% PCA/4% NaH2PO3 and then treated with 6.5% BTA/4% NaH2PO2 versus curing temperature.
All our findings on the cotton esterification mechanism by polycarboxylic acids are summarized as follows.

(1) Five-membered cyclic anhydrides form on cotton treated with polycarboxylic acids under curing conditions. The cyclic anhydrides function as reactive intermediates for the esterification of cotton cellulose. As an effective crosslinking agent for cellulose, a polycarboxylic acid must have three or more carboxyl groups bound to the adjacent carbons in its backbone.

(2) Formation of six-membered cyclic anhydride intermediates requires higher temperature, and six-membered cyclic anhydride intermediates are less reactive for esterifying cotton. A polycarboxylic acid forming a six-membered cyclic anhydride intermediate is a less effective crosslinker for cotton than those forming a 5-membered cyclic anhydride intermediate.

(3) Those carboxylic acids capable of forming both 5-membered and 6-membered cyclic anhydrides form only 5-membered anhydride intermediates on cotton under curing conditions.

(4) The reactivity of polycarboxylic acids for esterifying and crosslinking cotton is affected by their molecular sizes; smaller crosslinkers are more effective than larger ones.

(5) Polycarboxylic acids in a crystalline state start to form five-membered cyclic anhydrides when the temperature reaches its melting point. The intermolecular hydrogen-bonding between the carboxylic acid groups prevents formation of anhydride at low temperatures. Polycarboxylic acids in an amorphous state form anhydride at lower temperatures. When the acids are applied onto cotton, the temperature of forming the anhydrides is drastically reduced.
We also studied the effects of NaH$_2$PO$_2$ as a catalyst on the formation of 5-membered cyclic anhydride intermediates by polycarboxylic acids (41-43). We found the following:

(1) NaH$_2$PO$_2$ weakens the hydrogen bonding between carboxylic acid groups of BTCA, and only the carboxylic acid groups with weakened hydrogen bond are able to become free carboxylic acid groups, thus forming a cyclic anhydride.

(2) NaH$_2$PO$_2$ accelerates the formation of a 5-membered cyclic anhydride intermediate.

(3) In the presence of NaH$_2$PO$_2$, polycarboxylic acids form cyclic anhydride intermediates at significantly lowered temperatures and form more esters with cotton.

**New Nonformaldehyde DP Finishing Systems for Cotton**

BTCA was the most effective nonformaldehyde crosslinking agent among various polycarboxylic acids, but it was not only more expensive but also commercially unavailable until more recently. Our research on the development of nonformaldehyde DP finishing agents has focused on the use of MA, an abundant and the most cost effective bifunctional acid, as a crosslinking agent for cotton.

**Synergistic Combination of Citric Acid (CA) and Poly(maleic acid) (PMA)**

The application of CA as a DP finishing agent for cotton was first reported in 1991 (65). In our research. We discovered that CA was a significantly less effective crosslinker for cotton than PCA (18). PCA (Scheme 3) and CA have the same molecular structure except that PCA has no $\alpha$-hydroxyl group whereas CA does. The $\alpha$-hydroxyl group of CA interfered with its esterification with cotton cellulose (18). CA also demonstrated lower laundering resistance than
BTCA (18). Because CA had only three carboxylic acid groups, it could only form maximum of two ester linkages on cotton. CA showed yellowing effects on cotton due to dehydration by elimination of the a-hydroxyl under a curing condition (28).

We evaluated formation of the 5-membered anhydride intermediates of two polymeric acids, i.e., a homopolymer and a terpolymer of MA (PMA and TPMA, respectively), and found that PMA and TPMA had higher anhydride carbonyl band intensities and lower ester carbonyl band intensities than that treated with BTCA, indicating that the polymeric polycarboxylic acids were less effective crosslinking agents because of the low mobility of their anhydride intermediates to access cellulosic hydroxyl. Furthermore, the experimental evidence proved that CA esterified PMA and TPMA by reacting with the anhydride intermediates of PMA and TPMA on cotton, thus eliminating CA’s a-hydroxyl group and transforming CA from a tri-functional acid into an acid with much higher functionality as shown in Scheme 5 (18).

![Scheme 5. Reaction of PMA and CA](image)

Based on those findings, we developed a nonformaldehyde DP finishing system for cotton using the combination of CA and TPMA with an approximate 4.5:1.0 carboxy mole ratio (18-22). The cotton fabric was treated with CA/TPMA/NaH₂PO₄ solutions having the same total carboxyl mole concentration but different CA-to-TPMA ratios, and cured at 185°C for 3 min. The wrinkle recovery angle (WRA) and tensile strength retention of the cotton fabric thus treated is shown in Table 1. Before laundering, the WRA was 236° and 254° when the fabric was treated with TMPA or CA alone, respectively. It increased to 264° when 15% of CA was replaced by
After 10 laundering cycles, the fabric treated with 85/15 CA/TPMA also had significantly higher WRA (252°) than that treated with 100% CA or with 100% TPMA (237° and 231°, respectively). Thus, the data clearly demonstrated a synergistic effect for crosslinking cotton when TPMA was added to CA. This synergistic effect was contributed by two factors: increasing CA’s reactivity for esterifying cotton by eliminating CA’s α-hydroxyl group and increasing the functionality of CA from tri-functional to a much higher functionality.

