

Novel Strategy to fabricate Antiwrinkle Cotton fabrics with 1,2,3,4-Butanetetracarboxylic Acid under a Low Temperature

Hanchang Hu, Xia Dong, Qiangqiang Zhao, Rongliang Wu, Chen Meng, Jiani Xu, Tingwei Cai, Xin Wang, and Jinxin He*



Cite This: *ACS Omega* 2022, 7, 30093–30103



Read Online

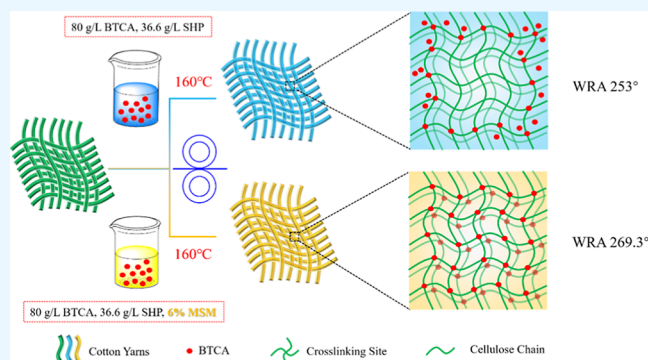
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: As a most promising formaldehyde-free crosslinking agent for the antiwrinkle treatment of cotton fabrics, 1,2,3,4-butanetetracarboxylic acid (BTCA) has been explored for many years to replace the traditional *N*-methylol resin. However, the current methodology for preparing antiwrinkle cotton fabrics with BTCA mainly highlights the troublesome problem of higher curing temperature. In this research, a novel strategy with the aid of dimethyl sulfone (MSM) was developed to decrease the curing temperature of BTCA for fabricating antiwrinkle cotton fabrics, which is an eco-friendly additive with low price and wonderful biocompatibility. Temperature-dependent Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, and computational simulations were employed to analyze the mechanism of MSM in the overall reaction between BTCA and cellulose. Based on the strong hydrogen-bond acceptor property of MSM, the noncovalent interactions in the crosslinking system could be easily interrupted, which facilitates the BTCA diffusion in amorphous regions of cellulose, anhydride formation, and the thermal vibration of cellulose chains during the processing. Physically and chemically speaking, both reactivities of grafting and crosslinking reactions of BTCA are significantly increased with the assistance of MSM, consequently reducing the curing temperature, which will hopefully help achieve the industrial-scale application of BTCA in antiwrinkle treatment.



1. INTRODUCTION

1,2,3,4-Butanetetracarboxylic acid (BTCA), a most effective nonformaldehyde crosslinking agent of poly-carboxylic acid, has been extensively investigated for many years to obtain high-performance antiwrinkle cotton fabrics in the presence of sodium hypophosphite (SHP).¹ However, the crosslinking process between BTCA and cotton fabrics requires a higher curing temperature (typically at 180 °C for 2 min) and acid condition (pH of finishing solution is typically at about 2.0), resulting in high strength loss of treated fabric and a huge amount of energy consumption, which impede its industrialized application in the antiwrinkle treatment of cotton fabrics.²

The mechanism of the reaction between BTCA and cellulose has been studied for many years; BTCA first dehydrates to form active anhydride intermediates under high temperature, and then, active anhydride intermediates esterify with hydroxyl groups in cellulose chains.^{3–5} The catalysis of SHP plays an important role in the esterification between BTCA and cellulose, which not only increases the reactivity of the reaction but also prevents cotton fabrics from being oxidized. However, under the catalysis of SHP, the antiwrinkle treatment based on BTCA still requires a high curing temperature, which urgently necessitates finding an

effective way to reduce the temperature for catering to the antiwrinkle treatment of BTCA.^{6,7} In our previous studies, we elaborately analyzed the impact of curing temperature on the overall reactions consisting of grafting and crosslinking reactions between BTCA and cellulose.⁸ Currently, we usually apply 80 g L⁻¹ BTCA to treat cotton fabrics for satisfactory antiwrinkle performance, and thus, the BTCA molecules in predried fabrics easily congregate together via the intermolecular hydrogen bonding effect, which restrains the diffusion of BTCA in the amorphous of cellulose as well as anhydride formation. The higher temperature could significantly break off the noncovalent interaction in the system and is beneficial for BTCA to diffuse to the inner fibers and, subsequently, form anhydride intermediates to esterify with cellulose.⁹ On the other hand, the motion of grafted BTCA is determined by the thermal vibration of cellulose chains. It is explicit that high

