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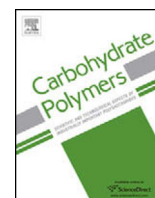
Authors

Qi, Huan
Huang, Yangen
Ji, Bolin
et al.

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Anti-crease finishing of cotton fabrics based on crosslinking of cellulose with acryloyl malic acid

Huan Qi[a], Yangen Huang[a], Bolin Ji[a], Gang Sun[c], Feng-ling Qing[a], Chunyan Hu[b,*], Kelu Yan[a,*]

[a] College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, PR China
[b] National Engineering Research Center for Dyeing and Finishing of Textiles, Donghua University, Shanghai 201620, PR China
[c] Division of Textiles and Clothing, University of California, Davis, CA 95616, United States

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ABSTRACT

Maleic acid (MA) has been explored to replace formaldehyde-based dimethylol dihydroxy ethylene urea (DMDHEU) for cotton anti-crease finishing. However, the resilience of treated fabrics was not satisfactorily improved. In this study, acryloyl malic acid (AMA) was synthesized and applied on fabrics as a novel crosslinking agent. The results showed that both crease recovery angle and whiteness index of treated samples were higher than those of MA in the presence/absence of catalyst sodium hypophosphite (SHP). Chemical structure of AMA was confirmed by NMR and MS spectra. The possible crosslinking mechanism between AMA and cellulose was investigated by means of ^{13}C NMR, MS, FTIR and phosphorus content analyses. It was found that AMA could form ester bonds with cellulose by formation of anhydride intermediate. Meanwhile, additional reaction of double bonds on AMA with another molecule or P—H of SHP residual has also contributed to the crosslinking. A reaction equation was proposed based on the analyses.

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1. Introduction

Cotton is one of the most favored textile materials because of its superior wearing comfort and excellent wearability. Unfortunately, cotton fabric wrinkles easily during home laundering and causes considerable inconvenience for users. The poor resiliency of cotton is caused by the structure of biopolymer-cellulose in fibers, as it has hydrogen bonds as the major intermolecular interactions but is lack of intermolecular chemical crosslinkages (Cai, 2009; Lewin, 2006). Crosslinking of cellulose with formaldehyde-based compounds, mainly dimethylol dihydroxy ethylene urea (DMD-HEU) was introduced to overcome winkles. DMDHEU has been used in cotton finishing for prominent wrinkle resistance property since 1950s (Harifi & Montazer, 2012; Petersen, 1987; Xu & Wang, 2012). However, when treated cotton fabric is subjected to multiple laundering cycles, ether linkages of DMDHEU gradually hydrolyze to become N-methylol groups. Hence, free formaldehyde releases continuously during the entire life of the treated garment. 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). Treated fabric releases formaldehyde which is extremely harmful to human health during the process of treatment and wearing (Kerfoot & Mooney, 1975).

Since early 1990s, extensive efforts have been made to develop formaldehyde-free crosslinking agents for cotton to replace the traditional formaldehyde-based reagents. Polycarboxylic acids were recognized as the most promising one among all formaldehyde-free alternatives since Welch found sodium hypophosphate as the most effective catalyst (Dehabadi, Buschmann, & Gutmann, 2013; Welch, 1992). It's reported that BTCA (1,2,3,4-butane tetracarboxylic acid) could be the most promising one to replace DMDHEU according to previous literatures. However, it was troubled with high production costs (Dehabadi et al., 2013; Hou & Sun, 2013a, 2013b; Yang & Wang, 1996a). Some unsaturated dicarboxylic acids, such as maleic acid (MA), were also used as crosslinking agents for cellulose when they were applied in the presence of a peroxide initiator and an esterification catalyst. However, the use of peroxide initiator caused fabric yellowing and strength loss (Choi, Welch, & Morris, 1993, 1994; Welch & Andrews, 1990). It's known that MA can only form a single ester linkage with cellulose, but it is not able to form the second cyclic anhydride intermediate for crosslinking.

Yang reported that wrinkle resistance of the cotton fabric treated by MA was significantly improved when NaH_2PO_2 was introduced without any radical initiator. The results showed 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 crosslinkage between two cotton cellulose molecules. Double bond of MA has participated in the crosslinking. SHP played a dual-role as a catalyst and a crosslinker in the finishing reaction (Peng, Yang, & Wang, 2012; Peng, Yang, Wang, & Wang, 2012; Yang, Chen, Guan, & He, 2010).

The reactivity of double bond is affected by steric hindrance (McMurry & Simanek, 2006). From the view of chemical structure, MA is a disubstituted unsaturated acid, its reactivity is lower than a mono-substituted one (Bartlett & Altschul, 1945; Moad & Solomon, 2005). Therefore, a mono-substituted unsaturated acid, acryloyl malic acid (AMA, 2-(acryloyl) succinic acid) was selected in this work as a potential crosslinking agent for cotton fabrics. Compared with MA, AMA has two functional groups of a vinyl and a dicarboxylic separately on either side. The vinyl group on the end of molecule could be more reactive in chemical reactions such as polymerizing and crosslinking. And for this reason, AMA may endow cotton fabric with a better resilience. Similar product acryloyl aspartic acid (AASPA) was synthesized and used as polymerizable monomers for dental applications (Xie, Chung, Wu, & Mays, 2004). As far as the author knows, no literature has reported the anti-crease finishing of cotton fabrics with AMA.

