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Esterification crosslinking structures of rayon fibers with 1,2,3,4-butanetetracarboxylic acid and their water-responsive properties

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Abstract

1,2,3,4-Butanetetracarboxylic acid (BTCA) was applied to crosslink amorphous regions of cotton-type rayon fibers via anhydride-mediated esterification for the purpose of enhanced mechanical properties. Crosslinking was conducted under a series of curing temperature with the presence of sodium hypophosphite (SHP) as the effective catalyst for anhydride formation. The conversion rate based on Fourier transform infrared (FTIR) spectra was in good agreement with that from the direct calculation based on titrated carboxyl groups and ester linkages. Crosslinking degree increased linearly with the curing temperature. The optimal tensile properties were derived from the curing temperature of 180 °C with an intermediate crosslinking degree. Moreover, the crosslinked structures of the rayon fibers had a great impact on absorption of liquid and gaseous water. The liquid water retention capacity diminished substantially with the crosslinking degree, while interaction between moisture and the fibers revealed that sorption–desorption cycles and concomitant hystereses were scarcely affected by the crosslinked fiber structures.

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Keywords: Butanetetracarboxylic acid; Esterification crosslinking of rayon fibers; Water-responsive properties

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1. Introduction

Natural cellulose fibers obtained from wood, cotton, straw, *etc*. have played a key role in the field of textile and paper industries for more than a century owing to remarkable chemical versatility and unique physical properties of cellulose so far not possible to be obtained from any other polymer. Crosslinking cellulose with *N*-methylol compounds has been extensively applied to generate cellulose-containing products with special features, namely better wet strength in the case of paper and better wrinkle-resistance in the case of textiles (Hernadi, 1999). However, the formaldehyde-based crosslinking agents have caused worldwide concern over their impact on human health and environment. There have been great endeavors to seek for nonformaldehyde alternatives to replace the traditional *N*-methylol compounds since the late 1980s (Chen, Yang, & Qiu, 2005; Gu & Yang, 2000; Mao & Yang, 2000, 2001; Yang & Wei, 2000). 1,2,3,4-Butanetetracarboxylic acid (BTCA) has attracted most attention among polycarboxylic acids as promising nonformaldehyde crosslinking agents for cellulose in that BTCA was proved to be the most effective (Gu & Yang, 2000; Mao & Yang, 2000, 2001; Yang & Wang, 1996a, 1996b; Yang & Wei, 2000). It was reported that BTCA imparted high levels of wrinkle-resistance and laundering durability to cotton (Andrews, Welch, & Trask-Morrell, 1989; Yang, Wang, & Kang, 1997), associated with sodium hypophosphite (SHP) as the most effective catalyst for crosslinking of cotton cellulose (Gu & Yang, 2000). Esterification of cellulose

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with BTCA proceeds in two steps: formation of a five-membered cyclic anhydride intermediate by anhydridisation of two adjacent carboxyl groups, and reaction between cellulose and the anhydride intermediate to form an ester linkage (Yang, Wang, & Lu, 2000). A major disadvantage of nonformaldehyde durable press finishing is severe tensile strength loss of cotton fabrics due to acid-catalyzed depolymerization and overcrosslinking (Kang, Yang, & Wei, 1998).

Development of alternative economical and environmentally-friendly processes of regenerated cellulose is still desirous because the current viscose technology is accompanied by hazardous carbon disulfide (CS_2). Much attention has been paid on environmentally compatible lyocell process utilizing *N*-methylmorpholine-*N*-oxide (NMMO) as the solvent, and carbamate process. But both of them have not yet replaced the viscose process. It was also reported that cellulose fibers were spun from environmental friendly NaOH/urea aqueous solution (Cai et al., 2004). So we are motivated to establish a new process of regenerated cellulose fibers to avoid toxic CS_2, in which chemical crosslinking is intended for improvement of wet tensile strength. Here, we describe intrafiber crosslinking of cotton-type rayon fibers with BTCA to acquire a good insight into the relationship between crosslinking degree of the rayon fibers and tensile properties by taking advantage of the cotton-type rayon fibers as a precursor. Water-responsive properties comprising of responses to liquid and gaseous water (moisture) are presented here as the interaction between water and the cellulose fibers is an important factor governing the mechanical properties.

2. Experimental

2.1. Materials

Never-dried cotton-type rayon staple fibers with an average length of 38 mm and linear density of 1.67 dtex were kindly supplied by Nanjing Chemical Fiber Co. Ltd. in China. BTCA was purchased from Aldrich. Monomethyl monopotassium malonate was obtained from Acros Organics. Other reagents were provided from commercial sources and used without further purification.

