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Catalytic actions of alkaline salts in reactions between 1,2,3,4-butanetetracarboxylic acid and cellulose: I. Anhydride formation

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Abstract 1,2,3,4-Butanetetracarboxylic acid (BTCA) reacts with cellulose in two steps: anhydride formation of adjacent carboxyl groups in BTCA and esterification of anhydride with cellulose, which are generally catalyzed by alkaline salts including sodium hypophosphite. The role of the salts in the reactions has been unclear. As an effort in fully understanding the catalytic effects of the salts, reaction mechanisms of alkaline metal ions and acid anions of the salts were investigated in details in the reactions. In this research, functions of alkaline metal ions on the formation of anhydride were studied. Results indicated that the existence of lithium, sodium or potassium promoted the formation of anhydride, and potassium ion was the most efficient one among these three ions. Besides, the reactions of a BTCA molecule with cellulose undergo a step-by-step process, i.e. formation of one anhydride and esterification of the anhydride with cellulose, and then formation of another anhydride and esterification of it to establish cross-linking by the BTCA.

Introduction

Polycarboxylic acids, such as 1,2,3,4-butanetetracarboxylic acid (BTCA) and citric acid, have been extensively investigated as cross-linking reagents for cellulose in production of wrinkle-free cotton fabrics (Welch 1988; Yang 1991a; Yao et al. 2013). BTCA has shown promising results under the catalysis of sodium hypophosphite (SHP) (Welch and Andrews 1990; Yang 2001), and has potential to replace the widely used N-methylol compounds in wrinkle-free treatment of cotton fabrics (Welch 1992). BTCA reacts with cellulose in two steps as reported in literatures (Gu and Yang 1998; Yang 1991a; Yang and Wang 1998): formation of an active intermediate anhydride and esterification of the anhydride with hydroxyl on the cellulose. Undoubtedly, the anhydride intermediate is very important in the reactions between BTCA and cellulose.

SHP has been proven effective in catalyzing the reactions between BTCA and cellulose. Rowland and Brannan (1968) suggested that SHP accelerated the formation of anhydride, but did not function in the second step of ester reaction. Laemmermann (1993) reported that the anhydride could be easily formed at high temperature, so the catalyst SHP really accelerated the esterification step. However, in Yang's

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opinion (Yang 2001), SHP worked in both formations of anhydride and esterification steps of BTCA reacting with cellulose. Besides SHP, many sodium phosphate salts and carboxylate salts (Welch and Andrews 1990; Andrews and Morris 1993), although less efficient than SHP, were also used as catalysts for the reactions between polycarboxylic acids and cellulose. Many hypotheses about the catalysis were proposed but without detailed chemical explanation or evidence (Welch and Andrews 1990).

Interestingly, a recent study carried out by this group has demonstrated that aromatic polycarboxylic acid could react with cellulose in a so-called direct esterification mechanism (Hou and Sun 2013), totally different from the two-step reaction mechanism of BTCA with cellulose. However, that reaction was also effectively catalyzed by the same salt, SHP. A more detailed investigation revealed that the direct esterification reaction follows the Fischer reaction mechanism, and anion concentrations of the catalyst salt could affect the reaction as well (Zhao and Sun 2015). The Fischer reaction is an acid catalyzed reaction and prefers low pH values in general, while SHP or other salts could provide more acid anion under relatively higher pH values to catalyze the reactions between aromatic polycarboxylic acid and cellulose.

Thus, it is quite curious for us to understand what catalytic actions of SHP in the reactions between aliphatic polycarboxylic acids, such as BTCA, and cellulose, since the formation of anhydride follows similar reaction mechanism as acid catalyzed reactions. The fact is that addition of SHP into BTCA solutions always results in increased pH values due to the slight alkalinity of SHP, while the anti-wrinkle properties of the fabrics treated by the solutions indeed are improved, i.e. increased esterification, contradictory to the regular acid catalyzed reactions (Wei and Yang 1999). Furthermore, other alkaline salts have demonstrated similar catalytic effects (Yang 1993), which were not observed in the reaction between aromatic polycarboxylic acid and cellulose. Here, the catalytic effects of the salts should be further investigated due to the nature of the two-step reaction mechanism of BTCA with cellulose (Gu and Yang 1998; Yang 1991a; Yang and Wang 1998). In addition, the use of SHP and any phosphorus-containing salt is a serious environmental concern. Understanding the catalytic actions of the salts on the

reactions would be critical for discovery of potential alternative catalysts.