In this study, AMA was synthesized by attaching an end vinyl group to malic acid. It was purified by flash chromatography on silica gel and chemically characterized by ^{1}H NMR and ^{13}C NMR, then applied on cotton fabrics as a novel crosslinking agent for anti-crease finishing. The performance of cotton treated by AMA and MA were compared. Fabric property was evaluated by measuring crease recovery angle (CRA). The performance indicators such as whiteness index (WI), tearing strength retention (TS%) were also included. The possible crosslinking mechanism between cellulose and AMA was investigated by means of ^{13}C NMR spectra, mass spectra analysis, Fourier transform infrared spectroscopy (FTIR) and phosphorus content on treated fabrics. A crosslinking mechanism was proposed according to the results.

2. Materials and methods

2.1. Materials

Cotton fabric used in this paper is plain weave ($40\,s \times 40\,s$, 133×72, weighing $108.6\,g/m^2$) desized, scoured, bleached and does not subject to any finishing processes. It was supplied by Youngor Group Co., Ltd. Acryloyl chloride (99%, J&K Scientific Co., Ltd.), maleic acid (99%, Sinopharm Chemical Reagent Co., Ltd.), sodium hypophosphite (99%, Sinopharm Chemical Reagent Co., Ltd.), malic acid (99%, Sinopharm Chemical Reagent Co., Ltd.), potassium bromide (99%, Sinopharm Chemical Reagent Co., Ltd.), soap flake (specially made for testing of textiles, Shanghai Soap Factory) were used as commercial products without any further purification.

2.2. Methods

2.2.1. Synthesis of AMA

Synthesis of AMA was carried out as shown in Scheme 1 according to the methods in previous papers but with some modifications (Cai, 1999; Xie et al., 2004). A 100 mL dry three-neck round-bottom flask was equipped with a magnetical stirrer, a reflux condenser with a drying tube and nitrogen inlet. Malic acid 13.40 g (100 mmol) and acryloyl chloride 18.10 g (200 mmol) were charged into the flask. The mixture was stirred at 50 °C overnight until the reaction solution became transparent. Evaporation of excess acetyl chloride

resulted to the mixture of acid anhydride with the desired product. Final product was extracted from water with ethyl acetate. The crude product was purified by flash chromatography on silica gel (eluent: ethyl acetate:petroleum ether = 2:1) to afford product (14.66 g, yield: 78%) as a pale yellow solid.

Chemical structure of AMA was confirmed by ^{1}H NMR and ^{13}C NMR. The results are presented as follows:

^{1}H NMR (400 MHz, DMSO-d_6): 12.61 (s, 2H), 6.38 (dd, J = 17.2, 1.4 Hz, 1H), 6.23 (dd, J = 17.3, 10.3 Hz, 1H), 6.02 (dd, J = 10.3, 1.3 Hz, 1H), 5.29 (dd, J = 8.6, 3.9 Hz, 1H), 2.88 (dd, J = 16.7, 4.0 Hz, 1H), 2.77 (dd, J = 16.8, 8.7 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.07 (—COOH), 170.45 (—COOH), 165.07 (—COOC), 133.15 (H$_2$C=C—), 128.05 (H$_2$C=C—), 69.11 (O—C(COOH)—), 36.19 (—CH$_2$—COOH); MS (ESI, m/z): 186.5 (M—H$^+$, 100).

2.2.2. Fabric treatment

Fabric sample was first immersed in an aqueous solution containing MA or AMA with other auxiliary agents, and then padded with two dips and two nips using a laboratory padder to reach a wet pickup of 90%. The impregnated fabrics were dried and then cured at a specified condition in a curing oven manufactured by Werner Mathis, Switzerland.

2.2.3. Fabric properties

Samples were conditioned for 4 h at $65 \pm 2\%$ relative humidity and $20 \pm 1\,°C$ conditions before measurements. Crease recovery angle (CRA) were tested according to AATCC Testing Method 66-2003 on SDL Atlas M003A tester. Tearing strength was measured according to ASTM Testing Method D-1424-1996 by a Thwing-Albert Elmendorf tearing machine, and tearing strength retention (TS%) was calculated using untreated sample as a control.

$$TS\% = \frac{T_t}{T_u} \times 100\%$$

T_t: tearing strength (cN) of treated sample; T_u: tearing strength (cN) of untreated sample. All measurements of mechanical properties were carried out on the weft direction. The whiteness index (WI) was determined according to AATCC Testing Method 11-2005. It was recorded and averaged from four different positions of the sample on Datacolor 650® Bench-Top Spectrophotometer.

