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Durable Press Finish of Cotton Fabric Using Malic Acid as a Crosslinker

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Abstract: It has been considered that malic acid, α-hydroxy succinic acid, could not form crosslinks in the cellulosic materials unless activated by other polycarboxylic acids such as butanetetracarboxylic acid or citric acid because there are only two carboxylic acids per molecule available for the formation of one anhydride intermediate. However we found that the dicarboxylic malic acid with sodium hypophosphite catalyst without the addition of other crosslinkers was able to improve wrinkle resistance of cotton up to 294° (dry WRA) and 285° (wet WRA), which is a measure of crosslinking level in cotton. ^{1}H FT-NMR, FT-IR and GPC analysis indicated the in-situ formation of an trimeric α, β-malic acid with a composition of 1:3 through the esterification between hydroxyl group and one of carboxylic groups in malic acid during curing. The crosslinking of cotton was attributed to the trimeric α, β-malic acid, a tetracarboxylic acid, which can form two anhydride rings during curing. The influence of crosslinking conditions such as concentrations of malic acid and catalyst, pH of the formulation bath, and curing temperature were investigated in terms of imparted wrinkle resistance and whiteness. The addition of reactive polyurethane resin in the formulation slightly increased the mechanical strength retention of crosslinked fabric coupled with additional increase in wrinkle resistance.

Keywords: Malic acid, Sodium hypophosphite, Crosslinking, Trimeric malic acid, Wrinkle resistance

Introduction

Polycarboxylic acids such as 1,2,3,4-butanetetracaboxylic acid(BTCA) and citric acid(CA) have been studied as formaldehyde-free crosslinkers for durable-press finish which could be substituted for conventional dimethyloldihydroxyethyleneurea(DMDHEU)[1,2]. Among the formaldehyde-free polycarboxylic acids, the BTCA with sodium hypophosphite(SHP) catalyst has been best known for superior performances such as excellent durable press appearance, high fabric strength retention and degree of whiteness, and durability to repeated laundering[3]. In spite of its highest effectiveness, the commercial use of BTCA treatment has been deterred due to the significantly higher cost of BTCA compared with the present formaldehyde-based agent. While CA can form durable crosslinking between cellulose molecules, the treatment inevitably causes excessive yellowing in spite of lower cost compared with BTCA treatment[2]. The esterifcation of cellulose by BTCA or CA occurs in two steps: the formation of a five-membered cyclic anhydride intermediate by the dehydration of two carboxyl groups, and subsequent esterification between the anhydride intermediate and the cellulose[4].

Malic acid, α-hydroxy succinic acid, has been considered as incapable of forming ester crosslinks between cellulose molecules and undergoing single-ended attachment to cellulose because three or more carboxyl groups per molecule are required for the generation of two anhydride intermediates during curing. Therefore moderate amount of tri- or tetra-carboxylic acids such as citric acid or BTCA were added, which couple and esterify the hydroxyl group of malic acid forming such intermediates as heptacarboxylic acid or other multicarboxylic acid during curing[5,6]. In the curing of the mixed formulation of tartaric acid and citric acid, the in-situ formation of hexacarboxylic acid or alternating copolymer were proposed to explain higher durable press appearance rating and wrinkle recovery angle of treated fabric[7]. It has been reported that polymers of maleic acid in combination with citric acid can synergistically improve the effectiveness of citric acid as a cellulose crosslinker by the esterification of hydroxyl group of citric acid with anhydride intermediate of poly maleic acid, as verified in the FT-IR analysis[8,9].

Although malic acid itself has not been used as an effective crosslinker unless activated with other polycarboxylic acids, we discovered that malic acid in combination with SHP catalyst enhanced the wrinkle recovery angle of cotton fabric up to 294°(dry WRA) and 285°(wet WRA), coupled with marginally decreased mechanical strength. The improvement in wrinkle resistance of treated fabric may be attributed to the existence of oligomers presumably having three or more carboxylic groups per molecule. From the analysis of purified oligomer formed under curing condition, it was found that trimeric α, β-malic acid, a tetracarboxylic acid, was formed under curing condition. The in-situ catalytic esterification of cellulose by the oligomeric malic acid would be responsible for the improved wrinkle resistance. The effect of polyurethane resin addition in the malic acid formulation was also investigated in relation with the mechanical properties of the crosslinked cotton.

