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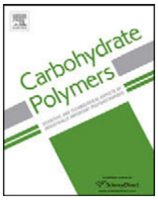

# Nonformaldehyde durable press finishing of cotton fabrics using the combination of maleic acid and sodium hypophosphite

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ABSTRACT

Polycarboxylic acids have been used as nonformaldehyde crosslinking agents for cotton with sodium hypophosphite ($NaH_2PO_2$) as the catalyst to replace the formaldehyde-based dimethyloldihydroxyethleneurea (DMDHEU). Maleic acid (MA), an α, β-unsaturated bifunctional carboxylic acid, can esterify cotton but is not able to form crosslinking between two cellulose molecules by itself. In this research, we discovered that the wrinkle resistance of the cotton fabric treated with MA and $NaH_2PO_2$ was significantly increased and phosphorus was bound to cotton when the treated fabric was exposed to temperatures higher than that required for esterification of cotton by MA. Elevation of the fabric wrinkle resistance and increase in quantity of the phosphorus bound to cotton had similar dependency on curing temperature, on MA concentration, and on $NaH_2PO_2$ concentration. All the data support the hypothesis that H–P–(residual of $NaH_2PO_2$) added to >C=C< of the MA already bound to cotton by esterification, thus forming a new crosslink between two cotton cellulose molecules. The cotton fabrics treated by MA/$NaH_2PO_2$ showed fabric wrinkle resistance similar to that treated with DMDHEU, but the breaking strength and tearing strength of the MA-treated cotton fabrics were significantly improved.

## 1. Introduction

Dimethyloldihydroxyethleneurea (DMDHEU) is a formaldehyde-based crosslinker for cotton and other cellulosic fibers. DMDHEU and its modified "low formaldehyde" versions form ether linkages with cellulose in the presence of a catalyst, such as magnesium chloride ($MgCl_2$). Those reagents have been widely used in textile industry to produce wrinkle resistant and easy-care cotton fabrics and garments since 1980s (Petersen, 1983). DMDHEU is a highly effective durable press finishing agent with excellent laundering durability, little fabric yellowing effects and good fabric hand properties. However, those reagents have fundamental disadvantages due to formaldehyde-release and severe decrease in fabric mechanical strength.

The effectiveness of DMDHEU is based on its two methylol groups, which releases free formaldehyde vapor from treated cotton fabrics during industrial production and home treatments such as laundering and ironing. When the cotton fabric crosslinked by DMDHEU is subjected to multiple laundering cycles, the ether linkages of DMDHEU gradually hydrolyze to become N-methylol groups. Consequently free formaldehyde is released continuously during the entire life of the finished garment (Scheme 1). Both textile workers and consumers are subjected to the health risk caused by formaldehyde vapor released during industrial production and consumer use of durable press finished cotton garments.

In 1987, the U.S. Environmental Protection Agency classified formaldehyde as "a probable human carcinogen" (Environmental Protection Agency, 1989). The risk of formaldehyde exposure was upgraded to "carcinogenic to humans" by the working group of WHO International Agency for Research on Cancer in 2004 (Cogliano et al., 2004). Five of seven most recent case-control studies showed increased risk for people exposed to formaldehyde. Epidemiology studies showed that individuals exposed to formaldehyde in their workplaces are at increased risk of leukemia and brain cancer compared with general public (Beane Freeman et al., 2009; Hauptmann et al., 2009). More specifically, a cohort study observed "an excess in leukaemia mortality among a cohort of formaldeyde exposed garment workers" and the mortality from leukaemia was greatest among workers first exposed in the earliest years and workers with 10 or more years of exposure (Pinkerton, Hein, & Stayner, 2004). Other epidemiology studies also indicated the increased cancer risk and mortality rate as a result of industrial formaldehyde exposure (Coggon, Harris, Poole, & Palmer, 2003; Hauptmann, Lubin, Stewart, Hayes, & Blair, 2003, 2004). The proven link between cancer and exposure to formaldehyde

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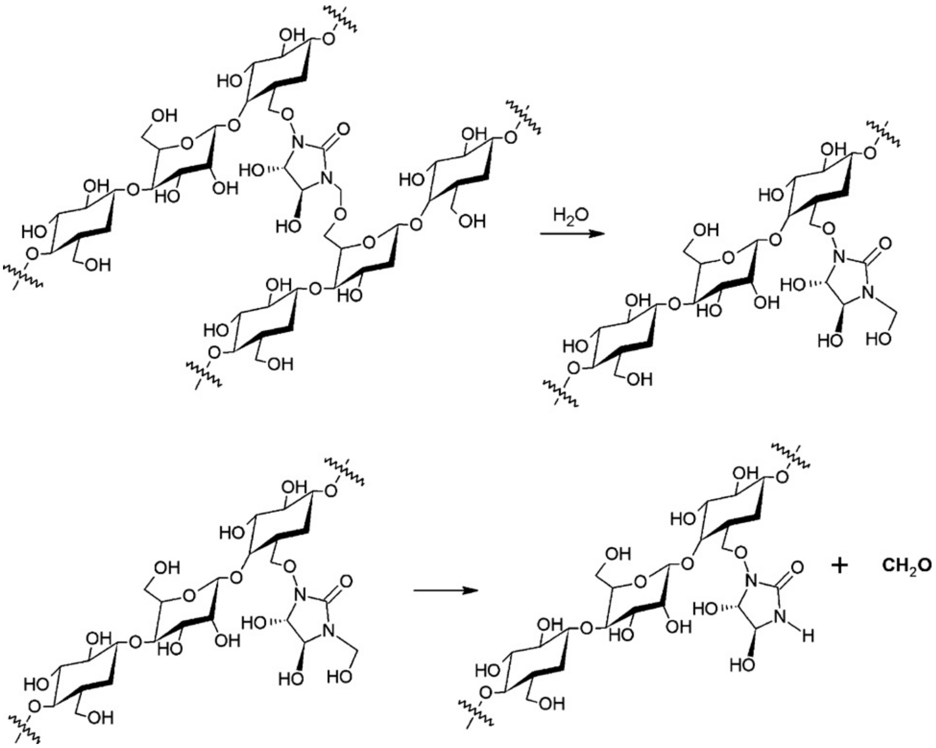


**Scheme 1.** Hydrolysis and formaldehyde release of cotton fabric crosslinked by DMDHEU.

for textile workers also makes it necessary to consider the health risk presented by formaldehyde-containing garments to the vast consumers since consumers are exposed to the low concentration formaldehyde vapor in their entire lives.