We compared the performance of the CA/TPMA system with the low formaldehyde DMDHEU system used in industry (19). The two fabric samples treated with CA/TPMA had significantly higher WRA and DP rating than the fabrics treated with DMDHEU, and they also had significantly higher tensile strength retention (Table 2). The CA/TPMA-treated cotton and that treated with DMDHEU also had similar tearing strength retention. The cotton fabric treated with CA/TPMA maintained a significantly higher WRA and DP rating that that treated with DMDHEU throughout the 30 launderings as shown in Table 3. We also applied the CA/TPMA system as the DP finishing agent to a cotton garment, and the data collected using garment finishing confirmed the superior performance of the CA/TPMA system (21). The disadvantages of the CA/TPMA system included (1) slightly lower whiteness for white cotton fabric due to use of CA and (2) higher curing temperature. The TPMA/CA system was patented in a number of countries in North America, Asia, Africa, and Europe (22).
Table 1. The WRA and tensile strength of the cotton fabric treated with CA/TPMA with different CA-to-TPMA ratios and cured at 185ºC for 3 min

<table>
<thead>
<tr>
<th>Carboxy Mole Ratio</th>
<th>Total -COOH (m)</th>
<th>WRA (º, w+f) before wash</th>
<th>WRA (º, w+f) after 10 washes</th>
<th>Tensile Strength Retention (% F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPMA</td>
<td>CA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>0.1980</td>
<td>236</td>
<td>237</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>0.1985</td>
<td>251</td>
<td>249</td>
</tr>
<tr>
<td>30</td>
<td>70</td>
<td>0.1956</td>
<td>262</td>
<td>249</td>
</tr>
<tr>
<td>25</td>
<td>75</td>
<td>0.1983</td>
<td>257</td>
<td>251</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>0.1964</td>
<td>255</td>
<td>246</td>
</tr>
<tr>
<td>15</td>
<td>85</td>
<td>0.1973</td>
<td>264</td>
<td>252</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>0.1953</td>
<td>255</td>
<td>243</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>0.1955</td>
<td>254</td>
<td>231</td>
</tr>
<tr>
<td>Control</td>
<td></td>
<td>0.0000</td>
<td>184</td>
<td>189</td>
</tr>
</tbody>
</table>

Table 2. The WRA, DP rating and tensile strength retention of the cotton fabric treated with TPMA/CA and DMDHEU*.

<table>
<thead>
<tr>
<th>DP Finish</th>
<th>pH adjustment</th>
<th>Curing Temp. (ºC)</th>
<th>WRA (º, w+f)</th>
<th>DP Rating</th>
<th>Tensile Strength Retention (% F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPMA/CA</td>
<td>2.4</td>
<td>185</td>
<td>285</td>
<td>4.1</td>
<td>65</td>
</tr>
<tr>
<td>TPMA/CA</td>
<td>2.7</td>
<td>185</td>
<td>283</td>
<td>4.1</td>
<td>62</td>
</tr>
<tr>
<td>DMDHEU</td>
<td>-</td>
<td>170</td>
<td>261</td>
<td>3.6</td>
<td>53</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>185</td>
<td>176</td>
<td>1.0</td>
<td>100</td>
</tr>
</tbody>
</table>

*The TPMA/CA system contained 9.4% (wob) CA, 2.0% TPMA, 6.8% NaH2PO2•H2O. The DMDHEU system contained 11.4% “low formaldehyde” DMDHEU with pre-mixed catalyst (“Premafresh EFC” supplied by Sequa). Both systems contained 3% polyethylene softener and 0.2% wetting agent. The curing time was 3 min for all samples.

Table 3. The WRA and DP rating of the cotton fabric treated with TPMA/CA and DMDHEU.

<table>
<thead>
<tr>
<th>DP System</th>
<th>WRA (º, W+F)</th>
<th>DP Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 5 10 20 30</td>
<td>0 5 10 20 30</td>
</tr>
<tr>
<td>TPMA/CA (pH 2.4)</td>
<td>285 276 263 255 250</td>
<td>4.1 3.9 3.7 3.4 3.4</td>
</tr>
<tr>
<td>TPMA/CA (pH 2.7)</td>
<td>283 267 250 249 247</td>
<td>4.1 3.6 3.4 3.3 3.2</td>
</tr>
<tr>
<td>DMDHEU</td>
<td>261 245 247 226 226</td>
<td>3.6 3.1 3.1 3.0 3.0</td>
</tr>
</tbody>
</table>

Oligomer of MA (OMA)

For the purpose of finding a more effective and low-cost crosslinking system, we investigated the in-situ polymerization of MA and itaconic acid (IA) on cotton (67-69). The application of in-situ polymerization of MA and IA as a crosslinking system on cotton had been reported.
previously (70). However, we discovered that the amount of the polymers formed by the in-situ polymerization of MA and IA on cotton is small using the formulas reported in the literature. Moreover, we discovered that the in-situ polymerization of MA and IA took place only when substantial amounts of K$_2$S$_2$O$_8$ and NaH$_2$PO$_2$ were present in the system. We also found that the amount of K$_2$S$_2$O$_8$ and NaH$_2$PO$_2$ played a decisive role on the in-situ polymerization and the performance of the treated cotton (69,70). We also found that the use of persulfate in the system caused significant loss of fabric strength because of its oxidative nature (71).

Based on the understanding of in-situ polymerization of MA on cotton, we studied the aqueous free radical polymerization of MA. Historically, MA is extremely difficult to polymerize in comparison to other substituted ethylenical acid monomers, such as acrylic acid, because of the strong electronic withdrawing effects and space hindrance caused by the two carboxyl groups. Polymers of MA were synthesized by free radical polymerization of maleic anhydride in organic solvents, such as toluene, to form poly(maleic anhydride) followed by hydrolysis of the anhydride (72). PMA and TPMA were synthesized by this method. We found that both PMA and TPMA were not effective crosslinking agents for cotton because of their relatively larger molecular sizes (18).