Experimental

Materials

Bleached plain weave cotton fabric(109 g/m^2) was used throughout this study. *d,l*-Malic acid(MA, hydroxybutanedioic

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*Corresponding author: sohkwonk@gong.snu.ac.kr acid) and sodium hypophosphite monohydrate ($NaH_2PO_2 \cdot H_2O$, SHP) were obtained from Junsei Chemical Co. and Shinyo Pure Chemical Co. respectively. Other chemicals used were all reagent grade. Triton X-100 was used as a wetting agent. As an additive, Elastron MF-25 and Elastron Catalyst 64, a water-soluble urethane resin and catalyst, were supplied from Daeyoung Chemical Co., which was formulated to improve mechanical properties of the crosslinked cotton fabrics. All chemicals were used as received.

Fabric treatment

All fabrics were impregnated by padding twice through the liquor trough to give an approximately 70±3% wet pick up with an aqueous formulation containing various amount of malic acid and SHP with 0.1%(w/w) Triton X-100. The padded samples were dried at 85°C for 3 min and cured at 180°C for 3 min on a pin stenter(Daiei Kagakuseiki Mfg. Ltd., Japan) unless indicated otherwise. The cured fabrics were washed with water at 50°C and dried as mentioned above.

Analysis of untreated and crosslinked cotton fabrics

The testing methods used to evaluate performance properties of the treated fabric were as the following: dry wrinkle recovery angle by AATCC 66-1984, breaking strength and elongation by ASTM D 5035-90(strip method), Elmendorf tear strength by ASTM D 1424-83, stoll flex abrasion resistance by ASTM D 3885-92 and whiteness index by AATCC 110-1989. Wet wrinkle recovery angle was measured by the same method described in the AATCC 66-1984 except that the samples were immersed in distilled water at least 20 minutes and excess water on the fabric was blotted with filter paper before testing.

FT-IR spectra of untreated and crosslinked cotton were also obtained with an FT-IR spectrophotometer(Perkin-Elmer 1725 X) using potassium bromide pellet technique. Ester carbonyl band in the infrared spectra was separated from the carboxyl carbonyl band by treating the finished fabric with 0.1 N NaOH solution for 2 minutes at room temperature. A Seiko SSC/5200 thermal analyser was used to perform thermogravimetric(TG) analysis of crosslinked cotton fabrics. A sample of constant weight was held at 50°C and heated to 500°C at a heating rate of 20°C/min.

Characterization of oligomeric malic acid

For the analysis of oligomeric malic acid formed during curing condition, oligomeric malic acid was prepared and purified as follows: 5 g malic acid and 0.8 g sodium hypophosphite were mixed together and the mixture, placed in a perforated aluminium container, was subsequently cured at 180°C for 3 min in the pin stenter. The unreacted malic acid, sodium hypophosphite, and other by products in the cured product were removed by the following purification steps:[10] the cured product was dissolved in tetrahydrofuran and the dissolved portion was then poured into excess amount of 1:1 n-hexane/diethylether (w/w) mixed solution. The reprecipitated oligomeric malic acid was used for analysis. FT-IR spectra of malic acid and oligomeric malic acid were obtained with an FT-IR spectrophotometer(Perkin-Elmer 1725 X). 500 MHz ^{1}H n.m.r. spectrum were recorded by using a Bruker FT-NMR spectrophotometer(DPX 500) in D_2O. Molecular weight and polydispersity of the oligomeric malic acid as referred to polystyrene standards were evaluated by using a Viscotek GPC apparatus(Model 250) equipped with a column and refractive index detection.

Results and Discussion

Effect of crosslinking conditions on wrinkle resistance

The amount of ester crosslinking formed on the fabric was estimated by the wrinkle recovery angles of the fabrics which was treated by a combination of such factors as malic acid concentration, catalyst concentration, pH of the formulation bath, and curing temperature, etc. The optimal crosslinking conditions of malic acid/SHP system were investigated in relation with wrinkle resistance and whiteness of treated cotton.