In our previous research, we found that magnesium chloride, the most commonly used catalyst for DMDHEU on cotton, caused significant degradation of cotton cellulose and significantly diminished the strength of cotton fabrics (Yang, Wei, & Lickfield, 2000). We found that the cotton fabrics treated with DMDHEU or its modified low formaldehyde versions lost 50–70% of their original breaking strength in order to achieve reasonably high levels of durable press performance (Wei & Yang, 1999, 2000). Severely decreased mechanical strength of the durable press finished cotton fabrics is a major limitation for the current durable press finishing technology based on DMDHEU.

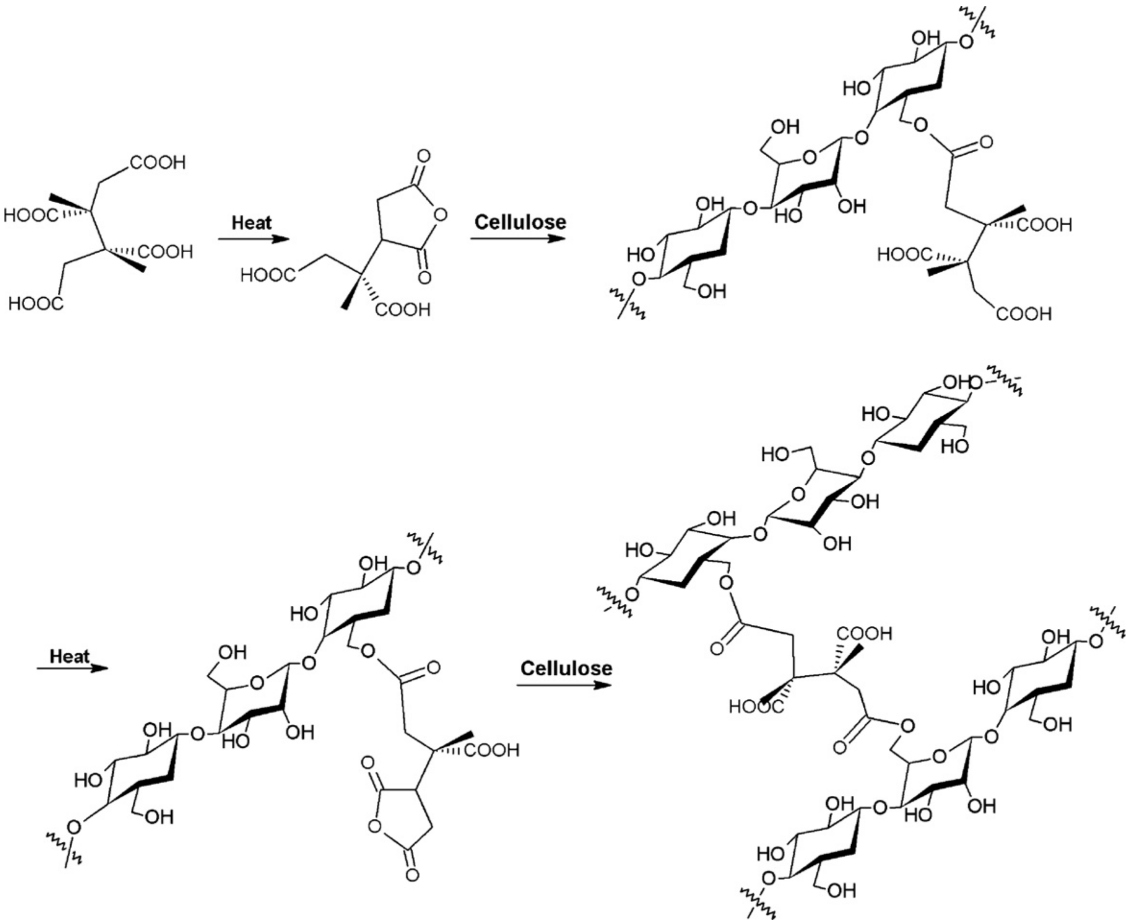
Since the late 1980s, extensive efforts have been made to develop formaldehyde-free crosslinking agents for cotton to replace the traditional formaldehyde-based reagents as durable press finishing agents for cotton (Welch, 1992, 2001). Among those agents investigated, multifunctional carboxylic acids have attracted most attention when Welch discovered sodium hypophosphite as the most effective catalyst (Welch, 1988; Welch & Andrews, 1989). In our previous research, we studied the mechanism of ester crosslinking of cellulose by polycarboxylic acids and found that a polycarboxylic acid esterifies cellulose through the formation of a 5-membered cyclic anhydride intermediate by the dehydration of two carboxylic groups bound to the adjacent carbons in their molecular backbone as shown in Scheme 2 (Yang, 1993; Yang & Wang, 1996a,b, 1997).

In our previous research, we found that oligomers of MA were able to impart high levels of wrinkle resistance to cotton fabrics (Chen, Yang, & Qiu, 2005). MA, an α, β-unsaturated dicarboxylic acid, can only form a single ester linkage with cellulose, and it is not able 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 $NaH_2PO_2$ was used as a catalyst. Such phenomenon was not observed when the cotton fabric was treated with combinations of succinic acid/$NaH_2PO_2$ or MA/$Na_2HPO_3$ (Yang, Chen, Guan, & He, 2010). Thus, the experimental evidence suggested that the reaction between $NaH_2PO_2$ and two MA molecules already esterified with cotton forms a crosslinkage between two cellulose molecules as shown in Scheme 3. The objective of this research was to evaluate the effectiveness of combination of MA and $NaH_2PO_2$ as a crosslinking system for cotton. We also compared the performance of MA/$NaH_2PO_2$ with that of DMDHEU as durable press finishing agents for cotton fabrics.