Received: May 19, 2022

Accepted: August 4, 2022

Published: August 22, 2022



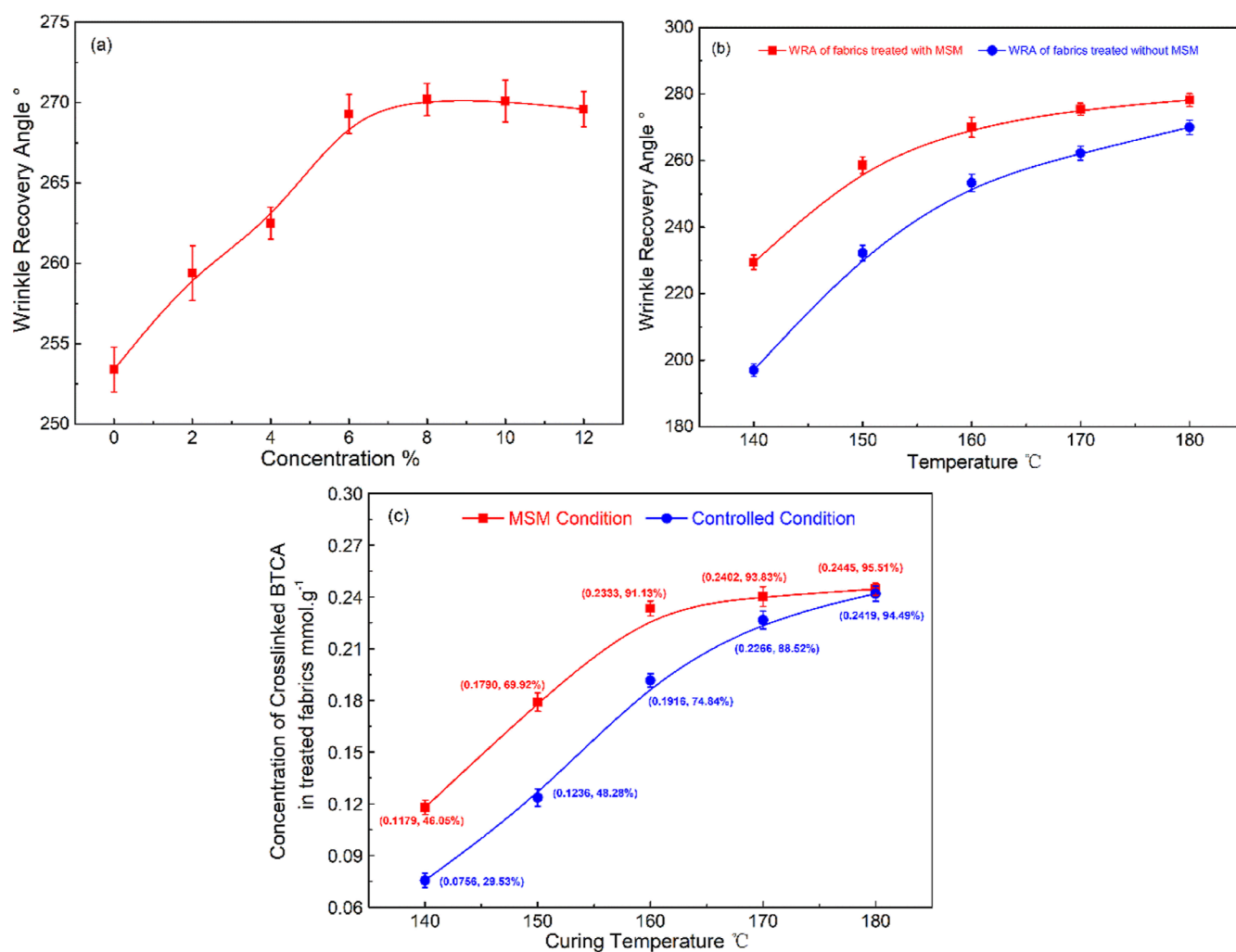


Figure 1. WRA and content of crosslinked BTCA in treated cotton fabrics. (a) Effect of concentration of MSM on WRA of finished fabrics. The finishing bath contained 80 g L⁻¹ BTCA and 36.6 g L⁻¹ SHP, and samples were cured at 160 °C for 3 min. (b) Effect of temperature on WRA of finished fabrics with or without MSM. The finishing bath contained 80 g L⁻¹ BTCA, 36.6 g L⁻¹ SHP, and 6 wt % MSM and was cured for 3 min. (c) Effect of curing temperature on the concentration of crosslinked BTCA in treated fabrics. The finishing condition was the same as that of (b).

temperature can promote the vibration of cellulose for crosslinking reaction between grafted BTCA and cellulose.^{10,11} Hence, decreasing the interactions between cellulose chains or BTCA molecules is conducive to de-escalate the curing temperature of BTCA, which might achieve the application of BTCA in the antiwrinkle treatment.

It is proposed in this article that if the hydrogen bonding in both BTCA molecules and cellulose chains was weakened by the plasticizing effect, the reaction efficiency between BTCA and cellulose macromolecules would be enhanced. The strong hydrogen bonding between cellulose chains could be weakened by water, causing cotton fabrics to swell rapidly.^{12,13} However, under the predrying process of antiwrinkle treatment, most hydrogen bonds both existing in BTCA molecules and cellulose chains could be reconstructed with the evaporation of water. Dimethyl sulfone (MSM) is an important chemical agent for human beings to synthesize the necessary collagen for supporting health and is usually applied in industrial chemical synthesis as a cheap high-temperature solvent due to its high boiling point of 238 °C.¹⁴ More importantly, MSM has two hydrogen-bond acceptors (HBA) and, thus, must have a wonderful performance to the weak hydrogen bonding effect between BTCA molecules or cellulose chains.^{15,16} Therefore,

the objective of this research is to verify whether the curing temperature of BTCA can be reduced by MSM and discuss the impact of MSM on grafting and crosslinking reactions between BTCA and cellulose from a kinetic perspective. In order to give a more reliable date, an acid-based back titration was applied to test the amount of ester-linkage in treated fabrics. In addition, temperature-dependent Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), and computational simulations were also employed to analyze the effect of MSM on the overall reaction.

2. RESULTS AND DISCUSSION

2.1. Wrinkle Recovery Angle of Cotton Fabrics Treated by BTCA with the Aid of MSM. First, the wrinkle recovery angle (WRA) of cotton fabrics finished by BTCA with the assistance of MSM was measured to verify the reduction effect of curing temperature. As indicated in Figure 1a, the WRA of treated cotton fabrics increased dramatically from 253 to 269.3° until the finishing concentration of MSM reached 6 wt %, which significantly indicated that MSM could improve the antiwrinkle performance of cotton fabrics finished by BTCA. Notably, the antiwrinkle performance of treated

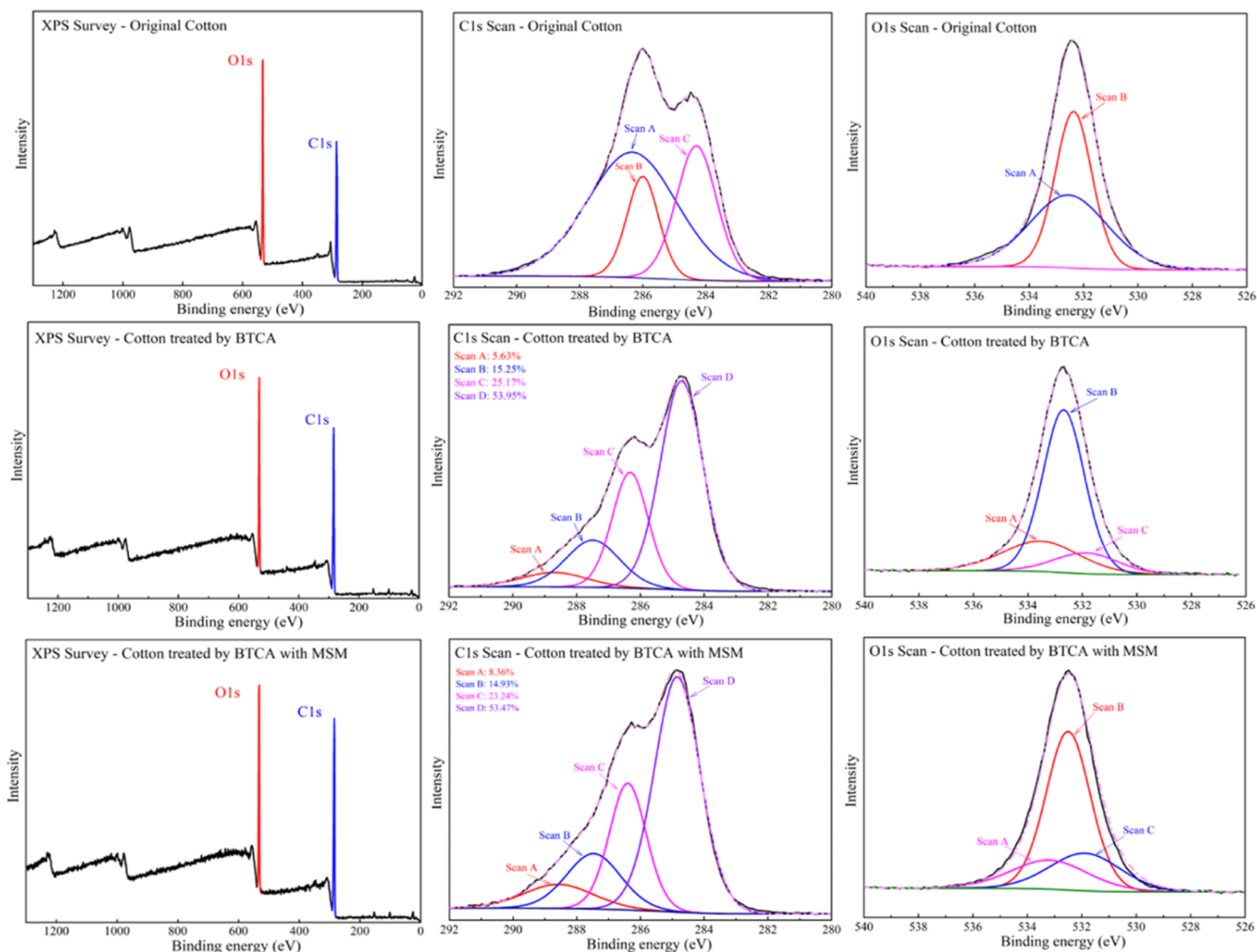


Figure 2. XPS spectra of cotton fabrics under different treatments.

cotton fabric with aid of MSM at 160 °C was almost equal to those of controlled antiwrinkle treatment at 180 °C (Figure 1b), which decreased the curing temperature by approximately 20 °C. This result demonstrated that the curing temperature of BTCA could be obviously reduced with the assistance of MSM, which is very promising for the extensive application of BTCA in the field of antiwrinkle treatment. Meanwhile, the content of crosslinked BTCA in fabrics was measured via a back-titration way, which is more identified evidence for the effect of MSM on the improved antiwrinkle performance of finished fabrics. As illustrated in Figure 1c, the content of crosslinked BTCA in fabrics was much higher than those without MSM, meaning the rate of the whole reaction became faster. Tables S1 and S2 presented grafted and crosslinked yield of BTCA with or without MSM in cotton fabrics under different curing times and temperatures. We usually treat cotton fabrics with BTCA under 180 °C for 2 min, and the crosslinked yield of BTCA under such conditions is about 90%. Regarding this crosslinked yield of BTCA as a standard, the optimized curing temperature and time required for the finishing method of BTCA with the help of MSM are 160 °C and 3 min, respectively. This methodology highlights a facile but highly effective strategy to reduce the curing temperature for fabricating cotton fabrics with satisfactory antiwrinkle performance.