The effect of malic acid application level on the wrinkle recovery angle was shown in Figure 1. The wrinkle recovery angle of treated cotton fabric increased proportionally with increasing malic acid concentration in the formulation from 4 to 16%(w/w), obviously implying that malic acid treatment introduced considerable crosslinkage in the treated cotton. However the extent of increase was leveled off at higher application level than 16% and thus following

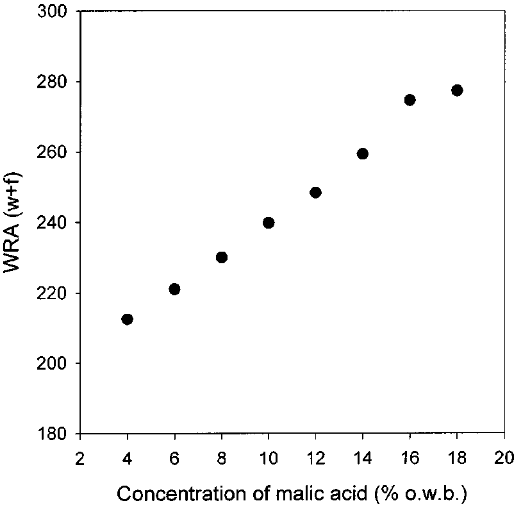


Figure 1. Effect of malic acid concentration on the wrinkle recovery angle of cotton fabrics. Treatment condition: SHP conc., 0.2 mol ratio with respect to mol malic acid; curing temperature, 170°C; curing time, 3 min.

experiments was done with optimal malic acid concentration of 16%. Higher application levels required, compared to BTCA or CA, implied that true crosslinker is not malic acid itself but oligomers of malic acid formed during curing as discussed later. Previous studies using malic acid as a crosslinker component did not report the remarkable crosslinking ability of malic acid possibly due to low application level they used[5,9].

The composition of SHP in the formulation, an esterification catalyst, also significantly affected the imparted crosslinking level as shown in Figure 2. While 0.1 mol ratio of SHP/malic acid was enough to achieve as high as 280 degree of wet wrinkle recovery angle, 0.2 mol ratio was required for both good dry and wet wrinkle resistance. Remarkably, the amount of SHP required in the malic acid finish was significantly lower than the usual amounts of SHP in BTCA or CA finishes, which can be another advantage of the malic acid/SHP system.

The influence of various curing temperatures on wrinkle recovery angle and whiteness were shown in Figure 3. Higher temperature curing caused higher wrinkle resistance but curing temperature higher than 180°C resulted in slight discoloration of the treated fabric. In the citric acid treatment, noticeable yellowing has been observed where unsaturated carboxylic acids such as aconitic acid, citraconic acid and itaconic acid was generated during curing[11]. Therefore curing temperature in the subsequent experiments was fixed at 180°C where crosslinked cotton produced little decrease in whiteness.

It has been known that it is necessary to choose the optimum pH of a treating bath in order to achieve the most effective esterificastion by a polycarboxylic acid because of pH-dependent ester crosslinking of cotton cellulose. In case of SHP/BTCA crosslinking system, optimum pH range was reported to be under 3.0 which determined by IR spectroscopic analysis[12]. In this study, the pH of finish was adjusted with nitric acid or sodium hydroxide and its effect on wrinkle resistance was measured after curing. As shown in Figure 4, malic acid crosslinking was little affected by the treating bath pH below 2.8, whereas higher pH caused wrinkle resistance to decrease.

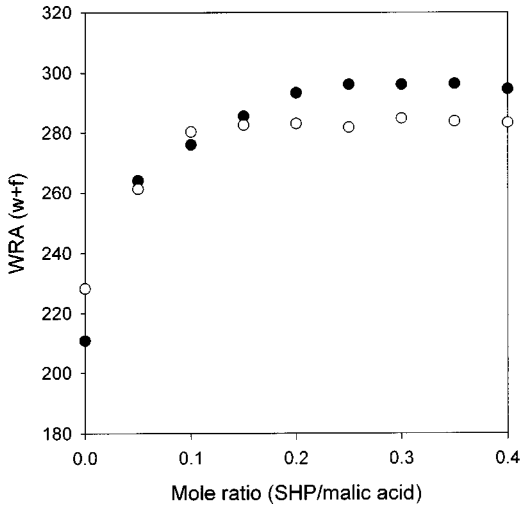


Figure 2. Effect of mole ratio of catalyst/malic acid on the dry and wet wrinkle recovery angle. Dry WRA, ●; wet WRA, O. Treatment condition: malic acid conc., 16%(w/w); curing temperature, 180°C; curing time, 3 min.