## 2. Experimental

### 2.1. Materials

Two cotton fabrics were used in this study: (a) a desized, scoured and bleached plain weave cotton printcloth weighing 109 g/m$^2$ (Testfabrics style 400) produced by Testfabrics, West Pittston, PA; and (b) a 3/1 twill weave Khaki cotton fabric weighing 264 g/m$^2$ produced by Milliken, Blacksburg, SC. MA and $NaH_2PO_2$ were reagent grade chemicals supplied by Aldrich, Milwaukee, WI. The modified low-formaldehyde DMDHEU with the trade name of "Freerez 845", which was 45% modified DMDHEU pre-mixed with the catalyst ($MgCl_2$), was supplied by Emerald Carolina Chemical, Charlotte, NC. The non-ionic wetting agent with commercial name of "Triton X-100" was supplied by Bio-Rad Laboratories, Hercules, CA. The aminofunctional silicon softener with the commercial name of "DM-3362" was supplied by Dymatic Chemicals, Shunde, China. The concentrations (w/w) of MA and $NaH_2PO_2$ were based on 100% active ingredient, whereas those of DMDHEU, the silicon softener and the wetting agent were based on the weight of commercial products.



**Scheme 2.** Ester crosslinking of cotton by BTCA.

### 2.2. Fabric treatment

A cotton fabric specimen was first impregnated in an aqueous solution containing a crosslinking agent, a catalyst and other additives, and then padded with two dips and two nips using a laboratory padder to reach average wet pickup of ∼100% and ∼80% (w/w) for the plain weave and the twill weave fabrics, respectively. The impregnated fabrics were dried at 85 °C for 3 min for the plain weave fabric and 5 min for the twill weave fabric, and finally cured at a specified temperature in a curing oven manufactured by Werner Mathis, Oberhasli, Switzerland. The fabric thus treated was finally subjected to one home laundering washing/drying cycle to remove the catalyst and other additives not bound to cotton according to AATCC Standard Method 124 using a standard reference detergent (“AATCC Detergent 1993”). The water temperature for laundering was approximately 46 °C.

### 2.3. Fabric performance evaluation

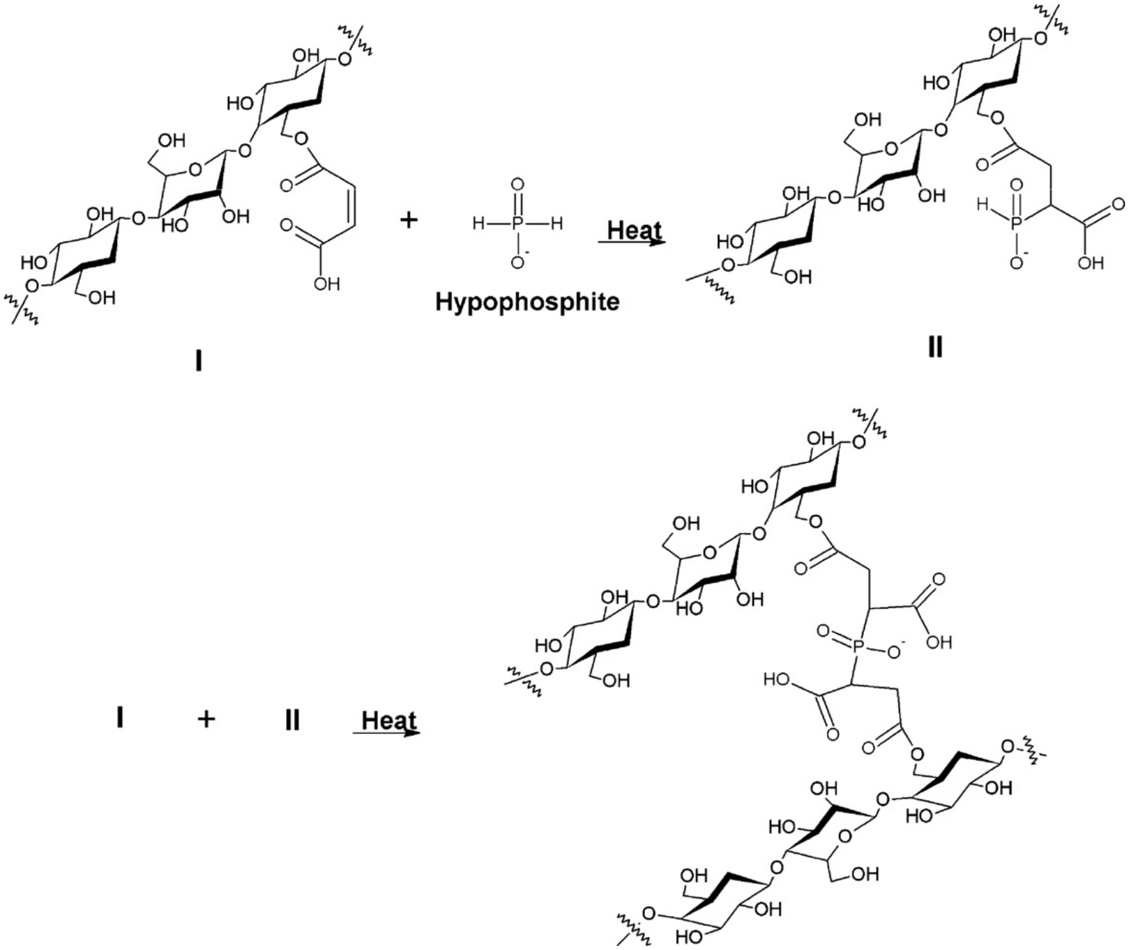
The treated samples were conditioned at 65 ± 2% relative humidity and 20 ± 1 °C at least for 24 h prior to testing. Breaking strength and tearing strength of the samples were measured in accordance with ASTM D5035 and ASTM D1424 (Elmendorf-Type), respectively. The conditioned wrinkle recovery angles (WRA) were evaluated according to AATCC Test Method 66 (Option 2).