2.2.4. NMR analysis of AMA before and after curing

NMR spectra of AMA was confirmed and recorded on a Bruker AM-400 spectrometer. 0.05 g sample was dissolved in 0.5 mL of dimethyl sulfoxide-d_6 (DMSO-d_6). The ^{13}C NMR of cured AMA was also recorded and analyzed.

2.2.5. Temperature-dependent FTIR spectroscopy of AMA

The sample was prepared by mixing AMA with SHP in a ratio of 2:1 (mole ratio), then dried under vacuum at the temperature of 50 °C for 2 h before measurement. Then samples were mixed with KBr and prepared by pressed-disk technique with a translucent disk. FTIR spectrum of the sample was measured on an Omnic Sampler of Nicolet 6700 FTTR spectrometer (Nicolet Analytical Instruments) with a scan range of 4000–400 cm^{-1} and a resolution of 8 cm^{-1}. The heating rate was 10 °C/min. The spectra were recorded at 140 °C, 160 °C and 180 °C for 2 min, respectively.

2.2.6. FTIR spectroscopy of treated cotton fabric

Fabric samples were dried under vacuum at the temperature of 50 °C for 2 h and grounded in a mill to form a powder. Then samples were mixed with KBr and prepared by pressed-disk technique before FTIR spectroscopy. FTIR spectra were measured on an Omnic Sampler of Nicolet 380 FTIR spectrometer (Nicolet Analytical Instruments) with a scan range of 4000–400 cm^{-1} and a resolution of 4 cm^{-1}.
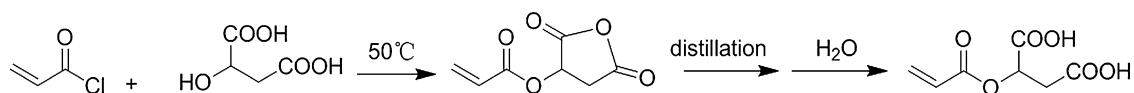
Scheme 1. Synthesis of AMA.

2.2.7. Phosphorus content of treated cotton fabric

Phosphorus content tests were measured by an IPC (Inductively Coupled Plasma) emission spectrometer (US Leeman Prodigy) in Research Center for Analysis & Measurement at Donghua University. Prior to testing, samples were soaped in the bath with 10 g/L soap flakes at 80 °C for 10 min, then washed with tap water until the water became clear. Samples were washed twice and dried at 85 °C for 5 min before phosphorus content test.

2.2.8. Mass spectrometric analysis of AMA

Pure AMA was measured by Varian 310 LC-MS/MS to confirm the molecular weight. Then AMA was cured at 160 °C for 5 min. The cured product was measured by MALDI-TOF-Mass on ABSciex 4800 to confirm the polymer molecular weight.

3. Results and discussion

3.1. Comparison of fabrics treated with AMA and MA

Properties of fabrics treated with AMA and MA in the presence/absence of SHP (NaH_2PO_2) are showed in Table 1. BTCA was also for comparison.

SHP is an effective catalyst for the reaction of polycarboxylic acids with cotton fabrics (Choi et al., 1993, 1994; Welch & Andrews, 1990). In the absence of SHP, as we can see from Table 1 that the crease recovery angle of treated cotton fabric with AMA increased more than that with MA under the same curing condition, suggesting that an additional reaction probably took place between AMA molecules and cotton, in addition to the esterification reaction. Both AMA and MA could form anhydrides and then react with cellulose to form a single ester bond, while double bonds in both AMA and MA could possibly have thermal addition reaction between the vinyl groups, which may contribute to crosslinking of cotton (Choi et al., 1993; Peng, Yang, & Wang, 2012; Yang et al., 2010). AMA showed better CRA performance than that of MA because that the reactivity of the double bond is affected by steric hindrance. MA is a disubstituted unsaturated acid (two —COOH groups on both sides of double bond) and its reactivity is lower than a mono-substituted AMA.

When SHP was added, as shown in Table 1, AMA treated fabrics also showed better wrinkle-free property and whiteness than

Table 1
Properties of fabrics treated with AMA and MA with and without SHP.[a]

	SHP	Curing condition	CRA (°)	WI	TS%[b]
Blank	–	–	118 ± 2.7	67.87	100
AMA	0	160 °C × 5 min	187 ± 1.5	52.86	62.2
		190 °C × 2 min	210 ± 2.5	34.06	37.2
MA	0	160 °C × 5 min	148 ± 2.1	46.91	41.7
		190 °C × 2 min	159 ± 1.8	19.14	20.8
AMA	AMA:SHP = 2:1[c]	160 °C × 3 min	230 ± 2.0	61.87	71.6
		180 °C × 2 min	261 ± 1.6	59.85	55.1
MA	MA:SHP = 2:1	160 °C × 3 min	216 ± 2.6	63.62	83.1
		180 °C × 2 min	245 ± 2.3	53.58	62.5
BTCA	BTCA:SHP = 2:1	160 °C × 3 min	245 ± 2.1	65.33	67.1
		180 °C × 2 min	271 ± 1.9	63.55	56.0