2.2. Determination of crystallinity of cellulose fibers

Crystallinity of the cellulose fibers was derived from wide angle X-ray diffraction (WAXD). WAXD was measured at a scanning rate of $0.02° s^{-1}$ in 2θ ranging from 5° to 60° on a Rigaku X-ray diffraction D/MAX 2580VB with high intensity Cu Kα radiation ($\lambda = 0.154056$ nm).

2.3. Crosslinking of rayon fibers

Initially, the rayon fibers were further desulfurized in a 2.5 wt% Na_2SO_3 aqueous solution at 75 °C for 1 h. After washing with a large amount of deionized water, the rayon fibers were impregnated in an aqueous solution containing 8.0 wt% BTCA and 5.0 wt% SHP, and then padded through two dips and two nips to reach an average wet pickup of 120%. After the treated fibers were fully dried at 40 °C in a vacuum, crosslinking of the fibers was conducted by curing the fibers at a specified temperature ranging from 160 to 200 °C for 5 min in a curing oven. The cured fibers were rinsed with a large amount of deionized water to remove residual BTCA and SHP for three times. Finally, the fibers were dried completely at 40 °C in a vacuum.

2.4. Measurement of tensile properties

Dry and wet tensile strength of the uncrosslinked and crosslinked rayon fibers were measured on a universal tensile tester (XQ-1, China Textile University) according to the standard method ASTM D3822-01. The fiber samples were preconditioned for 1 day so that they would reach the standard atmospheric equilibrium of 65% relative humidity (RH) at 20 °C. A gauge length of 20 mm was employed at a constant drawing rate of strain at 100% per min, or 20 mm/min. Fifty tests were completed for each result.

2.5. Fourier transform infrared (FTIR) measurement

FTIR absorption spectra were recorded with a Nicolet 670 spectrometer. A total of 10 scans for each sample were taken with a resolution of $2\,cm^{-1}$. The sample for FTIR analysis was prepared as follows. Cellulose fibers were cut into powder with a fiber microtome (Hardy's thin cross-section sampling device). Potassium bromide (KBr) powder was used as a reference to produce a background spectrum. The cured fibers were treated with a 0.1 M NaOH solution in advance for 3 min by vigorous stirring to convert carboxyl groups into carboxylate anions so as to separate absorption band of the ester carbonyl from that of the overlapping carboxyl carbonyl.

2.6. Titration of free carboxyl groups and ester linkages in crosslinked fibers

The concentration of carboxyl groups in 1 g of dry BTCA-treated rayon fibers before curing (C_0) was determined by first grinding them into a powder to improve sample uniformity. The powder sample was dispersed into distilled water and then titrated with a 0.0188 M NaOH solution as a titrant in the presence of phenolphthalein as an indicator. The NaOH solution had been previously standardized with potassium hydrogen phthalate. The concentrations of free carboxyl groups in 1 g of crosslinked fibers before washing (C_1) and after washing (C_2) were determined in the same way as described above. So the concentration of the ester linkages in 1 g of the crosslinked fibers could be determined indirectly, and it was equal to the difference between C_0 and C_1.

Concentration of carboxyl groups was C_3 via titration in the virgin cellulose fibers due to ageing or oxidation. Consequently, concentration of free carboxyl groups in the bonded BTCA could be estimated from the difference between C_2 and C_3.

2.7. Evaluation of moisture retention value (WRV)

WRV was measured by dispersing 0.5 g of the cured fibers in deionized water, soaking for 12 h, and then centrifuging the fibers in a tube at 1000*g* for 20 min with a porous screen at the bottom to separate water from the fibers. The centrifuged fibers were weighed to get the wet weight W_W. After a through drying of the centrifuged fibers in a vacuum at 40 °C, the dry weight W_D was reweighed. WRV was calculated as

$$\mathrm{WRV} = \frac{W_W - W_D}{W_D} \tag{1}$$

2.8. Sorption–desorption cycle

An absolutely dry system with RH 0% was created by adding P_2O_5 into a desiccator with a diameter of 180 mm. In a similar way, closed systems with RH of 23%, 33%, 43%, 52%, 75%, and 100% at 25 °C were generated by substituting P_2O_5 with saturated salt solutions of KAc, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, NaCl, and deionized water, respectively. After the rayon fibers were deposited into a weighing bottle and then placed in the desiccator with P_2O_5, the moisture sorption cycle was started by rising RH from 0% to 100% successively. The rayon fibers were conditioned in each desiccator for 24 h and weighed in the closed weighing bottle. Actually, 1 h was sufficient for each system to reach its equilibrium RH after unclosing and placing the rayon fibers by the assurance of a hygrometer, and 15 h was long enough for the rayon fibers to attain its equilibrium weight (Okubayashi, Griesser, & Bechtold, 2004, 2005). Desorption cycle was measured in the same way by stepwise decrease of RH.

