



Quantitative analysis of citric acid/sodium hypophosphite modified cotton by HPLC and conductometric titration

Tao Ye^{a,b}, Bijia Wang^{a,b}, Jian Liu^{a,b}, Jiangang Chen^{a,b}, Yiqi Yang^{a,b,c,d,*}

^a Key Laboratory of Science & Technology of Eco-Textiles, Ministry of Education, Donghua University, 2999 North Renmin Road, 201620 Shanghai, China

^b College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, 2999 North Renmin Road, 201620 Shanghai, China

^c Department of Textiles, Merchandising & Fashion Design, HECO Building, University of Nebraska-Lincoln, Lincoln, 68583-0802 NE, USA

^d Department of Biological Systems Engineering and Nebraska Center for Materials and Nanoscience, HECO Building, University of Nebraska-Lincoln, Lincoln, 68583-0802 NE, USA

ARTICLE INFO

Article history:

Received 19 September 2014

Received in revised form

18 November 2014

Accepted 3 December 2014

Available online 31 December 2014

Keywords:

Ester crosslinking

Cellulose

Citric acid

Sodium hypophosphite

HPLC

Conductometric titration

ABSTRACT

Isocratic HPLC was used in conjunction with conductometric titration to quantitatively examine the modification of cotton cellulose by citric acid (CA)/sodium hypophosphite (SHP). CA/SHP had been extensively used as a green crosslinking agent for enhancement of cellulose and other carbohydrate polymers without in-depth understanding of the mechanisms. The current study investigated all identifiable secondary polycarboxylic acids from CA decomposition in the CA/SHP-cellulose system under various curing conditions. It was found that CA decomposition was more sensitive to temperature compared with the desirable esterification reaction. Two crosslinking mechanisms, namely ester crosslinking and SHP crosslinking were responsible for the observed improvement in crease resistance of CA/SHP treated cotton fabrics. An oligomer of citraconic acid (CCA) and/or itaconic acid (IA) was identified as a possible contributor to fabric yellowing. Finally, the crease resistance of fabrics correlated strongly with CA preservation in polyol-added CA/SHP crosslinking systems. The dosage of polyol should be held below an inflexion point to keep the undesirable competition against cellulose minimum. The combination of HPLC and conductometric titration was demonstrated to be useful in studying the CA/SHP-cellulose crosslinking system. The findings have implications for better application of CA/SHP in polysaccharide modifications in general.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Citric acid (CA) has been extensively investigated as a crosslinking agent or modifier on carbohydrate polymers such as starch (Menzel et al., 2013; Olsson, Hedenqvist, Johansson, & Järnström, 2013; Reddy & Yang, 2010), alginate (Stone, Gosavi, Athauda, & Ozer, 2013), xylan (Shuaiyang et al., 2013), chitosan (Salam, Venditti, Pawlak, & El-Tahawy, 2011), and cellulose (Awada, Montplaisir, & Daneault, 2014; Feng, Xiao, Sui, Wang, & Xie, 2014; Fouda & Fahmy, 2011; Widsten, Dooley, Parr, Capricho, & Suckling, 2014) for property enhancement. Compared with the

other commonly employed polycarboxylic acid (PCA), namely 1,2,3,4-butanetetracarboxylic acid (BTCA), CA has the clear advantages of being non-toxic, renewable, and cost-effective. However, CA is not as effective as BTCA and causes severe yellowing which has undermined its applications in many fields, especially in functional finishing of cellulosic textiles (Harifi & Montazer, 2012). Moreover, the role of sodium hypophosphite (SHP), the widely accepted catalyst for ester-crosslinking with PCAs (Welch, 1988; Yang, 1993; Yang & Bakshi, 1996) in CA crosslinking was unclear (Widsten et al., 2014). Some researchers even doubted the necessity to use SHP in CA crosslinking (Coma, Sebti, Pardon, Pichavant, & Deschamps, 2003; Pantze, Karlsson, & Westermark, 2008).

Mechanistic study of the CA/SHP crosslinking system was challenging due to the complication of various secondary PCAs resulted from CA decomposition (Schramm & Rinderer, 2002). Our recent investigation revealed that SHP promoted thermal decomposition of CA by converting the unsaturated PCA products to 2-methylsuccinic acid (2MSA) (Yao, Wang, Ye, & Yang, 2013). Adding an appropriate polyol improved crease recovery performance and reduced the yellowing of the CA/SHP-cellulose crosslinking system. Although it was proposed that the polyol

Abbreviations: CA, citric acid; PCA, polycarboxylic acid; BTCA, 1*2*3*4-butanetetracarboxylic acid; CisAA, *cis*-aconitic acid; TransAA, *trans*-aconitic acid; 2MSA, 2-methyl succinic acid; CCA, citraconic acid; IA, itaconic acid; WRA, wrinkle recovery angle.

* Corresponding author at: University of Nebraska-Lincoln, Department of Biological Systems Engineering and Nebraska Center for Materials and Nanoscience, HECO Building, Lincoln, Nebraska 68583-0802, USA. Tel.: +1 4024725197; fax: +1 4024720640.

E-mail address: yyang2@unl.edu (Y. Yang).

might have functioned as crosslinking extenders and stabilized CA from decompositions, no direct evidence was observed. A quantitative analysis of the CA/SHP-cellulose crosslinking system with respect to varying curing conditions and added polyols would help to elucidate the underlying mechanisms for its better utilization.

