Research Article

Mechanism of Antiwrinkle Finishing of Cotton Fabrics Using Mixed Polycarboxylic Acids

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The kinetics, activation energy, and mechanism of esterification of cotton by mixed polycarboxylic acids, namely, 1,2,3,4-butanetetracarboxylic acid (BTCA) and citric acid (CA), were studied during the curing process of cotton fibers in comparison with the esterification by BTCA alone. The reaction rates of these two polycarboxylic acid finishing systems under different temperatures and the dependency of their reaction rate constants on temperature were studied. Consequently, in the temperature range from 120°C to 180°C, the activation energy of the mixed polycarboxylic acids (BTCA+CA) was obtained as $E_a = 40.7$ kJ/mol, which was slightly lower than that for the BTCA finishing system. The reaction occurring between the carboxylic acid group of BTCA and the hydroxyl group of CA was proposed. To confirm and prove the speculation, experiments were conducted to investigate the changes in wrinkle recovery angle and tensile strength retention by changing the concentration of both the single polycarboxylic acid and mixed polycarboxylic acids. The results show that, besides esterification of cotton fibers, citric acid probably functioned as an extender in the curing process, when it was combined with BTCA.

1. Introduction

Cotton is a natural cellulose fiber that is widely used in apparel textiles because of its desirable properties like softness, comfort, warmth, and hygroscopic nature. However, the slippage movement of the cellulose molecular chains which were held in position by interchain hydrogen bonds results in wrinkle and crease under external forces during use [1]. This drawback greatly restricts its practical applications. To overcome this problem and endow the cotton fabric with antiwrinkle property, cross-linking of cellulose chains (to inhibit their movement) using appropriate resins or polymers has proved to be effective [2–6]. Formaldehyde-based cross-linking agents were the first group of such finishing agents. Among these, dimethylol dihydroxyethyleneurea (DMDHEU) is one of the most widely used agents for producing intermolecular cross-linking to provide easy care properties to the fiber against deformation [7–9]. Moreover, it also improves the elastic recovery of the fiber after deformation with reactive *N*-methylol groups [3, 10, 11]. However,

the fabric treated with compounds containing *N*-methylol group has the problem of releasing formaldehyde, a probable human carcinogen, during manufacturing, wearing, and storage [1, 3]. Since the 1990s, extensive efforts [4, 5, 12–16] have been made to develop formaldehyde-free, durable, and press finishing agents. Polycarboxylic acids such as 1,2,3,4-butanetetracarboxylic acid (BTCA) and citric acid (CA) displayed interesting potential as cross-linking agents for substrates containing hydroxyl groups, including cellulose, starch, and chitosan [15, 17–20]. Many researchers are investigating the effectiveness of the polycarboxylic acid finishing systems for providing antiwrinkle property [5, 6, 21, 22] and the cross-linking mechanism of polycarboxylic acid with the treated cotton fabric [14, 23–25] and are finding appropriate catalysts [5, 24, 26, 27]. BTCA has proved to be the most effective cross-linking agent as it can impart excellent antiwrinkle properties to the finished fabric along with good and durable washability and whiteness. However, a higher cost is the most obvious barrier for BTCA that prevents its use at the technical scale. Methods to reduce the cost

of BTCA finishing technology have been investigated. These include combination with other carboxylic acids such as citric acid (CA) [28, 29] because CA is a sustainable chemical, cheap, and eco-friendly. However, it is an inferior wrinkle-resistant agent and leaves a yellowing effect on the CA-treated fabrics [30, 31].

In our previous work, we investigated the best conditions to optimize the wrinkle recovery properties and strength retention of cotton fabric with the BTCA and BTCA/CA finishing systems using the response surface methodology (RSM) and BBD (Box-Behnken design) [32, 33]. Moreover, we also investigated the influence of operating parameters and coupling effects between them. The results indicated that a combination of BTCA and CA could lead to an improvement in both wrinkle resistance and strength retention properties compared to a single BTCA finishing system under lower curing temperatures. This observation was interesting because CA usually performed well only under relatively harsher conditions [30, 31, 34]. As an attempt to evaluate the reactivity of BTCA/CA, the esterification kinetics of the BTCA/CA finishing system was investigated in comparison with that of the single BTCA system to prove the reactivity and the effectiveness of mixed polycarboxylic acids. The reaction rate constant and activation, as well as the possible mechanism, are also proposed.