3. Results and discussion

3.1. Esterification of rayon fibers

Cellulose fiber structures in a certain amount of the never-dried rayon fibers (corresponding to dry weight 5.0 g) were fully open and had a much greater tendency to receive 6.0 g of the mixed solution containing BTCA (0.48 g, 0.00205 mol) and SHP (3.0 g, 0.0283 mol) than a fiber which had been collapsed by drying and then rewet. It was determined by titration that 1.473×10^{-3} mol of BTCA (corresponding to 5.893×10^{-3} mol of carboxyl groups) had penetrated into amorphous regions of the never-dried rayon fibers before crosslinking, and esterified hydroxyl groups of cellulose molecules (Fig. 1). It should be noted that macromolecular chains of cellulose lie parallel to each other in a crystalline arrangement, making it impossible to initiate reaction with the hydroxyl groups. In other areas of the fibers, chains are jumbled together in a random arrangement that provides flexibility and accessibility to the fibers. It is in the accessible areas that reaction takes place (Rowell & Young, 1978). More hydroxyl groups become available for reaction if the fibers are swollen by water. Crystallinity of the rayon fibers was 50.2% determined by WAXD. The WAXD pattern showed the presence of diffraction peaks of 2θ at 12.4°, 10.4°, and 21.5°, corresponding to (1 0 1), (1 0 $\bar{1}$), and (0 0 2) planes, indicating the rayon fibers were typical cellulose II, or hydrate cellulose (Cai et al., 2004; Kaplan, 1998). Accordingly, accessible hydroxyl in the never-dried rayon fibers was estimated to be 0.0461 mol. Thus the feed molar ratio of accessible hydroxyl groups to carboxylic acid groups was 7.82. This ratio was kept constant to initiate all the crosslinking reactions of the rayon fibers in this research at the initial stage of crosslinking.

Exposure of the rayon fibers to BTCA and SHP made interior amorphous regions of each fiber available for the incoming reactants. BTCA forms a five-membered cyclic anhydride intermediate by the anhydridisation of two adjacent carboxyl groups catalyzed by SHP during curing, and

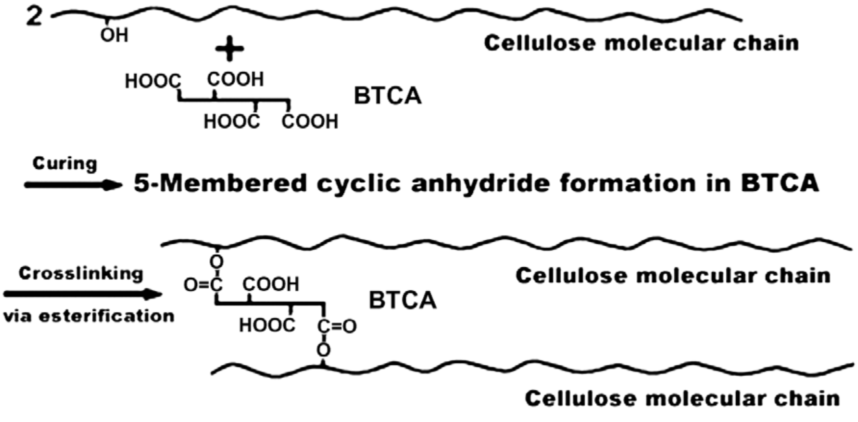

Fig. 1. Schemetic diagram of esterification between cellulose and BTCA.

the anhydride intermediate reacts with cellulose to form an ester linkage (Yang, 1991a, 1991b; Yang, 1993; Yang & Wang, 1996a, 1996b). Cellulose macromolecules consist of a series of glucose rings joined together. Protruding from the macromolecular chains are hydroxyl groups, which provide reactive crosslinking sites. There are two active five-membered cyclic anhydrides originated from each BTCA bearing four adjacent carboxyl groups. Therefore, an individual BTCA molecule is capable of esterifying more than one hydroxyl group of cellulose macromolecules. Numerous BTCA molecules within a rayon fiber are sufficient to form a 3-D network of cellulose, yielding an intrafiber crosslinked structure (Fig. 1).