Spectroscopic and thermal analysis of crosslinked cotton

It is known that crosslinked cotton has higher thermal stability compared to the untreated cotton due to effective

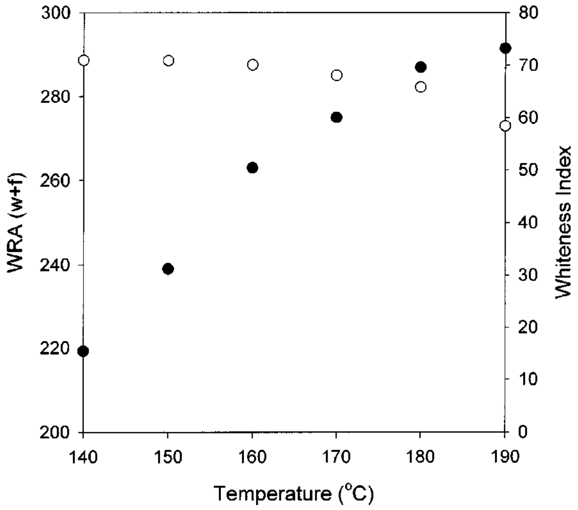


Figure 3. Effect of curing temperature on the wrinkle recovery angle and whiteness. Treatment condition: malic acid conc., 16% (w/w); SHP conc., 2.5%(w/w); curing time, 3 min.

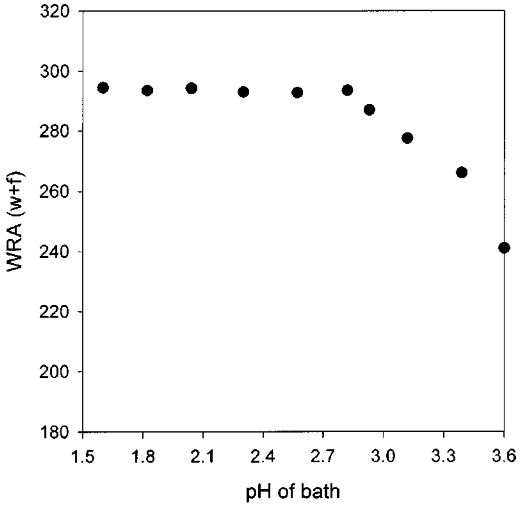


Figure 4. Effect of finish bath pH on wrinkle recovery angle of treated cotton. Treatment condition: malic acid conc., 16%(w/w); SHP conc., 2.5%(w/w); curing temperature, 180°C; curing time, 3 min.

crosslinks as indicated by higher % residues[13]. Thermogravimetric(TG) analysis of untreated and treated cotton fabric were carried out and shown in Figure 5.

For crosslinking of cotton, the cotton fabric applied with an aqueous solution of 16% malic acid and 2.5% SHP was cured at 140 or 180°C for 3 minutes after drying. As expected, % residue of crosslinked fabrics were higher than uncrosslinked cotton and higher curing temperature produced higher amount of char, indicating that crosslinks were formed in the cotton by the malic acid treatment.

Yang *et al.* used FT IR spectroscopy to demonstrate the ester crosslinkages of finished cotton with polycarboxylic acids[14]. The FT IR spectra of treated cotton fabric at 180°C before and after NaOH treatment were shown in Figure 6.

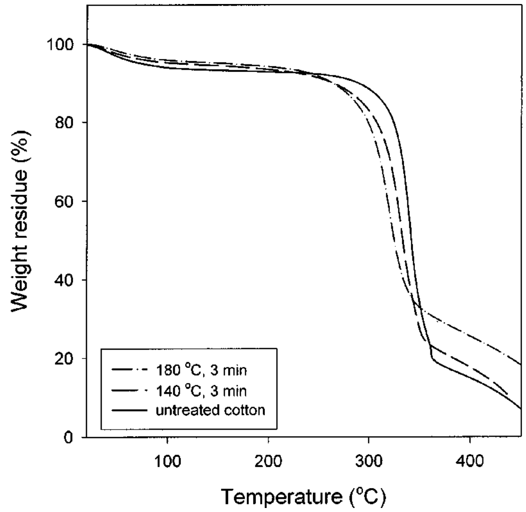


Figure 5. TGA thermograms of untreated and treated cotton fabric with malic acid. For treatment condition, see Figure 4.