To further demonstrate the influence of MSM on the reaction between BTCA and cellulose at a molecular level, the chemical components of treated cotton were determined by XPS.¹⁷ All the samples were washed after treatment and then cut into small powders for further test. As shown in Figure 2, the chemical shifts of carbon in original cotton were deconvoluted into three binding energy peaks using the peak-fitting of Gaussian curves, which correspond to C–C at 284.6 eV, C–O–C at 286.1 eV, and C–OH at 286.4 eV.^{18,19} After treating with BTCA, the chemical shifts of carbon in finished cotton were divided into four binding energy peaks at 288.5, 287.6, 286.4, and 284.5 eV, attributable to the O=C–O, C–O–C, C–OH, and C–C species, respectively. Importantly, the area of the peak corresponding to O=C–O at around 288.5 eV increased from 5.63% (controlled condition) to 8.36% (MSM condition), which obviously showed that MSM could promote the crosslinking of BTCA in cotton fabrics.

2.2. Effect of MSM on BTCA Anhydride Formation.

The mechanism of esterification between BTCA and cellulose depicts that active BTCA anhydride intermediates play a crucial role in the esterification process, and inter- or intramolecular H-bond between or within BTCA molecules could impede the formation of anhydrides because of the hindrance of rotation of the C–C bond between two adjacent carboxyl groups. MSM has two sites of hydrogen bond

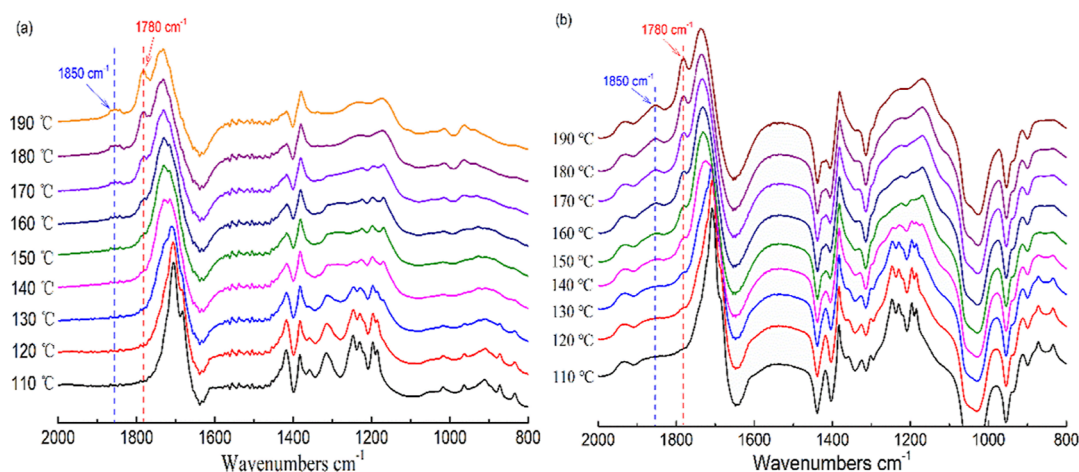


Figure 3. Temperature-dependent FTIR of pure BTCA (a) without or (b) with MSM.

acceptors and might decrease the H-bond effect of BTCA. Hence, a study on the effect of MSM on anhydride formation was designed to investigate the mechanism of affection between MSM and BTCA.

As shown in Figure 3, two obvious absorbance peaks at 1780 and 1850 cm^{-1} in FTIR of pure BTCA, representing the symmetric and asymmetric stretch vibration of carbonyl groups in anhydride respectively, were shown at 160 °C. However, the vibrational absorbances at 1780 and 1850 cm^{-1} on BTCA with MSM were clearly noticeable when the temperature was around 140 °C, which reflected that the temperature of anhydride formation could be reduced effectively with the aid of MSM. Thus, more anhydrides of BTCA can be produced and the formation of ester-linkage between BTCA and hydroxyl groups in cellulose would be promoted.

To further clarify the influence of MSM on the BTCA anhydride formation process, BTCA with or without MSM were heated up in the thermogravimetric analyzer under a nitrogen atmosphere. The weight loss of all samples with the increment in temperature was recorded in Figure 4. Pure BTCA began to lose weight at approximately 194 °C by the formation of anhydrides and continued to lose weight for the further degradation of compounds. The mixture of BTCA and SHP started losing weight at about 159 °C, which indicated that SHP can decrease the temperature of BTCA anhydride

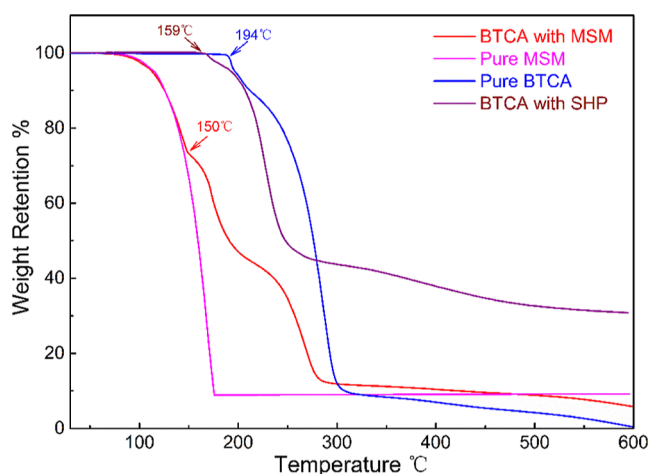


Figure 4. TGA curves of different chemical samples.

formation. MSM started to lose weight at around 100 °C which is consistent with its melt point, and its weight dramatically de-escalated with the increase in the temperature. However, there was an explicit inflection point showing at around 150 °C in the curve of the mixture of BTCA and MSM, which corresponds to the formation of BTCA anhydride, indicating that the anhydride formation temperature with the help of MSM was much lower than that of pure BTCA and a mixture of BTCA and SHP. This result was consistent with temperature-dependent FTIR and served as solid evidence for the promotion of esterification with the effect of MSM.

