Influence of Esterification Crosslinking Structures of Rayon Fibers with 1,2,3,4-Butanetetracarboxylic Acid on Tensile 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 a molecular-level control over macroscopic properties. Formation of intrafiber crosslinked structures of the rayon fibers was a facile and efficient method to diminish swelling degree and enhance tensile properties. Crosslinking was conducted under a series of curing temperature and various dosages of BTCA with the presence of sodium hypophosphite as the catalyst for anhydride formation. It was found that crosslinking conditions, both the curing temperature and dosage of the crosslinking agent, made notable impacts on the crosslinking behaviors of the rayon fibers. The dry and wet tensile strength of the rayon fibers were optimized for both the dosage of the crosslinking agent and the curing temperature. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 3553–3559, 2011

Key words: 1,2,3,4-butanetetracarboxylic acid; esterification crosslinking of rayon fibers; tensile properties

INTRODUCTION

Cellulose, the most important skeletal component in plants with fascinating structure and properties, is the most abundant natural polymer derived from plant photosynthesis from carbon dioxide and water. The end products of waste cellulose are also carbon dioxide and water, which join nature's cycle and be absorbed by plants. The very substantial, but so far little exploited cellulose resource is attracting increasing attention as an almost inexhaustible source of raw materials to replace petrochemically derived compounds in many cases.[1]

It was estimated that the reserves of the initial raw materials for many types of chemical fibers would be close to depletion.[2] Fortunately, rayon (viscose) fibers are the traditional types of cellulose fibers due to their excellent properties for a broad product range, from cottonlike textile fibers to technical fibers in the form of cord for use in high-performance tires. Expanding use of cellulose based on renewable resources must be further developed for fiber production utilizing both existing technologies and modification processes in the stages of fiber production or finishing of final textile materials.[3,4] Rayon fibers will retain their position both in the near future and for many years thereafter.[5,6] New frontiers of environmentally friendly cellulose fiber technologies are highlighted with future strategies and application.

The rayon process, well over 100 years old, still dominates cellulose fiber production methods in which pulp with carbon disulfide (CS_2) is converted into cellulose xanthogenate as a metastable intermediate. However, the use of CS_2 leads to environment loads. To decrease the emission of exhaust CS_2 gas to meet the environmental standards, different methods can be applied with particular regard to avoid the use of CS_2. We are motivated to establish a new process of cellulose fibers utilizing low-substituted hydroxyethyl cellulose (LSHEC) to replace cellulose xanthogenate in the rayon process because LSHEC is soluble in common NaOH aqueous solutions. It is advantageous that LSHEC fibers can be spun from the existing rayon spinning facilities. Dry tensile strength of the LSHEC fibers are comparable to that of commercial available rayon fibers, whereas the

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wet tensile strength is lower with the ratio of wet to dry tensile strength 0.3. The most important reason is that the swelling degree of the LSHEC fibers in water is higher than that of rayon fibers.

To diminish the swelling degree and enhance the tensile properties of cellulose fibers, especially the wet tensile properties, intrafiber crosslinked structures will be introduced into the LSHEC fibers. 1,2,3,4-Butanetetracarboxylic acid (BTCA) was proved to be the most effective crosslinking agent for cotton cellulose.[7–12] BTCA imparted high levels of wrinkle-resistance and laundering durability to cotton fabrics. A major disadvantage is severe loss of tensile strength due to acid-catalyzed depolymerization and overcrosslinking.[13] We have recently reported that water-responsive properties comprising of responses to both liquid and gaseous water (moisture) of chemically crosslinked cotton-type rayon fibers were indispensable to understand the tensile properties because the macroscopic properties relied extremely on molecular-level swelling of the cellulose fibers. Therefore, the interaction between liquid water and the crosslinked fibers is of decisive significance for the wet tensile properties of the crosslinked rayon fibers. Here, we describe the intrafiber crosslinking of cotton-type rayon fibers with BTCA to acquire a good insight into the relationship between the crosslinking degree of the rayon fibers and the tensile properties by taking advantage of the cotton-type rayon fibers as a precursor. Variation of the dry and wet tensile properties of the rayon fibers with the significant crosslinking conditions, the curing temperature and dosages of BTCA, were investigated in detail in this research.