### 2.4. FT-IR spectroscopy analysis

The FT-IR spectra were collected using a Nicolet 760 Magna FT-IR spectrometer with a Specac diffuse reflectance accessory. All the infrared spectroscopy data were diffuse reflectance spectra presented as absorbance ($-\log R/R_0$). There were 100 scans for each sample with a resolution of 4 $\text{cm}^{-1}$. No smoothing functions and baseline correlation were used. To measure the intensity of the ester carbonyl band, the treated cotton fabric was first subjected to one home laundering cycle to remove the unreacted acid and catalyst, and then treated with a 0.1 M NaOH solution at room temperature for 4 min to convert free carbonyl on the fabric to carboxylate anion so that the ester carbonyl band could be separated from that of the overlapping carboxylic acid carbonyl. The samples thus treated were dried at 90 °C for 2 min and finally ground in a Willey mill to form a powder before it was analyzed by the FT-IR spectrometer to quantify the amount of ester formed on a fabric sample. The ester carbonyl band absorbance in the infrared spectra was normalized against the 1317 $\text{cm}^{-1}$ band associated with the C–H bending mode of cellulose. This method was developed in our previous research (Yang, 1991; Yang & Andrews, 1991; Yang & Bakshi, 1996).

### 2.5. Determination of phosphorous concentration of treated cotton fabric

Prior to testing, the treated fabric samples were conditioned for 24 h. Approximately 2 g of the treated sample taken from five different parts in a “30 cm × 30 cm” fabric specimen were grounded in a Willey mill to form powder, and the powder was thoroughly mixed in the mill to achieve high uniformity. 2 mL of concentrated sulfuric acid was added to 0.1 g (precisely weighed) of the powder in a beaker. 10 mL of 30% hydrogen peroxide was slowly added dropwise to the mixture, allowing the reaction to subside between



**Scheme 3.** Crosslinking of cellulose by MA and $NaH_2PO_2$.

drops. The reaction mixture was heated at 250 °C to digest the powder and to evaporate the water until the dense $SO_3$ vapor was produced. The completely digested sample as a clear solution was transferred to a 50 mL volumetric flask and then diluted with deionized water to the mark. The sample thus prepared was analyzed with a Thermo-Farrell-Ash (Model 965) inductively coupled plasma atomic emission spectrometer to determine the phosphorus concentration.

## 3. Results and discussion

### 3.1. The chemical reactions of MA on cotton

Presented in Fig. 1A is the infrared spectrum of the untreated cotton fabric. The cotton fabric was treated with 6.0% MA, and its spectrum is shown in Fig. 1B. The intense and broad band at 1729 $cm^{-1}$ is due to the stretching mode of carboxy carbonyl of MA (Yang, 1991; Yang & Andrews, 1991). The treated cotton fabric was cured at 180 °C for 2 min (Fig. 1C). Two distinct bands at 1852 and 1778 $cm^{-1}$ appearing in Fig. 1C are due to the symmetric and asymmetric carbonyl stretching modes, respectively, of a 5-membered cyclic anhydride (Bellamy, 1975; Scocrates, 1994), and the carbonyl bands carboxy and ester, which was formed between MA and cotton at curing, overlaps at 1729 $cm^{-1}$ (Yang, 1991; Yang & Andrews, 1991). The broad bands at 1644 $cm^{-1}$ in Fig. 1A is due to the bending mode of the hydrogen-bonded hydroxy group of cellulose. It is evident that MA forms 5-membered anhydride on cotton under elevated temperatures as shown in Fig. 1C. The infrared spectra of the cotton fabrics treated with various polycarboxylic acids, including cotton, were discussed in details previously (Yang & Lu, 1999; Yang & Wang, 1996a). Previously, we also observed that the two anhydride carbonyl bands of MA at 1852 and 1778 $cm^{-1}$ increases their intensity as the curing temperature is increased from 130 to 180 °C, indicating that more anhydride is formed on the MA-treated cotton fabric at higher temperatures (Yang et al., 2010).

The cotton fabric treated with 6.0% MA and 4% $NaH_2PO_2$, and cured at different temperatures for 2 min was subjected to one

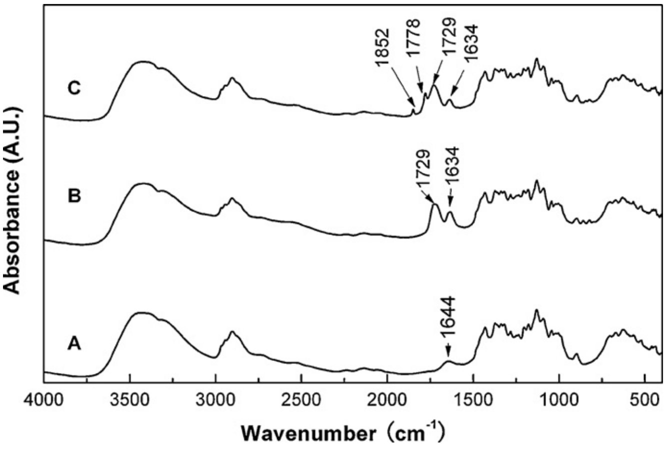


**Fig. 1.** FT-IR spectra of (A) untreated cotton, (B) cotton treated with 6.0% MA and dried at 80 °C and (C) cotton thus treated and cured at 180 °C for 2 min.