We discovered that MA can be polymerized to form an oligomer (OPMA) in an aqueous solution in the presence of both K$_2$S$_2$O$_8$ and NaH$_2$PO$_2$ (23,24). Presented in Fig. 5 are the FT-Raman spectra of the MA polymerization products with different polymerization times. The Raman spectrum of the polymerization mixture (MA and NaH$_2$PO$_2$) before the addition of Na$_2$S$_2$O$_8$ (Fig. 5a) showed the stretching modes of the carbon-carbon double bond (>$\text{C}=$<$\text{C}$) and the unsaturated =$\text{C}=$H of MA at 1648 and 3060 cm$^{-1}$, respectively (73). The band at 1708 cm$^{-1}$ was due to the stretching mode of the carboxylic carbonyl (>$\text{C}=$O) of MA, which was in conjugation with C=C. The strong band at 866 cm$^{-1}$ in Fig. 5 was due to the out-of-plane deformation of =$\text{C}=$H of MA. After the addition of Na$_2$S$_2$O$_8$ to the polymerization mixture and keeping the mixture at 70°C for 30 min, a
new band at 2939 cm\(^{-1}\) due to the saturated C-H stretching mode appeared whereas the intensity of all those bands associated with MA, which included the band at 3061 cm\(^{-1}\) due to stretching of =C-H, the band at 865 cm\(^{-1}\) due to out-of-plane deformation of =C-H, and the band at 1648 cm\(^{-1}\) due to stretching of C=C, decreased their intensity in the spectrum (Fig. 5b), indicating the polymerization of MA and formation of OPMA. The emerging band at 980 cm\(^{-1}\) in Fig. 5b was attributed to S=O stretching of HSO\(_4^-\), which resulted from the thermal decomposition of S\(_2\)O\(_8^-\). As the polymerization time increased from 0.5 to 6 h, the FT-Raman spectra (Figs. 1b-1f) showed the following changes: (1) the characteristic bands of MA at 3060, 1648, and 866 cm\(^{-1}\) gradually decreased their intensities and finally disappeared completely after the polymerization time reaches 6 h and (2) the characteristic bands of OPMA at 2942 cm\(^{-1}\) due to saturated C-H stretching and at 912 cm\(^{-1}\) due to OH···O out-of-plane deformation gradually increased their intensities. The frequency of the carboxylic carbonyl band gradually shifted from 1708 cm\(^{-1}\) in Fig. 5a to 1720 cm\(^{-1}\) in Fig. 5f. As MA polymerized to form OPMA, the C=C of MA was converted to saturated C-C, consequently, the carboxylic carbonyl is no longer conjugated with C=C and its vibrational frequency shifted to a higher frequency at 1720 cm\(^{-1}\) accordingly.

We also applied matrix-assisted laser desorption/adsorption mass spectroscopy (MALDI-MS) to determine the molecular weight (MW) of the OMA thus synthesized and to elucidate the polymerization mechanism. Shown in Fig. 6 is the MALDI mass spectrum of OMA. The MW of OMA was calculated by the formula \(\text{MW} = (n \times 116) + 66 + 23\), in which 116 was the MW of MA, 23 was the weight of Na\(^+\), 66 was the molecular weight of H\(_3\)PO\(_2\) and \(n\) was degree of polymerization (DP) of OMA. The peaks at 321, 537, 553, 669, and 785 are assigned to OMA with DP of 2, 3, 4, 5, and 6, respectively. The MS data reveal the structures of the polymerization products, as shown in Scheme 3. Based on the mass spectroscopy and also \(^{31}\)P nuclear magnetic resonance (NMR) spectroscopy data [42], we concluded that the products of aqueous polymerization of MA were indeed oligomers of MA with NaH\(_2\)PO\(_2\) (mostly between 2
and 5), and that the anion (H$_2$PO$_2^-$) from hypophosphite formed a free radical upon reaction with S$_2$O$_8^{2-}$ to initiate the polymerization. The polymerization mechanism is shown in Scheme 6. OMA is currently produced commercially by Dymatic Chemicals in China.

The OMA thus formed was applied to a plain weave cotton fabric and a twill weave cotton fabric in combination with NaH$_2$PO$_2$ as the catalyst. A low-formaldehyde DMDHEU DP finishing agent was included in the study for comparison. The formulas, curing conditions, WRA, DP rating, and strength of the treated plain weave cotton fabric are presented in Table 4. The fabric treated with OMA and DMDHEU had a WRA of 273° and 278°, respectively after one laundering cycle, and the WRA became 260 and 264°, respectively, after 20 laundering cycles (Table 4). The effectiveness of OMA as a DP finishing agent appeared to be very similar to that of the low-formaldehyde DMDHEU. The tensile strength retention for the fabric treated with OMA was 50% whereas that for the fabric treated with DMDHEU was only 35% (Table 4). The flex abrasion resistance for the cotton fabric treated with OMA was also significantly higher than that treated with DMDHEU (Table 4). Since the fabric treated with the two different crosslinking agents had similar wrinkle resistance, we can conclude that the OMA caused significantly less fabric tensile strength loss than did DMDHEU. The OMA-treated cotton fabric also showed much higher flex abrasion resistance (Table 4).
Fig. 5 FT-Raman spectra of the mixture of MA/NaH₂PO₄, (a) before adding Na₂S₂O₈; (b) after adding Na₂S₂O₈ and polymerized for 0.5 h; (c) polymerized for 1.0 h; (d) polymerized for 2.0 h; (e) polymerized for 4.0 h; and (f) polymerized for 6.0 h.

Mass (m/e)

Fig. 6 MALDI mass spectrum of OPMA.
Scheme 6. Polymerization mechanism of MA

We applied OMA and DMDHEU in combination with a silicone softener to treat a twill cotton fabric. The conditioned WRA and DP rating of the fabric thus treated are shown in Table 5. The cotton fabric treated with OMA had a WRA of 291° (123° higher than the control) after one home laundering cycle, and had a WRA of 256° (88° higher than the control) and DP rating of 3.0 after 30 home laundering cycles. Thus, the data indicate that OMA was an effective DP finishing agent and was able to impart a high level of wrinkle resistance to the cotton fabric. Both the WRA and the DP rating of the fabric treated with the different crosslinking agents after 1, 10, and 30 laundering cycles were very similar, indicating that the two DP finishing agents provide similar wrinkle-resistant performance under the curing conditions used, but OMA caused significantly less fabric tensile strength loss than DMDHEU (Table 5).

We measured the formaldehyde release from the plain weave cotton fabric treated with OPMA, a standard DMDHEU and a low-formaldehyde version of DMDHEU (Table 6). No formaldehyde was detected on the OMA-treated cotton fabric. The formaldehyde content for the cotton fabric samples treated with the standard and "low formaldehyde" DMDHEU was 360 and 204.
pm, respectively, before home laundering, and those values did not show significant reduction after one home laundering cycle.