[a] All finishing baths contained 0.8 mol/L AMA or MA, or 0.3 mol/L BTCA, two dips and two nips, wet pick-up 90%, pre-dried at 85 °C for 5 min and cured at different conditions.
[b] Tearing strength retention (TS%). All mechanical tests were carried out on weft direction.
[c] Mole ratio.

that of MA treated ones under the same condition. The addition of SHP was conducive to the vinyl crosslinking for both MA and AMA, evidenced by the increases in CRA values of fabrics. The fabric treated with AMA and SHP under curing temperature of 180 °C for 2 min reached the results of CRA at 261°, tearing strength retention (TS%) at 55.1% and whiteness index (WI) at 59.85. With the same condition, the MA treated one revealed CRA at 245°, tearing strength retention (TS%) and whiteness index (WI) at 62.5% and 53.58, respectively. The better performance of AMA showed that thermal induced vinyl addition reaction significantly improved the crosslinking between AMA and cellulose.

3.2. Proposed crosslinking mechanism

Above proposed crosslinking mechanism for anti-wrinkle treatment of cotton with AMA could explain the results but should be proved chemically and analytically. Thus, ^{13}C NMR analysis, mass spectrometric analysis, phosphorus content test, FTIR, temperature-dependent FTIR were employed in a systematic study.

3.2.1. Vinyl polymerization of AMA

Based on the CRA results of AMA treated fabrics without SHP, a possible thermal induced radical polymerization of vinyl groups was proposed. To prove such a hypothesis, pure AMA was cured at a special condition to simulate the finishing process. Chemical structures of AMA before and after curing were evaluated by ^{13}C NMR spectroscopy and mass spectrometric analyses and the results are shown in Figs. 1 and 2.

As shown in Fig. 1(a), ^{13}C NMR characteristic signal peaks of uncured AMA were presented as follow: 171.07 ppm (—COOH), 170.45 ppm (—COOH), 165.07 ppm (—COOC), 133.15 ppm (H$_2$C=C—), 128.05 ppm (H$_2$C=C—), 69.11 ppm (O—C(COOH)—), 36.19 ppm (—CH$_2$—COOH) (Callaghan, 1991; Ernst, Bodenhausen, & Wokaun, 1987; Pretsch et al., 2009). Compared Fig. 1(a) and (b), characteristic peaks of >C=C< double bonds (128.05 ppm, 133.15 ppm) disappeared after cured at 180 °C for 3 min, a 37.63 ppm and a 37.11 ppm of —CH$_2$— and —CH— peak appeared, respectively, indicating that >C=C< of AMA was converted to methylene group during the thermal induced polymerization reaction. In addition, new peaks appeared around 170 ppm can be attributed to carbonyl group of anhydride or new derivatives of carboxylic acid.

Moreover, pure AMA was cured at 160 °C for 5 min to simulate the treatment heating process. Mass spectrometric analysis of cured product of AMA was tested by MALDI-TOF-MS shown in Fig. 2. In the mass (m/z) range from 300 to 600, peaks at 375.0 (M−H$^+$) and 563.0 (M−H$^+$) are corresponding to dimers and trimers of AMA, respectively, revealing that the double bonds were likely to polymerize under elevated temperatures. The mass spectrometric analysis of the cured AMA also supported the hypothesis that thermal induced polymerization reaction of double bonds had participated in crosslinking.