Schramm and colleagues had demonstrated that isocratic HPLC could be used to quantify both fixed and unfixed acids in PCA crosslinking of cotton cellulose (Schramm, Rinderer, & Bobleter, 1998). One limitation of Schramm's pioneering work was that the amount of ester crosslinks could not be determined based on the HPLC results alone. Fras had shown that conductometric titration could be used to accurately determine the carboxylic groups on cotton fabrics (Fras et al., 2004).

The current study aimed to provide explanations for the observed trends in CA/SHP crosslinking of cellulose based on quantitative data obtained from HPLC and conductometric titration analysis. The findings have implications for CA/SHP crosslinking of carbohydrate polymers in general.

2. Materials and methods

2.1. Materials

The cotton fabric used in this study was desized, scoured, and bleached 40 × 40 cotton poplin weighing 123 g/m² kindly provided by the Esquel Group.

Citric acid monohydrate, sodium hypophosphite monohydrate, hydrochloric acid, sulfuric acid, nitric acid, 30% aqueous hydrogen peroxide, sodium hydroxide, sodium chloride, sodium carbonate anhydrous, PEG 200, glycerol and pentaerythritol were purchased from Sinopharm Chemical Reagent Co. Ltd. Xylitol, 2-methyl succinic acid, citraconic acid, itaconic acid, *cis*-aconitic acid, and *trans*-aconitic acid were purchased from Adamas-Beta Reagent. All chemicals were used as received.

Wetting agent JFC was obtained from the Waker Chemical Company. Laundry detergent was a non-bleaching product purchased from Shanghai White Cat Co. Ltd.

2.2. Fabric treatment

The cotton poplin was cut into 30 cm × 30 cm squares weighing roughly 10–11 g and padded with two dips and two nips using a finishing bath containing 125 g/L of citric acid, 63.1 g/L of SHP, and 2 g/L of JFC to give a wet pickup of 80%. A predetermined amount of polyol was also included in the bath for experiments as crosslinking extenders. No softener was applied in these investigations. The padded fabrics were dried at 85 °C for 5 min and cured at a predetermined temperature for 5 min.

2.3. Preparation of LC analytes

Wash liquor: Each treated fabric was washed with occasional stirring using 1 L of aqueous Na₂CO₃ solution (1 g/L) for 10 min at 50 °C and heated at 85 °C to dryness. The wash solution was allowed to cool and filtered before introduced into the LC systems.

Saponification liquor: The saponification reaction involved the following procedure: 200 mL 1 M NaOH were placed into a 500 mL two-necked round bottom flask equipped with a reflux condenser and a glass stopper. Approximately 8 g of the treated fabric was cut into small pieces, weighed accurately, and introduced into the flask. The solution was heated and refluxed for 60 min with occasional shaking. At the end of the reaction, the solution was poured into a 250 mL volumetric flask. The residual fabric was thoroughly washed twice with 20 mL 1 M NaOH. The extraction and wash solutions were combined and allowed to cool. Finally the volumetric

flask was adjusted to the mark with 1 M NaOH. The saponification analytes were filtered before introduced into the LC systems.

2.4. LC–MS characterizations

LC–MS analysis was done on a Varian 310-LC/MS quadrupole mass spectrometer equipped with an Aminex HPX-87H column. The mobile phase used was 0.01 M formic acid for protection of the system. The flow rate was 0.4 mL/min, the column temperature was 25 °C, and MS detector was set to ESI/negative ion mode. The injection volume was 20 µL.

2.5. HPLC experiments

A Shimadzu LC-20AT high performance liquid chromatography equipped with an Aminex HPX-87H column was used for the quantitative HPLC analysis. The mobile phase used was 0.01 M sulfuric acid, the flow rate was 0.6 mL/min, the column oven temperature was 40 °C, and the UV detector was set to 210 nm. The injection volume was 20 µL. Reference standard solutions of CA and the five major secondary PCAs were prepared to obtain the calibration curves accordingly. The calibration curves can be found in the Supplementary data (Fig. A.1) and the correlation coefficients were all greater than 0.998. PCA contents of the wash and saponification liquors were then determined based on the calibration curves. A typical LC chromatogram of the saponification liquor can be found in the Supplementary data (Fig. A.2).

2.6. Conductometric titration

Conductometric titration was done using a procedure modified from the one reported by Fras et al. (2004). Before titrations, the fabric was washed the same way as in preparation of the HPLC wash liquor analyte. The washed fabric was then dried to constant weight, cut and grinded into a powder using an IKA MF 10 Mill. About 1 g of the powdered fabric was weighed out and suspended in 100 mL solution of 0.001 M sodium chloride with stirring. Three to four drops of concentrated hydrochloric acid was then added to fully protonate the carboxylic groups. The conductivity of the suspension was measured using a Mettler Toledo S230 conductivity meter at room temperature. Marked increases or decreases in conductance are associated with the changing concentrations of the two most highly conducting ions, the hydrogen and hydroxyl ions. The powdered fabric samples were first treated with excess hydrochloric acid to convert all the carboxylic groups to the protonated form before they were titrated with a NaOH solution of known concentration. The titration curve of the fabric suspension was characterized by three distinct phases. Phase 1: neutralization of excess free protons marked by steady lowering of the conductivity; Phase 2: neutralization of carboxylic groups, during which the conductivity should remain constant. Phase 3: accumulation of OH[−] in excess leading to an increased conductivity. The total amount of carboxylic groups could be determined based on the amount of NaOH consumed in phase 2. The inflection points separating the phases were determined as the intersections of linearly fitted conductivity data.