EXPERIMENTAL

Materials

Never-dried cotton-type rayon fibers with an average length of 38 mm and linear density of 1.67 dtex were kindly supplied by Nanjing Chemical Fiber 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.

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).

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 % sodium hypophosphite (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 under a series of temperature and various BTCA amounts respectively 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.

Measurement of tensile properties

Dry and wet tensile strength of the uncrosslinked and crosslinked rayon fibers was 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 used at a constant drawing rate of strain at 100% min, or 20 mm/min. Fifty tests were completed for each result.

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.

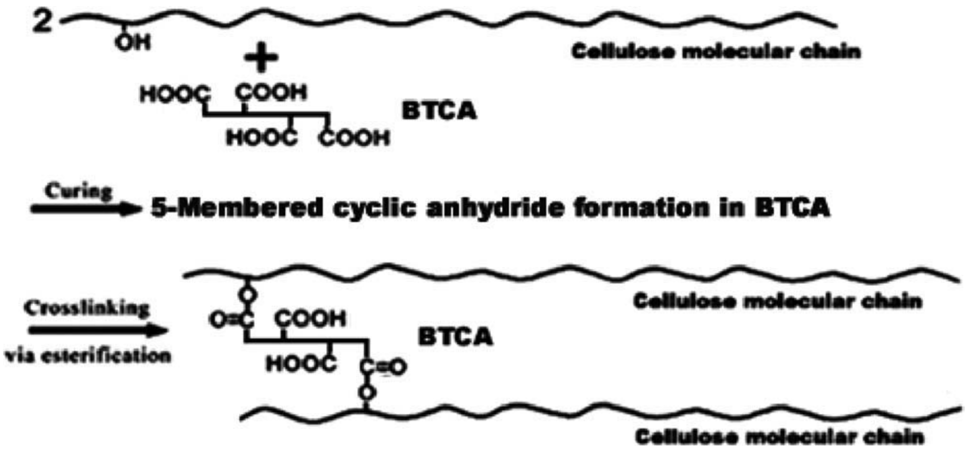

Figure 1 Schemetic diagram of esterification between cellulose and BTCA.

Evaluation of water 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

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

RESULTS AND DISCUSSION

Esterification crosslinking of rayon fibers

Polycarboxylic acids are used for nonformaldehyde anticrease finishing of cellulose fabrics, among which BTCA is the most effective crosslinking agent for cellulose in combination with the corresponding catalyst, SHP. Here the amorphous regions of the cotton-type rayon fibers were crosslinked by BTCA via esterification for the purpose of the formation of the intrafiber crosslinked structures of cellulose macromolecules to diminish the swelling degree and enhance the tensile properties. Esterification crosslinking of hydroxyl groups of cellulose macromolecules by BTCA was schematically illustrated in Figure 1. Esterification of cellulose with BTCA catalyzed by SHP proceeded 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.[14] Crosslinking of the rayon fibers occurred when an individual BTCA molecule reacted with more than two hydroxyl groups on different cellulose macromolecular chains. Actually, the esterification crosslinking was divided into two main stages, i.e., pendant attachment of BTCA via esterification with cellulosic hydroxyl groups [Fig. 2(a)], and its further reaction with another cellulosic hydroxyl group producing bridging crosslinking of the cellulose fibers [Fig. 2(b)]. It was reported that the rest two carboxyl groups in the crosslinked BTCA could be properly positioned for additional anhydride formation and, hence, could react with a cellulosic hydroxyl group in a third esterification reaction [Fig. 2(c)].[15]

Dependance of tensile properties on curing temperature

Exposure of the rayon fibers to BTCA and SHP made the interior amorphous regions of each fiber available for the incoming reactants. Influence of curing temperature on the esterification crosslinking structures of the rayon fibers with BTCA and their water-responsive properties has been reported in a previous research paper.[16] The variation of the curing temperature from 150 to 210°C had a great impact on the concentration of the crosslinked ester linkages and crosslinking degree, which resulted in less swelling of the rayon fibers in liquid water. Actually water-responsive properties of the crosslinked rayon fibers were correlated with the swelling behaviors of the crosslinked rayon fibers in liquid water. Therefore, the curing temperature affected the water-responsive properties of the crosslinked rayon fibers dramatically, but very little influence to gaseous water vapor was observed from the moisture sorption and desorption isothermals. The interesting results may have practical application for the BTCA-crosslinked rayon as a kind of textile fibers.

