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Multifunctional finishing of cotton fabrics with 3,3′,4,4′-benzophenone tetracarboxylic dianhydride: Reaction mechanism

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ABSTRACT

Aqueous solutions of 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BPTCD) were successfully employed in treatment of cotton fabrics to bring multiple functions onto the cotton cellulose. The overall reaction mechanism of the chemical finishing process was investigated. Results revealed that the dianhydride groups of BPTCD were hydrolyzed to tetracarboxylic acid groups, and the acid could directly react with hydroxyl groups on cellulose under the catalyst sodium hypophosphite to form ester bonds. Such a mechanism is different from the mostly recognized formation of anhydride from polycarboxylic acid and then esterification between the anhydride with hydroxyl groups. FTIR, DSC and thermogravimetric analyzer (TGA) were employed in the analysis of the reactions, respectively.

1. Introduction

Wrinkle-free treatment of cotton fabrics is generally achieved by chemically crosslinking cotton cellulose by using traditional formaldehyde containing N-methylol compounds or non-formaldehyde 1,2,3,4-butanetetracarboxylic acid (BTCA) (Hashem, Ibrahim, El-Shafei, Refaie, & Hauser, 2009; Lam, Kan, & Yuen, 2011; Yang & Wei, 2000a, 2000b). The ultraviolet (UV) protective function on the fabrics, which is important for protecting both materials and wearers (Gouda & Keshk, 2010; Lu, Fei, Xin, Wang, & Li, 2006), can be obtained by incorporating UV absorbents or UV blockers onto the fabric (Czajkowski, Paluszkiewicz, Stolarski, Kaźmierska, & Grzesiak, 2006; Hatch & Osterwalder, 2006; Hou, Zhang, & Wang, 2012; Ibrahim, E-Zairy, & Eid, 2010; Wang & Hauser, 2010). To obtain both functions, multi-step chemical treatments of cotton fabrics should be carried out, which could consume large quantity of water and energy and consequently increase costs and environmental impacts. Thus, development of energy efficient multi-functional finishing processes of textiles is extremely important.

In a previous research, 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BPTCD) was directly incorporated to cotton cellulose by using N,N-dimethylformamide (DMF) as a solvent (Hong & Sun, 2011). The results proved that the BPTCD could crosslink with cellulose, and the benzophenone group could introduce photo-active antimicrobial functions to the products. However, due to the use of DMF as a solvent, the treatment process is not practical to textile industry. Since the two anhydride groups in BPTCD could be hydrolyzed to tetracarboxylic acids, which will make the compound, benzophenone tetracarboxylic acid (BPTCA), soluble in hot water, direct use of BPTCD aqueous solutions as finishing baths of cotton fabrics is possible. Thus, a process of using hydrolyzed BPTCD in aqueous solutions in treatment of cotton fabrics was developed, and the process was successful and industrially practical. Based on the well-recognized reaction mechanism of polycarboxylic acids in crosslinking cellulose, the polycarboxylic acids should form anhydrides on cotton which then can form ester bonds with cellulose (Yang, 2003; Yang & Wang, 1996). Thus, the benzophenone tetracarboxylic acid should form BPTCD again on cellulose, and an esterification reaction should occur between the anhydride and hydroxyl groups on cellulose consequently under elevated temperatures. However, the results obtained in this treatment of cotton fabrics revealed that the polycarboxylic acids in the system could directly react with hydroxyl groups under the catalyst, sodium hypophosphite, and form ester bonds without going through the formation of anhydride. To further prove and understand the overall reactions of the benzophenone tetracarboxylic acid on cellulose, FTIR spectrometer, differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA) were employed in the structural analysis of the materials. The reaction condition and potential mechanism are discussed in this paper.