3.2. Conversion rate of carboxyl groups

After separation of the absorption bands of the ester carbonyl from those of overlapping carboxyl carbonyl in FTIR spectra, as shown in Fig. 2, by transformation of carboxyl groups into carboxylate anions via NaOH treatment, the absorption bands at 1716 and 1574 cm^{-1} were assigned to the ester and carboxylate carbonyl, respectively (Yang, 1991a, 1991b). It should be noted that there was no absorption corresponding to the ester or carboxylate carbonyl for the uncrosslinked rayon fibers. Conversion rate of carboxyl groups can be evaluated by comparison of absorption intensity of the ester and carboxylate carbonyl.

For the purpose of semiquantitative estimation of conversion rate of carboxyl groups into ester linkages at various curing temperatures, the quantitative analyses of relative amounts of the generated ester linkages and free carboxyl groups on bonded BTCA were made on the basis of the respective absorption peak areas in FTIR spectra via the Beer-Lambert law with an internal standard calibration technique. The intensity for the absorption bands at 1716 and 1574 cm^{-1} of equimolar ester and carboxylate carbonyl in the crosslinked fibers can be expressed as following:

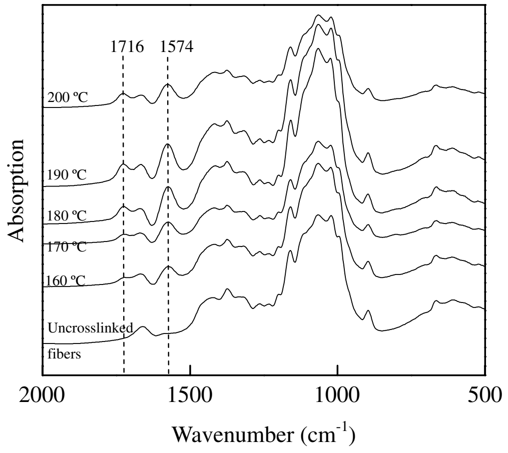

Fig. 2. FTIR absorption spectra for uncrosslinked rayon fibers, and crosslinked fibers at different curing temperature.

$$I_{1574} = kI_{1716} \tag{2}$$

where I_{1716} and I_{1574} were the absorption peak areas of the equimolar ester and carboxylate carbonyl, respectively. k was a constant relative to the molar absorption coefficient ratio of the two sorts of carbonyl. An initial value of k was 1.98 derived from the FTIR spectrum of a model compound, monomethyl monopotassium malonate, which contains equimolar ester and carboxylate carbonyl. However, the initial value was unable to be utilized directly as chemical environments of the crosslinked fibers were different from those of the model compound. In order to obtain a more precise value of k, the conversion rate of carboxyl groups into ester linkages was computed according to the following definition, which was modified from the reported criterion of intensity ratio of carbonyl band (ester/carboxylate) in FTIR spectra (Yang, 1991a, 1991b).

$$\begin{aligned}\text{Conversion rate} &= \frac{N_e}{N_{e\&f}} \times 100\% \\ &= \frac{A_{1716}}{A_{1716} + A_{1574}/k} \times 100\%\end{aligned} \tag{3}$$

where N_e is the number of the ester linkages derived from esterification in the crosslinked cellulose fibers. $N_{e\&f}$ is the total number of carbonyl of bonded BTCA. A_{1716} and A_{1574} were the absorption peak areas of the ester and carboxylate carbonyl, respectively, in the FTIR spectra of the crosslinked fibers. According to Eq. (2), A_{1574} was comparable with A_{1716} after dividing by k. k was 3.2, which was determined from the initial value 1.98 and corrected by conversion rate of carboxyl groups into ester linkages derived from the direct titration method. Conversion rate of carboxyl groups into ester linkages was calculated from the concentrations of the ester linkages and free carboxyl groups in the crosslinked fibers via titration according to Eq. (4).

$$\begin{aligned}\text{Conversion rate} &= \frac{N_e}{N_{e\&f}} \times 100\% \\ &= \frac{C_0 - C_1}{C_0 - C_1 + C_2 - C_3} \times 100\%\end{aligned} \tag{4}$$

A nearly linear relationship was observed between the conversion rate in the crosslinked rayon fibers and the curing temperature (Fig. 3). The conversion rate based on the FTIR spectra was in good agreement with that from the direct calculation based on the titrated carboxyl groups and ester linkages. More than half of the carboxyl groups were involved in the esterification when the curing temperature was 190 and 200 °C.