In order to further investigate how MSM interferes with the formation of anhydride, Gaussian 09W software was applied to simulate the formation process of BTCA anhydride under different environments with or without MSM and calculate the activation energy of anhydride formation under the B3LYP level at a basic set of 6-31G(d,p). The whole process of anhydride formation was presented in Figure 5. First, two adjacent carboxyl groups in BTCA rotated to available reaction sites through $\text{C}_1\text{-C}_3$, $\text{C}_3\text{-C}_{10}$, and $\text{C}_1\text{-C}_6$ single bond. After that, the carbon atom of C_{10} was attacked by the oxygen atom of O_8 , and the length of forming $\text{C}_{10}\text{-O}_8$ and $\text{O}_{12}\text{-H}_9$ bonds changed from 2.407 and 1.706 Å at reactant to 2.137 and 1.074 Å at the transition state and 1.764 and 0.977 Å at the product, respectively. Meanwhile, the length of breaking $\text{C}_{10}\text{-O}_{12}$ and $\text{O}_8\text{-H}_9$ bonds changed from 1.413 and 0.977 Å at reactant to 1.751 and 1.437 Å at the transition state and 2.071 and 1.995 Å at the product, respectively. Finally, a five-membered ring of anhydride and a water molecule would be produced. From the abovementioned process, the rotating competence of the bond and nucleophilic performance of the oxygen atom are the two main factors for the formation of anhydrides in BTCA. Besides, as depicted in Figure 6, the active energy (energy difference between TS and reactant) of anhydride formation with MSM (26.4801 kcal mol^{-1}) was lower than that without MSM (44.5479 kcal mol^{-1}), and thus, the temperature of anhydride formation could decrease to a low point, further facilitating the esterification between BTCA and cellulose. More elaborately, the electrostatics potential map of BTCA with the affection of MSM was also presented in Figure 7. Explicitly, the oxygen atom of MSM could form a H bond with the hydrogen atom of BTCA carboxyl groups, resulting in the negative oxygen atom of carboxyl groups becoming stronger for beneficially attacking

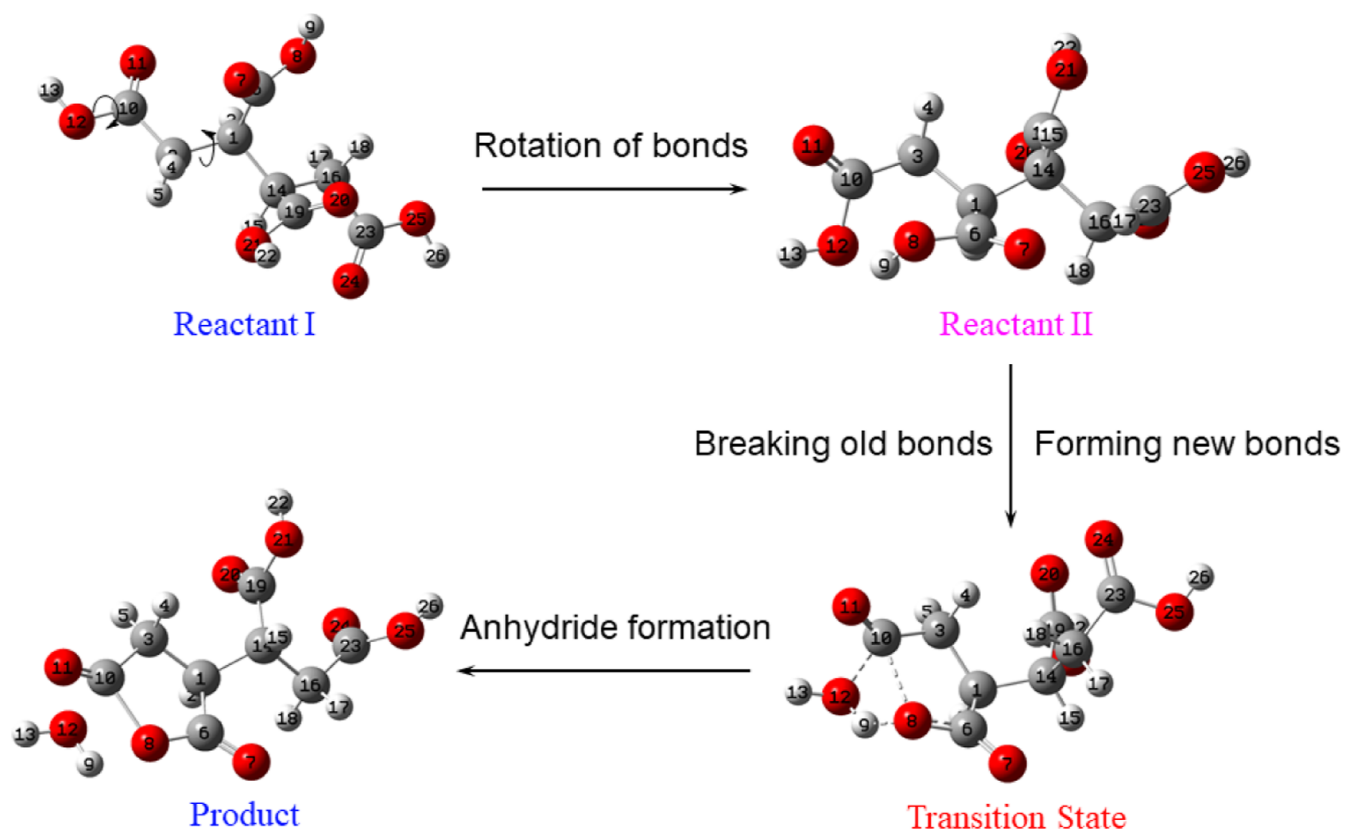


Figure 5. Process of forming anhydride in BTCA.

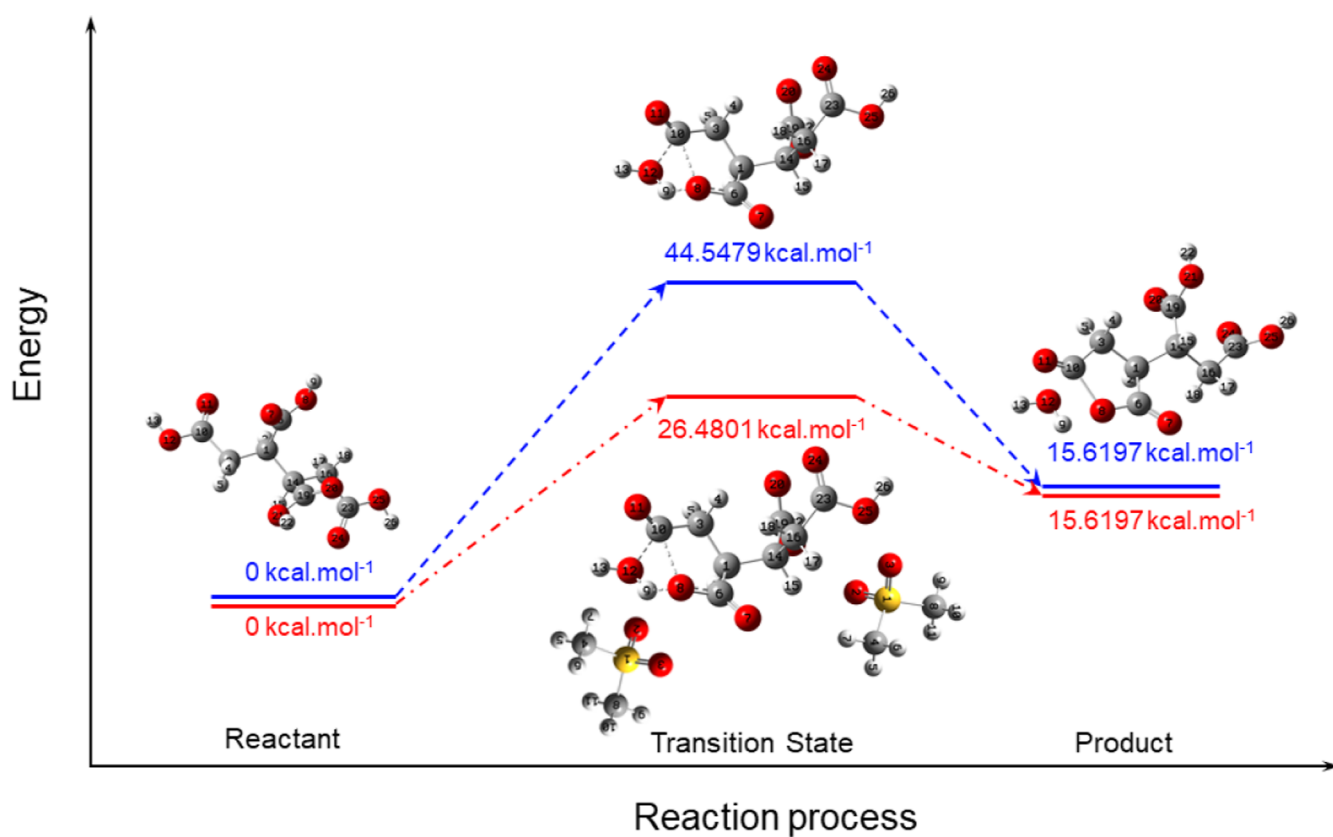


Figure 6. Variations of energy under different reaction processes with or without MSM.