2. Experimental

2.1. Materials. Desized scoured, bleached, and mercerized pure cotton plain-woven fabrics (weight: 140 g/m²; warp density: 52.4 ends/cm; weft density: 28.3 picks/cm; and yarn count: 14.75 tex × 14.76 tex) were purchased from Weifang Qirong Textile Co., Ltd., Weifang, China. 1,2,3,4-Butanetetracarboxylic acid (BTCA), sodium hypophosphite (SHP) monohydrate, and hydrochloric acid (HCl) were purchased from China National Pharmaceutical Group Co., Ltd., Shanghai, China. Sodium hydroxide (NaOH) was purchased from Kemiou Chemical Reagent Co., Ltd., Tianjin, China. Silver nitrate (AgNO₃) and barbituric acid were purchased from Xiya Reagent, Linyi, China. Calcium acetate was purchased from Tianjin Dingshengxin Chemical Co., Ltd., Tianjin, China. Cresol red was purchased from MACKLIN Reagent, Shanghai, China. Thymol blue sodium salt was purchased from Beichen Fangzheng Reagent, Tianjin, China. Barbituric acid was purchased from Shanghai Zhanyun Chemical Co., Ltd., Shanghai, China. Hydrochloric acid (HCl) and barbituric acid were of chemically pure grade, and other reagents were of analytical grade. All reagents were used without any further purification.

2.2. Fabric Treatment. The cotton fabric was first impregnated in an aqueous solution containing both BTCA and sodium hypophosphite (SHP); the pH of the solution was adjusted to 2.5 using 1 M NaOH. The samples were then padded through two dips and two nips to reach an average wet pickup of about 80%. They were then dried at 80°C for 5 min and cured at a specific temperature for a specific time in a curing oven. In case of investigation of kinetics, the cur-

ing process was set at 120°C, 140°C, 160°C, and 180°C for 30 s, 60 s, 90 s, 120 s, and 150 s.

For investigating the kinetics, the finishing solutions of (i) a BTCA/CA system containing 50 g/L of BTCA, 45 g/L of CA, and 38 g/L of SHP and (ii) a BTCA system containing 73 g/L of BTCA and 38 g/L of SHP were used to treat the fabrics. These two formulas were the best formula obtained, to optimize the wrinkle resistance and strength retention, in our previous work [32, 33].

In order to calculate the content of free carboxylic acid before the esterification reaction, fabrics were dipped and nipped two times, followed by drying at 80°C for 5 min without exposure to the curing process. Further, the washing process was omitted after curing to calculate the content of esters in the cured fabrics.

2.3. Characterization of Finished Fabrics

2.3.1. Wrinkle Recovery Angle (WRA). The WRAs of the treated fabrics were measured according to the American Association of Textile Chemists and Colorists (AATCC) method 66-1990 with an LFY-1 fabric wrinkle recovery tester. Each sample was measured twelve times in both the warp and weft directions to obtain the average value.

2.3.2. Tensile Strength (TS). The tensile strength of the finished fabrics was measured by using a YG026 electronic fabric strength tester according to the ASTM D 5035-90. All measurements were performed in the weft direction to characterize and calculate the strength retention of the treated fabrics.

$$\text{TS retention (\%)} = \frac{\text{TS}_i}{\text{TS}_0}, \quad (1)$$

where TS₀ and TS_i are the tensile breaking strengths (N) of the fabrics before and after the finishing treatment under various conditions, respectively.

2.3.3. Yellowness Index (YI). The yellowness index of all finished and control cotton fabrics was tested according to ASTM D 1925 (observer: 2°, illuminant: c) [27], which was carried out on a spectrophotometer (X-Rite, Inc., Grand Rapids, MI) under illuminant c using a 2° standard observer. Four measurements for each fabric sample were taken to obtain the average value.