Table 4. The conditioned WRA and mechanical strength of the plain weave cotton fabric treated with OMA, BTCA, and DMDHEU.

<table>
<thead>
<tr>
<th>CROSSLINKER (WOB)</th>
<th>CATALYST (WOB)</th>
<th>CURING CONDITION</th>
<th>WRA (°, W+F) (NO. LAUNDERING CYCLES) 1 5 10 20</th>
<th>TENS. STRENGTH RETENTION (% F)</th>
<th>FLEX ABRASION (CYCLES, W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8% OMA</td>
<td>2% NaH₂PO₄</td>
<td>180°C 1.5 min</td>
<td>27 3</td>
<td>261 261 260</td>
<td>50</td>
</tr>
<tr>
<td>10.5% DMDHEU</td>
<td>Pre-added catalyst</td>
<td>165°C 1.5 min</td>
<td>27 8</td>
<td>273 269 264</td>
<td>35</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>180°C 1.5 min</td>
<td>190</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5. The conditioned WRA and DP of the twill weave cotton fabric treated with OMA, BTCA and DMDHEU. (All the finish solutions contained 3.0% softener.)

<table>
<thead>
<tr>
<th>CROSSLINKER (WOB)</th>
<th>CATALYST (WOB)</th>
<th>CURING CONDITION</th>
<th>WRA (°, W+F) NO. LAUNDERING CYCLES</th>
<th>DP RATING NO. LAUNDERING CYCLES</th>
<th>TENS. STRENGTH RETENTION (% F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1% OMA</td>
<td>2.7% NaH₂PO₂</td>
<td>175°C 3 min</td>
<td>291</td>
<td>268 256</td>
<td>3.4 3.3 3.0</td>
</tr>
<tr>
<td>12.5% DMDHEU</td>
<td>Pre-catalyzed</td>
<td>160°C 1.5 min</td>
<td>292</td>
<td>265 253</td>
<td>3.5 3.4 3.0</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>-</td>
<td>168</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6. Formaldehyde release of the cotton fabric treated with OMA, standard DMDHEU and the modified low-formaldehyde DMDHEU.

<table>
<thead>
<tr>
<th>CROSSLINKER CONCENTRATION (WOB)</th>
<th>CATALYST CONCENTRATION (WOB)</th>
<th>SOFTENER CONCENTRATION (WOB)</th>
<th>CURING CONDITION</th>
<th>FORMALDEHYDE RELEASE (PPM) before wash after one wash</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.8% OMA</td>
<td>1.8% NaH₂PO₂</td>
<td>2.0%</td>
<td>175°C, 2 min</td>
<td>0</td>
</tr>
<tr>
<td>5.3% Standard DMDHEU</td>
<td>1.1% MgCl₂•6H₂O</td>
<td>2.0%</td>
<td>160°C, 2 min</td>
<td>360</td>
</tr>
<tr>
<td>8.4% Mod. DMDHEU</td>
<td>Pre-catalyzed</td>
<td>2.0%</td>
<td>160°C, 2 min</td>
<td>204</td>
</tr>
</tbody>
</table>

The Combination of MA and NaH₂PO₂
As we discussed previously, MA, an α, β-unsaturated dicarboxylic acid, could only form one single ester linkage with cellulose, and is unable to form the second cyclic anhydride intermediate for crosslinking cotton cellulose. However, we also discovered that the wrinkle resistance of the cotton fabric treated with MA was significantly improved when NaH₂PO₂ was used as a catalyst. Such phenomenon was not observed when cotton fabric was treated with combinations of MA and Na₂HPO₃ (31). We discovered that two reactions took place on cotton fabric treated with the combination of MA and NaH₂PO₂. First, NaH₂PO₂ functioned as the catalyst for the esterification of cotton by MA, which formed an ester linkage with cellulose. When the curing temperature reached to 160°C and higher, the 2nd reaction became predominant. The H-P-H of hypophosphite reacted with the >C=C< bonds of the two MA molecules already esterified with cellulose, thus forming a crosslinkage between two cellulose molecules shown in Scheme 7. This crosslinking mechanism was supported by the WRA, tensile strength, and phosphorus analysis data of the cotton fabric treated with MA and NaH₂PO₂ (30,31). We found similar results when cotton was treated with the combination of itaconic acid (another unsaturated bifunctional carboxylic acid) and NaH₂PO₂ (29).

The DP performance of the plain weave cotton fabric treated with MA/NaH₂PO₂ and that treated with a low-formaldehyde DMDHEU are presented in Table 7. The WRA of the cotton fabrics treated with MA/NaH₂PO₂ and with DMDHEU were 275° and 274°, respectively, after one laundering cycle. Both treated fabrics showed very similar DP ratings. During the 30 home laundering cycles, the two treated fabrics also had gradually reduced and very similar WRA and DP ratings (Table 7). After 30 home laundering cycles, the fabrics treated with MA/NaH₂PO₂ and with DMDHEU have WRAs of 254° and 257°, respectively. Apparently, the cotton fabric treated with MA/NaH₂PO₂ and that treated with DMDHEU demonstrated similar hydrolysis resistance and similar wrinkle resistance after 30 launderings. Thus, we can conclude that the cotton fabric
crosslinked by MA/NaH₂PO₂ has DP performance and laundering durability similar to fabrics crosslinked by DMDHEU under those curing conditions.

Scheme 7. The crosslinking of cotton by the combination of MA and NaH₂PO₂.

Shown in Table 8 are the breaking strength and tearing strength of fabric treated with MA/NaH₂PO₂.
with standard deviation included. Table 8 shows that the breaking strength of the fabric treated with MA/NaH$_2$PO$_2$ were 29 and 17 N higher in warp and filling directions, respectively, than fabric treated with DMDHEU, which represents 23% and 28% improvement, respectively. The data also show that the tearing strength of the fabric treated with MA/NaH$_2$PO$_2$ was 11% higher in the filling direction than fabric treated with DMDHEU. It was apparent that MA/NaH$_2$PO$_2$ as a DP system caused a significantly lower loss in fabric mechanical strength. We also applied the MA/NaH$_2$PO$_2$ system to a cotton twill fabric and the results were similar. Therefore, we conclude that the MA/NaH$_2$PO$_2$ system had effectiveness as a DP finishing agent similar to that of DMDHEU, but caused significantly less fabric strength loss. The combination of MA and NaH$_2$PO$_2$ was a formaldehyde-free, odor-free, and cost-effective DP finishing system with superior fabric strength retention.