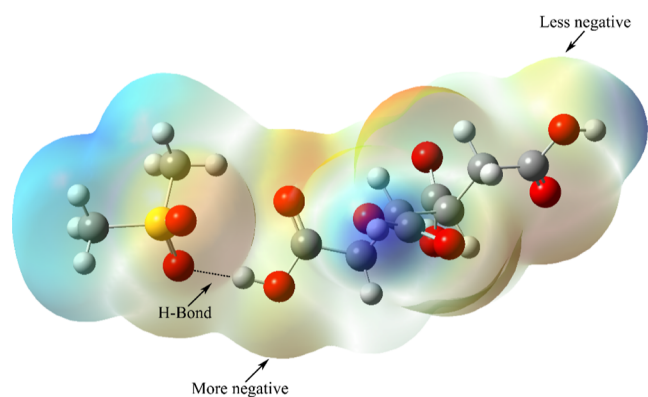


Figure 7. Electrostatics potential charge distribution map of BTCA with MSM.

the carbon atom of the adjacent carboxyl group to form anhydride.

2.3. Effect of MSM on the Overall Reactions Consisting of Grafting and Crosslinking Reactions from a Kinetic Perspective. Before our discussion, we gave some definitions for the reaction between BTCA and cellulose. The reaction between free BTCA and cellulose to form the first ester-linkage is regarded as a grafting reaction, and the reaction between grafted BTCA and cellulose to form the second ester-linkage is recognized as crosslinking reaction. Previous studies demonstrated that BTCA could not form two anhydrides simultaneously and the establishment of crosslinkers between cellulose chains follows a step-by-step process, which consists of grafting and crosslinking steps. Thus, a novel kinetic model for the overall reaction between BTCA and cellulose was built. For a more detailed deduction refer to the [Supporting Information](#) or published paper.⁸

The rate constants of grafting and crosslinking reactions under different conditions were measured from 120 to 180 °C at a 10 °C interval, and the detailed data can be displayed in [Tables S1 and S2](#). As presented in [Figure 8](#), the rate constants measured under the MSM circumstance were higher than those measured without MSM, indicating that MSM could promote both grafting and crosslinking reactions and, thus, significantly improve the antiwrinkle performance of treated cotton fabrics. Interestingly, the extent of increasing rate constants of crosslinking reactions was higher than those of

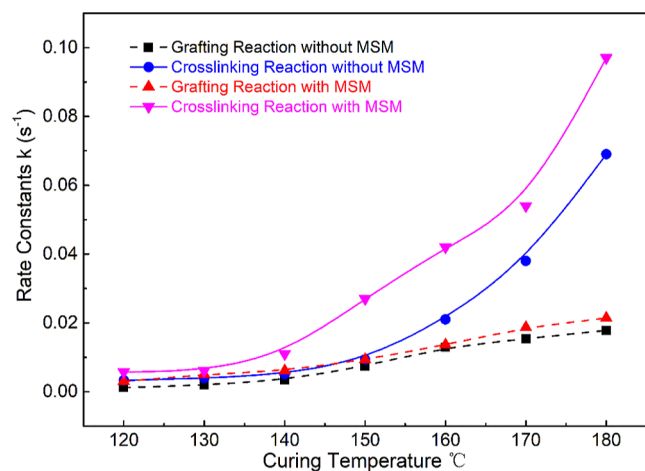


Figure 8. Rate constants of the overall reaction with or without MSM.

grafting reactions, showing that the impact of MSM on crosslinking reactions is more obvious. In addition, regression lines for the determination of Arrhenius activation energy and frequency factor were shown in [Figure 9](#). The Arrhenius

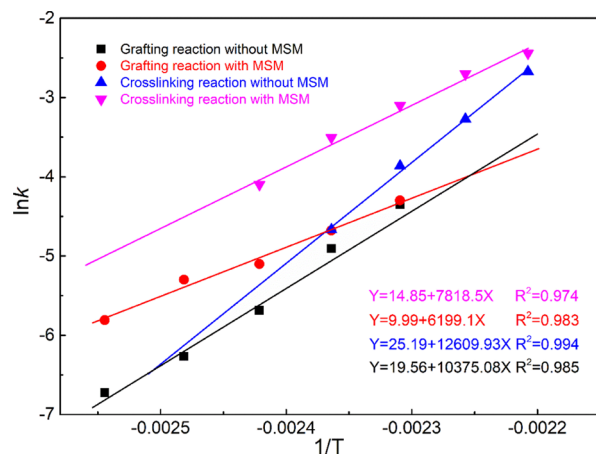


Figure 9. Regression lines for determination of the Arrhenius activation energy and frequency factor.

activation energies were 51.54 kJ mol⁻¹ for the grafting reaction and 65 kJ mol⁻¹ for the crosslinking reaction in the presence of MSM, while those without MSM were 86.3 and 104.84 kJ mol⁻¹, respectively, which indicated that crosslinking in cellulose macromolecular chains can be generated quickly at a relatively low curing temperature with the aid of MSM. According to the physical meaning of Arrhenius activation energy,²⁰ much more molecules can be activated in the reaction system if their Arrhenius activation energy is relatively low, which increases the probability of the effective collision between reactants for elevating reaction rates significantly. Thus, the curing temperature of antiwrinkle treatment of BTCA can be decreased.

To further understand the mechanism of elevating the rate of the overall reaction, ATR-FTIR was employed to identify the hydrogen bonding information of BTCA molecules and cellulose chains in finished cotton fabrics. [Figure 10](#) presented the FTIR of cotton fabrics treated in different conditions, and all fabric samples were only dried at 100 °C for 3 min. As indicated in [Figure 10](#), the characteristic peak corresponding to the stretching vibration of carbonyl groups in the FTIR spectrum of cotton fabrics treated by BTCA with MSM was at around 1714.3 cm⁻¹, which was higher than those without MSM, indicating that hydrogen bonding between BTCA molecules became much weaker. This reflected that the aggregation of BTCA was alleviated in the existence of MSM, which allows for the further dispersion of BTCA in amorphous regions and benefits its diffusion for grafting with cellulose. Importantly, weaker H-bond interactions between BTCA molecules promoted anhydride formation, which is also conducive to subsequent esterification. Thus, the rate constants of grafting reaction measured under the MSM condition were higher than those measured without MSM. On the other hand, an obvious characteristic broad peak at 3327.5 cm⁻¹ in FTIR spectra of untreated cotton fabric was observed, which is corresponding to the stretching vibration of hydroxyl groups with strong hydrogen bond interactions in cellulose. After the cotton fabric was padded and dried with 6 wt % MSM solution, double peaks which represented the two