In this research, new experimental conditions were designed by using different salts and alkaline metal ions as catalysts of BTCA reaction with cellulose. Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA) and Gaussian calculation were employed to analyze the treated cotton fabrics so as to characterize the catalytic mechanism of the ester formation between the aliphatic polycarboxylic acid and cellulose. This presentation will focus on the discussion of the catalytic actions of alkaline salts on the formation of anhydride step of reactions in detail.

Experiments

Materials

Desized, scoured, bleached and mercerized 40 s × 40 s plain-woven pure cotton fabric (weighing 117 g/m^2) was purchased from Hualun printing and dyeing Co., Ltd. (Shanghai, China). BTCA and lithium hydroxide (LiOH) were both analytical reagents and purchased from ACROS (New Jersey, USA). Sodium hydroxide (NaOH) and potassium hydroxide (KOH) were both purchased from EMD chemical Inc. (New Jersey, USA). SHP was obtained from Sigma-Aldrich Co. (St Louis, USA). And acetone was from Fisher Scientific Co. (New Jersey, USA).

Fabric treatment

Cotton fabric was dipped and padded two times in a 6.4 wt% (unless specified) BTCA aqueous solution with or without a catalyst. The amount of the catalyst was based on a 0.5 mole ratio to BTCA. The average wet pickup of the fabrics was 60 % (unless specified). And then it was dried at 80 °C for 5 min and cured at 160 °C for 3 min in a curing oven (Roaches International Ltd., Staffordshire, England). The treated fabrics were either immediately measured by FTIR, or were washed by tap water for 10 min and then a 0.1 mol/L NaOH solution for 4 min at room temperature, and dried at 80 °C for 5 min before FTIR measurements. Besides, some fabrics were washed by

acetone for 1 min at room temperature and air dried before FTIR measurements.

Characterization

Wrinkle recovery angle (WRA)

The WRA values of treated fabrics, which were washed by tap water for 10 min at room temperature to remove the unreacted BTCA and catalysts, were measured with a wrinkle recovery tester (T.J. Edwards, Inc., Boston, USA) according to the American Association of Textile Chemists and Colorists (AATCC) method 66-1990.

FTIR measurement

FTIR was used to determine the degree of cross-linking between polycarboxylic acid and cellulose (Morris et al. 1995). A Nicolet 6700 FTIR spectrometer (Thermo Electron Co., USA) was employed to collect the spectra at absorbance mode, at the range of 4000–400 cm^{-1} with 64 scans and a 4 cm^{-1} resolution for each sample. Sample mass and KBr mass were accurately weighed at 2.00 and 100 mg, respectively. All corresponding band intensities were normalized against the absorbance intensity of C–H bond at 2900 cm^{-1} (Hou and Sun 2013; Lam et al. 2011), which is not affected by the reactions. FTIR absorbance at 1780 cm^{-1} represents anhydride structures, and anhydride bond ratios were calculated based on FTIR band intensities of 1780/2900 cm^{-1}. Similarly, the peak at 1724 cm^{-1} is absorbance of the formed ester bonds (fabrics were washed in a NaOH solution), and ester bond ratios were calculated according to 1724/2900 cm^{-1}. Total anhydride (TA) bond ratios were calculated by [1780/2900 cm^{-1} (before alkaline washing) + 1724/2900 cm^{-1} (after alkaline washing)], since anhydride bonds on fabrics before washing were residual anhydride and any formed ester bonds, resulting from anhydride reacting with cellulose, could only be measured after alkaline washing.