The above conversion rate represents the fraction of the total carboxyl groups of bonded BTCA that were transformed into ester linkages. Conversion of reacted BTCA in Table 1 depicts the fractions of reacted BTCA with two or three ester linkages that actually contributed to the fiber crosslinking. The esterification crosslinking was divided into two main stages, i.e., pendant attachment of BTCA via esterification with cellulosic hydroxyl groups

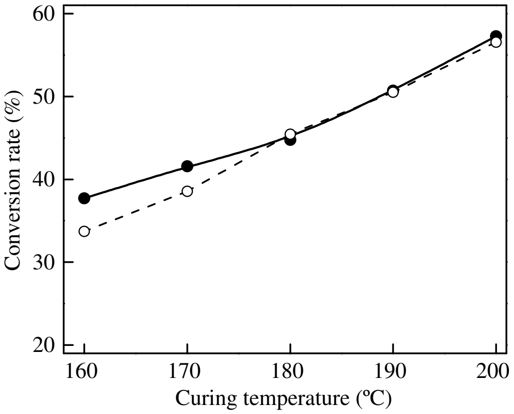

Fig. 3. Dependence of conversion rate of carboxyl groups into ester linkages calculated from titration (solid line) and FTIR spectra (dash line) on curing temperature.

(Fig. 4a), and its further reaction with another cellulosic hydroxyl group producing bridging crosslinking of the cellulose fibers (Fig. 4b). It was reported that the rest two carboxyl groups in the crosslinked BTCA could be properly positioned for additional anhydride formation and, hence, could reacted with a cellulosic hydroxyl group in a third esterification reaction (Fig. 4c) (Zhou, Luner, & Caluwe, 1995).

In 1 g of the crosslinked fibers, it was supposed that there was X mmol of monoesterified BTCA and Y mmol of twice esterified BTCA. The following simultaneous equations could be expressed as:

$$X + 2Y = C_0 - C_1 \tag{5}$$

$$3X + 2Y = C_2 - C_3 \tag{6}$$

where C_0, C_1, C_2, and C_3 were in mmol/g fiber. The total ester linkages in 1 g of the crosslinked fibers, $C_0 - C_1$, were given by the contribution of both the monoesterified BTCA, X, and twice esterified BTCA, $2Y$. The total free carboxyl groups in 1 g of the crosslinked fibers, $C_2 - C_3$, was given by the contribution of the monoesterified BTCA, $3X$, and twice esterified BTCA, $2Y$. By solving simultaneous Eqs. (5) and (6) simultaneously, X and Y were given by

$$X = (-C_0 + C_1 + C_2 - C_3)/2 \tag{7}$$

$$Y = (3C_0 - 3C_1 - C_2 + C_3)/4 \tag{8}$$

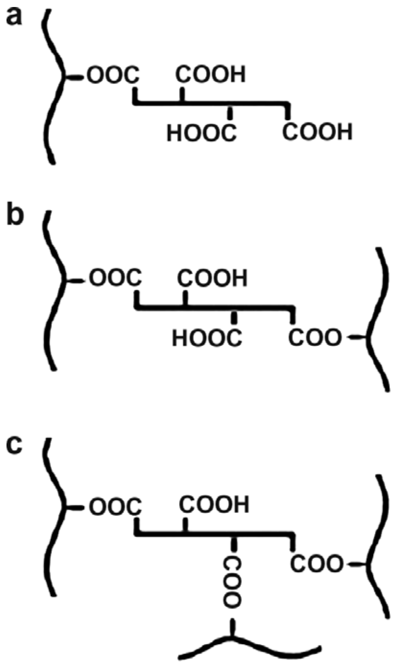

Fig. 4. Schematic diagram of three possible esterification patterns of (a) monoesterification, (b) twice esterification, and (c) 3-time esterification in reacted BTCA molecules.

3-Time esterification of BTCA was considerably more difficult to occur and it was expected to occur only at sufficiently high curing temperature. It was supposed that 3-time esterification occurred when the simultaneous Eqs. (5) and (6) were unsolvable, and there was Z mmol of 3-time esterified BTCA in 1 g of the crosslinked fibers. Thereby the simultaneous Eqs. (9) and (10) were derived in a similar way under the assumption that no monoesterified BTCA in the form of ester appendage was left.

$$2Y + 3Z = C_0 - C_1 \tag{9}$$

$$2Y + Z = C_2 - C_3 \tag{10}$$

By solving simultaneous Eqs. (9) and (10), Y and Z were given by

$$Y = (-C_0 + C_1 + 3C_2 - 3C_3)/4 \tag{11}$$

$$Z = (C_0 - C_1 - C_2 + C_3)/2. \tag{12}$$

Finally, the amounts of the monoesterified, twice esterified, and 3-time esterified BTCA were obtained for the BTCA-crosslinked fibers as listed in Table 1. The amount

Table 1
Conversion of BTCA and esterification patterns of BTCA molecules under various curing temperature