BTCA was reported to cause loss of mechanical properties when it was used as a durable press finishing agent for cellulose fabrics due to acid-catalyzed depolymerization and interfiber over crosslinking. However, the densely packed intrafiber

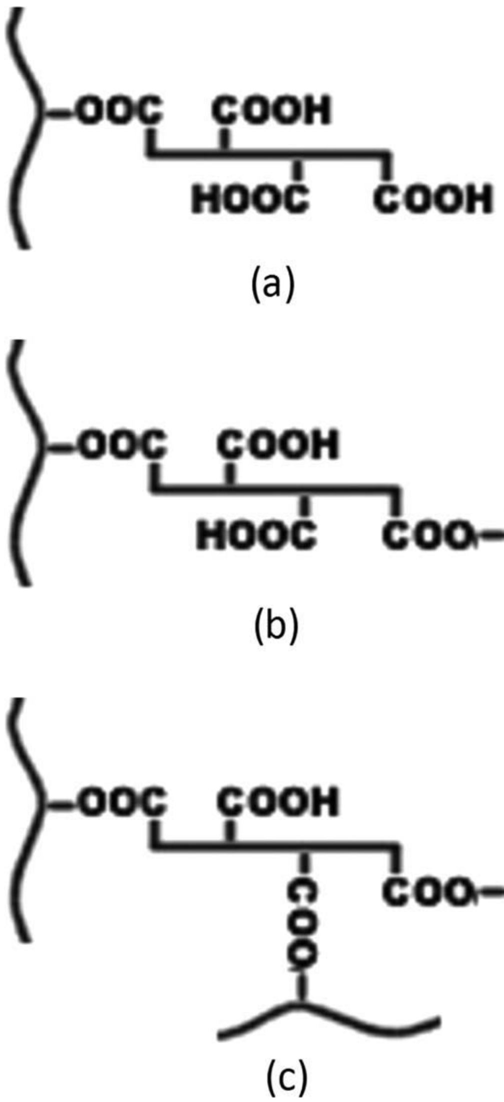

Figure 2 Schematic diagram of three possible esterification patterns of (a) monoesterification, (b) twice esterification, and (c) 3-time esterification in reacted BTCA molecules.

crosslinked structures and less swelling of the crosslinked rayon fibers accounted for their enhanced dry and wet tensile strength (Fig. 3) based on the tensile properties of virgin rayon fibers (Table I).

In Figure 3(a), the dry and wet tensile strength first increased rapidly with the curing temperature and decreased subsequently. The optimal dry and wet tensile strength was achieved under the curing temperature 180°C. Based on the tensile strength of the virgin rayon fibers, the optimal dry tensile strength 2.57 ± 0.02 cN/dtex increased 20.7%, and the optimal wet tensile strength 1.42 ± 0.02 cN/dtex increased 27.9%, respectively. The crosslinked cellulose macromolecular chains were tied together at the crosslinking sites in the amorphous regions of an individual rayon fiber, which prevented the slippage of the cellulose macromolecular chains past one another and led to the increased dry tensile strength and decreased dry elongation at break. When the rayon fibers were immersed in water, the cellulose macromolecular chains moved apart and gave room for the penetration of liquid water into the amorphous regions. However, the ingress of water was strongly restricted by the crosslinks in the amorphous regions, which prevented the cellulose macromolecular chains from breaking apart and thus enhanced the wet tensile strength and diminished the wet elongation at break. As we reported, the crosslinking degree increased linearly with the curing temperature.[16] Obviously, higher curing temperature favored the esterification crosslinking and formation of the intrafiber network structures of the rayon fibers. Nevertheless, insufficient or over crosslinking of the rayon fibers might occur under the curing temperature lower or higher than 180°C, which caused the variation of the dry and wet tensile strength in Figure 3(a).