2.7. Determination of CA crosslinks on cotton

If all acids reacted with cotton cellulose for only once, the theoretical amount of free carboxylic groups on fabric ([COOH]_T) could be calculated as follows:

$$[\text{COOH}]_T = 2 \times ([\text{CA}]_F + [\text{CisAA}]_F + [\text{TransAA}]_F) + [\text{MSA}]_F + [\text{CCA}]_F + [\text{IA}]_F$$

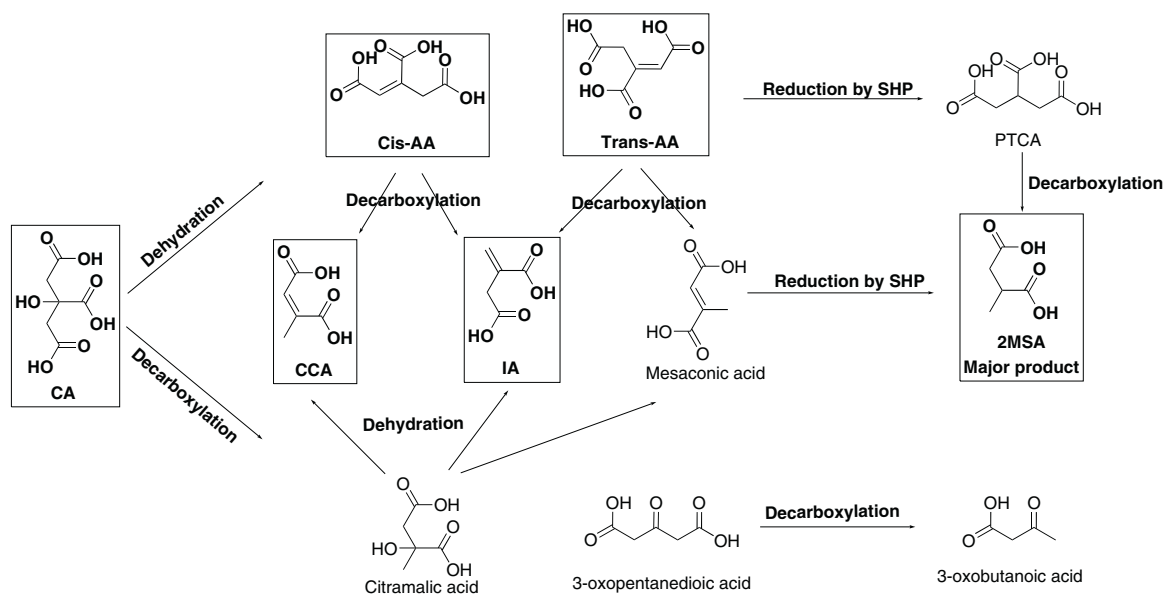


Fig. 1. Possible thermal decomposition pathways of citric acid. (The PCAs detected by LC–MS are highlighted with frames.)

where $[CA]_F$, $[CisAA]_F$, $[TransAA]_F$, $[2MSA]_F$, $[IA]_F$, and $[CCA]_F$ were the corresponding concentration of PCAs fixed on the fabric determined by the HPLC experiments. The amount of ester crosslinks on fabric ($[crosslink]$) was the difference between $[COOH]_T$ and the actual amount of free carboxylic groups measured by conductometric titration ($[COOH]_A$).

$$[crosslink] = [COOH]_T - [COOH]_A$$

2.8. Analysis of phosphorus concentration of the treated fabrics

The treated cotton fabric samples were washed with aqueous Na_2CO_3 solution as described in Section 2.3. Approximately 2 g of the washed fabric samples taken from three different parts in a fabric specimen were ground in a Wiley mill into a powder, and the powder was thoroughly mixed to improve sample uniformity. Approximately 0.10 g of cotton powder was placed in a 100 mL Teflon digestion tank, to which 3 mL concentrated HNO_3 , and 1 mL 30% H_2O_2 , and 2 mL concentrated H_2SO_4 were added subsequently. The reaction mixture was microwaved to allow complete digestion and diluted to 50 mL with distilled water. The sample thus prepared was analyzed with a Leeman Prodigy inductively coupled plasma atomic emission spectrometer to determine the phosphorus concentration (w/w).

2.9. Measuring physical properties of cotton fabrics

The cured fabrics were machine washed and tumble dried using a XQG50-1 washer-dryer according to AATCC Test Method 124 before testing. The control samples that underwent sodium carbonate wash and saponification were prepared as follows. Washed fabric: a cured fabric was washed with occasional stirring using 1 L of aqueous Na_2CO_3 solution (1 g/L) for 10 min at 50 °C and heated at 85 °C to dryness. Saponified fabric: A washed fabric was refluxed with occasional shaking in 250 mL of 1 M aqueous NaOH solution for 60 min, rinsed with 160 mL \times 3 deionized water, and heated at 85 °C to dryness.

The wrinkle recovery angle (WRA) was measured according to the American Association of Textile Chemists and Colorists (AATCC) Testing Method 66-2003.

