

Preparation and Properties of Cross-Linked Regenerated Cellulose Fibers

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Abstract

Butane-tetra-carboxylic acid (BTCA) and sodium hypophosphite (SHP) were added into cellulose spinning solution. The cross-linked regenerated cellulose fibers were prepared by spinning the solution into a coagulation bath of distilled water and then cured at high temperature. The optimum conditions were obtained according to the single factor experiments. The properties and structure of the fibers were investigated. FTIR and XRD show that the cross-linked fibers were prepared successfully and the crystal form of the fibers remain the same before and after cross-linking. The results indicate that the regenerated cellulose fibers prepared in this study possess more excellent wrinkle recovery ability and wash durability than those treated by finishing process.

Keywords: Preparations; Properties; Cellulose; Wet spinning; Crosslink; Wrinkle recovery

Introduction

Cellulose fiber has advantages of high wet adsorption, wearing comfort and low price, but it shows poor wash durability, easy deformation, low size stability and low wet elasticity, which influence its service performance significantly [1,2]. At present, cellulose fiber mainly employs the after finish mode. Firstly, wash and wear finisher and cross-linked agent are applied on textiles through impregnation and padding. Secondly, the finishing agent and cellulose macromolecules make cross-linked reactions through high-temperature curing, thus improving morphological stability of textiles. However, the easy-care anti-crease finishing of textiles based on after finish mode will result in hardening of hand feeling, easy yellowing and sharp strength reduction [3-6].

Ionic liquid is an emerging green solvent system in recent years. Many scholars have studied dissolution and regeneration of cellulose fiber based on ionic liquid. In 1934, Graenacher discovered the first organic fuse salt (N-ethylpyridine chloride) that can dissolve fiber, but it failed to be used extensively due to the high melting point (118–120°C) [7]. In 2002, Swatloski et al. discovered for the first time that fiber can be dissolved in ionic liquid without activation, which opened a new field for new cellulose solvent system [8]. In 2005, Zhu et al. synthesized the chlorination1-(2-ethoxy)-3-methylimidazole ([HeMIM] Cl) ionic liquid and found that the solubility of activated microcrystalline cellulose in [HeMIM] Cl under 70°C reaches 5%–7%. Cellulose/ionic liquid solution can regenerate cellulose through coagulating bath with water, acetone and ethyl alcohol [9]. Zhang et al. pointed out from X-ray diffraction research that the crystal form of cellulose changes from I-type to II-type after cellulose pulp is dissolved and regenerated in [AMIM] Cl [10].

In this paper, blend spinning solution was prepared by dissolving cellulose pulp, wrinkle proofing agent and crosslink agent into the ionic liquid. The prepared blend spinning was regenerated in weak acid coagulation bath by wet spinning technology, followed by drafting, precur and curing process, finally getting cross-linked regenerated cellulose fiber.

Experiment

Preparation of cross-linked regenerated cellulose fiber

BTCA and SHP (mass ratio of BTCA: SHP=8:5) were added into the ionic liquid. The mixture was heated to 60°C and stirred continuously. The vacuum dried cellulose pulp was added and the solution was heated

to 80°C while stirring, getting the blend spinning solution. Next, the blend spinning solution was filtered and degassed for 24 h in vacuum environment. Subsequently, 1 wt% dilute sulfuric acid solution was prepared and heated to 40°C for later use. The spinning solution arrived at the prepared dilute sulfuric acid solution under the pressure of nitrogen after passing through the spinneret plate, and then solidified for 30 s. Next, two-stage drafting (draft multiple of each is 1.5 times) was implemented, getting the shaped fiber. The shaped fiber was put into a dryer for procuring (90°C, 2.5 min), curing, washing and drying, thus getting the BTCA cross-linked regenerated cellulose fiber.

Test of fiber carboxyl and ester bond contents

In this paper, 0.01 mol/L calcium acetate solution was prepared. Then, 1.00 g fiber was weighted accurately and grinded into powder which was immersed in the calcium acetate solution. The mixture was put under constant temperature (8°C) for 2 h and then titrated by NaOH standard solution.