Dry and wet elongation at break of the crosslinked rayon fibers decreased substantially with the curing temperature in Figure 3(b), indicating that the intrafiber crosslinked structures suppressed the relative movement among the cellulose macromolecular chains and the elongation at break relied on the density of the crosslinks. The dry and wet elongation at break was 15.82 ± 0.55% and 18.34 ± 0.59%, respectively, under the curing temperature 180°C, which decreased 30.9 and 33.9%, respectively, based on the dry and wet elongation at break of the virgin rayon fibers in Table I. It should be noted that the lower dry and wet elongation at break arising from the post crosslinking of the drawn rayon fibers did not deteriorate the extensibility of cellulose polymeric chains in the drawing process followed the spinning of the rayon fibers.

The intrafiber crosslinked structures of the rayon fibers improved the capability to resist elastic deformation. Consequently, the dry and wet initial modulus of the crosslinked rayon fibers increased with the curing temperature, as shown in Figure 3(c). Low initial modulus is preferred from the viewpoint of wear comfort. In contrast, low initial modulus makes rayon fibers not resilient. So anticrease finishing is often applied to rayon fabrics because they wrinkle easily. An adequate increase in dry and wet initial modulus might lead to the resistance to small deformation of rayon fibers in constant wear of rayon fabrics. Figure 3(c) indicates that dry and wet initial modulus increased with curing temperature remarkably. The dry and wet initial modulus under the curing temperature 180°C was 57.43 ± 0.58 and 15.28 ± 0.46 cN/dtex, respectively, which increased 30.11 and 118.29%, respectively, based on the initial modulus of the virgin rayon fibers. As a result, the intrafiber crosslinked structures of the rayon fibers improved the tensile properties and dimensional stability.

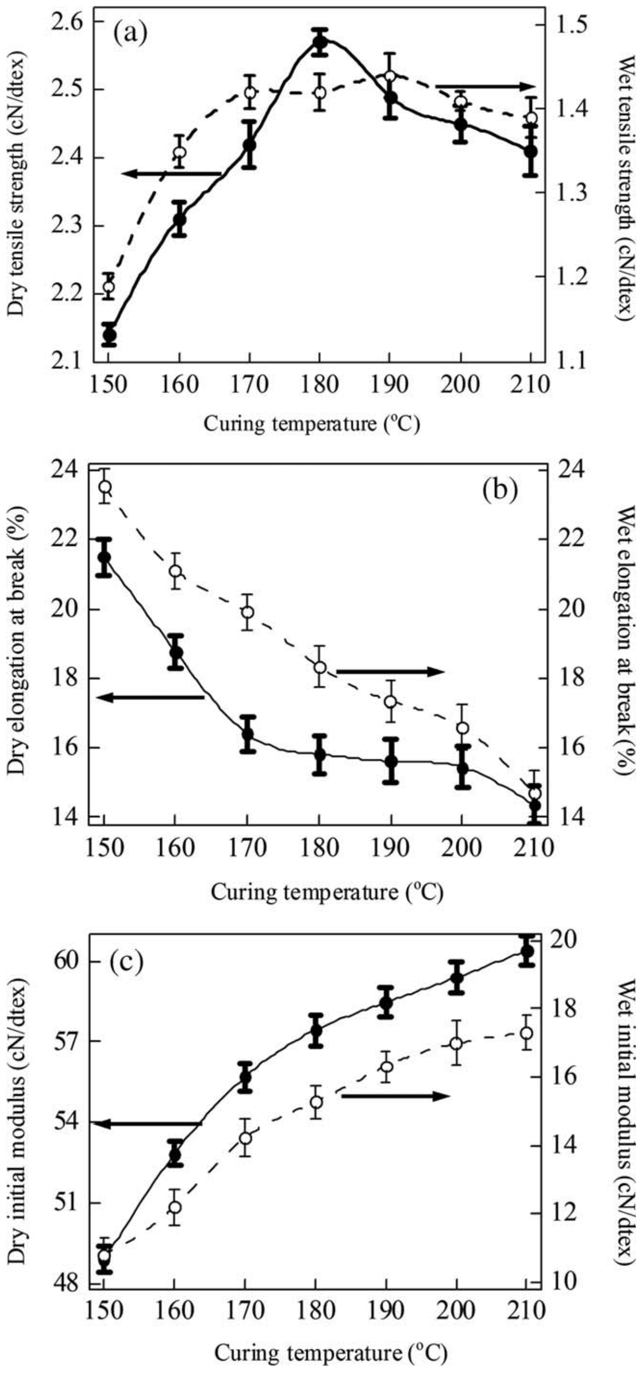

Figure 3 Dependance of dry (solid line) and wet (dash line) tensile properties of rayon fibers crosslinked with BTCA on curing temperature. (a) tensile strength, (b) elongation at break, and (c) initial modulus.