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2. Experimental

2.1. Materials

Desized, scoured, and bleached pure cotton plain woven fabrics (#400) were purchased from Test Fabrics, Inc. (West Pittston, PA). 3,3′,4,4′-Benzophenone tetracarboxylic dianhydride (BPTCD) and sodium hypophosphite monohydrate were purchased from Sigma Chemical Co. (Louis, MO, USA). All other chemicals were purchased from Fisher Scientific (Pittsburgh, PA, USA). All reagents were used as received without any further purification.

2.2. Preparation of functional cotton fabrics

BPTCD was dissolved in distilled water in a concentration of 70 g per liter (70 g/L) at 70–80 °C under agitation. Sodium hypophosphite monohydrate was added as a catalyst to the BPTCD solution based on a molar ratio of the catalyst versus BPTCD (Yang, 2003; Yang & Wang, 1996). The cotton fabric was first impregnated in the solution containing both BPTCD and the catalyst, then padded through two dips and two nips to reach an average wet pickup of 120%, dried at 80 °C for 5 min, and cured in a curing oven (Roaches International Ltd., Staffordshire, England) at a specified temperature for 3 min. And finally the treated fabrics were washed with water. Additional washing in sodium hydroxide (0.1 N) was performed for FTIR analysis only.

2.3. Characterization of treated fabrics

Fourier transform infrared (FTIR) spectroscopy was performed with a Nicolet 6700 FTIR spectrometer (Thermo Electron Co., USA) with a resolution of 4 cm^{-1}, and measurements were carried out by using KBr pellets. Differential scanning calorimeter (DSC) and Thermogravimetric analysis (TGA) of samples were carried out using a Shimadzu DSC-60 and TGA-60 system (Shimadzu Science Instruments, Inc., USA) at a heating rate of 10 °C/min from room temperature to 500 °C under a nitrogen atmosphere.

3. Results and discussion

3.1. BPTCD treatment of cotton fabrics

The anhydride groups in BPTCD are both reactive with water and hydroxyl groups in cellulose structure, and the reactions between these groups can lead to formations of carboxylic acids and ester bonds quickly (Yang, 2003; Yang & Wang, 1996). When BPTCD is added into hot water, the anhydride will be hydrolyzed to polycarboxylic acids, making the compound soluble in water. The solution was applied onto fabrics by a dip-nip-dry-cure process. Fabrics were treated with a solution of 70 g/L of BPTCD in a wet pick up rate of 120%, dried at 80 °C. The chemical structures of the aqueous BPTCD solution treated cotton fabrics were examined by using FTIR. Fig. 1 shows FTIR spectra of the untreated (control) cotton fabric (Fig. 1a), the fabric treated with the BPTCD solution (70 g/L), dried at 80 °C, and cured at 160 °C (Fig. 1b), cured and after regular washing (Fig. 1c), and cured and after alkaline washing (Fig. 1d), respectively. The formation of carbonyl bonds at 1722 cm^{-1} on the cotton sample treated with BPTCA is clearly noticeable in Fig. 1b–d. Regular washing did not remove the incorporated chemical (Fig. 1c). After alkaline (0.1 N NaOH) washing, the band at 1722 cm^{-1} weakened but a strong new band at 1586 cm^{-1} appeared, which is corresponding to carboxylate ions (COO$^-$), indicating that free carboxylic acids are converted to the salt of the acid. The vibrational absorbance at 1722 cm^{-1} in Fig. 1d is a clear signal of formation of ester bonds between the benzophenone derivative and cellulose, while the existence of free acid show overlapped band at 1722 cm^{-1}. The alkaline washing treatment of the fabric also proved durable ester bond connection between BPTCA and cotton cellulose.