Table 7. The DP performance of the plain weave cotton fabric treated with MA/NaH$_2$PO$_2$ and DMDHEU.

<table>
<thead>
<tr>
<th>Formulation %</th>
<th>Curing Condition</th>
<th>WRA (w+f, degree)</th>
<th>DP Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>No. of Laundering Cycles</td>
<td>No. of Laundering Cycles</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>8.0 MA 5.0 NaH$_2$PO$_2$</td>
<td>175°C 2min</td>
<td>275</td>
<td>262</td>
</tr>
<tr>
<td>10.5 DMDHEU</td>
<td>160°C 2min</td>
<td>274</td>
<td>262</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>190</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 8. The mechanical properties of the plain weave cotton fabric treated with MA/NaH$_2$PO$_2$ and DMDHEU

<table>
<thead>
<tr>
<th>Formulation %</th>
<th>Curing Condition</th>
<th>Breaking Strength (N)/SD</th>
<th>Tearing Strength (N)/SD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Warp</td>
<td>Filling</td>
</tr>
<tr>
<td>8.0 MA 5.0 NaH$_2$PO$_2$</td>
<td>175°C 2 min</td>
<td>153/4</td>
<td>91/8</td>
</tr>
<tr>
<td>10.5 DMDHEU</td>
<td>160°C 2 min</td>
<td>124/5</td>
<td>74/13</td>
</tr>
<tr>
<td>Control</td>
<td>-</td>
<td>296/4</td>
<td>197/10</td>
</tr>
</tbody>
</table>
Fabric Strength Loss of Cotton Crosslinked by a Polycarboxylic Acid

Crosslinking cotton cellulose imparted wrinkle resistance and smooth drying properties to cotton fabrics, and reduced tensile strength of the treated cotton fabric (74). Strength loss was the major disadvantage for DP finished cotton textiles. We studied the mechanism of strength loss of fabric treated with polycarboxylic acids. Because the strength loss for a cotton fabric treated with a polycarboxylic acid is the combined effects of acid degradation and crosslinking of cellulose, it is necessary to separate contributions by those two factors quantitatively.

We used alkaline hydrolysis to remove the ester crosslinking in the cotton fabric treated with BTCA (44). The untreated cotton fabric was first heated at 180°C for 2 min, then treated in 0.1 M NaOH at 50°C for 96 h. We found that fabric strength loss of the cotton fabric thus treated was negligible. The cotton fabric treated with 6% BTCA/4% NaH2PO2 was cured at 180°C for 2 min, washed, and then hydrolyzed in a 0.1 M NaOH solution at 50°C. The WRA and tensile strength retention of the cotton fabric thus treated was plotted against the hydrolysis time (Figs. 7 and 8, respectively). The WRA decreased as the hydrolysis proceeded, and it was reduced to the level of an untreated cotton fabric sample (~200°) after 24 h of hydrolysis in the NaOH solution, indicating complete removal of the ester crosslinking on the cotton fabric. Further hydrolysis had no effects on the WRA of the fabric (Fig. 7). The fabric tensile strength gradually increased in both warp and filling directions as the hydrolysis of the crosslinked fabric progressed as shown in Fig. 7, indicating that the lost fabric tensile strength due to crosslinking was gradually restored as the crosslinked cotton fabric was hydrolyzed. The data clearly demonstrated that the fabric strength loss caused by crosslinking of cellulose molecules was reversible. The fabric strength retention at both warp and filling direction increased markedly for the first 10 h of hydrolysis, then reached approximately 80% after 24 h of hydrolysis in both the filling and warp direction (Fig. 8). The portion of fabric strength loss (approximately 20%) not recovered by hydrolysis was evidently caused by acid...
degradation. The data showed that the strength loss caused by crosslinking and that caused by cellulose degradation could be separated and measured quantitatively for the fabric crosslinked by a polycarboxylic acid (44).

Fig. 7. The WRA of the cotton fabric treated with 6.0% BTCA/4.0% NaH₂PO₄, cured at 180°C for 2 min, and hydrolyzed at 50°C for different time.

Fig. 8. The tensile strength retention (%) the cotton fabric treated with 6.0% BTCA /4.0% NaH₂PO₄, cured at 180°C for 2 min, and hydrolyzed at 50°C for different time.

In our research on this topic, we also had the following additional discoveries:

(1) The magnitude of irreversible fabric strength loss caused by acid degradation is affected by curing temperature and time, the dissociation constant of the acid, the concentration of the acid, and pH of the finish solution applied to the fabric. The magnitude of the reversible fabric strength loss caused by fabric crosslinking increased as the degree of crosslinking increased (44).
(2) The relationship between tensile strength loss and wrinkle recovery angle for cotton fabric treated with BTCA and all-cis-1,2,3,4-cyclopentanetetracarboxylic acid is essentially equivalent. The cotton fabric treated with DMDHEU and DHDMI showed the same phenomenon. Therefore, all data indicate that the tensile strength loss of crosslinked cotton fabric appeared to be independent of the molecular structure and the reactivity of the crosslinking agents (46).

(3) Both polycarboxylic acids and Lewis acids (such as MgCl2) used as the catalyst for DMDHEU on cotton, catalyzed degradation of cotton cellulose, thus reducing tensile strength. The tensile strength loss of the cotton fabric treated with a Lewis acid or a carboxylic acid was the direct result of cellulose depolymerization (47).

(4) A direct linear correlation exists between the cellulose MW of the treated cotton fabric and the fabric tensile strength (47).