Calculation method: if the carboxyl group contents (mmol/g fiber) on fiber before and after cross-linked are C_1 and C_2 , the carboxyl group content on fiber after washing is C_3 and the carboxyl group content on non-cross-linked fiber is C_0 , then the carboxyl group content after cross-linked and washing is $C_3 - C_0$, the ester bond content is $C_1 - C_2$, the carboxyl group content participating in the esterification reaction is $C_1 - C_2 + C_3 - C_0$, and the conversion rate of carboxyl group is $(C_1 - C_2) / (C_1 - C_2 + C_3 - C_0) \times 100\%$.

Structural characterization of cross-linked regenerated cellulose fiber

FTIR: Fiber samples were grinded into powder and scanned by NICOLET5700 infrared spectrometer by the potassium bromide pellet technique. The resolution, scanning times and scanning rate were set 4 cm^{-1} , 32 and 0.2 cm/s , respectively.

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XRD: DX2700 X-diffractometer using Cu target K line was applied for XRD. Tube pressure, tube current, scanning angle range and scanning rate were 40 kV, 40 mA, 5°–60° and 5°/min, respectively.

Mechanical property test

Breaking strength and elongation at break of fiber were tested by LLY-06 single fiber strength tester. The stretching velocity and clamping interval were 20 mm/min and 10 mm. Each kind of samples has 20 test samples and means results were used. The relative humidity and temperature were tested 65% and 20°C.

Results and Discussions

FTIR analysis of cross-linked fiber

It can be seen from Fig. 1 that the peak at 1117.2 cm⁻¹ is contributed by stretching vibration of C-O-C and the peak at 2900.1 cm⁻¹ is contributed by stretching vibration of C-H. There's a strong absorption peak at 1723.3 cm⁻¹, which is the stretching vibration peak of ester bond carbonyl. It is the additional peak compared to fiber before cross-linked and is mainly caused by the esterification reaction between BTCA and cellulose hydroxyls (Figure 1).

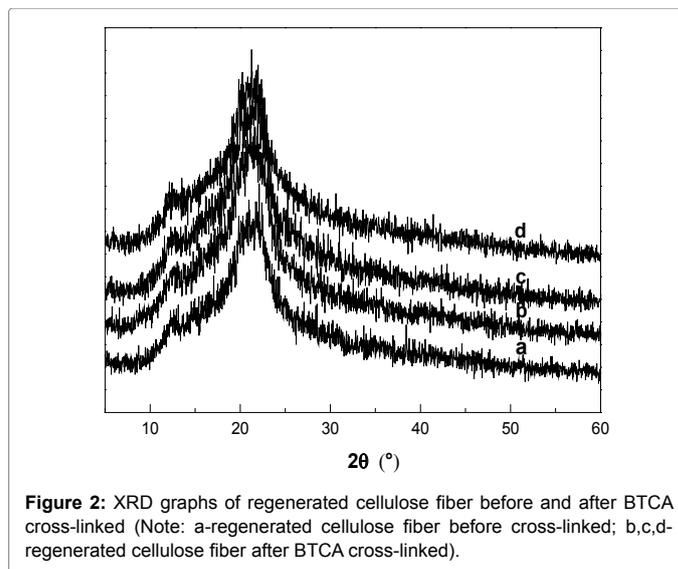
XRD analysis of cross-linked fiber

Compared with non-cross-linked fiber, the regenerated cellulose fiber after BTCA cross-linked (b, c and d) keeps basically same XRD spectra (Figure 2). They have characteristic peaks of fiber II close to 2θ=11.8° (101), 19.9° (10) and 21.6° (002). Cellulose is dissolved in ionic liquid directly. Only the cellulose I is converted into cellulose II, but no other derivative reactions occurs. The cross-linked reaction occurs in the accessible region of the regenerated cellulose, mainly between carboxyl groups of C6-OH and BTCA. Nevertheless, crystal form of cellulose is same before and after cellulose cross-linked, showing cellulose II-type crystal form. Based on calculation of Jade 5.0 software, the degree of crystallinity of fiber after curing and cross-linked is higher than that before the curing, indicating the II-type cell parameters of cellulose change slightly. This might be attributed to the formation of "quasi-crystal" structure in amorphous region of cellulose (Figure 2).