CIE whiteness index (WI) measurements were made according to AATCC Testing Methods 11-2005.

The tear strength (TS) of the treated fabrics was measured according to the American Society of Testing Materials (ASTM) Testing Method D-1424-1996 using a Thwing-Albert Elmendorf tearing tester.

All mechanical tests were carried out in the fill direction. All tests were carried out after one home laundering if not specified.

3. Results and discussion

3.1. Identification of carboxylic acids in the saponification and washing liquors

Fig. 1 shows the possible decomposition pathways of CA in the presence of SHP. Previous NMR experiments had revealed that 2MSA was the major product (Yao et al., 2013) and several other unsaturated PCAs were also present. CA and all its decomposition products were able to form ester linkages with cellulose and contribute to the change in its macroscopic properties. LC experiments were carried out to identify and quantify PCAs in the CA/SHP-cellulose crosslinking system. To prepare the analytes, treated fabrics were subjected to Na_2CO_3 washes and NaOH saponifications subsequently as described in Section 2.3. Based on the WRA measurements of the washed and saponified fabrics (Table A.5), the washes only removed the unfixed PCAs, while the saponification treatment were sufficient in hydrolyzing all ester linkages. PCAs fixed and unfixed to cellulose could be analyzed separately by subjecting the saponification and wash liquors to LC–MS and HPLC. A typical chromatogram is shown in Fig. A.2 and the results are summarized in Table 1. The elution conditions used were slightly different for LC–MS and HPLC experiments, resulting in different retention times.

Based on the LC–MS data, CA, 2MSA, CisAA, TransAA, CCA, IA and a derivative later recognized as oligomer of IA and/or CCA were found to be the major constituents of both analytes. No citramalic acid or 3-oxopentanedioic acid were detected, indicating that CA first underwent dehydration rather than decarboxylation upon heating. Decarboxylation of TransAA may give rise to IA or mesaconic acid (MCA). However, no MCA was detectable in either

Table 1

LC–MS results of the saponification and wash liquors of a CA/SHP treated cotton fabric.

Peak no.	Retention time (min)		MS fragments	Identity
	LC/MS	HPLC ^a		
1	8.63	5.92	388.31, 259.96, 194.71, 176.73, 163.10	Oligomer of IA and/or CCA
2	9.07	7.63	173.76, 130.63	CisAA
3	10.51	7.78	191.77, 111.90	CA
4	11.39	10.08	129.72, 111.92	CCA
5	12.57	11.04	173.98, 130.73	TransAA
6	17.86	12.28	131.67	2MSA
7	18.28	12.60	129.68	IA

^a The eluent conditions used for quantitative HPLC analysis was different from that used for LC/MS.

the wash or saponification liquor, indicating that TransAA was preferentially converted to IA.

3.2. Decomposition and esterification as affected by temperature

The concentrations of six major detectable PCAs were calculated based on the HPLC peak integrals and the calibration curves of the corresponding standards. The oligomer was not included in the quantitative analysis due to unavailability of the standard. It was noticed that the elution peak from 2MSA (peak 6) could be overshadowed by the IA peak because the two peaks partially overlapped and the extinction coefficient of 2MSA was two order of magnitudes less than that of IA. This is likely the reason that 2MSA had been mostly neglected in the previous HPLC studies of the CA crosslinking system (Schramm & Rinderer, 2002; Schramm et al., 1998). As the dominant product of CA decomposition, 2MSA has profound impact on the crosslinking efficiency and should not be omitted in a quantitative study. Deconvolution of the chromatogram was performed to obtain the proper integrals for 2MSA and IA. The results of the HPLC experiments could be found in the Supplementary data. (Tables A.1 and A.2) In all conditions studied, CA and 2MSA were the major acids found in both saponification and wash liquors.

Ideally, the total moles of PCAs found in both liquors should be equal to the moles of CA applied. As shown in Fig. 2, at all curing temperatures, the moles of all PCAs added up to over 92% of the added CA. At 200 °C, slightly more acids were lost from the

system due to the evaporation of lower-boiling derivatives. The ratio of esterified CA to decomposed CA kept decreasing as the temperature went up. Apparently, the decomposition reaction was more sensitive to temperature change compared with the desirable esterification reaction. Therefore, to maximize crosslinking efficiency of CA, it should be more desirable to allow the reaction to run at lower temperatures for longer time.

The concentration of ester crosslinks on fabric ([XL-PCA]) could be determined as described in Section 2.7 using the HPLC and conductometric titration data. [XL-PCA] was calculated for fabric samples cured at various temperatures and shown in Table 2. The results showed that [XL-PCA] peaked at 170 °C and slowly went down as the curing temperature increased. This was understandable because higher temperature favored decomposition and generated products incapable of forming ester crosslinks. However, the WRA of treated fabrics kept increasing with temperature. These observed trends were not consistent with the generally accepted notion that crease-resistant property is a result of cellulose ester crosslinking. The result of a linear regression analysis [Table 3, entry 2] showed that WRA and [XL-PCA] were apparently not correlated.