2.3.4. Carboxyl Content Determination. Calcium acetate titration [35, 36] was used for the determination of the carboxyl content of the treated cotton fabrics. This method is based on ion exchange and involves the reaction of the carboxyl groups with calcium acetate, as shown in Scheme 1.

Before titration measurement, the treated fabric was divided into single yarns, kept at room temperature for 24 h, and then dried at 80°C to yield a constant weight. About 500 mg of the fabric was placed in a 100 mL ground-glass-stoppered Erlenmeyer flask, and 25 mL of an aqueous solution of 0.1 M fresh (CH₃COO) Ca was added to it. The blank test was performed separately. After shaking for 2 h at room temperature, ten drops of the mixed indicators thymol blue

SCHEME 1: Ion exchange between the carboxyl group and calcium acetate.

and cresol red were added into the flask. Titration was carried out using 0.01 M NaOH solution until the color of the solution changed from yellow to violet.

Carboxylic acid content ($c_{(\text{PCA})}$) of the treated fabric, i.e., the nonreacted free carboxylic acid after the curing process, was calculated according to the following equation:

$$c_{(\text{PCA})} = \frac{V \times c}{W} \left(\frac{\text{mmol}}{\text{g}} \right), \quad (2)$$

where V is the volume of consumed NaOH solution, c is the concentration of standard NaOH solution, and W is the weight of the treated fabric used for titration.

The consumed carboxylic acid was calculated by $c_{0(\text{PCA})} - c_{(\text{PCA})}$. Here, $c_{0(\text{PCA})}$ is the carboxylic acid content before curing, and $c_{t(\text{PCA})}$ is the nonreacted carboxylic acid content after being cured for a given period of time.

3. Results and Discussion

3.1. Consumption of Polycarboxylic Acids. In order to determine the curing time and temperature range for calculating the kinetics data of esterification, the amount of carboxylic acid consumed in the esterification process during the curing step under different temperatures was measured by the calcium acetate titration as shown in Figures 1 and 2. The temperatures 120°C, 140°C, 160°C, and 180°C were selected in this investigation. We saw that the consumption of carboxylic acids increased as the curing time prolonged, and a higher amount of carboxylic acids was consumed under higher temperatures for both the finishing systems. This showed that the esterification of carboxylic acids with cellulose was accelerated by temperature. In addition, the consumption increased and was then maintained at a nearly constant level under higher temperatures when the curing time was longer than 120 s. This indicated that the reaction had approached an equilibrium condition.

3.2. Calculation of the Rate Constant of Esterification. According to the reaction mechanism, polycarboxylic acids react with the hydroxyl groups in the cellulose to form an ester linkage and impart wrinkle recovery properties to the treated fabrics. As previously reported, the kinetics of esterification [37, 38] between the polycarboxylic acids and the cellulosic hydroxyl groups can be depicted as a pseudo-first-order reaction with respect to the carboxylic acid concentration; the reaction rate τ was calculated according to the following equation:

$$\tau = -\frac{dc_{(\text{PCA})}}{dt} = k c_{(\text{PCA})}^{\alpha} c_{(\text{CAT})}^{\beta} c_{(\text{OH})}^{\gamma}, \quad (3)$$

where k is the reaction rate constant, $c_{(\text{PCA})}$, $c_{(\text{CAT})}$, and $c_{(\text{OH})}$ are the concentrations of the carboxylic acid, catalyst, and hydroxyl groups in cotton cellulose, respectively. α , β , and γ are the orders of the reaction. As the concentration of the catalyst was considered to be constant, the hydroxyl group was considered to be in excess in comparison with the amount of PCA. Hence, it could be assumed to be constant and Equation (3) was transformed into Equation (4) as below:

$$\tau = -\frac{dc_{(\text{PCA})}}{dt} = k_1 c_{(\text{PCA})}. \quad (4)$$

By taking the logarithm of both sides of Equation (4), Equation (5) was obtained.

$$\ln c_{0(\text{PCA})} - \ln c_{t(\text{PCA})} = k_2 t, \quad (5)$$

where $c_{0(\text{PCA})}$ is the concentration of carboxylic acids before curing, i.e., the carboxylic acid content at the beginning of the esterification, and $c_{t(\text{PCA})}$ is the concentration of carboxylic acids that have not reacted after curing for a specific time. The nonreacted carboxylic acid content in the fabrics, which have undergone curing for different time points, was calculated from the calcium acetate titration method. Thus, we plotted $\ln c_{0(\text{PCA})} - \ln c_{t(\text{PCA})}$ against the curing time (t) and obtained the value of the slope that represented the constant rate.