3.2.2. Anhydride intermediate of AMA

A hydroxyl containing bifunctional carboxylic acid in proper configuration is liable to form a five- or six-membered lactone units under heat condition (Yang & Wang, 1996a). SHP could promote dicarboxylic acid to form a cyclic anhydride intermediate, which is more reactive with hydroxyl group on cellulose to form ester bond.
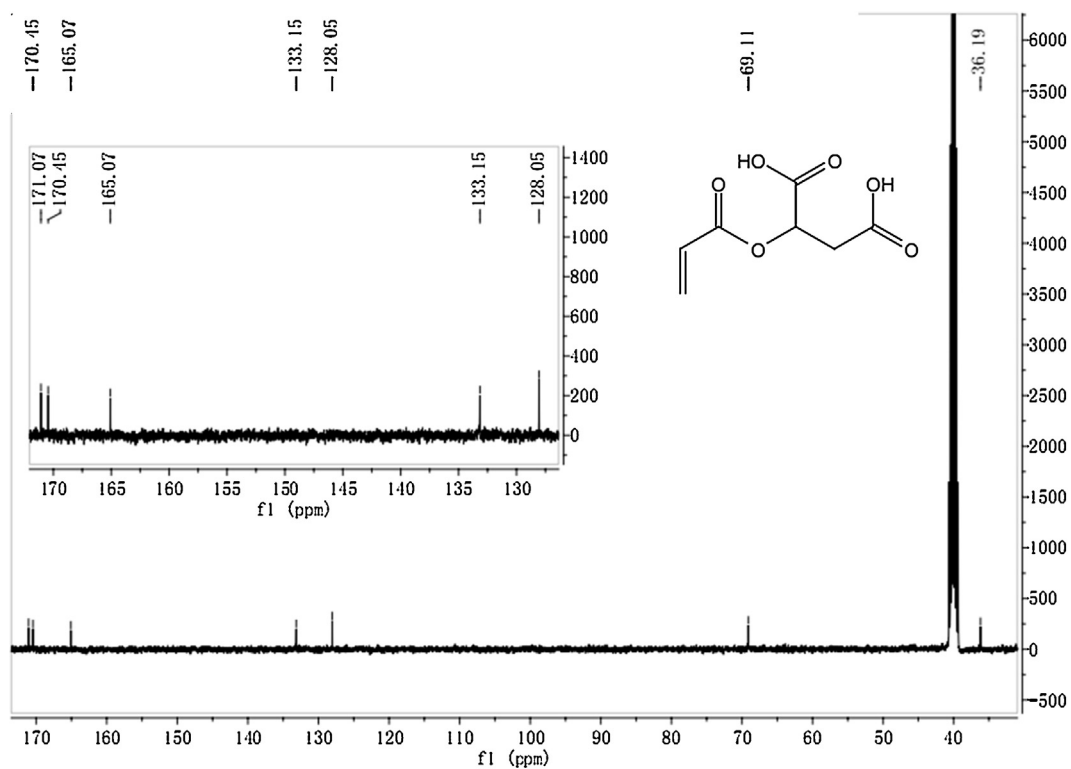
(a) Pure AMA
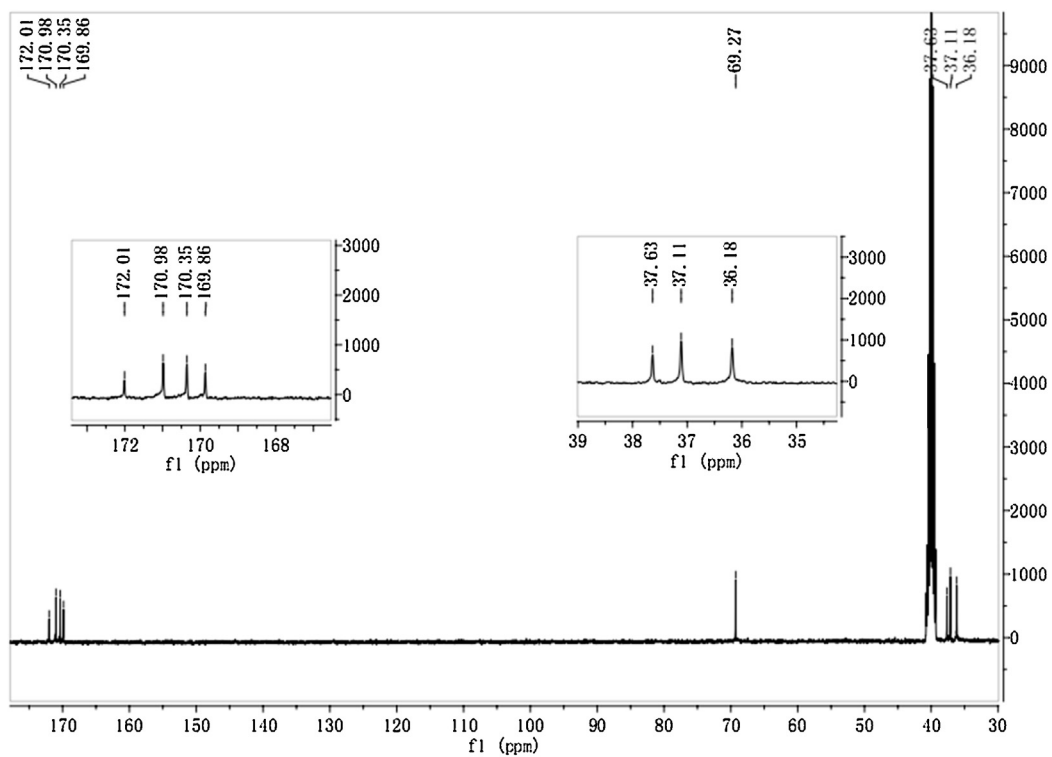
(b) Pure AMA cured at 180℃ for 3 min