TGA

TGA of sample was performed by using a TGA-60 system (Shimadzu Science Instruments, Inc., USA) following such procedures: Sample was first heated up to 120 °C from room temperature in a heating rate of 10 °C/min in a nitrogen atmosphere to completely eliminate free or crystal water in samples. After cooling down to room temperature, the sample was then heated again to 500 °C and weight losses were recorded. The sample mass used was about 5–8 mg.

Gaussian calculation

Geometry structures of molecules were optimized by using Gaussian 09 W software (Ramnial et al. 2003) with Density Functional Theory (DFT) and ub3lyp/6-31G (Krest'yaninov et al. 2014) under the vacuum condition. Hydrogen bond interactions between molecules were analyzed.

Results and discussion

Alkaline metal ions as catalysts for anhydride formation

The reaction between BTCA and cellulose undergoes two steps, formation of anhydride and esterification of anhydride with cellulose (Gu and Yang 1998; Yang 1991a; Yang and Wang 1998). The formation of anhydride is a key step in the reaction but is determined by the right conformation of vicinal carboxylic groups in BTCA, mostly affected by the rotation of the end carboxylic acid groups to the proper position (Scheme 1a). The intermolecular and intramolecular hydrogen bonds existing between and within BTCA are the major barriers of rotation, which need high temperature to overcome. So the formation of anhydride of BTCA requires 180 °C or higher temperature (Morris et al. 1996). Also, the anhydride is more reactive with cellulose than acid. The catalytic effect of SHP on the overall reaction is known but is not clear on this step of the reaction. Hence, a study on reactions between SHP and BTCA was designed and conducted in order to investigate the effect of SHP on the anhydride formation.

As a comparison, NaOH, another source of sodium ion, was employed in the study. Presented in Fig. 1 are FTIR spectra of four different chemicals. Comparing to the spectra of BTCA (Fig. 1a) and SHP (Fig. 1b), the spectrum of BTCA/SHP showed absorbance peak at 1618 cm^{-1} (Fig. 1c), associated with $-COO^{-}$ carboxylate ions (Ning 2000), proving that some

Scheme 1 Proposed formation of anhydride (**a**), and a step-by-step reaction mechanism of BTCA with cellulose (**b**)
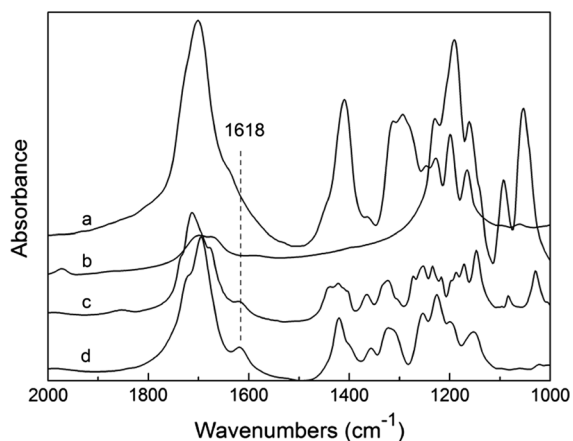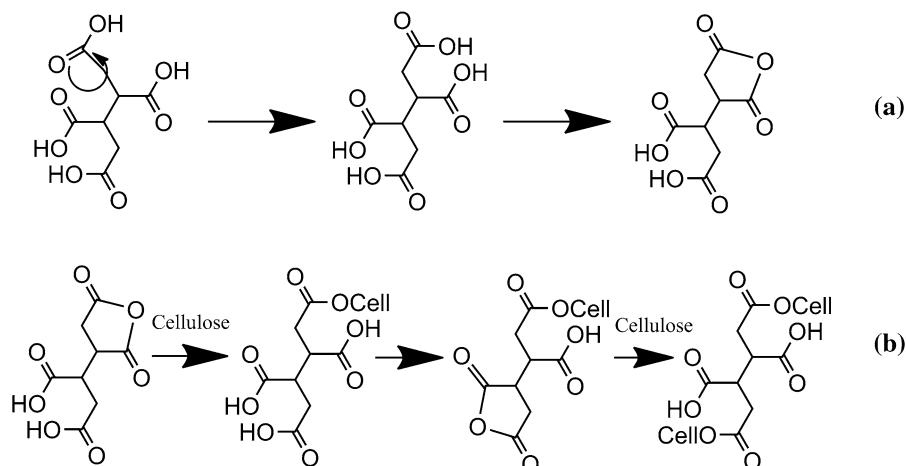