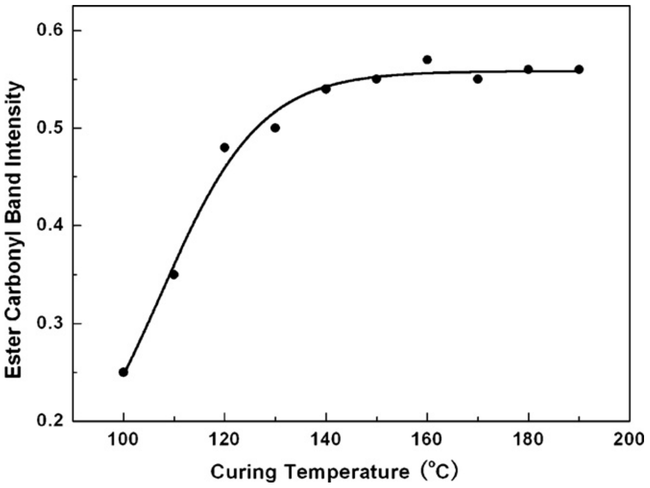


**Fig. 2.** The ester carbonyl intensity of the cotton fabric treated with 6.0% MA and 4.0% $NaH_2PO_2$, cured at different temperatures for 2 min, subjected to 1 home laundering cycle and finally with a 0.1 M NaOH solution.

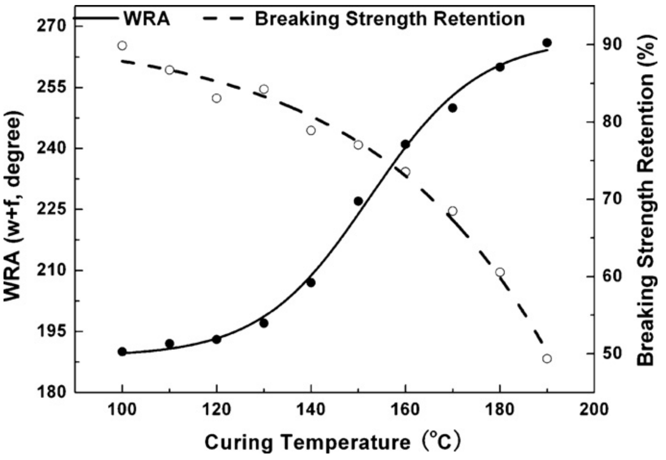


**Fig. 4.** The WRA and breaking strength retention of the cotton fabric treated with 8.0% MA and 4.0% $NaH_2PO_2$, cured at different temperatures for 2 min, and subjected to 1 home laundering cycle.

home laundering cycle followed by treatment using 0.1 M NaOH to convert the free carboxylic group to carboxylate anion so that the intensity of the ester band around 1730 $cm^{-1}$ could be used as the basis for quantitative measurement of the ester formed on the treated cotton fabric (Yang, 1991; Yang & Andrews, 1991). The intensity of the ester carbonyl band of the cotton fabric thus treated is presented against the curing temperature in Fig. 2. The ester carbonyl band intensity increases significantly from 0.25 to 0.54 as the curing temperature is increased from 100 to 140 °C, respectively, indicating that the esterification of cotton cellulose by MA is accelerating as the curing temperature is increased. As the curing temperature is increased further from 140 to 190 °C, the ester carbonyl band intensity shows little increase (Fig. 2). Thus, the data presented here demonstrated that in the presence of $NaH_2PO_2$ as the catalyst, the esterification of MA took place at low curing temperatures, and the esterification reaches the maximum range when the curing temperature reaches ≥140 °C (Fig. 2).

The cotton fabric was treated with 8.0% MA and 4% $NaH_2PO_2$, cured at different temperatures for 2 min and subjected to one home laundering cycle. The phosphorus concentration of the cotton fabric thus treated is presented as a function of curing temperature in Fig. 3. Phosphorus concentration of the treated cotton fabric increases modestly from 0.026% to 0.146% as the curing temperature is increased from 100 to 140 °C, indicating the bonding of $NaH_2PO_2$ to cotton cellulose. $NaH_2PO_2$ has been used as a catalyst for the esterification of cotton by a polycarboxylic acid (Welch, 1992, 2001). The data presented in Fig. 3 also indicate that the bonding of $NaH_2PO_2$ accelerates as the curing temperature is increased above 140 °C. When the curing temperature is increased form 140 to 190 °C, the phosphorus concentration is increased drastically from 0.146% to 0.813% (Fig. 3). It is evident that the bonding of $NaH_2PO_2$ to cotton and the esterification of cotton by MA have different temperature-dependency, and that the bonding of $NaH_2PO_2$ to cotton requires significantly higher temperature than the esterification of cotton by MA.

We further investigated the wrinkle resistance and breaking strength of the cotton fabric treated described above (Fig. 4). The WRA of the plain weave cotton fabric is 190 before treatment, and it increases slightly from 190 to 207 °C as the curing temperature is increased from 100 to 140 °C, indicating little crosslinking on the cotton fabrics. As the curing temperature is increased from 140 to 190 °C, however, the WRA of the treated fabric is increased considerably from 207 to 266° (Fig. 4). The slope of the WRA versus temperature curve shows a significant rise as the curing temperature is increased above 140 °C (Fig. 4). Elevation of WRA of the treated cotton fabric is a convincing evidence of crosslinking of

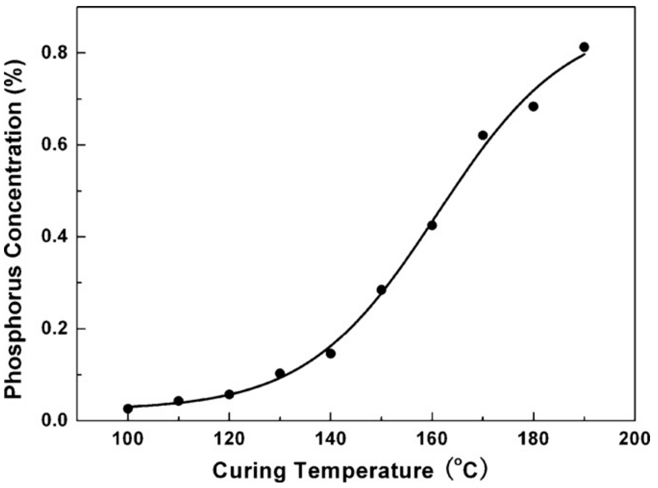


**Fig. 3.** The phosphorus concentration of the cotton fabric treated with 8.0% MA and 4.0% $NaH_2PO_2$, cured at different temperatures for 2 min, and finally subjected to 1 home laundering cycle.