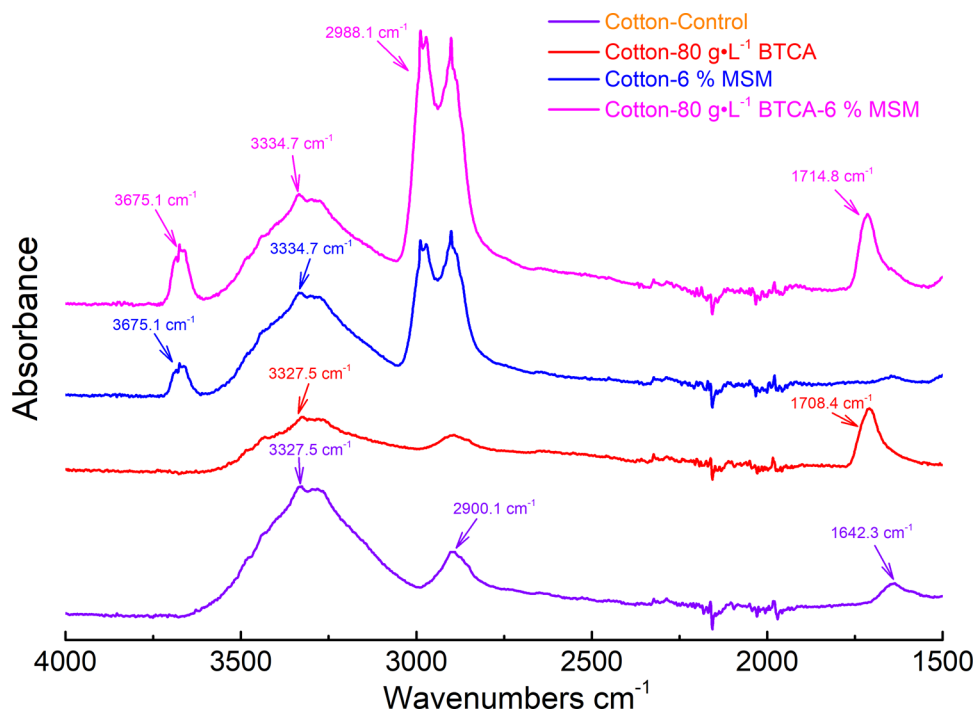


Figure 10. FTIR of cotton fabrics treated in different conditions. Note: all fabric samples were only dried at 100 °C for 3 min.

methyl groups in MSM clearly showed up at 2988.1 cm^{-1} , indicating MSM padded into the fabric. Interestingly, the absorbance peak of hydroxyl groups in cellulose with MSM shifted to 3334.7 cm^{-1} , showing that the intra- or intermolecular hydrogen bonding of cellulose chains in treated fabric was weaker than those of untreated cotton. It was revealed that the hydrogen bonding was interrupted by MSM and, thus, their thermal vibration was intensified, increasing the rate constants of crosslinking reaction between grafted BTCA and cellulose chains. Therefore, the amount of crosslinked BTCA in the fabric containing MSM was significantly higher than that without MSM (Figure 1c). In addition, the absorbance peaks of hydroxyl groups still located at 3334.7 cm^{-1} , showing hydrogen bonding between carboxyl in BTCA and hydroxyl in cellulose was not formed, otherwise it would be observed at the location of lower wavenumber, which is also good conducive to promoting the diffusion of BTCA in amorphous regions and formation of crosslinking between cellulose chains.

Computational modeling was conducted to deepen our comprehension of the plasticizing effect of MSM in crosslinking esterification. The thermal motion of BTCA and vibration of cellulose polymer chains could be reflected by the relationship between their MSD and simulation time. Moreover, one-sixth of the slope of their MSD against simulation time is usually defined as the diffusion coefficient. As illustrated in Figure 11a,b, both the diffusion coefficient of BTCA and cellulose chains were higher than those without MSM, especially in the diffusion coefficient of cellulose chains, which was almost 5 times that of untreated fabrics. This made clear that MSM obviously promoted BTCA diffusion in amorphous regions and thermal vibration of cellulose chains for proceeding with the reaction between BTCA and cellulose, which is in good accordance with the previous results in ATR-FTIR.

In order to further demonstrate the noncovalent interactions in cellulose crosslinking systems, an RDG analysis was employed.²¹ The cellulose was replaced by modified glucose (MG) so as to simplify the calculation, in which two hydroxyl groups of $\text{O}_{(4)}\text{H}$ and $\text{O}_{(1)}\text{H}$ were substituted by OCH_3 .²² In BTCA aggregation, MG aggregation, BTCA-MSM aggregation, and MG-MSM aggregation, hydrogen bonding was investigated by the noncovalent interaction index of RDG plots. The stronger hydrogen bonding interactions within $-\text{C}(=\text{O})\text{OH}$ of BTCA_1 and $-\text{C}(=\text{O})\text{OH}$ of BTCA_2 in BTCA aggregation and those within $-\text{OH}$ of MG_1 and $-\text{OH}$ of MG_2 in MG aggregation were confirmed from intensified scatter points ($I_2 < 0$) (Figure 12a,e and b,f). The relatively weaker hydrogen bonding interactions within $-\text{C}(=\text{O})\text{OH}$ of BTCA and $-\text{S}(=\text{O})_2$ of MSM in BTCA-MSM aggregation and those within $-\text{OH}$ of MG and $-\text{S}(=\text{O})_2$ of MSM in MG-MSM aggregation were also identified from reduced scatter points ($I_2 < 0$) (Figure 12c,g and d,h). This is because MSM is an HBA instead of a hydrogen-bond donor and hydroxyl or carboxyl groups are both hydrogen bond acceptors and donors, which means that BTCA-MSM or MG-MSM aggregation can only form one hydrogen bond, while BTCA or MG aggregation can produce two hydrogen bonds. As depicted in Figure 13, the strong chain-chain hydrogen bonds were energetically established in cotton fabrics, which limited the thermal vibration of the cellulose chain and, thus, decreased the reactivity of hydroxyl groups in them. In addition, some BTCA molecules formed micro-aggregations via their intermolecular hydrogen bonding, hindering the diffusion of BTCA in amorphous regions. MSM is known to be a strong HBA, which has capable of forming hydrogen bonding with hydroxyls or carboxyl groups due to its special structure. It thereby affected the intra- or intermolecular hydrogen bonds among cellulose chains or BTCA. Thus, the strong hydrogen bonding of chain-chain or BTCA-BTCA was replaced by relatively weaker bonding of chain-MSM or BTCA-MSM,

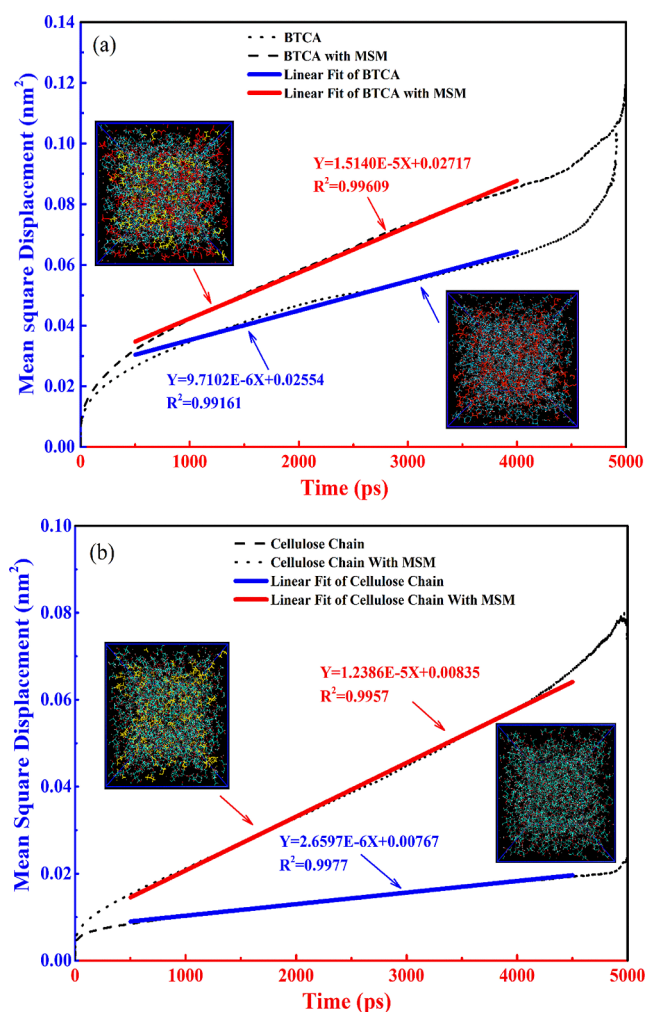


Figure 11. Mean square displacement (MSD) curves of (a) BTCA and (b) cellulose chains.

interrupting their nonvalent interactions and, consequently, promoting both BTCA diffusion and thermal vibration of cellulose chains for subsequent crosslinking reaction.