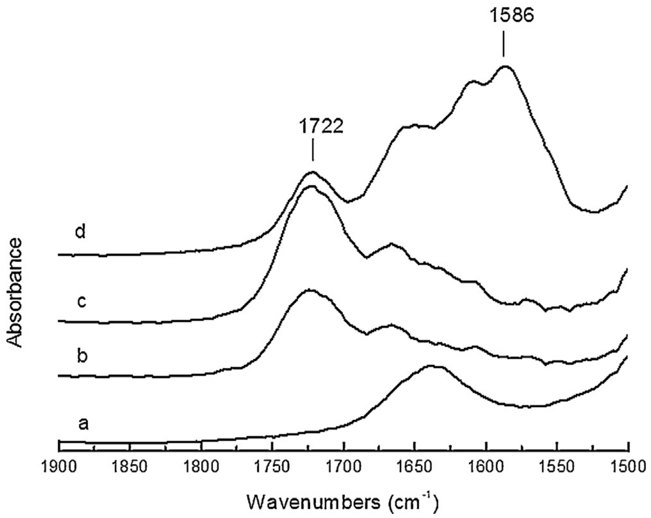


Fig. 1. FTIR spectra of: (a) untreated (control) cotton fabric; (b) fabric treated with BPTCD solution (70 g/L) and cured at 160 °C; (c) cured and after regular washing; and (d) cured and after alkaline washing.

3.2. Whether anhydride is formed first?

According to the reaction mechanism of butane tetracarboxylic acid (BTCA) reaction on cellulose, the polycarboxylic acid groups will form anhydride, and then the active anhydride will react with hydroxyl groups of cellulose to form ester bonds under a catalyst, sodium hypophosphite and an elevated temperature (Yang, 2003; Yang & Wang, 1996). Such a mechanism was our initial speculation on this treatment process. Thus, 3,3′,4,4′-benzophenone tetracarboxylic acid (BPTCA) on the finished cotton fabrics should return to its original anhydride structure of BPTCD, and then the anhydride group will react with hydroxyl group, during curing. The formed anhydride group should be observed in the infrared spectrum of the treated cotton. However, the FTIR of the treated fabric sample (cured at 160 °C for 3 min) did not show a clear signal of the expected anhydride group (Fig. 1b). Instead, strong vibrational absorbance at around 1722 cm^{-1}, representing both ester and carboxylic acid groups, is shown. This result was unexpected and consequently raised questions on the reaction mechanism of BPTCA with cellulose. Thus, a series of experiments were designed and conducted on the BPTCD treated cotton fabrics to confirm the observations from FTIR analysis. Fabric samples impregnated in an aqueous solution containing 70 g/L of BPTCD (catalyst in a molar ratio of 0.5) were treated in the following steps, (a) only dried at 80 °C for 5 min and no washing; (b) dried at 80 °C for 5 min and cured at 160 °C for 3 min without washing; (c) dried at 80 °C for 5 min and cured at 200 °C for 3 min without washing. FTIR spectra of the samples were carefully taken and are shown in Fig. 2.

The spectrum (a) in Fig. 2 confirmed that the chemical applied onto the cotton is mostly an acid or polycarboxylic acid not an anhydride since no characteristic anhydride peaks (1855 cm^{-1} and 1778 cm^{-1}) are existing in the FTIR spectrum (Fig. 2a). After the fabric was cured at 160 °C for 3 min, the FTIR spectrum (Fig. 2b) did not show clear signal of anhydride peaks either. However, after cured at a higher temperature, 200 °C, for 3 min, the spectrum revealed quite weak but noticeable anhydride peaks (Fig. 2c), meaning that anhydride groups were formed at 200 °C. Such a result is very interesting and different from the literatures (Yang, 2003; Yang & Wang, 1996), indicating that at 160 °C almost no anhydride group was formed but ester bonds between BPTCD and cellulose were indeed