(a)

(b)

Fig. 1 FTIR spectra of different chemicals: *a* BTCA; *b* SHP; *c* BTCA + SHP; and *d* BTCA + NaOH

carboxyl groups are converted to carboxylates. This effect is similar to the system of BTCA/NaOH without SHP, showing the exact peak at 1618 cm^{-1} (Fig. 1d). Such results indicated that SHP was functioning somewhat similar to the sodium ions in NaOH, possibly due to the mild alkalinity of SHP. If the sodium ions could have the same effect as SHP on the reaction, addition of NaOH into the BTCA and cotton fabric system probably should provide catalytic effect as well. Indeed, NaOH demonstrated certain catalytic effect on the reaction of BTCA with cellulose based on the increases of ester bond and total anhydride ratios, and WRA values compared with that of the fabric treated by BTCA only (Table 1). In fact, not only NaOH, other alkaline metal ions, such as lithium and

potassium, also showed the same effects on the treated fabrics (Table 1).

Interestingly, the pH values of BTCA with alkalines and SHP are all higher than that of BTCA only (Table 1), though overall the systems are still under acidic conditions which are needed for the esterification reaction. But the added chemicals all increased cross-linking efficiency of BTCA, reflected by the increased ester bond ratios (1724/2900 cm^{-1}), total anhydride bond ratios and WRAs, different from the normal trend of regular acid catalyzed reactions. Carefully comparing the results of ester bond ratios and WRA values of the treated fabrics, a trend of changes of the cross-linking efficiency to alkaline metal ion size can be found (Table 1). The radii of the alkaline metal ions are 0.76 Å (Li$^+$), 1.02 Å (Na$^+$) and 1.38 Å (K$^+$) (Shannon 1976), respectively, while total anhydride bonds (TA) and cross-linking effect (WRA) were increased in the same order, i.e. the larger the size of the metal cations, the better cross-linking effects were observed. According to the known reaction mechanism of formation of anhydride and esterification of anhydride with cellulose, it seems that these metal ions could only be involved in the step of the anhydride formation instead of the esterification, since the addition of alkaline metal ions could react with the carboxylic acid to form corresponding carboxylates (as observed in Fig. 1). The carboxylates then could affect H-bond interactions between carboxylic acid groups within or between BTCA molecules and possibly improve the formation of the anhydride. The large ions could further reduce the interactions. In fact, if proton ion (H$^+$) is considered as another

Table 1 Properties of BTCA treated fabrics with addition of different alkalines and SHP

Catalyst[a]	pH of finishing bath	Anhydride ratio	Ester ratio	Total anhydride ratio	WRA (°)
NC	1.84	0.054	0.054	0.108	193.0
LiOH	3.19	0.042	0.159	0.201	235.5
NaOH	3.27	0.045	0.164	0.209	242.0
KOH	3.26	0.061	0.180	0.241	248.0
SHP	2.21	0.090	0.227	0.317	259.3

All data are averages of two tests. The radii of cations are -0.38 Å (H^+); 0.76 Å (Li^+), 1.02 Å (Na^+) and 1.38 Å (K^+), respectively