Figures 3 and 4 show the esterification kinetics of carboxylic acid under different temperatures in the BTCA and BTCA-CA finishing systems, respectively. To calculate the esterification rate constant, the regression lines of $\ln c_{0(\text{PCA})} - \ln c_{t(\text{PCA})}$ were plotted against the curing time (t). Additionally, the reaction rate constants under different temperatures (120°C, 140°C, 160°C, and 180°C) were calculated from which the activation energy was calculated. Each set of data gave a straight line, as shown in Figures 3 and 4, indicating first-order kinetics with respect to the free carboxylic acid content in the treated fabrics. The slopes of the regression lines were the values of the esterification rate constants. The resulted values are listed in Table 1, showing that the rate constants increased with an increase in the curing temperature. This demonstrated that the esterification reaction was faster under higher temperatures.

3.3. Calculation of Activation Energy. Higher temperatures accelerated the process of esterification. The temperature dependence of the rate constant followed the Arrhenius equation, as shown in Equation (6). By taking the logarithm of both sides of Equation (6), a new equation was obtained.

$$k = A e^{(-E_a/RT)}, \quad (6)$$

$$\ln k = \ln A - \frac{E_a}{RT}, \quad (7)$$

where A is the frequency factor, E_a is the Arrhenius activation energy, R is the gas constant (8.314 J/(mol·K)), and T is the

FIGURE 1: Effect of curing time on the consumption of carboxylic acids in the BTCA finishing system.

FIGURE 2: Effect of curing time on the consumption of carboxylic acids in the BTCA/CA finishing system.

temperature. According to Equation (7), E_a was calculated by plotting $\ln k$ against $1/T$. By adding the values of the rate constants from Table 1 and those of the corresponding temperature into Equation (7), the fitting curves of $\ln k$ against $1/T$ were plotted in Figures 5 and 6.

The slopes and the intercepts of the corresponding regression lines represented $-R/T$ and $\ln A$, respectively.

The overall apparent activation energy using mixed acids of BTCA/CA esterification with hydroxyl groups during the curing process was calculated to be 40.70 kJ/mol that was slightly lower than the values for the BTCA esterification (44.4 kJ/mol) (Table 1). This suggested that by combining CA in the BTCA finishing system, the esterification process was easier. This was an interesting observation of a possible

FIGURE 3: Esterification kinetics plot for the BTCA finishing system under various temperatures.

FIGURE 4: Plot of the esterification kinetics for the finishing system combining BTCA and CA under various temperatures.

reaction between BTCA and CA since it was earlier reported that CA had a weaker reactivity than BTCA [37].

4. Mechanism Analysis

As shown in the previous report, the α -hydroxyl groups in the citric acid molecule hindered its esterification with cellu-

lose [39]. Moreover, the presence of other polycarboxylic acids, such as homopolymers and terpolymers, reacted with the hydroxyl group and transformed CA from trifunctional to tetrafunctional molecule. Therefore, the increased reactivity of the BTCA/CA system was interpreted by similar esterification of the carboxylic acids in the BTCA molecule with the hydroxyl groups of citric acid, correspondingly increasing

TABLE 1: Kinetics data of esterification during the curing process for both the BTCA and BTCA/CA system.