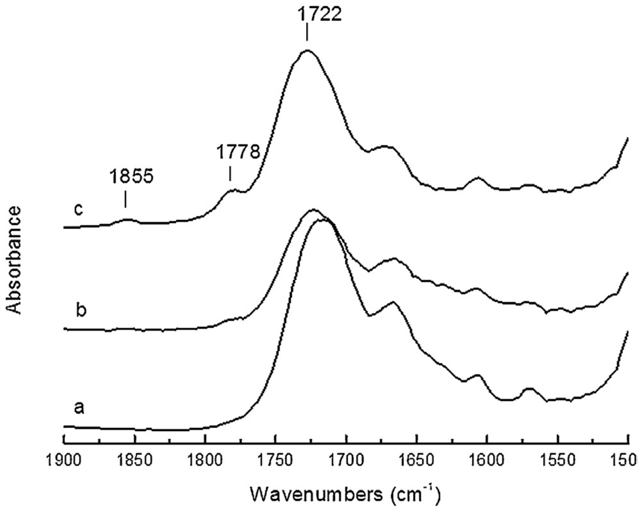


Fig. 2. FTIR spectra of cotton fabric treated with 70 g/L of BPTCD without washing: (a) only dried at 80 °C for 5 min; (b) dried at 80 °C for 5 min and cured at 160 °C for 3 min; and (c) dried at 80 °C for 5 min and cured at 200 °C for 3 min.

established. It suggested that a direct esterification process between polycarboxylic acid and cellulose occurred. FTIR results also confirmed formation of anhydride of BPTCA on the cellulose under a much higher temperature (200 °C), which could cause more negative impacts on the treated fabrics. However, the newly formed anhydride groups should be able to react with cellulose to produce ester bonds or crosslinking cellulose as well.

3.3. *Catalytic effect of sodium hypophosphite*

To further confirm the observation from FTIR, BPTCD was hydrolyzed in hot water again, and its acid derivative, 3,3′4,4′-benzophenone tetracarboxylic acid (BPTCA), was produced. Pure BPTCA was heated up to decomposition in both DSC and TGA apparatuses with and without the catalyst, respectively. Based on the DSC of BPTCA without the catalyst, an endothermic peak at 234 °C on DSC (Fig. 3a) appeared. Thermogram of BPTCA without the catalyst reveals a major weight loss at around 200 °C. The weight loss within this range was 9.28% (200–265 °C), equivalent to losing two water molecules from BPTCA (Fig. 3a and b). This is the formation process of the original anhydride compound, BPTCD. Afterward, the chemical degradation begins, resulting in another major weight loss. The addition of the catalyst did not obviously alter the formation temperature of the anhydride rings and the decomposition temperature of the compound according to the TGA (Fig. 3c). The slight loss of weight in the thermogram is caused by hydrate molecules in the catalyst. However, there is no evidence showing that the addition of the catalyst affected formation of anhydride structure of this polycarboxylic acid (BPTCA).

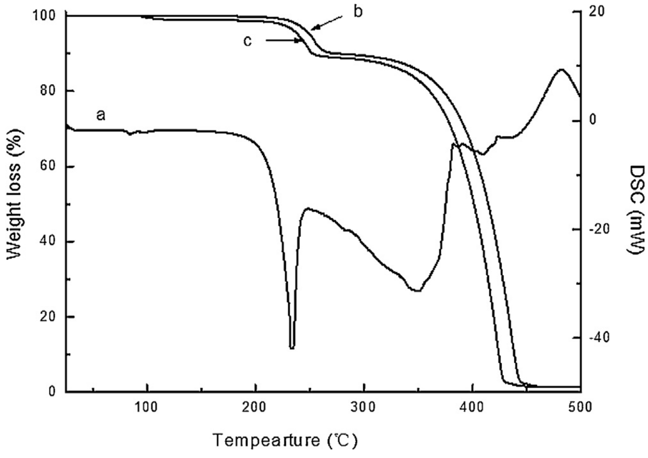


Fig. 3. TGA and DSC of BPTCA with and without the catalyst: (a) DSC of pure BPTCA; (b) TGA of pure BPTCA; and (c) TGA of BPTCA with catalyst (catalyst molar ratio at 0.5).