(5) When cotton fabric is crosslinked by a crosslinking agent, its abrasion resistance decreases as the amount of crosslinks increase. The reduction in abrasion resistance for the cotton fabric treated with a polycarboxylic acid can be attributed to irreversible acid-catalyzed degradation and reversible crosslinking of cellulose molecules. MgCl2 used as a catalyst for DMDHEU also causes significant reduction in fabric abrasion resistance (48).

(6) Both the effectiveness of BTCA as a crosslinking agent for cotton and the strength loss for the cotton fabric crosslinked by BTCA are pH-dependent. The effectiveness of BTCA for esterifying and crosslinking cotton remained steady in the 2.2-2.8 pH range, and declined as the pH further increased. The strength loss due to acid-catalyzed degradation for the treated cotton fabric crosslinked by BTCA decreased as the pH increased. Therefore, BTCA at pH ~2.8 provided optimum effectiveness for crosslinking cotton with minimized fabric strength loss (45).
Improvement of the Abrasion Resistance of Crosslinked Cotton Fabric

In addition to reducing cotton fabric tensile strength, crosslinking agents also reduce fabric abrasion resistance. Significantly reduced abrasion resistance shortens wear life of garments and is the chief obstacle for applications of crosslinking agents to a wider range of cellulosic fabrics and garments. Fabric softeners were used to improve the abrasion resistance of DP finished cotton fabric with limited success. A DP finishing agent forms covalent crosslinkages between cellulose molecules in cotton fibers to impart wrinkle-resistance to cotton fabric. The wrinkle resistance of a crosslinked cotton fiber was determined by the amount of crosslinking across an entire fiber. The abrasion and wear of a crosslinked cotton fiber, on the other hand, takes place on the surface of a fabric. Thus, we were able to develop a new approach to improve the abrasion resistance of DP finished cotton fabric by reducing the cellulose crosslinking on the surface without reduction in the bulk of the fabric. If the crosslinking on a fiber’s surface could be reduced while the crosslinking in the interior of the fabric was maintained, the abrasion resistance of a DP finished cotton fabric could be improved without sacrificing its wrinkle-resistance. We used a high molecular weight poly(vinyl alcohol) (PVA) as an additive, which stayed on the surface to react with the crosslinker, to improve the abrasion resistance of the treated cotton fabric without diminishing its DP performance (75).

The PVA sample having MW range of 146,000-186,000 with a hydrolysis rate of 98.0%-98.8%, was the most effective one among several samples we evaluated. The cotton fabric was first treated with 6% BTCA and 4% NaH₂PO₂ in combination with PVA at concentrations ranging from 0.05% to 0.90%, cured at 180°C for 2 min, and finally subjected to one home laundering cycle. The flex abrasion resistance of the cotton fabric thus treated was plotted against the PVA concentration in Fig. 9. The data presented here clearly demonstrated that the addition of PVA at a concentration ≥ 0.60% significantly improved the abrasion resistance of the DP finished cotton fabric.
Data collected after the treated cotton was subjected to five laundering cycles also confirmed the above observation. The fact that the superior abrasion resistance of the fabric treated with BTCA/PVA remained after laundering indicated that PVA must have reacted with BTCA, because any PVA physically absorbed onto the fiber without covalent bonding to the fiber must have been washed off after five home laundering cycles (75).

The improved abrasion resistance of the cotton fabric treated with BTCA/PVA was most likely a result of the reaction between BTCA and PVA. Because of its large molecular size, PVA stays on the surface of the cotton fiber, whereas BTCA penetrated into the fiber interior to form crosslinking among cellulose molecules. Three different reactions (crosslinking among cellulose, crosslinking among PVA, and crosslinking between cellulose and PVA) took place on the cotton fiber surfaces when the treated cotton fabric was cured at an elevated temperature. Because PVA and cotton cellulose competed to esterify BTCA, the amount of crosslinking among cellulose on the surfaces of the cotton fiber was reduced when PVA was added. The reduced cellulose crosslinking on the fiber surface improved the abrasion resistance of the fabric. When the cotton fabric was treated with BTCA/PVA, PVA went onto pores and cracks on the fiber surface under capillary force. Thus, PVA might also repair the weak points on the cotton fiber surface. Thus, the crosslinking between cellulose and PVA made those PVA molecules durable to home laundering. Formation of a film was observed between two cotton fibers in the scanning electron microscopy (SEM) micrograph (Fig. 10). The film was probably the crosslinked networks of PVA/BTCA. The networks must have covalently bound to the fibers through BTCA because the film was observed after one home laundering cycle. The crosslinked networks of PVA/BTCA on the cotton fiber surfaces may also contribute to the improved abrasion resistance of the cotton fabric treated with BTCA/PVA (75).
Fig. 9. The flex abrasion resistance of the cotton fabric treated with 6% BTCA and 4% NaH₂PO₄ in combination with 0.60% PVA cured at 180°C for 2 min, and finally subjected to one laundering cycle.

Fig. 10 The micrograph of the cotton fabric treated with 6% BTCA, 4% NaH₂PO₄ and 0.6% PVA cured at 180°C or 2min, and after one laundering cycle.

Flame Retardant Finishing of Cotton and Cotton Blends

Treatment of Cotton Fleece with Polycarboxylic Acids
Cotton fleece fabrics are among the most flammable textile fabrics. Without flame retardant treatment, almost all fleece fabrics made of 100% cotton are not able to meet the flammability requirement specified in the federal regulation “16 CFR 1610”, and therefore cannot be sold in the US (76). The flammability standard for general wearing apparel (“16 CFR 1610”) is a US federal regulation that applies to all apparel textiles and defines the flammability ranking and the testing method for cotton fleece fabrics.

Blanchard first reported the use of polycarboxylic acids, including BTCA and CA, as flame retardants for 90/10 cotton/polyester carpet with sodium hypophosphite as the catalyst (77). We successfully applied various polycarboxylic acids, including BTCA, succinic acid (SUA), CA, malic acid, OMA and combinations of MA and NaH₂PO₂ as the catalyst, to treated cotton fleece fabrics (62,78-80). Cotton fleece treated with those acids achieved "Class 1" flammability (low flammability), whereas the fabric had "Class 3" flammability (high flammability) before the treatment. Such a change in fabric flammability took place only when those treated cotton fleece underwent a curing process (80).