Fig. 1. ^{13}C NMR analysis of AMA. The pure AMA cured at 180 °C for 3 min, then dissolved in DMSO-d$_6$ for a ^{13}C spectrum, compared it to an uncuring AMA. The multiple peaks around 40 ppm were DMSO signals.
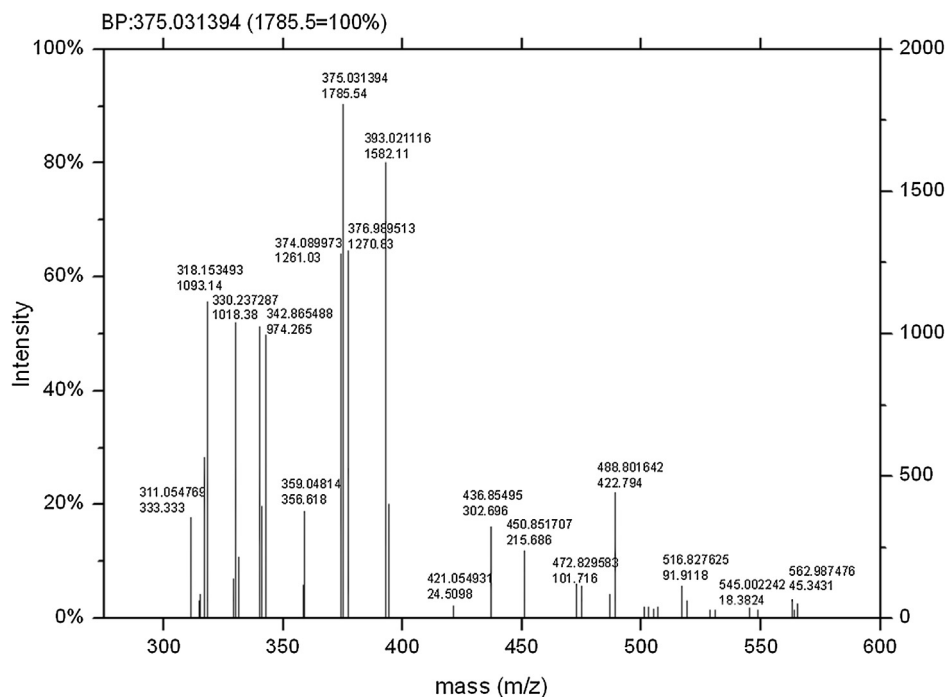
Fig. 2. Mass spectrometric analysis of cured AMA. The pure AMA cured at 160 °C for 5 min, then dissolved in CH₃OH for MS analysis by MALDI-TOF-MS.

To confirm the formation of anhydride intermediate instead of lactone, temperature dependent FTIR spectra of AMA are shown in Fig. 3.

As shown in Fig. 3, when curing temperature increased from 140 °C to 180 °C, two distinct bands appeared at 1850 cm⁻¹ and 1780 cm⁻¹. The bands are due to the symmetric and asymmetric carbonyl stretching vibration modes, respectively, of a 5-membered cyclic anhydride (Yang, 1991, 1993; Yang & Wang, 1996a, 1996b, 1997; Pretsch et al., 2009). It is evident that AMA can form 5-membered anhydride under elevated temperatures. It's also observed that the two anhydride carbonyl bands of AMA at 1850 cm⁻¹ and 1780 cm⁻¹ increases their intensity with the curing temperature increased from 140 °C to 180 °C, indicating that more anhydride can be formed under higher temperatures. The anhydride is able to react with the hydroxyl group of cellulose to form ester under higher temperature further.

3.2.3. New ester bonds between AMA and cellulose

In addition, FTIR spectra of uncured and cured fabrics treated with AMA and SHP are compared in Fig. 4. As can be seen from Fig. 4, curve(a), the sharp absorbance peak at 1725 cm⁻¹ is due
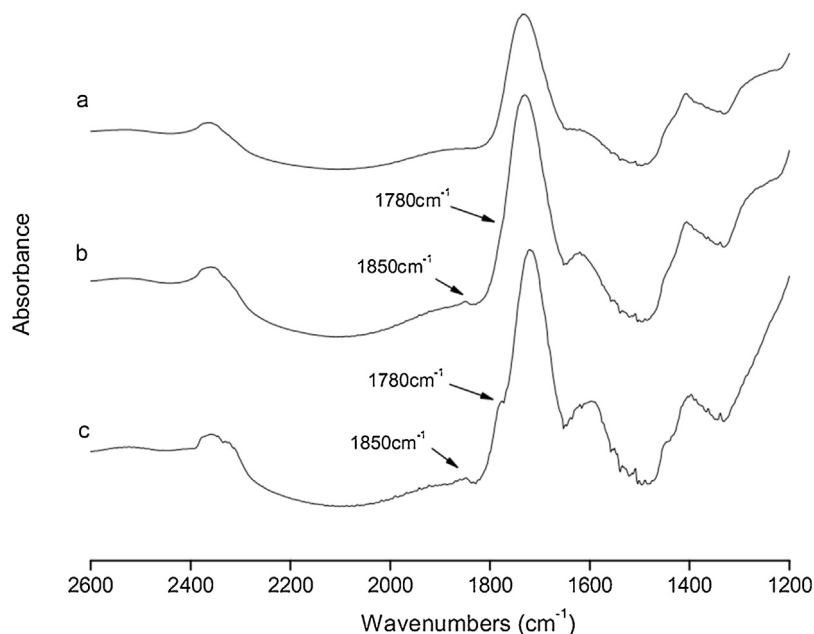