Charles Q. Yang and colleagues had reported that the P-H bonds on SHP would add to >C=C< on unsaturated PCAs (MA or IA) that already esterified with cellulose, resulting in an alternative crosslinkage (Peng, Yang, Wang, & Wang, 2012; Yang, Chen, Guan, & He, 2010). Similarly, the various unsaturated secondary PCAs formed from CA decomposition may also participate in cellulose crosslinking by reacting with SHP. The SHP crosslinks on treated fabrics ([XL-SHP]) could be quantified by measuring the phosphorous concentration on treated and washed fabrics as described in Section 2.8. As shown in Tables 2 and 3, the results indicated a moderate positive correlation of WRA and [XL-SHP]. The adjusted R^2 from the linear regression analysis of WRA and [XL-SHP] was 0.7783, meaning 77.83% of the variation in WRA could be explained by change in [XL-SHP].

The imparted crease resistance of treated fabric should be resulted from both ester and SHP crosslinks. Therefore, a multiple linear regression was performed to obtain the predicted equation for WRA with both [XL-PCA] and [XL-SHP] as variables. The predictive equation was found to be:

$$\text{WRA} = 576.98 \times [\text{XL-PCA}] + 229.27 \times [\text{XL-SHP}] + 150.58$$

Table 2

WRAs and concentrations of ester and phosphorous crosslinks of fabrics treated at various temperatures.

Curing temp.	[XL-PCA] (mmol/g)	[XL-SHP] (mmol/g)	WRA
160	0.1445	0.0565	247
170	0.1675	0.0716	264
180	0.1568	0.1242	269
190	0.1475	0.1765	275
200	0.1464	0.1906	280

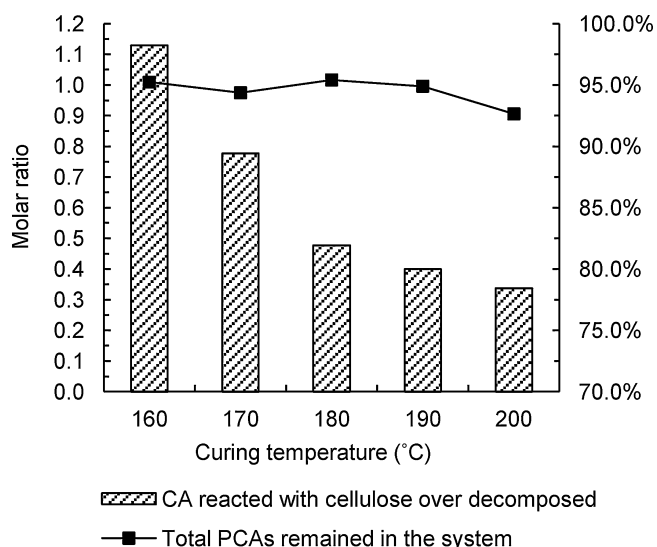


Fig. 2. The molar ratio of CA underwent esterification to decomposition and percentage of total PCAs remained in the system under various curing temperatures. (Add-on was 10% for CA and 5% for SHP. Padded fabrics were predried at 85 °C and cured at predetermined temperature for 5 min.)

Table 3
Linear regression results on the correlation of [XL-PCA] and [SHP] to WRA.

No.	Variant	R^2	Adjusted R^2	F value	t Stat	P value
1	[XL-SHP]	0.8337	0.7783	15.04	3.88	0.030
2	[XL-PCA]	0.0073	−0.3333	0.0002	0.01	0.991
3	[XL-PCA], [XL-SHP]	0.9950	0.9900	198.07	[XL-PCA] [XL-SHP]	8.01 19.9 0.015 0.003

The adjusted R^2 was found to be 0.9900, meaning that 99% of the variation in WRA was explained by [XL-SHP] and [XL-PCA]. The results were statistically significant judging from the corresponding P values. The results unambiguously confirmed our hypothesis that the crease resistant properties of treated fabrics were resulted from both ester crosslinks and SHP crosslinks.

3.3. Effect of various polyols

In our previous study, it was found that polyols could be used as extenders in the CA/SHP-cellulose crosslinking system for better treatment results (Yao et al., 2013). Depending on the structure, polyols may be more effective in enhancing whiteness or crease resistance of the treated cotton fabric. In this study, the effects of four different polyols, namely PEG-200, glycerol, pentaerythritol, and xylitol on the CA/SHP-cellulose crosslinking system were reexamined on the molecular level by HPLC analysis.

The amount of PCAs in terms of molar percentage to added CA found on fabrics cured with and without polyols are plotted in Fig. 3. Due to the competition of carboxylic groups by the added polyols, the total amount of fixed PCAs decreased from 92% to about 80% in all cases. However the proportion and the absolute amount of fixed CA increased appreciably in the presence of all polyols, indicating they were effective in preventing CA from decomposition. In the best case observed with adding xylitol, more than 50% of the original CA reacted with cellulose without decomposition. PEG-200 was the least effective, with which the amount of fixed CA only increased by 4.1%.

As shown in Fig. 3, the amount of unsaturated PCAs fixed on fabric was reduced upon adding polyols. A maximum drop was observed for fabrics finished with pentaerythritol, which contained two thirds less unsaturated PCAs than the control. The linear regression analysis (Fig. A.5 in Supplementary data) of fabric white index (WI) and the amount of fixed unsaturated acids showed an adjusted high correlation coefficient of 0.9772. Considering none of the four identifiable unsaturated PCAs absorbs in the range of visible light, the yellow color must be caused by a secondary product of these acids. In the HPLC experiments, the

unidentified species eluted out at 5.92 min (8.63 min in LC-MS) was found to absorb strongly at 380 nm. The corresponding mass spectrum showed two peaks at m/z = 259.96 and 388.31 respectively, which fitted with the protonated molecular ion peaks for CCA/IA dimer (260.05) and trimer (388.06), respectively. Therefore, it is reasonable to attribute the yellowing effect to oligomers of IA or CCA.