Influencing factors of wrinkle recovery of cross-linked fiber

Effect of BTCA dose on wrinkle recovery of cross-linked fiber:

In Figure 3, both dry and wet wrinkle recovery angles of the fiber increase with the increase of mass fraction of BTCA. When the mass



fraction of BTCA is smaller than 4 wt %, the wrinkle recovery angle of fiber increases quickly with the increase of mass fraction of BTCA, but such growth slows down when the mass fraction of BTCA is higher than 4 wt%. Under different concentrations of BTCA, the cross-linked degrees of BTCA and cellulose are different. The cross-linked under low concentration of BTCA is more effective, but weakens under high concentration. This is because under low concentration, BTCA can make cross-linked reaction with carboxyl groups on cellulose more effectively, but under high concentration, each carboxyl group in molecule will make competitive reaction with -OH. Therefore, some carboxyl groups will be failed in the competition and some BTCA can only react with one carboxyl group that is, grafting reaction. Accordingly, WRA curve soars up and then becomes stable with the increase of BTCA concentration. Reactions between BTCA and cellulose include three types: intermolecular cross-linked, intermolecular cross-linked and grafting formed by one carboxyl group and cellulose. The first two types are major reactions under low concentration of BTCA, but the third type increases gradually under high concentration (Figure 3).

Effect of cross-linked temperature on wrinkle recovery of fiber

Figure 4 shows that the wrinkle recovery angle and wrinkle recovery rate of fiber increase as the cross-linked temperature rises. Due to the heat absorption equilibrium reaction during esterification, temperature rise is conducive to facilitate the esterification toward the cross-linked reaction [11]. The esterification of carboxylic acid and alcohol is called the reversible reaction [12]. The reaction isn't thoroughly under general situations. With respect to one reversible reaction, the same equilibrium state could be established under certain conditions no matter whether the reaction starts from the positive reaction or the reverse reaction. This means the same equilibrium state could be realized under different initial conditions. If influencing factors (e.g., concentration, temperature and pressure) of the equilibrium state are changed, the equilibrium will move to the direction that could weaken such change (Figure 4).

Effect of cross-linked time on wrinkle recovery of fiber

It can be seen from Figure 5 that the wrinkle recovery angle and wrinkle recovery rate of fiber increase gradually as the cross-linked continues. From 1.5-3 min, the wrinkle recovery angle achieves a straight growth trend, but such growth trend slows down after 3 min.

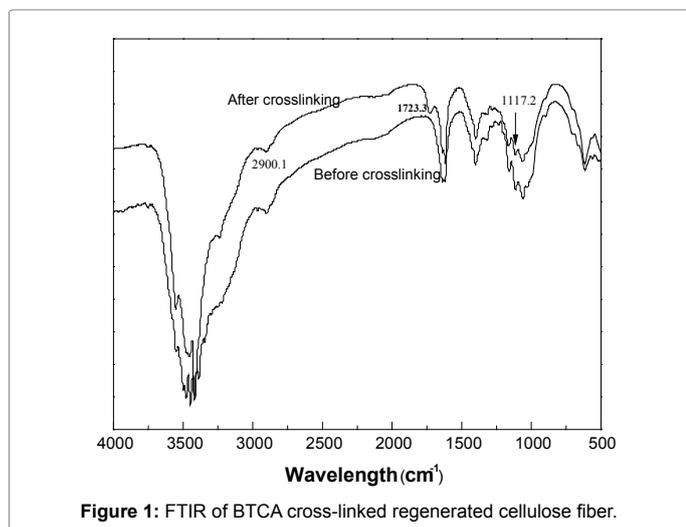


Figure 1: FTIR of BTCA cross-linked regenerated cellulose fiber.