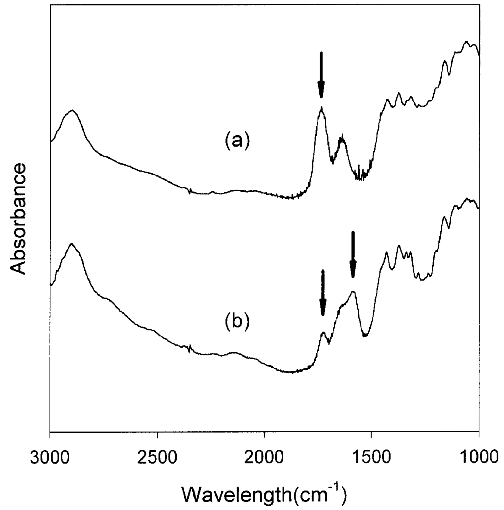


Figure 6. FT-IR spectra of cotton fabric treated with malic acid at 180°C. (a) without NaOH treatment; (b) with NaOH treatment; for treatment condition, see Figure 4.

Ester carbonyl band at 1720 cm^{-1} verifies the existence of ester crosslinks in the spectrum of malic acid-treated fabric even after the NaOH treatment which modifies unreacted carboxylic acids to carboxylate salt without affecting the ester groups. The carbonyl stretching band of the carboxylate appeared at 1587 cm^{-1}. From the results mentioned above, it is apparent that malic acid treatment catalyzed by SHP introduced ester crosslinks in the cotton fabric.

Analysis of purified oligomeric malic acid

Polycondensation of *d,l*-malic acid occurs at 110-140°C in vacuo even without catalyst and a random sequence of both α-and β-type units in equal ratio can be produced if polymerization time was more than several hours[10]. Although condensation of malic acid did not occur without SHP catalyst under the curing condition used in this study(at 180°C and 3 minute), it was found that oligomeric α, β-malic acid can be produced in the presence of SHP at the same curing condition. Oligomeric malic acid can be formed through esterification between OH group and either of carboxylic acids in malic acid. The reaction mixture of malic acid and SHP was purified as described in experimental section.

The FT-IR spectum of the purified oligomeric malic acid was compared with that of malic acid, as shown in Figure 7. The two bands at 1735 and 1190 cm^{-1} correspond to C=O and C-O stretching vibration of main chain ester in the oligomalic acid respectively. The out-of-plane OH bending vibration of carboxylic acids and secondary alcohol in malic acid were significantly reduced at 950 and 665 cm^{-1}.

The FT-NMR spectra of oligomeric malic acid recorded in D_2O were shown in Figure 8. The signals of methylene and methine protons of malic acid at 2.70-2.83 ppm and 4.46-4.50 ppm, respectively, showing that certain amount of malic acid was remained after purification. The signals at

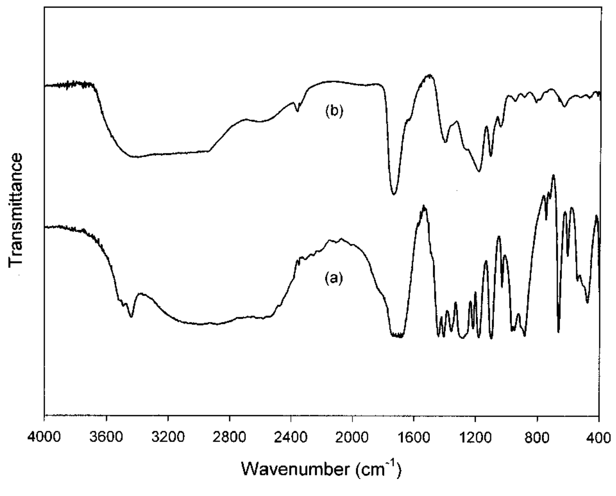


Figure 7. FT-IR spectra of malic acid and purified malic acid oligomer. (a) malic acid; (b) purified malic acid oligomer.