Curing temperature (°C)	Total amount of reacted BTCA (mmol/g fiber)	Conversion of reacted BTCA (%)	Amount of reacted BTCA with the following ester linkage number per molecule (mmol/g fiber)		
			1	2	3
160	0.197	50.76	9.7×10^{-2}	10.0×10^{-2}	0
170	0.267	66.29	9.0×10^{-2}	17.7×10^{-2}	0
180	0.271	78.97	5.7×10^{-2}	21.4×10^{-2}	0
190	0.280	100	0	27.2×10^{-2}	0.8×10^{-2}
200	0.285	100	0	20.2×10^{-2}	8.3×10^{-2}

of 3-time reacted BTCA was relatively small, which showed an increase by raising the curing temperature from 190 to 200 °C. Apparently, the third anhydride formation was less effective than the monoanhydride and dianhydride formation. We found that the crosslinked fibers became brittle and lost strength with a higher concentration of 3-time reacted BTCA under the curing temperature 210 °C. Conversion of BTCA increased with the curing temperature, that is, more BTCA was involved in crosslinking and pendant BTCA became less under the enhanced curing temperature. Moreover, BTCA with three ester linkages was generated under the curing temperature of 190 and 200 °C. In addition, Table 1 illustrated that total amount of the reacted BTCA increased with the curing temperature.

3.3. Crosslinking degree of rayon fibers

To understand the crosslinking details of the crosslinked fibers, pendant and crosslinked ester linkage concentrations in Fig. 5 were computed from the titrated results in Table 1. The concentration of crosslinked ester linkages increased with the curing temperature, while free carboxyl concentration first increased to its maximal value and decreased subsequently. Pendant ester linkage concentration was relatively very low, which confirmed that the two five-membered cyclic anhydrides originated from the curing of BTCA were extremely active.

Crosslinking degree (CD) is defined as the number ratio of hydroxyl groups involved in crosslinking via ester linkages in the amorphous region of a cellulose fiber sample to total accessible hydroxyl groups for the crosslinking agent located in the amorphous region of the same cellulose fiber sample (Eq. 13).

$$\mathrm{CD} = \frac{N_e}{\frac{W \cdot f_a}{162} \times 3 \times 1000} = \frac{C_0 - C_1}{\frac{f_a}{162} \times 3 \times 1000} \qquad (13)$$

where W is the weight of the cellulose fiber sample in g. N_e is the number of hydroxyl groups in mmol involved in crosslinking via ester linkages in the W g of the cellulose fiber sample, which was determined indirectly from the amount of the reacted BTCA esterified twice and 3-time listed in Table 1. f_a is the weight fraction of the amorphous region of the cellulose fibers obtained from WAXD. One hundred and sixty-two is the molecular weight of a glucopyranose ring, and there are three hydroxyl groups in each glucopyranose ring. C_0 and C_1 are in mmol/g fiber. In Fig. 6, a nearly linear relationship between crosslinking degree and the curing temperature was observed. Obviously, higher curing temperature favored crosslinking of the rayon fibers, and thus a more densely packed interior network structure was formed at a higher curing temperature. Both the dry and wet tensile strength were optimized at the intermediate crosslinking degree of 4.64×10^{-2} under the curing temperature of 180 °C. The optimal dry and wet tensile strength was 2.57 and 1.42 cN/dtex, respectively. Based on the dry tensile strength 2.13 cN/dtex and wet tensile strength 1.11 cN/dtex of the virgin rayon fibers, the optimal dry and wet tensile strength increased 20.7% and 27.9%, respectively.

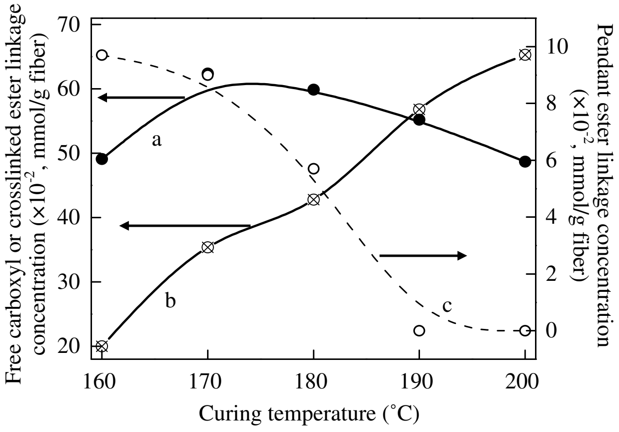

Fig. 5. Concentration variation with curing temperature of (a) free carboxyl groups, (b) crosslinked, and (c) dangled ester linkages in crosslinked fibers.