3. CONCLUSIONS

In this study, we provided a novel strategy of MSM in the cellulosic crosslinking system for fabricating antiwrinkle cotton fabrics with BTCA, which can reduce the curing temperature of BTCA by approximately 20 °C. This methodology could, remarkably, promote the diffusion of BTCA to disperse homogeneously in amorphous regions of cellulose, thereby enhancing the effectiveness of BTCA grafting as well as benefiting anhydride formation for subsequently reactions. Importantly, the thermal vibration of cellulose polymer chains was also intensified by the interruption of hydrogen bonding of cellulose by MSM, which is beneficial for the crosslinking reaction and increasing the content of crosslinked BTCA in fabrics. Moreover, the Arrhenius activation energies of grafting and crosslinking reactions were obviously reduced by the plasticizing effect of MSM, which provides a solid theory for decreasing curing temperature in the antiwrinkle field of textile.

4. MATERIALS AND METHODS

4.1. Materials. Desized, scoured, bleached, and mercerized 40s*40s plain-woven pure cotton fabric (weighing 117 g m⁻²)

was provided by Hualun printing and dyeing Co., Ltd (Shanghai, China). BTCA was purchased from Energy Chemical (Shanghai, China). SHP was offered by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). MSM and hydrochloric acid (HCl) were supplied by Lingfeng Reagent Co., Ltd (Shanghai, China). Sodium Hydroxide (NaOH) was provided by Aldrich Chemical Reagent Co., Ltd (Shanghai, China). All the reagents were used directly without purification.

4.2. Preparation of Treated Cotton Fabrics. Cotton fabrics were impregnated in a finishing bath containing BTCA and SHP with a molar ratio of 1:1, with or without MSM. No other chemical agents were added. Then the cotton sample was pressed through a two-roll laboratory padder (Rapid Company, Taiwan, China) two times, which controlled wet pick-up at the 85% level based on the weight of the fabric. After that, all the fabrics were dried at 100 °C for 3 min and cured at different special temperatures for a designated time in the curing oven (DHE65002, Werner Mathis, Switzerland). Finally, all the treated fabrics were subject to home washing and drying to remove unreacted BTCA and other chemical compounds.²³

4.3. Fabric Performance. The WRAs were measured with a wrinkle recovery tester (M003A, SDL company, USA) according to the America Association of Textile Chemist and Colorists (AATCC) method 66-1990.

4.4. Titration Analysis. In order to determine the amount of each component in cured cotton fabrics, an acid–base titration method was employed to make quantitative measurements of two concentrations.^{2,24} (1) Carboxylic concentration was determined by a back-titration way as followed steps: cured fabric samples weighing approximately 1.000 g were cut into small pieces and put into an Erlenmeyer flask, which contained an excess amount of 25 mL standardized 0.05 mol L⁻¹ NaOH solutions. The mixture was stirred vigorously for about 5 min to make sure all the carboxylic acids convert into carboxylic anions. The remaining NaOH was titrated with standardized 0.05 mol L⁻¹ HCl solutions, and the concentration of carboxyl groups in cured fabrics was equal to the difference between the original content of NaOH and the remaining content of NaOH; we described it as $-\text{COOH}_1$. The content of carboxyl groups in dried but not cured fabrics was also tested by the abovementioned method, and we described it as $-\text{COOH}_2$. The concentration of ester bonds in cured fabrics is equal to the difference between $-\text{COOH}_1$ and $-\text{COOH}_2$. From published literature, the hydrolysis of ester in cured cotton fabrics was very minimal under such low concentrations of NaOH and short reaction times.²⁴ (2) Amount of unreacted BTCA in cured cotton fabrics: we used the abovementioned back-titration to determine carboxyl group concentrations in the cured fabrics washed with distilled water and described it as $-\text{COOH}_3$. The amount of unreacted BTCA is determined by the difference between $-\text{COOH}_1$ and $-\text{COOH}_3$.

The concentration of total BTCA ($C_{\text{BTCA-total}}$), unreacted BTCA ($C_{\text{BTCA-unreacted}}$), and ester bonds (C_{ester}) in the fabric, respectively, could be determined using the following equations

$$C_{\text{BTCA-total}} = C_{\text{BTCA-free}} + C_{\text{BTCA-graft}} + C_{\text{BTCA-cross}} \quad (1)$$