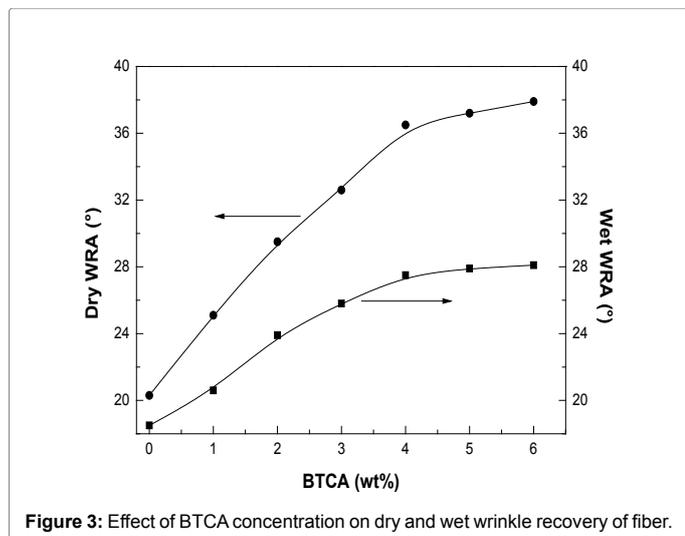


Figure 3: Effect of BTCA concentration on dry and wet wrinkle recovery of fiber.

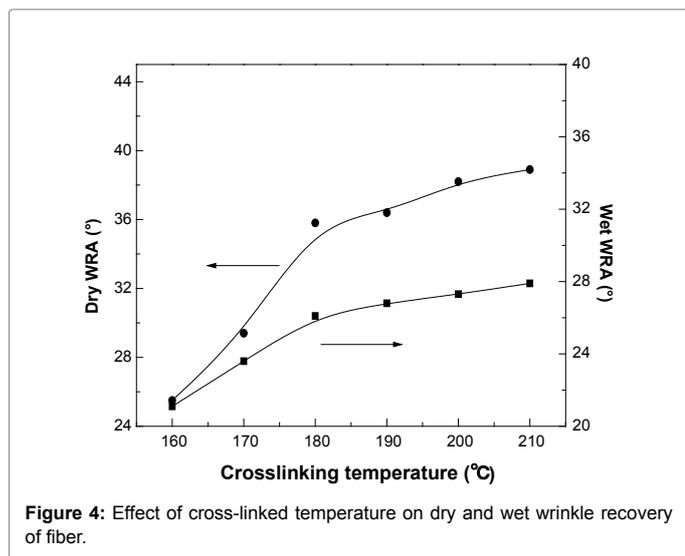


Figure 4: Effect of cross-linked temperature on dry and wet wrinkle recovery of fiber.

In the beginning, each BTCA molecule has one or two carboxyl groups that make the esterification. As time goes on, each molecule has two or three or all carboxyl's groups participating in the reaction, indicating that long cross-linked time is in favour of esterification. Figures 3-5 also reveal that the dry wrinkle recovery of fiber is significantly better than the wet wrinkle recovery. Since fiber uses dry cross-linked, water and finishing agent have different accessibilities in fiber. Water molecules which are smaller than finishing agent molecules are easier to penetrate into crystal region edges with high lateral order (Figure 5) [13].

Influencing factors of mechanical properties of cross-linked fiber

Effect of BTCA mass fraction on mechanical properties of fiber:

Figure 6 reflects the positive correlation between ester bond content and BTCA mass fraction. In the beginning, the conversion rate of carboxyl groups increases slowly with the increase of BTCA mass fraction and reaches the maximum (48.5%) at 4 wt% of BTCA mass fraction. With the further increase of BTCA mass fraction, the conversion rate of carboxyl groups decreases.

The esterification which pertains to an equilibrium reaction will approach to the equilibrium state. Further increase of BTCA mass fraction after reaching the equilibrium state won't influence the conversion rate of carboxyl groups significantly, but will waste the BTCA. For the purpose of material saving, BTCA dose is chosen 4 wt% (Figure 6).