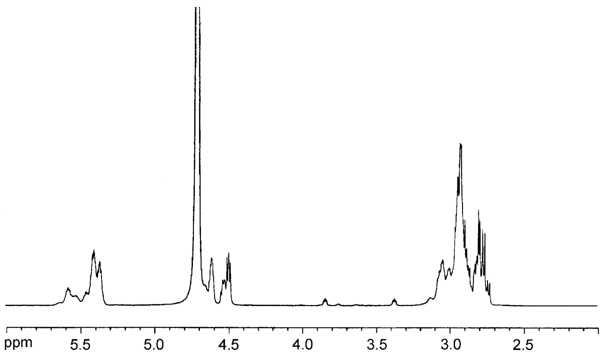


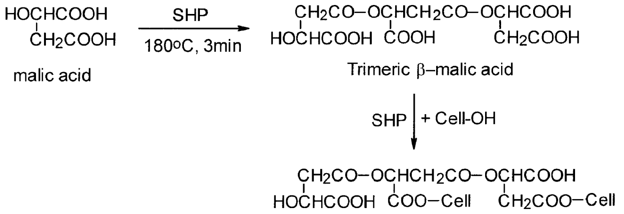
Figure 8. FT-NMR spectrum of purified malic acid oligomer.

2.83-3.20 ppm and 5.33-5.68 ppm were assigned to the methylene and methin protons of oligo-malic acid. A composition of 25% α-malic acid unit and 75% β-malic acid unit in the oligomer was calculated from the integration of the signals observed at 5.52-5.68 and 5.33~5.52 ppm, which correspond to methine protons of α- and β-esters, respectively [15]. Also each ester signal shows typical triad structure of methine protons implying heterotactic sequence. From GPC measurement of oligomeric malic acid dissolved in tetrahydrofuran, the number averaged molecular weight of the oligomer was estimated to be 360 with a polydispersity index of 1.25, indicating a trimer of malic acid. Therefore primary crosslinker active in malic acid/SHP system is considered to be a trimeric α, β-malic acid.

One of possible crosslinking mechanisms of a trimeric β-ester of malic acid with cellulose molecules may be proposed as shown in Scheme 1. However the reaction scheme does not exclude other possible mechanisms such as the attachment of malic acid to cellulose by esterification and then the polymerization of the malic acid because of apparently similar reactivity of secondary hydroxyl groups of cellulose and malic acid. In summary malic acid can be in situ polymerized to form trimeric α-, β- ester of malic acid followed by crosslinking of cellulose molecules or simultaneous polymerization and ester crosslinking of malic acid with cellulose.

Effect of an additive on the mechanical strength of crosslinked cotton

Malic acid finish had detrimental effect on the mechanical properties of the crosslinked cotton fabric as usually appeared in most of durable press finish(Table 1). Mechanical strength loss of durable press finished cotton fabric with polycarboxylic acids has been attributed to two factors: irreversible acid degradation and reversible cellulose crosslinking[16].



Scheme 1. Proposed crosslinking mechanism of malic acid.

Table 1. Effects of an additive on the mechanical strength of crosslinked cotton

Treatment	%	WRA	BS	TS	AR
Malic acid	0	164	100	100	100
	12	267	66	50	24
	16	294	58	40	24
Malic acid (12%) + Polyurethane	2	279	69	51	26
	4	286	69	52	27
	6	296	68	53	28
	8	298	66	53	28
	10	299	68	54	28

WRA is wrinkle recovery angle; BS, TS and AR denote retention of breaking strength, tearing strength, stoll flex abrasion, respectively; Treatment condition: 16 or 12%(w/w) of malic acid and 2.5 or 1.9%(w/w) of SHP respectively at 180°C for 3 minute with/without various amount of polyurethane resin.

A water-soluble polyurethane resin and its catalyst, 10%(w/w) of the polyurethane resin, were added to the formulation to improve the strength retention. It is surprising that mechanical strength retention was slightly improved even with increased wrinkle resistance. It may be caused by the formation of additional elastic and flexible polyurethane crosslinks on the fabric surface. The durability of malic acid crosslinking to laundering is under study and will be reported later.

Conclusions

Malic acid/SHP treatment without other polycarboxylic acids produced highly wrinkle-resistant cotton fabric in a relatively large amount of malic acid concentration. Treating conditions such as malic acid and SHP concentraton, pH of the finishing bath, and curing temperature on the crosslinking performance were investigated. The extraordinary crosslinking of cotton by malic acid treatment was attributed to the in-situ formation of trimeric α- and β- esters of malic acid, which was verified by GPC, IR and NMR analysis. Also the existence of ester crosslinking between cellulose was also studied with FT-IR and thermogravimetric analysis. In addition polyurethane resin was effective in improving the wrinkle resistance of crosslinked cotton additionally. The cost effectiveness of malic acid treatment would encourage the commercial exploitation of nonformaldehyde durable press finish in cellulosic materials.

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