TABLE I
Tensile Properties of Virgin Rayon Fibers

Virgin rayon fibers	Dry	Wet
Tensile strength (cN/dtex)	2.13 ± 0.03	1.18 ± 0.02
Elongation at break (%)	22.90 ± 0.48	27.75 ± 0.54
Initial modulus (cN/dtex)	44.14 ± 0.52	7.00 ± 0.23

Dependance of swelling degree on curing temperature

The curing temperature had a great impact on the crosslinking degree and retention of liquid water,[16] which was essential to understand the above-mentioned dry and wet tensile properties. The apparent crosslinking degree (ACD) was 2.32×10^{-2}, and

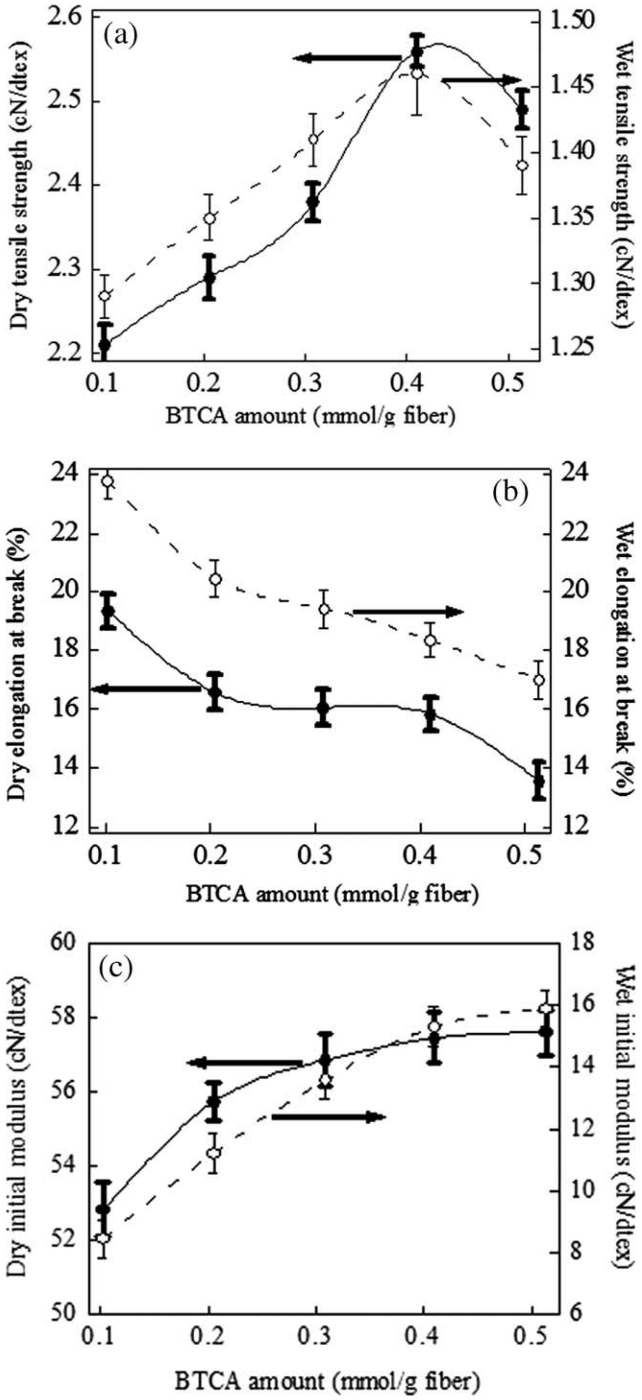

Figure 4 Dependance of dry (solid line) and wet (dash line) tensile properties of rayon fibers crosslinked with BTCA on BTCA amount. (a) tensile strength, (b) elongation at break, and (c) initial modulus.