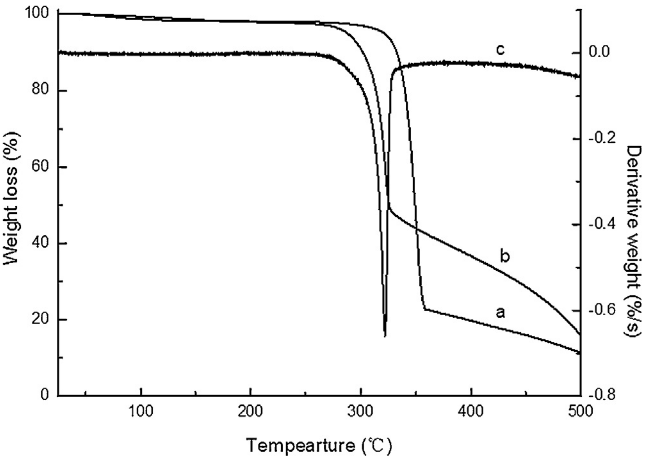
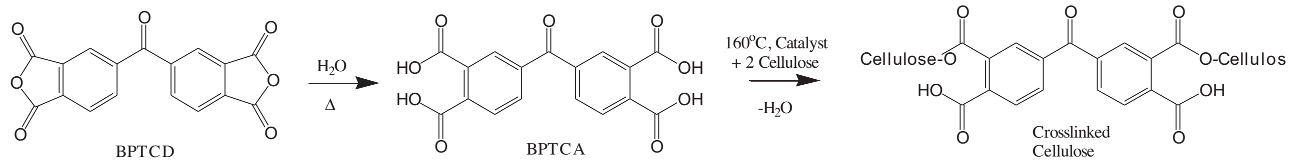


Fig. 4. TGA of pure cotton and TGA and first derivative of TGA of BPTCD treated cotton with the catalyst: (a) TGA of pure cotton; (b) TGA of BPTCD treated cotton with the catalyst; and (c) first derivative of TGA of BPTCD treated cotton with the catalyst.

Then, both pure cotton and a cotton fabric sample impregnated with a solution containing 70 g/L BPTCD and a catalyst in a molar ratio of 0.5 and dried at 80 °C were subjected to similar TGA tests. TGA spectra of the fabric samples are shown in Fig. 4. The TGA of the treated cellulose shows smooth and continuous weight reduction (1.44%) in a temperature range of 100–200 °C (Fig. 4b), while the pure cotton exhibited only 0.50% weight loss in the same temperature range (Fig. 4a). First derivative of the TGA curve (Fig. 4b) did not reveal any peak (Fig. 4c), a sign of continuous dehydration reaction (loss of water) during the temperature range. Both anhydride formation and direct esterification reactions could release water, resulting in related weight loss during the heating. Since FTIR of the cotton sample cured at 160 °C only showed exclusively ester bond (1722 cm^{-1}) (Fig. 2b), confirming that the direct esterification reaction happened, while no anhydride rings were formed, at 160 °C in this process. Thus, we believe that basically the weight loss of the samples was the esterification reaction between BPTCA and cellulose. However, the function of the catalyst in the reaction should be explored.

To further view the function of the catalyst on the reactions on cellulose, TGA of cotton fabric samples treated by 70 g/L of BPTCD in a wet pick up rate of 120%, dried at 80 °C without using the catalyst and with different amounts of the catalyst were carried out and are shown in Fig. 5. All three TGA thermograms show similar weight loss patterns without major difference. In fact, the catalyst itself may also lose water in its monohydrate crystal and cause weight loss (Brenda & Choi, 1994). The increased amount of sodium hypophosphite could interfere with the thermogravimetric analysis. Thus, a limited temperature range of 100–160 °C was selected since the catalyst weight loss is minimal. The weight losses of the samples in the temperature range are listed in Table 1, indicating that the addition of the catalyst indeed have accelerated the weight loss of the samples during heating, a sign of accelerated reactions. More interestingly, the increased dehydration effect was more significant at the temperature range of 100–160 °C than 160–200 °C, which could have more impact on selection of curing temperatures.