It can be seen from Figure 7 that with the increase of BTCA mass fraction, wet modulus of regenerated cellulose fiber increases from 8.5 cN/dtex to 15.9 cN/dtex, while the wet breaking strength presents an inverted U-shaped variation law, reaching the peak (1.43 cN/dtex, 24.43% higher) at 4 wt%. Therefore, increasing BTCA mass fraction can improve the wet breaking strength of cross-linked fiber significantly (Figure 7).

Effect of cross-linked temperature on mechanical properties of fiber:

In Figure 8, conversion rate of carboxyl groups and ester bond content increase gradually as cross-linked temperature rises. Under 160°C the conversion rate of carboxyl groups is only 39.5% and the ester bond content is 0.32 mmol/g, which increase to 50.1% and 0.45 mmol/g under 180°C. The conversion rate of carboxyl groups further increases to 63.2% under 210°C. This proves that higher cross-linked temperature can promote esterification between BTCA and

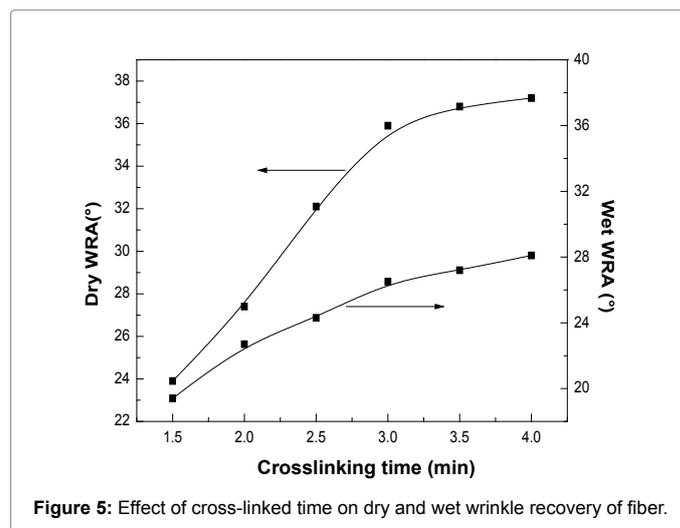


Figure 5: Effect of cross-linked time on dry and wet wrinkle recovery of fiber.

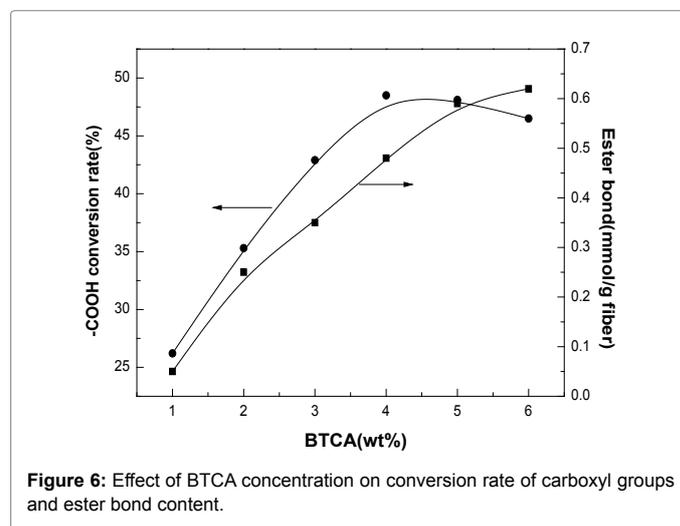


Figure 6: Effect of BTCA concentration on conversion rate of carboxyl groups and ester bond content.