Fig. 3. Temperature-dependent FTIR spectral analysis of mixed AMA:SHP = 2:1 (mole ratio). (a) Mixture cured at 140 °C for 2 min; (b) mixture cured at 160 °C for 2 min; and (c) mixture cured at 180 °C for 2 min.
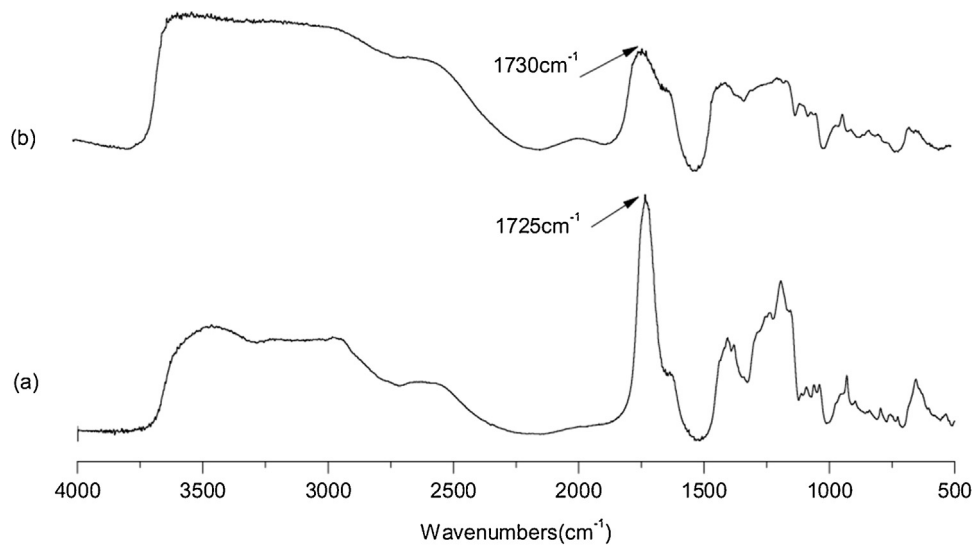
Fig. 4. FTIR spectra of uncured and cured fabric. (a) Uncured fabric treated with AMA and SHP and (b) cured fabric treated with AMA and SHP.

to the carbonyl (>C=O) stretching vibration of carboxylic acid and ester bonds overlapped on fabrics (Yang & Wang, 1996a, 1996b, 1997). Sharp absorbance peak around 1725 cm^{-1} broadened after curing, curve(b), indicating that the carboxylic acid group reacted with hydroxyl or some other groups and new carbonyl (>C=O) absorbance peak appeared around 1730 cm^{-1}. FTIR spectroscopy results presented in Figs. 3 and 4 supported the cellulose esterification mechanism that AMA esterified to cotton by the formation of a cyclic anhydride intermediate.

3.2.4. Relationship between phosphorus content and winkle recovery angle

To investigate phosphorus included in the crosslinking reaction on cotton fabric, phosphorus content on fabrics treated with 0.8 M AMA and 0.4 M NaH$_2$PO$_2$ were tested as shown in Fig. 5. Phosphorus content increased from 2.89 mg/g to 5.54 mg/g as the curing condition varied from 160 °C × 3 min to 180 °C × 2 min, indicating

that potential bonding of P compound or element on the treated cellulose. The increase of phosphorus content on the treated fabrics showed the same trend with CRA values under harsher baking condition. Such dependency of both CRA and phosphorus content on the curing condition provides another hypothesis that the P—H in SHP may also participate in an addition reaction with AMA to form crosslinking on the treated cotton fabric. The results were consistent with Yang's previous research on MA crosslinking mechanism that SHP reacted with the >C=C< bonds of two MA molecules (Peng, Yang, & Wang, 2012; Peng, Yang, Wang, et al., 2012). The results showed that SHP also played as a role as a catalyst and a crosslinker in the crosslinking of AMA with cellulose.