The sample finished with added xylitol gave the highest WRA and the best DP rating. Regression results showed that WRA of treated fabric correlated positively to the concentration of fixed CA (adjusted R^2 = 0.9489), and negatively to that of other PCAs (adjusted R^2 = 0.9188) (Fig. A.7). The result indicated that CA was much more effective in enhancing crease resistance than its derivatives.

3.4. Effect of xylitol dosage on the fate of CA

Xylitol was found to be the most effective in preserving CA and imparting crease resistant properties to the cotton fabric. The effect of xylitol dosage on the CA/SHP-cellulose crosslinking system was also investigated. Amounts of the PCAs fixed on fabric in the presence of varying amounts of xylitol were calculated from the corresponding HPLC results and presented in Table A.4 of the Supplementary data. Although, the total mass of fixed PCA was almost invariant to xylitol dosage, the molar ratio of fixed PCAs continued to decrease with increasing xylitol dosage as shown in Fig. 4a. This was because xylitol compete with cellulose in reacting with the PCAs, causing more PCAs to remain unfixed. Fortunately, this competition was not overwhelming at the dosages applied. Upon adding 0.6 equivalents of xylitol, which theoretically could consume all the carboxylic groups in CA, the amount of PCAs fixed to cellulose still accounted for about 80%. On the other hand, the molar percentage of fixed CA continued to increase with xylitol dosage. This indicated that the mono ester of CA and xylitol are more thermally stable and tend to react with cellulose rather than go through decomposition.

As shown in Fig. 4b, both whiteness and tear strength (fill direction) of the treated fabric improved with increasing xylitol dosages.

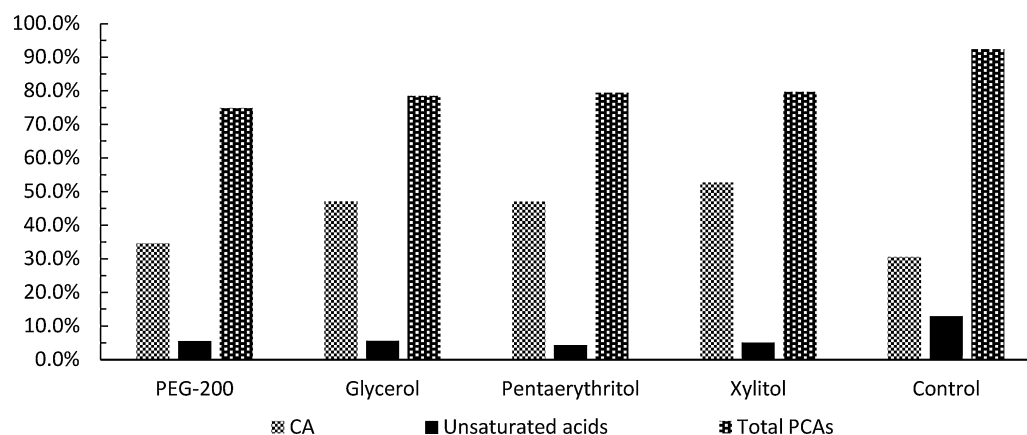


Fig. 3. Effect of polyols on molar percentage of PCAs found on the fabrics. (Add-on was 10% for CA and 5% for SHP. Polyols were added in a 1:1 OH/COOH molar ratio to CA. Padded fabrics were pre-dried at 85 °C and cured at 180 °C for 5 min.)