Scheme 1. Reaction mechanism of BPTCD with cellulose.

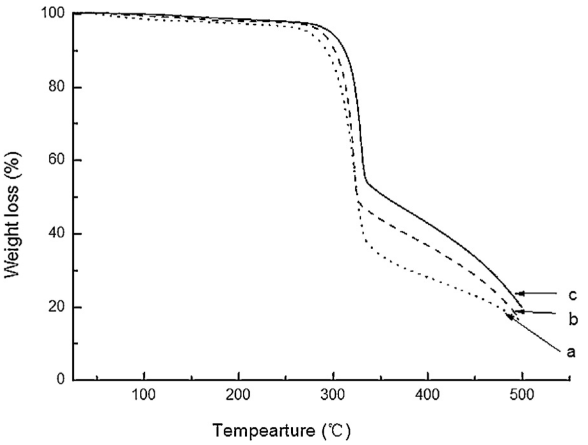


Fig. 5. TGA of cotton fabrics treated with BPTCD 70 g/L with and without the catalyst: (a) without catalyst; (b) catalyst molar ratio at 0.5; and (c) catalyst molar ratio at 2.

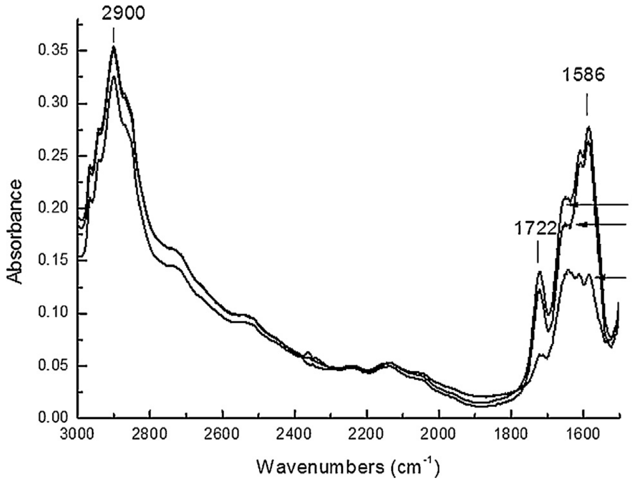


Fig. 6. FTIR spectra of cotton treated by BPTCD after washing in 0.1 M NaOH solution: (a) without catalyst; (b) catalyst molar ratio at 0.5; and (c) catalyst molar ratio at 2.

3.4. *Reaction mechanism*

Based on the above analysis, we would like to propose an overall reaction mechanism for this treatment process as the following (Scheme 1). The BPTCD is hydrolyzed to BPTCA in hot water, which is then applied onto cellulose together with the catalyst, sodium hypophosphite. Under an elevated temperature (160 °C), BPTCA could directly react with hydroxyl groups of cellulose to form ester bonds. Normal esterification reaction of acids with alcohols is slow and reversible. However, the esterification of BPTCA with cellulose could be exceptional since the treatment process has the following features: (1) relatively low pH (2–4); (2) vast majority of hydroxyl groups in cellulose to react with acid groups; and (3) rapid removal of water at a curing temperature above 100 °C. The removal of water molecules breaks the balance of the reaction and drives the reaction forward. The thermograms of three samples (Fig. 5) could partially prove the proposed mechanism since without catalyst esterification also occurred. FTIR spectra of the cotton samples that were used in the TGA studies were also taken (Fig. 6). The three infrared spectra are identical, though peak intensities are different at certain level. This is another solid evidence of esterification reaction occurred between BPTCA and cellulose with or without any catalyst.