3.4. Retention of liquid water

The cellulose molecules in the amorphous regions were undoubtedly far more densely packed compared with the uncrosslinked cellulose molecules. The crosslinked fibers were held together by the crosslinkages under wet conditions, which inhibited swelling of the crosslinked fibers by the absorbed water in the amorphous regions. Because the ordered regions (crystalline) did not contribute significantly to the process of water adsorption (Strnad, Kreze, Stana-Kleinschek, & Ribitsch, 2001), the rubber-like network structures within the crosslinked rayon fibers are largely responsible for uncommon behavior of transverse and axial swelling when absorbing water, which has technical consequences in tensile strength and dimensional stability of cellulose fabrics. WRV of the crosslinked fibers was an indicator to demonstrate interaction between liquid water

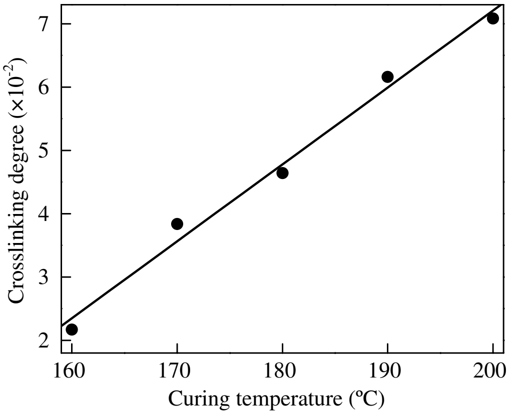

Fig. 6. Dependence of crosslinking degree on curing temperature.

and the fibers. WRV of the virgin rayon fibers was 0.972 g/g. In Fig. 7, WRV of the crosslinked rayon fibers reduced evidently with the curing temperature or crosslinking degree. WRV of the crosslinked fibers cured at 190 °C was almost half of that of the uncrosslinked fibers. The absorbed water drained out under high centrifugal fields, but a stage was reached eventually in which the water remained held by surface tension in capillary spaces within a fiber (Morton & Hearle, 1997). The exact form of these spaces depended on the way in which cellulose macromolecules were packed together within a fiber. Higher crosslinking degree accounted for the more densely packed network structures with less swelling of the cellulose molecules in the amorphous regions. The network structures effectively screened the cellulose molecules in the interior of the fibers from dissolution in incoming water. So less water was retained in the crosslinked network structures, and hence swelling and WRV of the fibers diminished substantially as a result of crosslinking.

3.5. Absorption of moisture

Dry cellulose is an exceedingly hygroscopic material withdrawing water vapor from atmosphere. This moisture absorption capacity, regarded as a function of the amorphous regions, is of paramount importance in the processing and use of cellulose for textiles. The moisture absorption capacity relies closely on the internal fiber surfaces because moisture was attached only to fiber surfaces as well as multilayer stacking. As the crosslinked fibers cured under 180 °C were of optimal mechanical properties, and those under 190 °C were of relatively high crosslinking degree, both the crosslinked fibers were chosen as representatives to study interaction between moisture and the crosslinked fibers. Moisture regain increased remarkably with RH in the sorption and desorption isotherms (Fig. 8). The equilibrium curves had a typical sigmoidal shape due to strong moisture uptake and release at very low or high RH. There was a significant amount of capillary water present only at RH greater than 99% (Morton & Hearle, 1997). The sorption–desorption cycles of the uncrosslinked and crosslinked rayon fibers were extremely similar, illustrating that crystal structure of cellulose II was hardly altered (Morton & Hearle, 1997). Because the crosslinking degree in Fig. 6 varied slightly from the minimal 2.169×10^{-2} (corresponding to curing temperature 160 °C) to maximal 7.081×10^{-2} (200 °C), it is reasonable to suppose that the internal surfaces of the crosslinked cellulose fibers were not varied greatly by the crosslinkages. Moreover, the equilibrium moisture isotherms showed concomitant hystereses between the sorption and desorption cycles, indicating structural variation of the rayon fibers caused by the interaction with moisture.

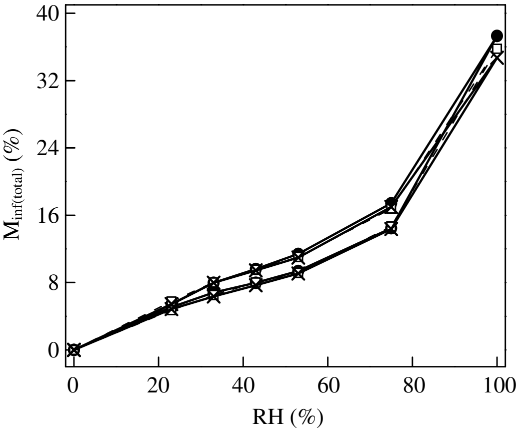

Fig. 8. Equilibrium moisture sorption and desorption isothermals of (a) uncrosslinked fibers (●), crosslinked fibers cured under (b) 180 °C (□), and (c) 190 °C (×).