NC no catalyst

[a] The mole ratio of catalyst to BTCA was 0.5:1
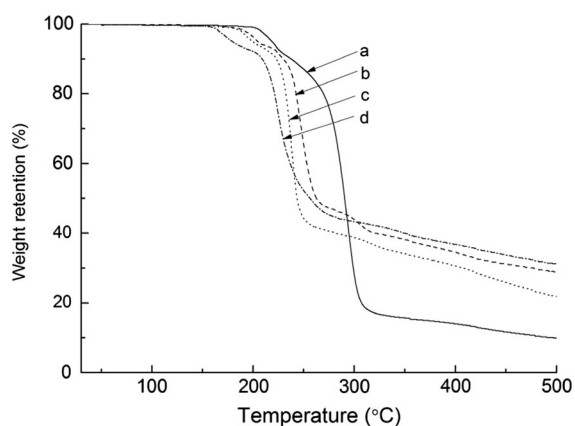

Fig. 2 TGA curves of BTCA chemicals with different alkaline catalysts: *a* BTCA; *b* BTCA + LiOH; *c* BTCA + NaOH; *d* BTCA + KOH

smaller cation, which is the case of without these metals ions (NC in Table 1), the formation of anhydride is even more difficult. The results are consistent with the trend. Thus, the catalytic effects of SHP in the formation of anhydride should come from its sodium ion in the reaction of BTCA with cellulose.

In order to further clarify the catalytic effect of metal ions in promoting the formation of anhydride, BTCA with different alkaline catalysts were heated up in the thermogravimetric analyzer under nitrogen atmosphere. The samples were prepared by dissolving BTCA and alkalines in distilled water, and then heated at 40 °C to constant weights, respectively.

The weight losses of BTCA with different alkaline bases under increased temperatures are shown in Fig. 2. Without the addition of any metal ions, BTCA started losing weight (water) at 204 °C by forming anhydride and continued with further weight loss

corresponding to degradation of the compound (Morris et al. 1996). But, the addition of three bases all lowered the temperature of the initial weight loss of BTCA, with LiOH and NaOH decreasing to about 194 and 187 °C (Fig. 2), respectively. However, KOH is more efficient in lowering the temperature of the formation of anhydride, decreasing the temperature to near 165 °C, and the weight loss occurred rapidly at a lower temperature range than those of the other two samples (Fig. 2). These results are consistent with these of esterification and WRA values (Table 1), serving as solid evidence of the alkaline metal ions affecting the formation of anhydride. Therefore, sodium ion in SHP plays this role in catalyzing the reaction of BTCA with cellulose.

To further understand how the alkaline metal ions interfere the formation of anhydride, a computational modeling study was conducted, focusing on the inter- and intra-molecular hydrogen bond interactions of BTCA with existence of three different alkaline metal ions (Krest'yaninov et al. 2014).