We applied BTCA and succinic acid (SUA) to the cotton fleece and to study the change in PHRR of the cotton fabric as a result of the esterification of cotton cellulose by those acids. The heat release rate of the cotton fabric, treated with 6.3% BTCA and that treated with 6.4% SUA, in combination with 3.2% NaH₂PO₂ as a catalyst, cured at 180°C for 2 min, and subjected to one home laundering cycle, are presented against the heating temperature in Fig. 11. The untreated cotton fabric started decomposition at ~320°C, and its heat release rate reached the maximum (234 w/g) at 378°C. When cotton fabric is treated with BTCA and SA, the fabric started to decompose at ~280°C, and the PHRR of the treated fabric became 147 w/g for BTCA and 179 w/g for SUA (Fig. 11). Evidently, both acids were effective in significantly reducing PHRR of the cotton fabric, and BTCA was more
effective than SA. The acids also reduce the starting temperature of decomposition by ~40°C.

Fig. 11. The heat release rate of the cotton fabric treated with BTCA and SUA and cured at 180°C for 2 min versus temperature.

Fig. 12. The peak heat release rate of the cotton fabric treated with BTCA and SUA, cured for 2 min and subjected to one home laundering cycle versus curing temperature.

Fig. 13. The percent char yield of the cotton fabric treated with BTCA and SUA, cured for 2 min and subjected to one home laundering cycle versus curing temperature.
The cotton fabric samples treated with BTCA and SA were cured at different temperatures. The PHRR versus curing temperature curve of the fabric treated with BTCA was significantly lower than that treated with SUA as shown in Fig. 12, indicating a significantly lower fire hazard. The heat release capacity of the treated cotton fabric had the same trend (80). The percent char yield versus curing temperature curves for the BTCA- and SUA-treated fabric shown in Fig. 13 demonstrated that the esterification of cotton by both acids caused a remarkable increase in the char yield and that the BTCA-treated cotton causes higher char yield. The significantly increased char yield of the treated cotton demonstrated that the polycarboxylic acids on cotton functioned as condensed phase flame retardants to promote char formation.

We also studied the heat release properties of the cotton fabric treated with MA in combination with NaH$_2$PO$_2$. Presented in Figs. 14 and 15 are the peak heat release rate versus curing temperature curves of the fabric treated with (a) 6% MA and (b) the combination of 6.0% MA and 3.0% NaH$_2$PO$_2$. The cotton fabric treated with the combination of MA and NaH$_2$PO$_2$ had a significantly lower peak heat release rate and significantly higher char yield than that treated with MA as shown in Figs 14 and 15. This was due to the bonding of the phosphorus of NaH$_2$PO$_2$ to the cotton fabric through the reaction between NaH$_2$PO$_2$ and the MA esterified with cotton (63). Esterification of cotton by MA reduced the PHRR and increased in percent char yield of the treated cotton fabric. For the cotton fabric treated with MA and NaH$_2$PO$_2$, the reaction between NaH$_2$PO$_2$ and MA bound NaH$_2$PO$_2$ to cotton further enhanced the flame redundancy of the MA-treated cotton fabric as indicated by more significant decrease in PHRR, TPHRR, and a more significant increase in the char formation.
Fig. 14. The PHRR of cotton fabric treated with (a) 6.0% MA and (b) 6.0% MA and 3.0% NaH$_2$PO$_2$, cured at different temperatures and subjected to 1 home laundering cycle.

Fig. 15. The char retention of cotton fabric treated with (a) 6.0% MA and (b) 6.0% MA and 3.0% NaH$_2$PO$_2$, cured at different temperatures and subjected to 1 home laundering cycle.

**Treatment of Nomex/Cotton Blend Military Fabric**

Nomex has been commonly used to make fire-resistant protective clothing. The high cost of Nomex and low comfort of Nomex due to fabric stiffness and low moisture regain limited its wider uses (81). Blending Nomex with cotton not only reduces the cost but also improved its comfort. Because cotton is a highly flammable fiber, a Nomex/cotton blend fabric containing more than 20% cotton is not self-extinguishable (82). Therefore, a flame-retardant finishing treatment becomes necessary to make such Nomex/cotton blend fabric flame resistant if it contains more than 20% cotton. We developed a flame retardant finish system for cotton based on a hydroxyl-functional organophosphorus oligomer (HFPO) shown below as the flame retardant and BTCA as the bonding agent. BTCA was able to function as a nonformaldehyde crosslinker to esterify the hydroxyl groups of both cotton cellulose and HFPO (83,84). We used triethanolamine (TEA) as a co-reactant to provide synergistic nitrogen to enhance the performance of HFPO and to reduce the deposition of
calcium by forming calcium salts of BTCA on cotton. We applied this system as a flame retardant finishing system for the 65/35 Nomex/cotton blend military fabric (85).

![Molecular formula of HFPO](image)

Scheme 8. Molecular formula of HFPO

The phosphorus concentration of the 65/35 Nomex/cotton blend fabric treated with 24% HFPO, 8% BTCA, and 2.5% H₃PO₂ in combination with TEA at different concentrations and subjected to different home laundering cycles is presented in Fig. 16. The phosphorus concentration on the treated Nomex/cotton blend fabric first increased, then decreased as the TEA concentration increased in the range from 1.0% to 10.0%. Maximum phosphorus concentrations on the treated fabric were achieved at 4% TEA (Fig. 16). The use of TEA increased the percent phosphorus retention on the fabric after multiple laundering cycles. TEA has three hydroxyl groups in its molecule and was able to react with the carboxylic acid groups of BTCA by esterification. BTCA also reacted with HFPO and cotton to form a BTCA/HFPO/TEA/cotton crosslinked network as shown in Scheme 9, thus improving the laundering resistance of the HFPO on cotton. The data presented in Fig. 16 also show that further increasing TEA concentration from 4% to 10% reduced the retention of HFPO after multiple launderings on the treated fabric (85). Because TEA, HFPO, and cotton all have hydroxyl groups, they competed to react with BTCA, and the presence of excessive amount of TEA reduced the reaction of BTCA with HFPO and cotton, thus reducing the fixation of HFPO on cotton.
Fig. 16 The phosphorus concentrations of the Nomex/cotton blend fabric treated by 24% HFPO, 8% BTCA, and 2.5% H₃PO₄ as a function of TEA concentration.