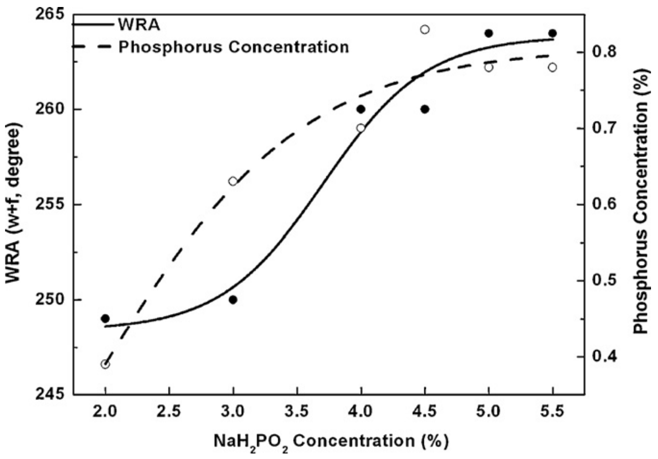


**Fig. 5.** The WRA and phosphorus concentration of the cotton fabric treated with 8.0% MA and $NaH_2PO_2$ of different concentrations, cured at 180 °C for 2 min and subjected to 1 home laundering cycle.

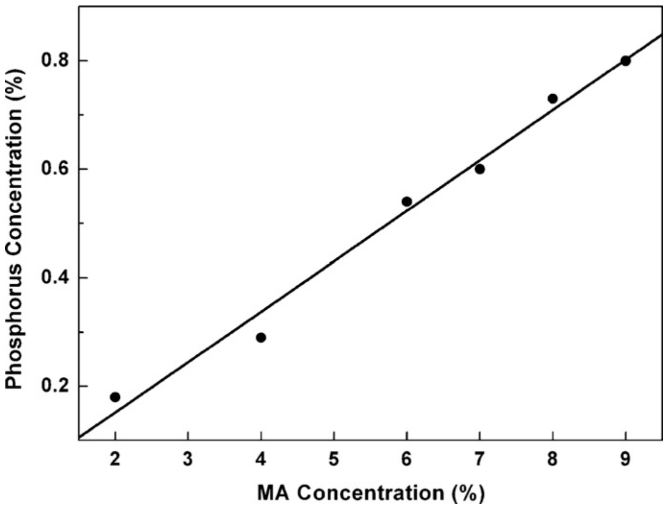


**Fig. 6.** The phosphorous concentration of the cotton fabric treated with 5.0% $NaH_2PO_2$ and MA of different concentrations, cured at 180 °C for 2 min, and subjected to 1 home laundering cycle.

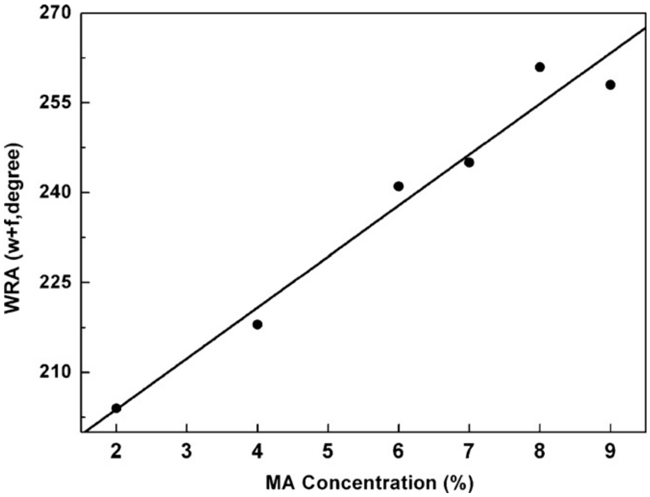


**Fig. 7.** The WRA of the cotton fabric treated with 5.0% $NaH_2PO_2$ and MA of different concentrations, cured at 180 °C for 2 min, and subjected to 1 home laundering cycle.

cotton cellulose as reported previously (Wei & Yang, 1999). Comparing the WRA versus curing temperature curve in Fig. 4 with the phosphorus concentration versus curing temperature curve in Fig. 3 reveals that those two curves have very similar slope, indicating crosslinking of cellulose and bonding of phosphorus to cotton have similar temperature-dependency. Figs. 3 and 4 also show that the bonding of $NaH_2PO_2$ to cotton and crosslinking cotton are taking place simultaneously at the same temperature range. The data presented here support the hypothesis that H–P–H of $NaH_2PO_2$ adds to >C=C< of the MA bound to cotton by esterification, thus bonding phosphorus to cotton. Crosslinking cotton cellulose takes place when one $NaH_2PO_2$ molecules react with two MA molecules as shown in Scheme 3.

In our previous research, we reported that the strength loss of the cotton fabrics crosslinked by a polycarboxylic acid was caused by acid-catalyzed cellulose depolymerization and crosslinking of cotton cellulose (Kang, Yang, Wei, & Lickfield, 1998). Presented in Fig. 4 is the percent breaking strength retention of the treated cotton fabric in warp direction, which is calculated based on the breaking strength of the fabric before and after the MA/$NaH_2PO_2$ treatment. When the treated fabric was cured at 100 °C, its breaking strength retention is 90%. The strength retention decreases to 79% as the curing temperature is increased to 140 °C, which represents 11% decrease of the original fabric strength. We observe in Fig. 4 that as the curing temperature is increased above 140 °C, the slope of the strength retention versus temperature curve becomes more negative, indicating an increase in the magnitude of strength loss as a function of higher curing temperature. The strength retention decreases from 79% to 49% as the curing temperature is increased from 140 to 190 °C. Such a change shown in Fig. 4 is obviously due to the crosslinking of cotton taking place above 140 °C. Thus, the fabric strength data presented in Fig. 4 support the hypothesis that the reaction between $NaH_2PO_2$ and MA forms crosslinking on the cotton at higher curing temperature as discussed above.