As shown in Fig. 3, hydrogen bond interactions between two BTCA molecules under the existence of alkaline metal ions are presented based on the computer modeling using Gaussian 09 W (Ramnial et al. 2003). BTCA could have up to four hydrogen bond interaction sites between two molecules (Fig. 3a). However, only one hydrogen bond appears if one Li^+ ion is added into one BTCA (Fig. 3b). When Na^+ and K^+ ions are added into BTCA molecules, respectively, no hydrogen bond could be formed between these molecules (Fig. 3c, d). Obviously, when the metal cation size becomes large enough, it could completely eliminate intermolecular hydrogen bond interactions, which could possibly
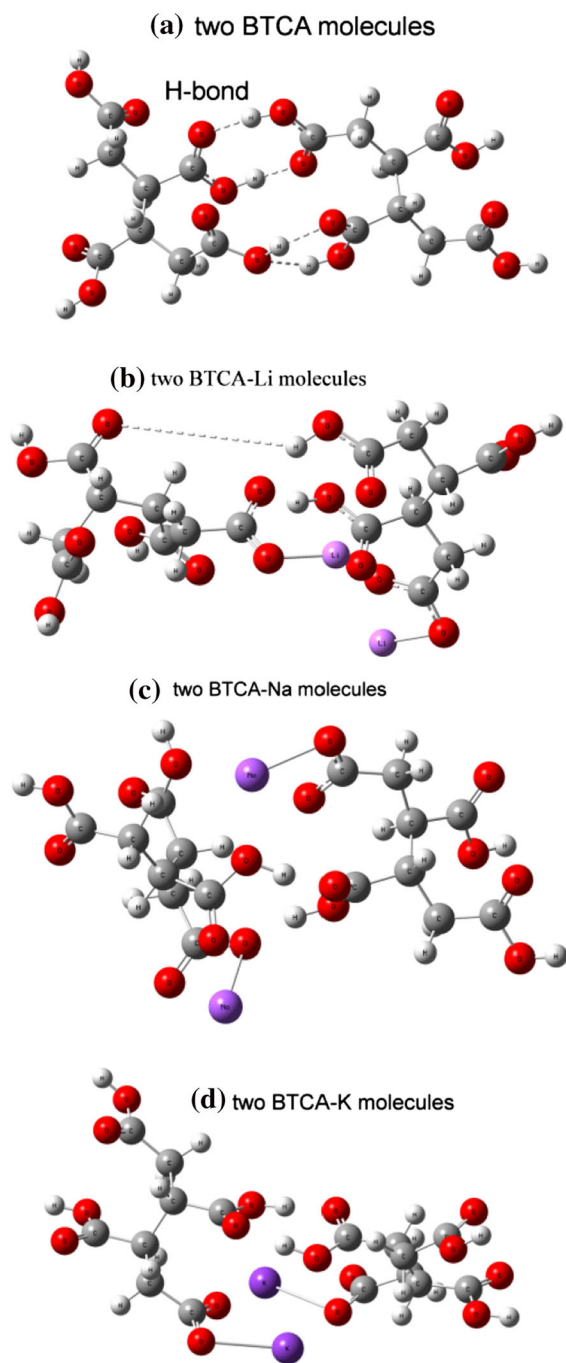
(a) two BTCA molecules

(b) two BTCA-Li molecules

(c) two BTCA-Na molecules

(d) two BTCA-K molecules

Fig. 3 The optimized conformations and the H-bonds of BTCA molecules with alkaline metal ions by Gaussian 09 W (*single dash line* means H-bond): The *white ball* is hydrogen atom, the *grey ball* is carbon atom, the *red ball* is oxygen atom, and the *blue ball* is lithium atom (**b**), sodium atom (**c**) and potassium atom (**d**), respectively

make the rotation of the end carboxylic group in BTCA easier and consequently formation of anhydride at lower temperatures. These results again support that alkaline metal ions are the catalysts in the formation of anhydride of BTCA.

Step-by-step anhydride formation

There are four carboxylic groups in each BTCA molecule, and two anhydrides can be formed under the same condition theoretically (Yang 1991a). However, it is not clear whether both anhydrides are formed simultaneously or separately before reacting with cellulose. Since one mole alkaline ion (mole ratio of $Na^+/BTCA = 1.0$) could catalyze the formation of one anhydride according to the above mechanism, more alkaline ion above one mole should be able to catalyze the formation of two anhydrides simultaneously. Here, to answer such a question, BTCA was mixed with NaOH at different mole ratios with intention to promote formation of two anhydrides on the molecule. Table 2 shows the weight loss results of the mixtures under programmed heating conditions since only the formation of anhydride could result in weight losses.

The pH values and theoretical weight losses of the mixtures corresponding to one water molecule are listed, together with weight losses measured from TGA data in two temperature ranges, 120–160 and 120–200 °C. Interestingly again, when NaOH/BTCA mole ratio was raised from 0.25 to 1.25, the weight losses of the samples due to the formation of anhydride, were gradually reduced, instead of increased. This looks surprising but is normal since the pH values of the systems are also increased as more NaOH is added, which could inhibit the formation of anhydride and even esterification reactions. Thus, raising the mole ratio of $Na^+/BTCA$ was unable to promote the formation of two anhydrides structures of BTCA. So we believe that the formation of anhydride of esterification with cellulose probably follows a step-by-step pattern under such reaction conditions, meaning that the first anhydride is formed and esterifies with cellulose, and then the second one will be formed and consequently reacts with cellulose again, resulting cross-linking of cellulose (Scheme 1b).