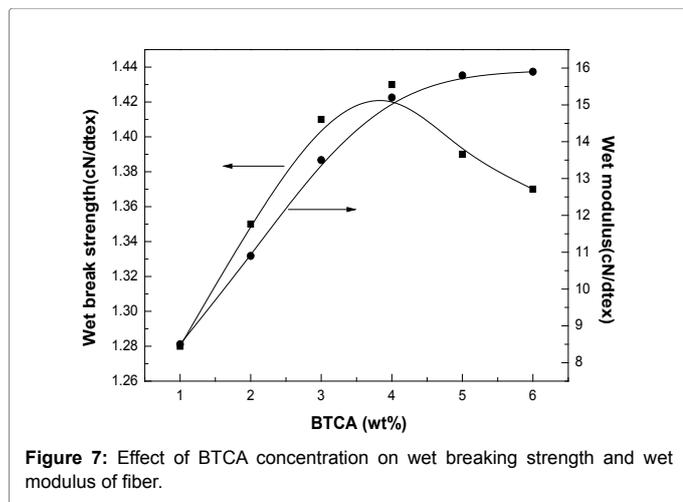


Figure 7: Effect of BTCA concentration on wet breaking strength and wet modulus of fiber.

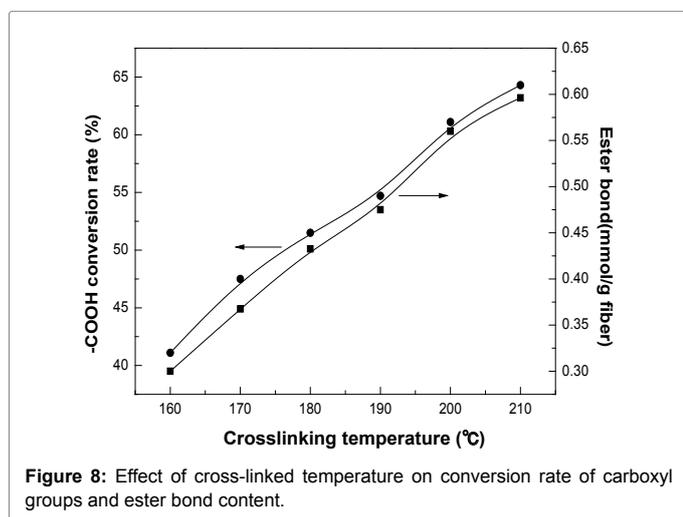


Figure 8: Effect of cross-linked temperature on conversion rate of carboxyl groups and ester bond content.

regenerated cellulose fiber. This is because the esterification is a heat absorption equilibrium reaction and higher temperature will facilitate the esterification toward the cross-linked reaction [14] (Figure 8).

Figure 9 shows that with the increase of cross-linked temperature, wet module of cross-linked fiber increases from 12.5 cN/dtex to 17.3 cN/dtex. Initial modulus represents fiber resistance to small deformation. If the initial modulus is high, the fiber is difficult to be deformed under small load and the fiber has good wrinkle recovery performances. However, excessive initial modulus will affect the breaking strength of the fiber. The wet breaking strength of fiber increases firstly and then decreases as the cross-linked temperature rises, reaching the peak (1.45 cN/dtex) at 180°C. The maximum wet breaking strength is 16% higher than that of regenerated cellulose fiber. With the continuous increase of temperature, breaking strength declines slightly. Different from cotton fiber, regenerated cellulose fiber has lower relative molecular mass, lower degree of polymerization and degree of crystallinity. The hydrogen bond density between molecular chains in regenerated cellulose fiber is small and there are inadequate hydrogen bonds to resist external forces, which will cause breaking failure and relative slippage between macromolecular chains and basic structural unit of the fiber, thus resulting in fiber breakage [15]. After esterification cross-linked of BTCA, the involvement of covalent cross-linked supplements

and enhances molecular acting force, which makes it difficult to cause slippage failure of the regenerated cellulose fiber. Hence, strength of fiber increases significantly (Figures 9-11).