We evaluated the WRA and phosphorus concentration effected by changes of concentrations of $NaH_2PO_2$ and MA. The cotton fabric is treated with the combination of 8.0% MA and $NaH_2PO_2$ at different concentrations and then cured at 180 °C for 2 min. The WRA and phosphorus concentration of the cotton fabric thus treated are presented in Fig. 5. The data presented here demonstrate that both WRA and phosphorus concentration of the cotton fabric treated with 8.0% MA increases as the concentration of $NaH_2PO_2$ increases (Fig. 5). The similar dependency of WRA and phosphorus concentration of the treated cotton on the $NaH_2PO_2$ concentration shown in Fig. 5 supports the hypothesis that a chemical reaction takes place between MA/$NaH_2PO_2$ and cotton (Scheme 3).

Presented in Fig. 6 is phosphorus concentration of the cotton fabric treated with 5.0% $NaH_2PO_2$ and MA at different concentrations and cured at 180 °C for 2 min. Only 0.18% of phosphorus is bound to cotton when the MA concentration is 2.0%. As the MA concentration is increased to 8.0%, the phosphorus concentration also increases to 0.72% (Fig. 6). The phosphorus concentration versus MA curve appears to have a perfect linear correlation with $R^2 = 0.99$ in Fig. 6. The WRA of the cotton fabric treated with 5.0% $NaH_2PO_2$ and MA is shown against the MA concentrations in Fig. 7. The WAR versus MA concentration curve also show a linear correlation with $R^2 = 0.98$ in Fig. 7. The same dependency of both WRA and phosphorus concentration on the MA concentration demonstrated in Figs. 6 and 7 provides another piece of evidence to support the hypothesis that the reaction between $NaH_2PO_2$ and MA to form crosslinking on the treated cotton fabric.

The cotton fabric was first treated with 10.0% MA in combination with 4.0% $NaH_2PO_4$ as a catalyst, and was then cured at 160 °C for 2 min and subsequently subjected to 1 home laundering cycle. $NaH_2PO_4$ was reported as one of the effective catalysts for the

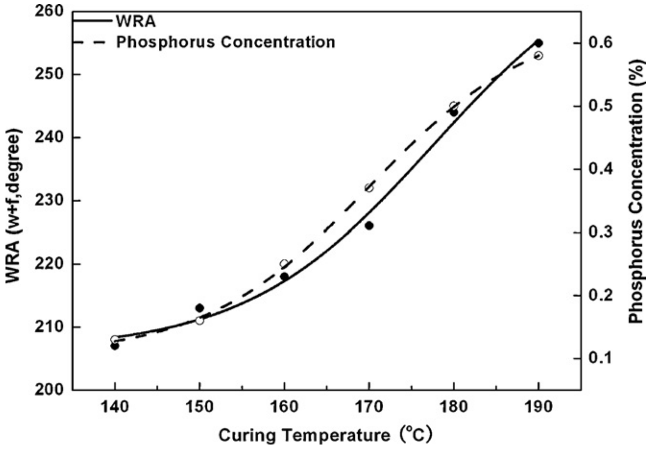


**Fig. 8.** The WRA and phosphorous concentration of the cotton fabric first treated with the combination of 10.0% MA and 4.0% $NaH_2PO_4$, cured at 160 °C for 2 min and subjected to 1 home laundering cycle, and was then treated with 6.0% $NaH_2PO_2$, cured at different curing temperatures (140–190 °C) and finally subjected to 1 home laundering cycle.

**Table 1**
The durable press performance and mechanical properties of the plain weave cotton fabric treated with MA/$NaH_2PO_2$ and DMDHEU.

| Finish formulation[a] (%) | Curing condition | WRA (w + f, degree) | | | | DP rating | | | | Breaking strength (*N*) ± SD[b] | | Breaking strength retention (%) | | Tearing strength (*N*) ± SD | Tearing strength retention (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | No. of laundering cycles | | | | | | | | Warp | Filling | Warp | Filling | Filling | Filling |
| | | 1 | 10 | 20 | 30 | 1 | 10 | 20 | 30 | | | | | | |
| 8.0MA; 5.0 $NaH_2PO_2$ | 175 °C 2 min | 275 | 262 | 256 | 254 | 3.7 | 3.4 | 3.3 | 3.0 | 153±4 | 91±8 | 52 | 46 | 12.9±0.5 | 57 |
| 10.5 DMDHEU | 160 °C 2 min | 274 | 262 | 257 | 257 | 3.6 | 3.4 | 3.2 | 3.0 | 124±5 | 74±13 | 42 | 38 | 11.6±0.4 | 51 |
| Control | – | | | | 190 | | | | – | 296±4 | 197±10 | – | – | 22.7±0.4 | – |

[a] The formulations contain 3.0% silicon softener and 0.1% wetting agent.
[b] SD: standard deviation.

**Table 2**
The durable press performance and mechanical properties of the twill weave cotton fabric treated with MA/$NaH_2PO_2$ and DMDHEU.

| Finish formulation[a] (%) | Curing condition | WRA (w + f, degree) | | | | DP rating | | | | Breaking strength (*N*) ± SD[b] | | Breaking strength retention (%) | | Tearing strength (*N*) ± SD | Tearing strength retention (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | No. of laundering cycles | | | | | | | | Warp | Filling | Warp | Filling | Filling | Filling |
| | | 1 | 10 | 20 | 30 | 1 | 10 | 20 | 30 | | | | | | |
| 8.0MA; 5.0 $NaH_2PO_2$ | 175 °C 3 min | 260 | 250 | 241 | 234 | 3.7 | 3.5 | 3.2 | 3.0 | 371±9 | 218±4 | 56 | 58 | 16.5±0.3 | 100 |
| 12.5 DMDHEU | 160 °C 3 min | 257 | 249 | 243 | 239 | 3.8 | 3.5 | 3.3 | 3.0 | 298±6 | 149±12 | 45 | 40 | 14.2±0.4 | 87 |
| Control | – | | | | 170 | | | | – | 662±4 | 377±10 | – | – | 16.4±0.4 | – |

[a] The formulations contain 3.0% silicon softener and 0.1% wetting agent.
[b] SD: standard deviation.