Table 2 Results of TGA weight-losses and other properties of treated fabrics

NaOH mole ratio	pH value of solution	Theoretical weight-loss[a] (%)	Weight-loss of TGA test (%)		TA[b]	WRA (°)
			120–160 °C	120–200 °C		
NC	1.84	7.69	0.065	0.130	0.108	193.0
0.25	2.80	7.51	0.182	5.557	0.303	244.6
0.50	3.17	7.34	0.019	4.324	0.473	268.0
0.75	3.45	7.18	0.127	2.306	0.424	263.0
1.00	3.69	7.03	0.055	0.496	0.452	262.7
1.25	3.91	6.88	0.051	1.423	0.337	260.8

[a] Values are based on formation of a single anhydride

[b] TA means the total anhydride bond ratio

To further prove the hypothesis of the step-by-step reaction mechanism, fabrics were treated with BTCA in different mole ratios of NaOH/BTCA. Total anhydride (TA) bond intensities [(1780 + 1724)/2900 cm^{-1}], and WRA values of the treated fabrics are presented in Table 2. The total anhydride (TA) ratios of the fabrics reached the highest at 0.5 mol ratio of NaOH/BTCA and gradually decreased with the increasing mole ratio (Table 2). However, the WRA values of the treated fabrics were almost unchanged after reaching the maximum at NaOH/BTCA mole ratio = 0.5. Overall, increasing NaOH/BTCA mole ratio did not achieve corresponding increases in anhydride and WRA, consistent with the TGA results shown in Table 2, supporting a step-by-step reaction mechanism.

In addition, we would like to quantitatively measure the amounts of anhydride structures on the treated fabrics. In order to retain the reactive anhydride groups but remove unreacted BTCA on the treated fabrics, acetone was employed as a washing solvent. The BTCA (9.0 % instead of 6.3 %) treated fabrics with or without acetone washing were both measured by FTIR. The higher concentrations of BTCA in the treatment solutions make the comparison of anhydride and ester band intensities under different metal cations easier.

Anhydride bond intensity ratios (1780/2900 cm^{-1}) (Fig. 4a) for different catalysts before acetone washing were almost 3 times stronger than those ratios in Table 1, and after acetone washing, the corresponding ratios were also very strong, indicating that many anhydride did not react with cellulose during the reaction. The total anhydride (TA) band ratio and ester
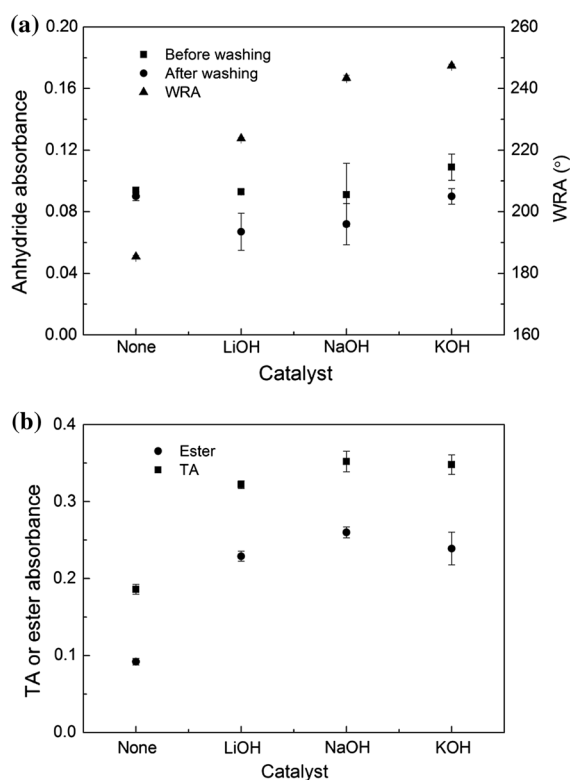