The moisture absorption occurred primarily on the internal surfaces of the hygroscopic cellulose, while the liquid water retention of the crosslinked fibers was due to the penetration of water into the amorphous regions and swelling of the cellulose molecules. Fortunately, water regain reduced little after crosslinking, indicating fabrics from the crosslinked fibers may be as comfortable as uncrosslinked fibers to wear because of its maintenance of moisture balance with respect to human skin. Reduction

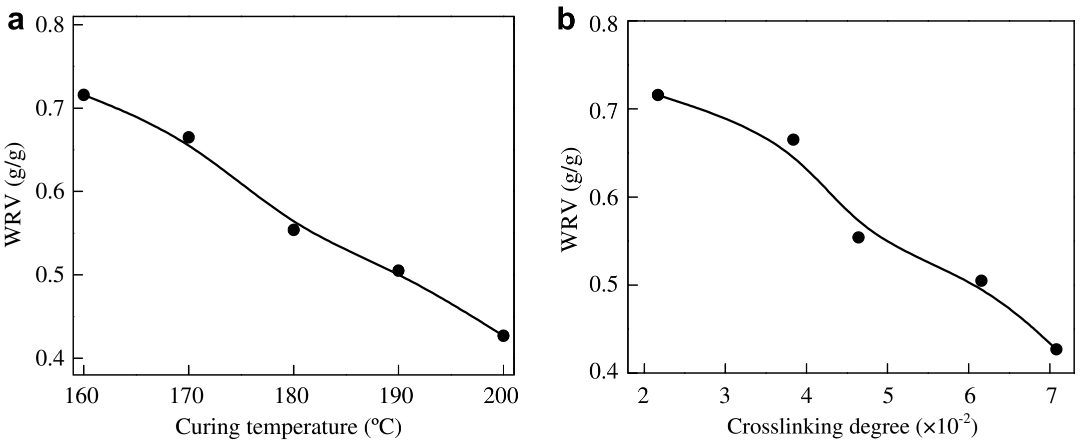

Fig. 7. Dependence of WRV on (a) curing temperature, and (b) crosslinking degree.

of retained water in the crosslinked fibers is of great significance to economize on energy in the process of drying from the viewpoints of both rayon industry and daily use of rayon fabrics. Moreover, wet tensile strength and dimensional stability of cellulose fabrics could be improved by the diminished swelling arising from crosslinking as well.

4. Conclusions

BTCA, as the most efficient crosslinking agent of cellulose, was applied to crosslink the amorphous regions of the cotton-type rayon fibers via esterification through the formation of the cyclic anhydride intermediates for the purpose of a molecular-level control over the macroscopic properties of water responses, although BTCA was reported to cause loss of mechanical properties when it was used as a durable press finishing agent for cellulose fabrics. Semiquantitative quantification of the conversion rate of carboxyl groups into ester linkages was proposed on the basis of the FTIR spectra, in which the constant k was necessary to standardize the absorption intensity of the ester and carboxylate carbonyl. The value of k was estimated from the FTIR spectrum of the model compound associated with the titration results. The crosslinked ester linkages were separated from the pendant ones as only two of the three esterification patterns were responsible for crosslinking. The curing temperature had a great impact on the concentration of the crosslinked ester linkages and crosslinking degree.

It has been found that the crosslinking reaction made a notable impact on the crosslinked fiber response to liquid water as shown by the WRV results, but very little influence to gaseous water vapor as can be seen from the moisture sorption and desorption isothermals. It is believed that the WRV is correlated with the swelling behaviors of the crosslinked cellulose fibers, while the sorption and desorption isothermals are correlated with the total accessible water molecule absorption sites over their internal surfaces. These interesting phenomena may have valuable utility for the BTCA-crosslinked rayon as a textile fiber because the interaction between liquid water or moisture and the crosslinked fibers is of decisive significance for the wet mechanical properties of the crosslinked rayon fibers. The densely packed fiber structures and less swelling of the crosslinked fibers accounted for their enhanced dry and wet tensile strength.

Interpretation of the water-responsive properties of the crosslinked fibers is indispensable to understand the mechanical properties of the crosslinked fibers as macroscopic properties, such as wet mechanical properties and resiliency, rely extremely on molecular-level swelling of cellulose fibers. The current research results provide a good insight into the relationship between the fiber structures and properties for the rayon cellulose fibers, which lays a foundation for searching more effective crosslinking agents beneficial to mechanical properties of polysaccharide fibers or proteinous fibers.

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