Effect of cross-linked time on mechanical properties of fiber: It can be seen from Figure 12 that conversion rate of BTCA carboxyl

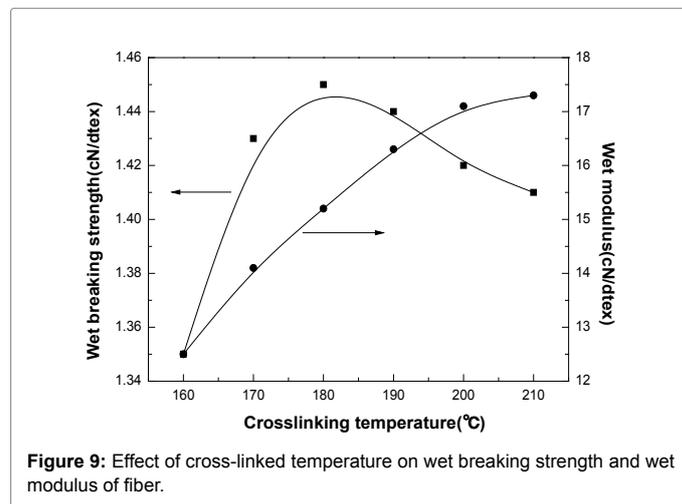


Figure 9: Effect of cross-linked temperature on wet breaking strength and wet modulus of fiber.

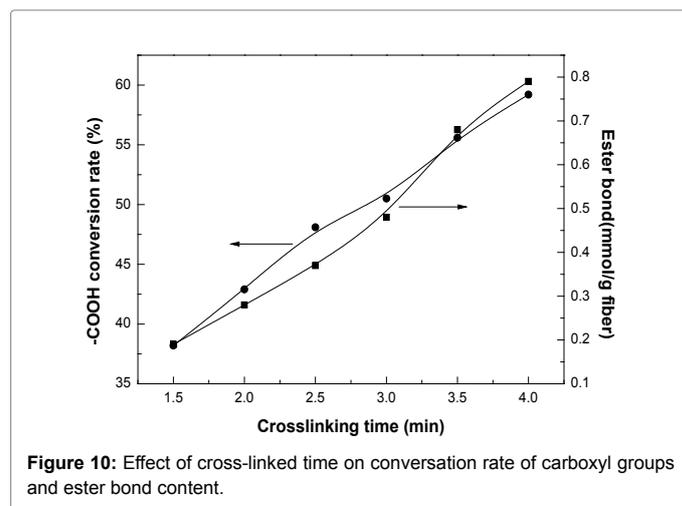


Figure 10: Effect of cross-linked time on conversion rate of carboxyl groups and ester bond content.

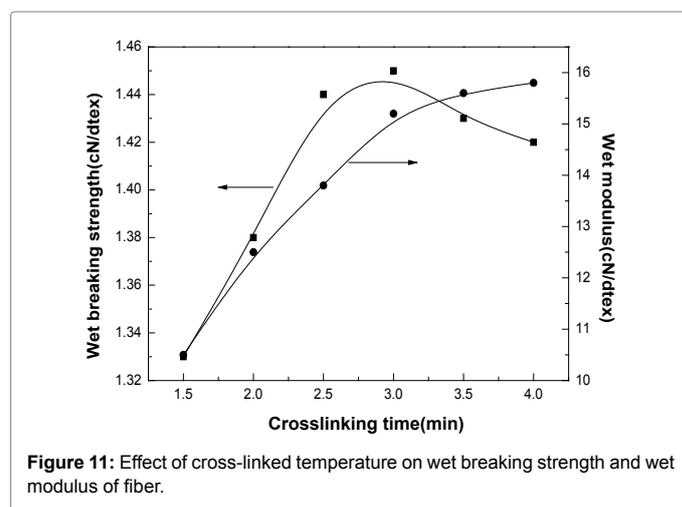


Figure 11: Effect of cross-linked time on wet breaking strength and wet modulus of fiber.

groups and ester bond content increase continuously with the increase of cross-linked time. From 1~3 min of cross-linked, the conversion rate of BTCA carboxyl groups increases from 38.2% to 50.5%, indicating that there are one or two carboxyl groups in involved carboxylic acids have participated in the esterification reaction. Subsequently, conversion rate of BTCA carboxyl groups increases gradually and exceeds 50% after 3.5 min, indicating that there are two or three carboxyl groups in each involved BTCA molecule have participated in the cross-linked reaction. This also reveals that longer cross-linked time is conducive for cross-linked between BTCA and regenerated cellulose, thus increasing the conversion rate of carboxyl groups (Figure 10).