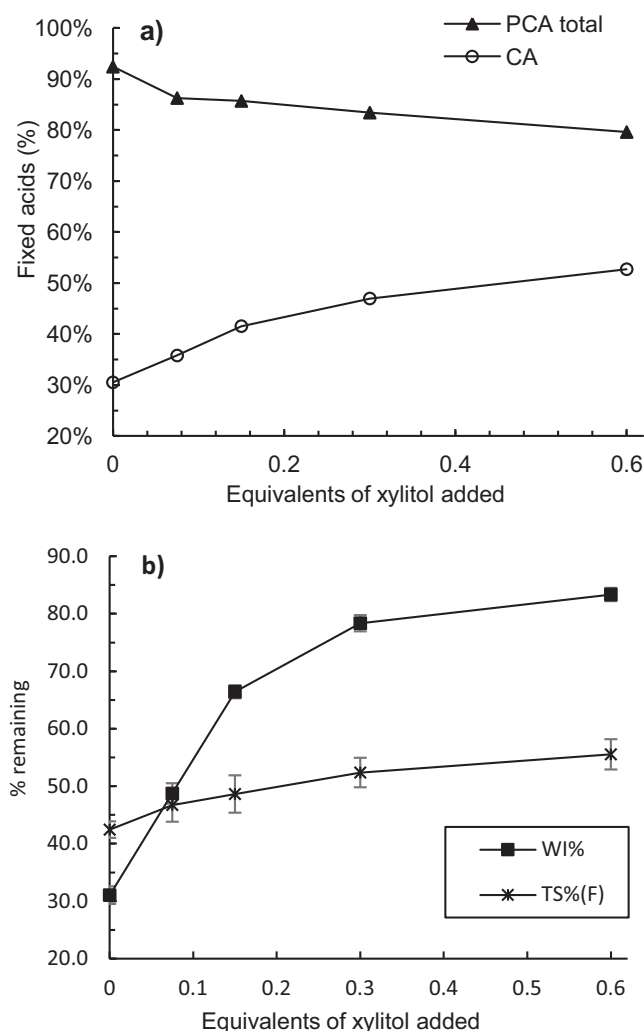


Fig. 4. Effect of xylitol dosage on (a) molar percentage of CA and total PCAs fixed on the fabric and (b) percentage remaining of whiteness and tear strength (F). (Add-on was 10% for CA and 5% for SHP. Padded fabrics were pre-dried at 85 °C and cured at 180 °C for 5 min.)

Good correlation between fabric whiteness and molar percentage of fixed unsaturated acids was observed (adjusted $R^2 = 0.9560$) for similar reasons as described above. The tear strength improvement could be rationalized by the “extension” effect of xylitol. That is some of the crosslinks bridging the two cellulosic hydroxyls became CA-xylitol-CA instead of the monomeric CA. The larger and more flexible CA-xylitol-CA crosslinks would cause less intermolecular strain than monomeric CA crosslinks. An increasing of CA-xylitol-CA crosslinks resulted in improved tear strength retention.

The concentrations of free carboxylic groups on fabrics treated with different xylitol dosages were determined by conductometric titration and plotted in Fig. 5. Adding xylitol could affect [COOH] on the treated fabric in two opposite manners. On one hand, it helped to stabilize PCAs from decarboxylation. On the other hand, it reacted with the carboxylic groups and reduced the chance for PCA fixation. It was found that [COOH] on fabric remained mostly constant up to the xylitol dosage of 0.15 equivalents. Beyond that dosage, a plunging in [COOH] was observed. 0.15 equivalents of xylitol corresponded to a $\text{—OH}:\text{—COOH}$ ratio of 1:2. The results indicated that formation of cellulose-PCA linkages would be adversely affected when more than half of the —COOH could be consumed by xylitol. Therefore, it should be more desirable to use no more than 0.15 equivalents of xylitol. The actual WRA values also

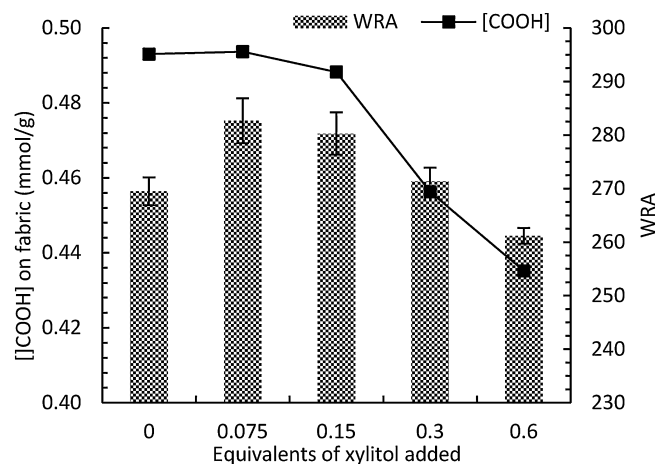


Fig. 5. Effect of xylitol dosage on WRA and [COOH] of the fabrics. (Add-on was 10% for CA and 5% for SHP. Padded fabrics were pre-dried at 85 °C and cured at 180 °C for 5 min.)

showed that fabrics finished with 0.075–0.15 equivalents of xylitol had the best crease resistant properties. Similar trend should hold for other polyols and the specific inflexion dosage could be predicted based on the trend observed in this work.

4. Conclusions

In conclusion, we have studied the chemical modification of cotton cellulose by CA/SHP under various conditions using the combination of HPLC and conductometric titration. The six major PCAs present in the CA/SHP crosslinking system and the amount of free carboxylic groups on cotton were quantified. Major finding of the current work is as follows:

- (1) Temperature has a more significant influence on decomposition of citric acid than on the esterification between CA and cellulose. Therefore it is desirable to apply CA/SHP at ambient temperature for extended amount of time for maximized crosslinking efficiency.
- (2) In CA/SHP crosslinking of cellulose, the improvement in crease resistance or WRA results from both ester crosslinking and SHP crosslinking. The co-existence of two distinct crosslinking mechanisms distinguishes the CA/SHP crosslinking system from systems based on other PCAs such as BTCA and MA.
- (3) The whiteness of treated fabric corresponded well with the sum of identifiable unsaturated PCAs found on fabric. The yellow species contributing to fabric yellowing was likely to be an oligomer of IA and/or CCA.
- (4) Adding polyol was confirmed to effectively inhibit CA decomposition. The crease resistant properties correlate strongly with CA preservation. The dosage of polyol should be kept below an inflexion point so that the undesirable competition against cellulose remained minor. For the best extender, xylitol, the inflexion point was at 0.15 equivalents to CA.

The combination of HPLC and conductometric titration had been demonstrated to be useful in understanding the CA/SHP-cellulose crosslinking system. The findings of this study have implications for improving and broadening the applications of CA/SHP in polysaccharide modifications in general.