	120°C	140°C	160°C	180°C	E_a (kJ/Mol)	A
BTCA	0.00057	0.001	0.002	0.00337	44.4	441.98
BTCA/CA	0.00034	0.0006	0.0009	0.0016	40.7	77.9

FIGURE 5: Linear fitting plot of $\ln k$ with $1/T$ of reaction constants of BTCA. FIGURE 6: Linear fitting plot of $\ln k$ with $1/T$ of reaction constants of BTCA and CA.

the effectiveness of the BTCA/CA finishing system. With such a possible reaction mechanism in mind, a series of experiments were designed and conducted with the cross-linking of either BTCA or CA or a combination of these

two. The fabric samples were impregnated in the following four groups of aqueous solutions: (a) BTCA (from 10 to 90 g/L), (b) CA (from 10 to 90 g/L), (c) BTCA (50 g/L)+CA (from 20 to 70 g/L), and (d) CA (40 g/L)+BTCA (from 10

FIGURE 7: (a) WRA and TS retention of fabrics treated with BTCA. (b) WRA and TS retention of fabrics treated with CA. (c) Effect of changing concentration of CA on fabrics treated with BTCA/CA combination with 50 g/L BTCA. (d) Effect of changing concentration of BTCA on fabrics treated with BTCA/CA combination with 40 g/L CA.

to 50 g/L). SHP (38 g/L) was the catalyst in all the finishing baths. Subsequently, the impregnated fabrics were dried at 80°C for 5 min and cured at 170°C for 90 s.

From Figures 7(a) and 7(b), it was seen that the fabrics treated with either BTCA or CA alone possessed higher WRA and lower tensile strength. It has been demonstrated in earlier reports that the loss of strength in the treated fabrics was attributed to ester cross-linking between polycarboxylic acid and cellulose, besides the process of acidic degradation. However, fabrics treated with the combination of BTCA and CA displayed a different pattern than that shown by fabrics treated with BTCA or CA alone. As seen in Figure 7(c), a slight increase in the strength of the fabric was observed when the concentration of CA increased from 20 to 40 g/L in the presence of 50 g/L BTCA. This phenomenon could

possibly be explained by the esterification of carboxylic acids in BTCA and that of the hydroxyl groups in the CA molecule, which formed longer and flexible cross-linking bridges between the cellulose chains. This bridge formation was very similar to the role of an extender [31]. In addition, this kind of esterification was expected to take place when sufficient BTCA and CA were present as no increase in strength was observed (Figure 7(d)). A possible cross-linking pathway is presented in Scheme 2. The results indicated that there was a coupling effect between BTCA and CA and the fabrics treated with the combination of BTCA (50 g/L) and CA (about 40 g/L) displayed a compromised WRA and tensile strength, which was consistent with our previous report [29]. In addition, using mixed polycarboxylic acids also has an advantage of decreasing the yellowness of the treated

SCHEME 2: Possible cross-linking between polycarboxylic acids and cellulose.

fabric when compared to that treated with CA alone, as shown in Table 2, possibly, partially due to the reaction of hydroxyl groups of CA to the carboxylic acid groups in BTCA and inhibiting formation of unsaturated aconitic acid [22, 31].

5. Conclusion

The kinetics and activation energy for the esterification of cotton fabric were investigated using different polycarboxylic acids, namely, a combination of BTCA and CA and CA alone. The activation energy of 40.7 kJ/mol of BTCA/CA was slightly lower than that of BTCA (44.4 kJ/mol); this demonstrated a possibly higher reactivity for the BTCA/CA finishing system. A probable reason for this observation was proposed. The proposed mechanism was proved when a change was observed in the pattern of the WRA and tensile strength of the fabrics treated with increasing concentrations of polycarboxylic acids in the BTCA, CA, and BTCA/CA fin-

TABLE 2: Yellowness index of fabrics treated with polycarboxylic acids.

Samples	YI
Control cotton	4.80
BTCA ^a	8.85
BTCA/CA ^b	11.53
CA ^c	13.26

^aFinishing solution: 73 g/L BTCA and 38 g/L SHP, cured at 170°C for 90s.

^bFinishing solution: 50 g/L BTCA, 45 g/L CA, and 38 g/L SHP, cured at 170°C for 90s. ^c100 g/L CA and 38 g/L SHP, cured at 170°C for 90s.

ishing systems. The results indicated that CA performed as an extender when sufficient BTCA and CA were present.

Data Availability

All datasets for this study are included in the manuscript.

Conflicts of Interest

The authors declare that they have no competing interests.

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