TABLE II
Esterification Patterns of BTCA Molecules Under Various BTCA Amounts

Amount of BTCA (mmol/g fiber)	Conversion of reacted BTCA (%)	ACD	Amount of reacted BTCA with the following ester linkage number per molecule (mmol/g fiber) 1	2	3
0.103	26.11	1.79×10^{-3}	3.05×10^{-2}	0.127×10^{-2}	0
0.205	38.39	9.27×10^{-3}	5.20×10^{-2}	5.95×10^{-2}	0
0.308	41.12	1.36×10^{-2}	5.45×10^{-2}	9.83×10^{-2}	0
0.410	49.56	2.58×10^{-2}	0.447×10^{-2}	23.6×10^{-2}	0
0.513	49.50	3.10×10^{-2}	0.597×10^{-2}	28.3×10^{-2}	0

WRV was 0.554 g/g for the crosslinked rayon fibers cured under 180°C in comparison with WRV 0.972 g/g of the uncrosslinked rayon fibers. Accordingly, the macroscopic tensile properties of the rayon fibers were altered significantly by the crosslinked network structures in the amorphous regions of the rayon fibers.

Dependance of tensile properties on BTCA amount

The dosage of the crosslinking agent affected the crosslinking reaction, which influenced the tensile properties inevitably. Figure 4(a–c) depicts dependance of dry and wet tensile strength, elongation at break, and initial modulus of the crosslinked rayon fibers on BTCA amount under the curing temperature 180°C. The variation of the tensile properties in Figure 4 could be interpreted by the crosslinked structures of the rayon fibers as well. The amounts of the monoesterified, twice esterified, and 3-time esterified BTCA were estimated based on the titration results of free carboxyl groups and ester linkages in the crosslinked rayon fibers,[16] as shown in Table II.

No 3-time reacted BTCA was generated, whereas the amounts of both monoesterified and twice esterified BTCA increased with the amount of BTCA. Pendant attachment of monoesterified BTCA with cellulosic hydroxyl groups first increased and then decreased with the amount of BTCA. However, the monoesterified BTCA was irrelevant with the variation of the tensile properties of the crosslinked rayon fibers. Only bridging crosslinking of two hydroxyl groups on two different cellulose macromolecular chains caused one crosslinking site via a twice esterified BTCA molecule, which played a major role for the variation of the tensile properties of the crosslinked rayon fibers as shown in Figure 4.

ACD was defined as the number ratio of bridgeable crosslinkages formed from pairs of the generated ester linkages in the amorphous regions of cellulose fibers to the total accessible hydroxyl groups for the crosslinking agent.

$$\mathrm{ACD} = \frac{0.5\mathrm{N_e}}{\frac{\mathrm{W.f_a}}{162} \times 3 \times 1000} = \frac{0.5(\mathrm{C_0} - \mathrm{C_1})}{\frac{\mathrm{f_a}}{162} \times 3 \times 1000}$$

where *W* is the weight of the cellulose fibers in g. $0.5\mathrm{N_e}$ means the number of bridgeable crosslinkages in mmol formed from pairs of the generated ester linkages in the cellulose fibers. f_a is the weight fraction of the amorphous regions of the cellulose fibers derived from WAXD. f_a was 0.498. 162 is the molecular weight of a glucopyranose ring. $\mathrm{C_0}$ and $\mathrm{C_1}$ are in mmol/g fiber. ACD was adopted here to evaluate the crosslinking efficiency because the pendant ester linkages made no contribution to crosslinking. More BTCA gave rise to higher ACD of the rayon fibers in Table II. The dry and wet tensile strength was optimized when the BTCA amount was 0.410 mmol/g fiber in Figure 4(a). The lower tensile strength corresponding to the BTCA amount other than 0.410 mmol/g was possibly interpreted by the insufficient or over crosslinking of the rayon fibers. When the BTCA amount was 0.410 mmol/g fiber, dry and wet elongation at break decreased by ~ 7% in Figure 4(b), and dry and wet initial modulus increased by 7 cN/dtex. Both the decreased elongation at break and