Obviously, the peak intensities of ester and carboxylate groups are different from the spectra (Fig. 6). A quantitative analysis of the peak intensities was carried out, and the results are listed in Table 2. The absorbance intensities at 2900 cm^{-1} (representing vibrational band of C—H of cellulose) was employed as a base, and peak intensities at 1722 cm^{-1}, representing ester bonds, and 1586 cm^{-1}, representing carboxylate, COO^- bonds, were divided by that of the base peak. The relative intensities, ratios of the intensities in Table 2, represent the amounts of ester and carboxylate groups on the treated cellulose. Clearly, without the catalyst, sodium hypophosphite, BPTCA can be incorporated onto cellulose by directly forming ester bonds. At 160 °C, addition of the catalyst at 0.5 molar ratio to BPTCD increased the intensities of carboxylate and ester groups 78% (0.42–0.75) and 84% (0.19–0.35), respectively (Table 2). Increase of the catalyst molar ratio from 0.5 to 2 raised more ester intensity (11%, from 0.35 to 0.39) than that of carboxylate group (4%, from 0.75 to 0.78). The relative amount of carboxylate groups versus the ester groups decreased from 2.25 to 2.14, and then 2, respectively, indicating that more carboxylic groups formed ester bonds when the catalyst was increased in the system.

At 200 °C, anhydride groups could form (Fig. 2c), which are more reactive with cellulose than acid groups, thus the esterification reactions should proceed through two mechanisms, one by direct esterification and another by reaction of anhydride with hydroxyl groups. As a result, the relative intensities of ester and carboxylate groups are increased in most samples, and the relative amount of carboxylate groups versus ester groups was further reduced to 1.80 from 2.14, revealing more ester bonds formed under the higher temperature. And more interestingly, the relative intensity of

Table 1
Weight loss of the treated fabrics.

Catalyst ratio	Weight loss (%)	
	100–160 °C	160–200 °C
0	0.76	0.51
0.5	0.99	0.45
2	0.88	0.48

Note: Catalyst ratio = catalyst molar ratio to BPTCD.

Table 2
Relative peak intensities of infrared absorbance under different amount of catalyst.

Temperature	160 °C			200 °C		
Catalyst ratio	0	0.5	2	0	0.5	2
1586 cm^{-1}/2900 cm^{-1}	0.42	0.75	0.78	0.63	0.86	0.74
1722 cm^{-1}/2900 cm^{-1}	0.19	0.35	0.39	0.29	0.43	0.41
1586 cm^{-1}/1722 cm^{-1}	2.25	2.14	2	2.14	2	1.80

Note: Catalyst ratio = catalyst molar ratio to BPTCD.

carboxylate groups first showed increase and then rapidly decreased when the catalyst was increased to a molar ratio of 2. The reduced relative intensity of carboxylic groups was even lower than that at 160 °C with the same amount of catalyst. Since the intensity change of the ester bonds was very small, overall effects of temperature and catalyst further increased ester bond crosslinking reactions between BPTCA and cellulose.

According to the above results, the catalyst indeed promoted esterification reactions between the acid and hydroxyl groups under this treatment process. It seems more catalyst could increase more ester bonds. High temperature could lead to formation of anhydride which could increase the esterification reaction. However, one noticeable change on the high temperature treated cotton is its yellow color, possibly caused by oxidation of cellulose, making the curing temperature of 160 °C a feasible and practical selection.

4. Conclusion

3,3′,4,4′-Benzophenone tetracarboxylic dianhydride (BPTCD) was hydrolyzed to its acid derivative, 3,3′,4,4′-benzophenone tetracarboxylic acid, BPTCA, and the acid was able to directly react with hydroxyl groups on cotton cellulose to form ester bond crosslinkings at an elevated temperature. Direct esterification between BPTCA and cellulose was confirmed by using both thermogravimetric and infrared analyses and could be promoted by addition of a catalyst, sodium hypophosphite. More catalyst and higher curing temperature promoted esterification reaction. However, higher temperature may cause unnecessary oxidation of cotton cellulose.

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