esterification of cotton by polycarboxylic acids even it is less effective than $NaH_2PO_2$ (Brown & Tomasino, 1991). After one home laundering procedure, abundant singly bound MA exists on the treated cotton fabric. The fabric thus treated is further treated with 6.0% $NaH_2PO_2$ in a second step, cured at different curing temperatures for 2 min and finally subjected to another home laundering cycle. The WRA and phosphorus concentration of the cotton fabric treated with the 2-step procedure described above are presented in Fig. 8. When the treated fabric is cured at 140 °C in the 2nd step treatment, the WRA and phosphorus concentration are 207° and 0.13%, respectively, indicating that the wrinkle resistance of the treated fabric is limited and the phosphorus concentration is small. As the curing temperature is increased $\geq$150 °C, both phosphorus concentration and WRA increase significantly. The temperature dependency of phosphorus concentration and WRA on curing temperature shown in Fig. 8 appears to be almost identical, and they are also similar to that of the cotton fabric treated with the combination of MA and $NaH_2PO_2$ shown in Figs. 3 and 4. It is evident that $NaH_2PO_2$ is able to react and to crosslink the cotton fabric already esterified by MA. This is yet another piece of experimental evidence to support the reaction mechanism shown in Scheme 3. It should be pointed out that bonding phosphorus to cotton reduces flammability of the treated cotton (Yang, He, & Voncina, 2011).

### *3.2. Performance of the cotton fabrics treated with MA/$NaH_2PO_2$*

The durable press performance and mechanical properties of the plain weave cotton fabric treated with MA/$NaH_2PO_2$ and that treated with a modified low-formaldehyde DMDHEU are presented in Table 1. The WRA of the cotton fabrics treated with MA/$NaH_2PO_2$ and with DMDHEU are 275° and 274°, respectively, after one laundering cycle. Both treated fabrics show very similar DP rating. During the 30 home laundering cycles, the two treated fabrics also have gradually reduced and very similar WRA and DP ratings (Table 1). After 30 home laundering cycles, the fabrics treated with MA/$NaH_2PO_2$ and with DMDHEU have WRA of 254° and 257°, respectively. Apparently, the cotton fabric treated with MA/$NaH_2PO_2$ and that treated with DMDHEU demonstrate similar hydrolysis resistance and similar wrinkle resistance after the 30 launderings. Thus, we can conclude that the cotton fabric crosslinked by MA/$NaH_2PO_2$ has durable press performance and laundering durability similar to that crosslinked by DMDHEU under those curing conditions.

Also shown in Table 1 are the breaking strength and tearing strength of the fabric treated with MA/$NaH_2PO_2$ with standard deviation included. The data presented in Table 1 show that the breaking strength of the fabric treated with MA/$NaH_2PO_2$, are 29 and 17 N higher in warp and filling directions, respectively, than that treated with DMDHEU, which represents 23% and 28% improvement, respectively. The data also show that the tearing strength of the fabric treated with MA/$NaH_2PO_2$ is 11% higher in the filling direction than that treated with DMDHEU. It is apparent that MA/$NaH_2PO_2$ as a durable press system causes significantly lower loss in the mechanical strength of the durable press finished cotton fabrics.

The MA/$NaH_2PO_2$ and DMDHEU systems are also applied to a twill weave cotton fabric. The durable press performance and mechanical properties of the cotton fabrics thus treated are listed in Table 2. The cotton fabric treated with MA/$NaH_2PO_2$ has WRA of 260° after one laundering cycle whereas that treated with DMDHEU has WRA of 257° (Table 2). The WRA and DP rating of the cotton fabrics treated with MA/$NaH_2PO_2$ and with DMDHEU are very similar during the entire 30 laundering cycles as shown in Table 2. However, the breaking strength of the fabric treated with MA/$NaH_2PO_2$ is 24% and 46% higher in the warp and filling directions, respectively, than those treated with DMDHEU, whereas the tearing strength of the same treated fabric is 15% higher in the filling direction. Thus, the data presented here provide ample evidence to show the superior mechanical strength of the cotton fabric treated with the MA/$NaH_2PO_2$ system.

In this research, we applied those two durable press finishing systems to two fabrics which have different thickness, different structures and different wet pick-up. Those two fabrics represent the majority fabrics treated by durable press finishes in the industry. We included standard deviation (SD) for the breaking strength and tearing strength data in Tables 1 and 2. We can see that the breaking strength of plain weave fabric at filling direction has much higher SD and higher coefficient of variation than those for the other strength data (Tables 1 and 2). Nevertheless, both the data of the plain weave fabric and that of the twill weave fabric demonstrate the same phenomenon that the fabrics treated with MA/$NaH_2PO_2$ have higher breaking strength and higher tearing strength.

Severely reduced fabric mechanical properties, including breaking strength, tensile strength and abrasion resistance, are a major downside of the wrinkle-resistance cotton fabrics (Kang et al., 1998; Yang, Qian, & Lickfield, 2001). The significantly improved mechanical properties must be considered as a major advantage of the MA/$NaH_2PO_2$ system over the traditional formaldehyde based DMDHEU system.

## 4. Conclusions

The wrinkle resistance of the cotton fabrics was achieved by the following two reactions: (1) the esterification of cotton cellulose by MA; and (2) the addition of H–P–(residual of $NaH_2PO_2$) to >C=C< of MA, which takes place at temperatures significantly higher than those of the esterification of cellulose. The addition reaction crosslinks cotton cellulose, thus imparting wrinkle resistance to the cotton fabrics.

The cotton fabrics treated by the combination of MA and sodium hypophosphite showed fabric wrinkle resistance similar to that treated with an N-methylol reagent (DMDHEU) with significantly less fabric strength loss. The combination of MA and $NaH_2PO_2$ is a formaldehyde-free, odor-free and cost-effective durable press finishing system with superior fabric strength retention. Therefore, it has potential to become an effective and low cost alternative nonformaldehyde durable press finishing system to replace the formaldehyde-based DMDHEU currently used in the textile industry.

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