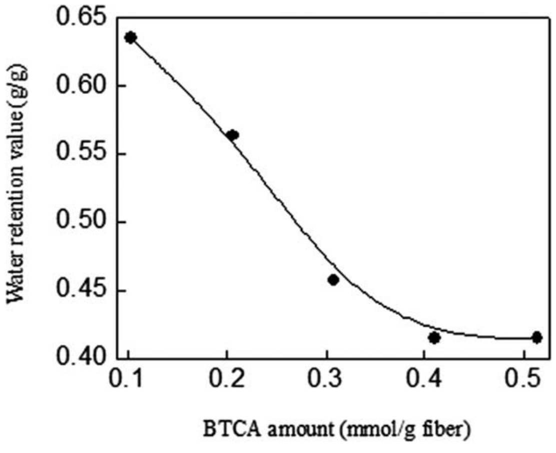

Figure 5 Dependance of water retention value of crosslinked rayon fibers on BTCA amount.

increased initial modulus were advantageous to dimensional stability of the rayon fibers.

Dependance of swelling degree on BTCA amount

The variation of the wet tensile properties could be further explained by WRV of the rayon fibers crosslinked with the different amounts of BTCA in Figure 5. When absorbing liquid water, the crosslinked network structures of the rayon fibers were responsible for diminished swelling, which had technical consequences in the tensile properties and dimensional stability of the cellulose fabrics. WRV of crosslinked fibers was an indicator to demonstrate swelling equilibrium between liquid water and the rayon fibers. In Figure 5, WRV of the crosslinked rayon fibers reduced evidently with the amount of BTCA, or ACD. In contrast, WRV of the uncrosslinked rayon fibers was 0.972 g/g. When the amount of BTCA was 0.410 mmol/g fiber, the optimal wet tensile strength 1.46 ± 0.03 cN/dtex corresponded to WRV 0.415 g/g and ACD 2.58×10^{-2}. So less liquid water was retained in the crosslinked network structures, and swelling of the rayon fibers diminished substantially as a result of crosslinking. It is not difficult to understand that less swelling accounted for the enhanced wet tensile properties.

CONCLUSIONS

BTCA was regarded as the most efficient crosslinking agent for nonformaldehyde anticrease finishing of cellulose fabrics. BTCA was hence used as the crosslinking agent to crosslink the amorphous regions of the cotton-type rayon fibers in this research. The formation of the intrafiber crosslinked structures in the amorphous regions of the rayon fibers enhanced the tensile properties, which was a facile and an efficient method to establish the relationship between the macromolecular structures and macroscopic properties of the rayon fibers.

The esterification crosslinking proceeded in two steps, i.e., pendant attachment of BTCA via esterification with a cellulosic hydroxyl group, and its further reaction with another cellulosic hydroxyl group in a different cellulose macromolecular chain producing bridging crosslinking of the rayon fibers. The amounts of the monoesterified, twice esterified, and 3-time esterified BTCA were estimated on the basis of the titration results of the free carboxyl groups and ester linkages in the crosslinked fibers. The pendant ester linkages made no contribution to crosslinking, whereas the esterification crosslinking of the rayon fibers occurred when an individual BTCA molecule reacted with more than two hydroxyl groups on different cellulose macromolecular chains. So ACD was defined to evaluate the crosslinking efficiency accordingly.

It was found that both the amount of the crosslinking agent and curing temperature made notable impacts on the esterification crosslinking behaviors of the rayon fibers. The dry and wet tensile strength of the rayon fibers, 2.57 ± 0.02 and 1.42 ± 0.02 cN/dtex, were optimized under the curing temperature 180°C, corresponding to ACD 2.32×10^{-2} and WRV 0.554 g/g. On the other hand, the optimized dry and wet tensile strength, 2.56 ± 0.02 and 1.46 ± 0.03 cN/dtex corresponded to ACD 2.58×10^{-2} and WRV 0.415 g/g when the amount of BTCA was 0.410 mmol/g fiber and the curing temperature was 180°C. The optimized tensile strength was in good agreement in both cases due to their almost identical ACD and swelling in water.

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