3.2.5. Suggested crosslinking mechanism

According to the above results, ^{13}C NMR and mass spectrometric analyses indicated that thermal induced addition reaction of vinyl bond in AMA has participated in crosslinking cellulose.
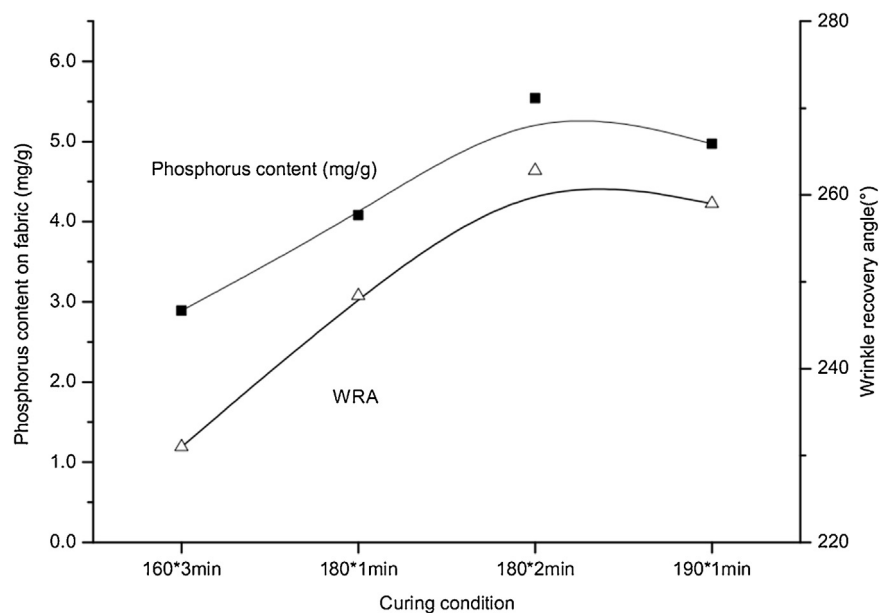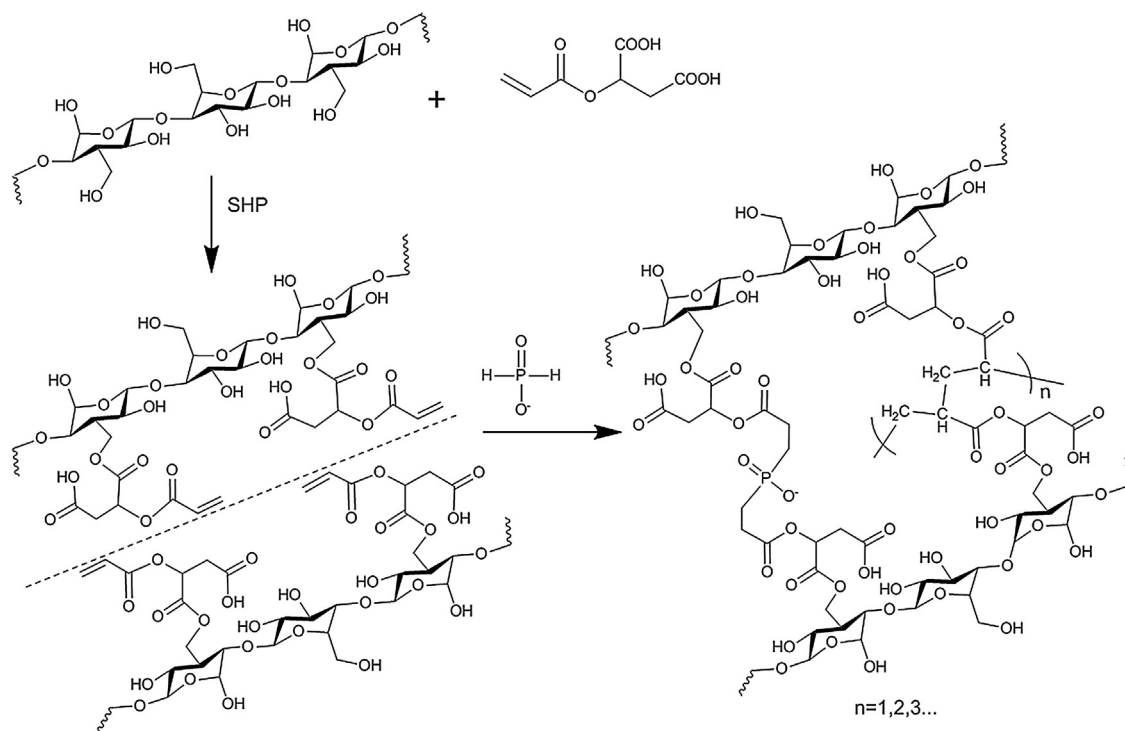

Fig. 5. Phosphorus content of cured fabric with different conditions. The finishing baths contained 0.8 mol/L AMA, AMA:SHP = 2:1, the treated method was the same as in Table 1. Finished samples were washed twice before measuring. Washing process: 5 g/L soap flakes at 80 °C for 10 min, then washed with tap water until clarified, dried at 85 °C for 5 min.

Scheme 2. Possible reaction mechanism between cellulose and AMA.

FTIR spectroscopy analysis showed that AMA can esterify cotton by the formation of a cyclic anhydride intermediate. More anhydride could be formed under higher temperatures. The relationship between CRA and phosphorus contents of the treated fabrics provides an evidence of the reaction between NaH_2PO_2 and >C=C< of AMA to form crosslinking on the fabrics. Two types of addition reaction on the vinyl site and the esterification are the total possible reactions between cellulose and AMA, as shown in Scheme 2. Thus, AMA molecules imparted better anti-crease property to fabrics.

4. Conclusion

AMA was synthesized and applied as an effective crosslinking agent for anti-crease finishing of cotton fabrics. Due to the higher reactivity of double bonds, fabrics treated with AMA showed better anti-wrinkle properties and whiteness than that of MA. Wrinkle resistance property of treated fabrics was obtained by the following three reactions: (1) esterification between cotton cellulose and AMA; (2) thermal induced polymerization reaction of >C=C< of AMA, (3) the addition of H—P—(NaH_2PO_2) to >C=C< of AMA. The three types of additional reaction and esterification resulted in the crosslinking formation, thus endowed the fabric with anti-crease property.

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