In Figure 11, wet breaking strength of fiber increases firstly and then decrease slowly with the increase of cross-linked time, reaching the peak (1.45 cN/dtex) after 3 min. Later, the wet breaking strength declines slightly, which is related with excessive modulus and increasing fragility of fiber. With the continuous increase of wet modulus, the wet modulus of the original regenerated cellulose fiber is 5.6 cN/dtex and increases by 1.7 times to 15.2 cN/dtex after 3 min of curing. Therefore, the curing time shall be chosen 3 min (Figure 11).

Wash durability analysis of cross-linked fiber

The optimal proportion and spinning technology are concluded from above discussions. The dry and wet wrinkle recovery angles of the regenerated cellulose fiber prepared by adding 4 wt% BTCA (BTCA:SHP=8:5) into cellulose spinning solution, 30 s coagulating bath by 1% sulfuric acid, two-stage drafting (draft multiple of each is 1.5 times), procuring, curing, washing by warm temperature and drying are 35.8° and 26.1°, which are 76.4% and 41.1% higher than those of the non-cross-linked cellulose fiber. Wash durability test results of dried fiber are shown in Figure 12. The dry wrinkle recovery angle of cross-linked fiber only decreases by 7.3% after 10 washing times and still can maintain over 85.5% after 30 washing times, higher than BTCA easy-care effect of viscose fabric. It also saves finishing agent significantly. This is because finishing agent which are added in the spinning solution can disperse to cellulose matrix more evenly and effectively and increase intermolecular contact, which can increase the esterification cross-linked efficiency (Figure 12).

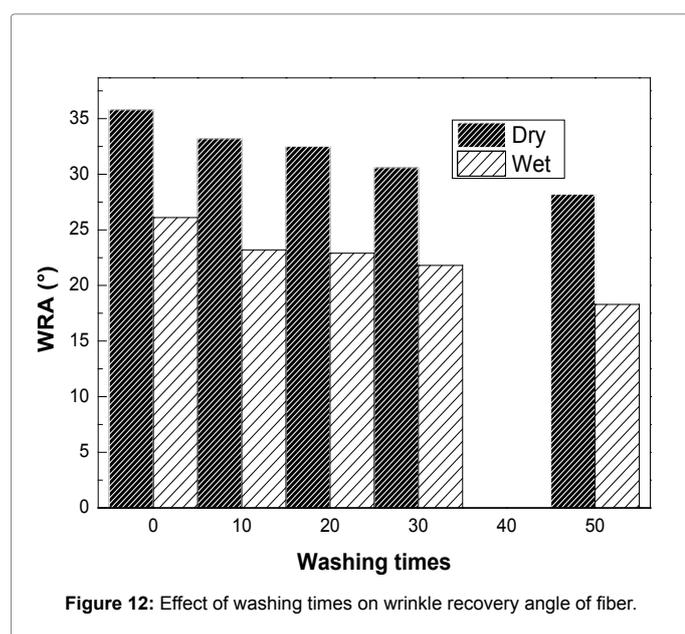


Figure 12: Effect of washing times on wrinkle recovery angle of fiber.

Conclusions

The cross-linked regenerated cellulose fibers were prepared by spinning the blend solution containing cellulose, BTCA and SHP into a coagulation bath of distilled water and then cured at high temperature. The optimal preparation condition was obtained according to the single factor experiments. Dry and wet wrinkle recovery angles of the cross-linked fibers are improved by 76.4% and 41.1%, separately. Moreover, it was indicated from the XRD analysis results that the crystal form remains unchanged (cellulose II-type), while the cell parameters of cellulose II change and the degree of crystallinity increases to some extent. This new approach offers great potential for cellulose fibers to get better wrinkle recovery ability with shorter production cycle compared with traditional ways.

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