Scheme 9. Formation of BTCA/HFPO/TEA crosslinked network on cotton

The Nomex/cotton fabric was treated with 24% HFPO, 8% BTCA, 2.5% H₃PO₄, and TEA at different concentrations. The fabric thus treated was cured at 180°C for 3 min. The limiting oxygen index (LOI, %) of the fabric thus treated showed increased from 37.2% to 40.6% as the TEA concentration increased from 0.0% to 8.0%. Thus, the data demonstrate the phosphorus-nitrogen synergistic effect of TEA in the HFPO/BTCA/ H₃PO₄/TEA system on the Nomex/cotton blend fabric. Previously, we found that the calcium deposit that formed on the cotton treated with HFPO/BTCA during laundering diminished the flame resistant performance of the

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treated cotton fabric (85). We found that the calcium concentration on the fabric after multiple launderings decreased as the TEA concentration increased.

The Nomex/cotton blend fabrics were treated with 24% HFPO, 8% BTCA, 2.5% H₃PO₂, and TEA at different concentrations. The Nomex/cotton blend fabric thus treated was cured at 180°C for 3 min and finally subjected to 1, 10, and 25 laundering cycles. The LOI of the fabric thus treated is shown against the TEA concentration (Fig. 17). After one laundering cycle, the LOI of the treated Nomex/cotton blend fabric first increased from 32.1% without TEA to its maximum (36.3%) when 6.0% TEA was used. Further increasing the TEA concentration reduced the LOI of treated Nomex/cotton blend fabric. Similar trends are observed on the treated fabric subjected to 10 and 25 laundering cycles. The optimum TEA concentration for the finish solution was in the 4.0%-6.0% range. After 25 laundering cycles, the LOI of the fabric treated using 6.0% TEA was 30.5% (85).

![Graph showing LOI of Nomex/cotton blend fabric treated with 24% HFPO, 8% BTCA, and 2.5% H₃PO₂ in combination with TEA as a function of TEA concentration.]

Fig. 17 The LOI of the Nomex/cotton blend fabric treated by 24% HFPO, 8% BTCA, and 2.5% H₃PO₂ in combination with TEA as a function of TEA concentration.

The Nomex/cotton blend fabrics was treated with HFPO/BTCA/TEA (weight ratio:3.0/1.0/0.75) at different concentrations and cured at 180°C for 3 min. The HFPO concentration increased from 12% to 24%, and the BTCA and TEA concentration were increased accordingly. The LOI and
vertical flammability (char length) of the treated fabric after different laundering cycles are presented in Tables 9 and 10, respectively. The LOI of the Nomex/cotton blend fabric without treatment is 22.9% and it failed the vertical flammability test. All the Nomex/cotton fabric samples treated with the four HFPO/BTCA/TEA formulas pass the vertical flammability test after 30 laundering cycles. The fabric treated with 12% (w/w) HFPO finishing solution (approximately 8% [w/w] HFPO on the fabric) had an LOI of 26.5% and char length of 48 mm after 30 laundering cycles, demonstrating excellent flame retardant performance and superior laundering durability at a small add-on concentration on the fabric (85).

Table 9. The LOI of the Nomex/cotton fabric treated with HFPO/BTCA/H$_3$PO$_2$/TEA at the weight ratio of 24/8/2.5/6 and cured at 180°C for 3 min.

<table>
<thead>
<tr>
<th>HFPO (%)</th>
<th>BTCA (%)</th>
<th>H$_3$PO$_2$ (%)</th>
<th>TEA (%)</th>
<th>Number of Home Laundering Cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>No Wash</td>
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<tr>
<td>12</td>
<td>4</td>
<td>1.25</td>
<td>3.0</td>
<td>35.7</td>
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<tr>
<td>18</td>
<td>6</td>
<td>1.88</td>
<td>4.5</td>
<td>38.8</td>
</tr>
<tr>
<td>24</td>
<td>8</td>
<td>2.50</td>
<td>6.0</td>
<td>40.7</td>
</tr>
<tr>
<td>30</td>
<td>10</td>
<td>3.13</td>
<td>7.5</td>
<td>40.6</td>
</tr>
<tr>
<td>Control</td>
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</tr>
</tbody>
</table>

Table 10. The char length of the Nomex/cotton blend fabric treated with HFPO/BTCA/H$_3$PO$_2$/TEA at the weight ratio of 24/8/2.5/6 and cured at 180°C for 3 min.

<table>
<thead>
<tr>
<th>HFPO (%)</th>
<th>BTCA (%)</th>
<th>H$_3$PO$_2$ (%)</th>
<th>TEA (%)</th>
<th>Number of Home Laundering Cycles</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
<td></td>
<td></td>
<td>No Wash</td>
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</table>
Conclusions

Multifunctional carboxylic acids, such as BTCA and OPMA are a practical nonformaldehyde alternative for cotton DP finishing. The chemical reactions of the polycarboxylic acids on cotton are well elucidated. Compared with the formaldehyde-based DMDHEU currently used by the industry to produce easy-care cotton fabrics and garments, the nonformaldehyde systems are as or more effective in imparting wrinkle-resistance to cotton fabrics with a very limited increase in cost. Fabrics treated with polycarboxylic acids also demonstrate higher strength retention than those treated with DMDHEU. Considering the fact that formaldehyde is a carcinogen for humans, it is critically important to use nonformaldehyde alternatives to protect the health of consumers. The capability of polycarboxylic acids to impart flame resistance to cotton provides additional benefits for consumers.

References