Fig. 4 Anhydride bond ratios with or without acetone washing and WRA values of treated fabrics (**a**); and ester bond ratio and total anhydride ratios of treated fabrics (**b**) under different catalysts (BTCA = 9.0 %)

bond ratio (Fig. 4b) were about 1.6 and 1.1 times stronger than the corresponding ratios in Table 1, respectively. Due to the fact that anhydride once formed should react with cellulose rapidly, more ester bonds should be formed if anhydride was produced
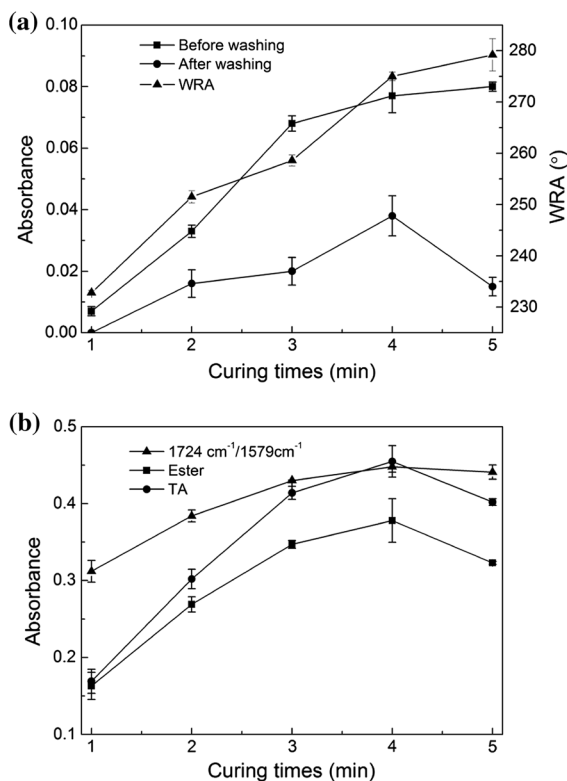
Fig. 5 Anhydride bond ratios with or without acetone washing and WRA values of treated fabrics (**a**); and 1724/1579 cm^{-1} band intensity ratio, ester bond ratio and total anhydride ratios (TA) of treated fabrics (**b**) under different curing times

initially. Thus, the results of more anhydride bonds left on the treated fabrics support the step-by-step process.

In addition, the effects of curing time on the formation of anhydride and ester structures were studied, and BTCA treated fabrics were cured for different times with NaOH (0.5 mol ratio) as a catalyst. As the curing time was increased from 1 to 5 min, the anhydride bond ratios after acetone washing decreased significantly (Fig. 5a). WRA values of the treated fabrics always increased with the prolonged curing time. The changing patterns of ester and TA bond ratios versus curing time were same, and reached the strongest value at 4 min (Fig. 5b). The FTIR absorbance ratios of 1724/1579 cm^{-1} indicate that the average ester bond numbers formed from the carboxyl groups in each BTCA molecule (Yang 1991b) increased as the curing time was prolonged in general. This result explains the reason of continuous increase in WRA values as curing time was increased (Fig. 5a), because the second anhydride is

continuously formed and consequently reacts with cellulose, increasing the cross-linking between BTCA and cellulose. Again, such results support the hypothesis of the step-by-step reaction mechanism.

Conclusion

Proper amount of alkaline metal ions could catalyze the formation of BTCA anhydride by decreasing hydrogen bond interactions between molecules, which is one of the catalytic effects of sodium hypophosphite. Based on the results of FTIR analyses and WRA values of treated fabric, several alkaline metal ions provided the same effects and potassium cation was the most effective one among Li$^+$, Na$^+$ and K$^+$ in catalyzing the reaction. The temperatures of forming BTCA anhydride were lowered following the same trend of the ion size changes according to TGA results. Moreover, the results all support a hypothesis of step-by-step esterification mechanism of BTCA with cellulose, which can explain the increased cross-linking effect under prolonged reaction times.

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