Acknowledgements

The authors wish to thank the Chinese National High Technology Research and Development Program 863 Project (2013AA06A307)

and Agricultural Research Division, Multi-State Project S-1054 (NEB 37-037), USDA Hatch Act for funding the research.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.carbpol.2014.12.028>.

References

- Awada, H., Montplaisir, D., & Daneault, C. (2014). Cross-linking of papers based on thermomechanical pulp fibers by polycarboxylic acids: Influence on the wet breaking length. *Industrial & Engineering Chemistry Research*, 53(11), 4312–4317.
- Coma, V., Sebti, I., Pardon, P., Pichavant, F. H., & Deschamps, A. (2003). Film properties from crosslinking of cellulosic derivatives with a polyfunctional carboxylic acid. *Carbohydrate Polymers*, 51(3), 265–271.
- Feng, X., Xiao, Z., Sui, S., Wang, Q., & Xie, Y. (2014). Esterification of wood with citric acid: The catalytic effects of sodium hypophosphite (SHP). *Holzforschung*, 68(4), 427–433.
- Fouda, M. M. G., & Fahmy, H. M. (2011). Multifunctional finish and cotton cellulose fabric. *Carbohydrate Polymers*, 86(2), 625–629.
- Fras, L., Laine, J., Stenius, P., Stana-Kleinschek, K., Ribitsch, V., & Doleček, V. (2004). Determination of dissociable groups in natural and regenerated cellulose fibers by different titration methods. *Journal of Applied Polymer Science*, 92(5), 3186–3195.
- Harifi, T., & Montazer, M. (2012). Past, present and future prospects of cotton cross-linking: New insight into nano particles. *Carbohydrate Polymers*, 88(4), 1125–1140.
- Menzel, C., Olsson, E., Plivelic, T. S., Andersson, R., Johansson, C., Kuktaite, R., et al. (2013). Molecular structure of citric acid cross-linked starch films. *Carbohydrate Polymers*, 96(1), 270–276.
- Olsson, E., Hedenqvist, M. S., Johansson, C., & Järnström, L. (2013). Influence of citric acid and curing on moisture sorption, diffusion and permeability of starch films. *Carbohydrate Polymers*, 94(2), 765–772.
- Pantze, A., Karlsson, O., & Westermark, U. (2008). Esterification of carboxylic acids on cellulosic material: Solid state reactions. *Holzforschung*, 62, 136–141.
- Peng, H., Yang, C. Q., Wang, X., & Wang, S. (2012). The combination of itaconic acid and sodium hypophosphite as a new cross-linking system for cotton. *Industrial & Engineering Chemistry Research*, 51(35), 11301–11311.
- Reddy, N., & Yang, Y. (2010). Citric acid cross-linking of starch films. *Food Chemistry*, 118(3), 702–711.
- Salam, A., Venditti, R. A., Pawlak, J. J., & El-Tahawy, K. (2011). Crosslinked hemicellulose citrate–chitosan aerogel foams. *Carbohydrate Polymers*, 84(4), 1221–1229.
- Schramm, C., & Rinderer, B. (2002). Identification and quantification of non-formaldehyde crosslinking agents by HPLC. *AATCC Review*, 2(6), 37–40.
- Schramm, C., Rinderer, B., & Bobleter, O. (1998). Quantitative determination of BTCA bound to cellulosic material by means of isocratic HPLC. *Textile Research Journal*, 68(11), 821–827.
- Shuaiyang, W., Huiling, L., Junli, R., Chuanfu, L., Feng, P., & Runcang, S. (2013). Preparation of xylan citrate—A potential adsorbent for industrial wastewater treatment. *Carbohydrate Polymers*, 92(2), 1960–1965.
- Stone, S. A., Gosavi, P., Athauda, T. J., & Ozer, R. R. (2013). In situ citric acid crosslinking of alginate/polyvinyl alcohol electrospun nanofibers. *Materials Letters*, 112, 32–35.
- Welch, C. M. (1988). Tetracarboxylic acids as formaldehyde-free durable press finishing agents. Part I: Catalyst, additive, and durability studies. *Textile Research Journal*, 58(8), 480–486.
- Widsten, P., Dooley, N., Parr, R., Capricho, J., & Suckling, I. (2014). Citric acid crosslinking of paper products for improved high-humidity performance. *Carbohydrate Polymers*, 101, 998–1004.
- Yang, C. Q. (1993). Infrared spectroscopy studies of the cyclic anhydride as the intermediate for the ester crosslinking of cotton cellulose by polycarboxylic acids. I. Identification of the cyclic anhydride intermediate. *Journal of Polymer Science, A: Polymer Chemistry*, 31(5), 1187–1193.
- Yang, C. Q., & Bakshi, G. D. (1996). Quantitative analysis of the nonformaldehyde durable press finish on cotton fabric: Acid–base titration and infrared spectroscopy. *Textile Research Journal*, 66(6), 377–384.
- Yang, C. Q., Chen, D., Guan, J., & He, Q. (2010). Cross-linking cotton cellulose by the combination of maleic acid and sodium hypophosphite. 1. Fabric wrinkle resistance. *Industrial and Engineering Chemistry Research*, 49, 8325–8332.
- Yao, W., Wang, B., Ye, T., & Yang, Y. (2013). Durable press finishing of cotton fabrics with citric acid: Enhancement of whiteness and wrinkle recovery by polyol extenders. *Industrial & Engineering Chemistry Research*, 52(46), 16118–16127.