$$C_{\text{ester}} = C_{\text{BTCA-graft}} + 2C_{\text{BTCA-cross}} \quad (2)$$

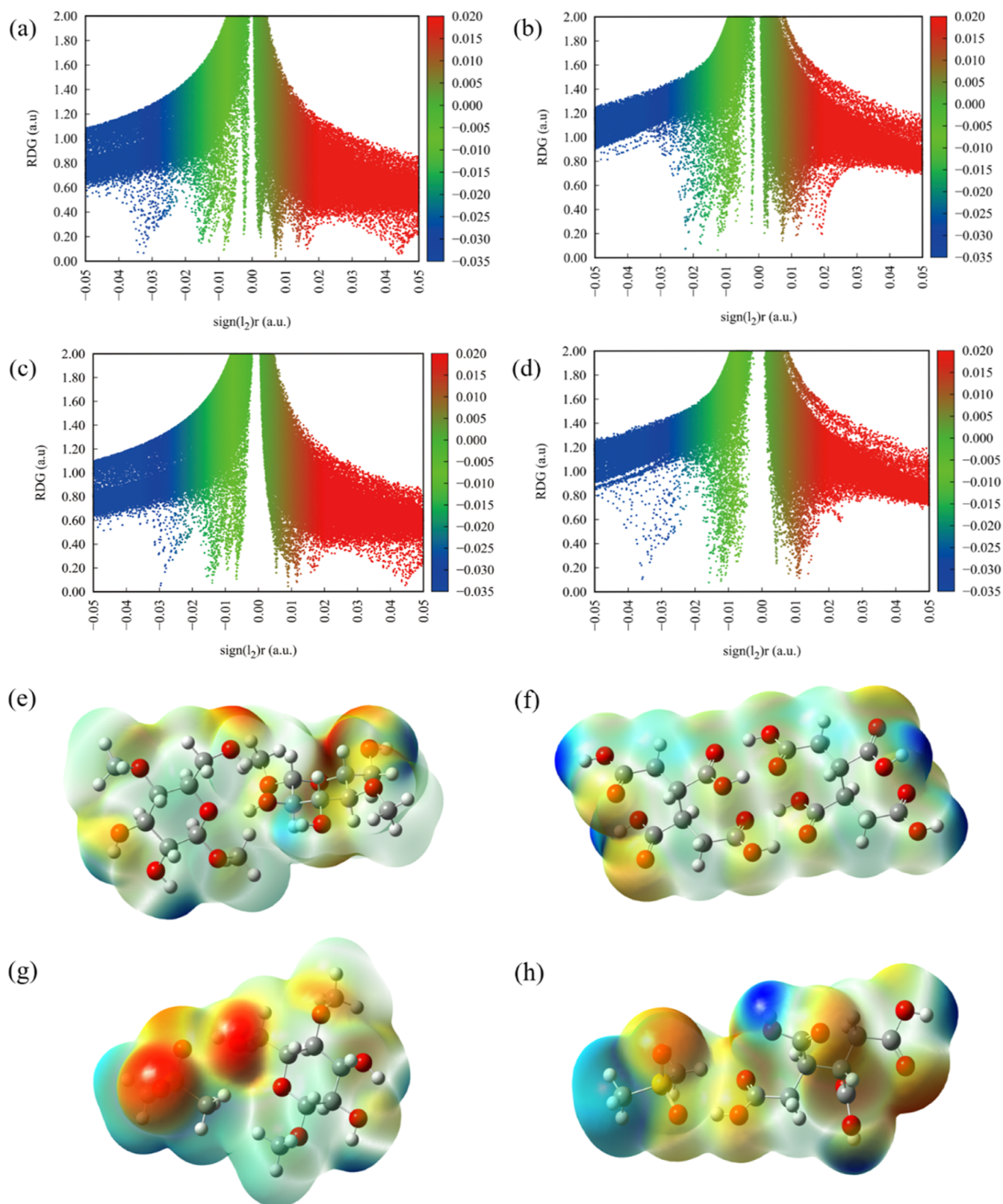


Figure 12. RDG plot of different compound aggregations. (a) MG aggregation, (b) BTCA aggregation, (c) MG-MSM aggregation, and (d) BTCA-MSM aggregation; 3D electrostatic potential charge distribution of (e) MG aggregation, (f) BTCA aggregation, (g) MG-MSM aggregation, and (h) BTCA-MSM aggregation.

$$C_{\text{BTCA-unreacted}} = C_{\text{BTCA-free}} \quad (3)$$

$$C_{\text{BTCA-graft}} = 2C_{\text{BTCA-total}} - 2C_{\text{BTCA-unreacted}} - C_{\text{ester}} \quad (4)$$

The expression of $C_{\text{BTCA-graft}}$ and $C_{\text{BTCA-cross}}$ could be deduced from eqs 1–3

$$C_{\text{BTCA-cross}} = C_{\text{ester}} - C_{\text{BTCA-total}} + C_{\text{BTCA-unreacted}} \quad (5)$$

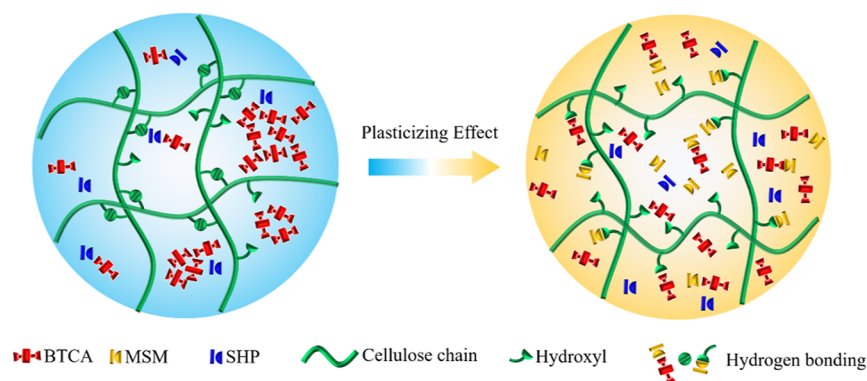


Figure 13. Schematic illustration of the plasticizing effect of MSM on the crosslinking system.

4.5. X-ray Photoelectron Spectroscopy. The chemical composition of the cotton sample was measured by an X-ray photoelectron spectrometer (ESCALAB 250Xi, Thermo Fisher Scientific, USA).

4.6. FTIR Analysis. Cotton samples under different treatments were quickly saved in ziplock bags to avoid exposure to moisture in air. Then, all the samples were measured by a Nicolet 6700 FTIR spectrometer for ATR–FTIR measurements in a range of 4000 to 400 cm^{-1} and at a resolution of 16 cm^{-1} .^{25,26}

Temperature-dependent FTIR was used to analyze the changes of BTCA with or without MSM under different temperatures. Approximately 2.00 mg of powdered samples were mixed with 200.00 mg of KBr to prepare a transparent pellet for the FTIR test. The pressed pellet was heated with a heating rate of 10 $^{\circ}\text{C}/\text{min}$. FTIR spectra were recorded from 110 to 190 $^{\circ}\text{C}$ in a 10 $^{\circ}\text{C}$ interval on a Nicolet 6700 FTIR spectrometer (Thermo Fisher Co., USA) in a range of 4000 to 400 cm^{-1} and at a resolution of 16 cm^{-1} .

4.7. Thermogravimetric Analysis. The sample powders were first heated up to 80 $^{\circ}\text{C}$ from ambient temperature under vacuum conditions and kept for 2 h to eliminate free or crystal water in samples. After cooling down, approximately 5.00 mg of the sample was heated up to 600 $^{\circ}\text{C}$ from the environment temperature at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ by using a thermal gravimetric analyzer (TG209F1, NETZSCH Company, Germany). The analytic spectrum was recorded by a computer.

4.8. Gaussian Calculation. The process of anhydride formation was simulated in Gaussian 09W software. First, the geometry structure of the BTCA molecule underwent optimization on the B3LYP level 6-31G(d,p). After that, the energy of the BTCA molecule was flexibly scanned with different atom distances of $\text{C}_{10}\text{--O}_8$ and $\text{O}_{12}\text{--H}_9$ to get the potential energy surface of forming anhydride, which could find the initial structure of the transition state. Finally, the initial structure of the transition state was optimized by TS selection on the B3LYP level 6-31G(d,p) to get an accurate structure of the transition state. The transition state has been checked by frequency analysis, showing one imaginary vibration. The molecular orbitals and electrostatic potential distribution maps of different compounds were visually presented in GaussView 5.0.9 software after undergoing geometric optimization.¹⁵

4.9. MSD Calculation. Crosslinking models were constructed by Gromacs 5.0.7 software, which consisted of 30 cellulose polymer chains containing 20 1,4- β -cellobiose units, 100 BTCA molecules, and 300 MSM molecules.²⁷ The initial

model underwent energy minimization by the algorithm of steepest descent, *NPT* compression at 1000 bar and 298 K for 5000 ps, *NVT* relaxation at 800 K for 2000 ps, and *NPT* equilibration at 1 bar and 433 K for 5000 ps four steps. The force field was selected for OPLS-AA. Finally, the MSD and hydrogen bond could be analyzed by the software, and the diffusion coefficients are equal to the one-sixth slope of MSD against simulation times.

4.10. Reduced Density Gradient Analysis. The RDG of compounds was analyzed by Multiwfn 3.7 software and gnuplot software. After finishing geometric optimization, the compound structure was submitted to Multiwfn 3.7 software for hydrogen bonding analysis, and the RDG scatter plot was calculated by gnuplot software.²⁸

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c03131>.

Concentration of different components in fabric with or without MSM under different curing times and temperatures and deduction of the kinetic model for the reaction between BTCA and cellulose (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Jinxin He – College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, PR China; The Key Laboratory of Textile Science and Technology, Ministry of Education, Shanghai 201620, China; orcid.org/0000-0003-1379-6610; Phone: +86 21 67792602; Email: jxhe@dhu.edu.cn; Fax: +86 2167792608

Authors

Hanchang Hu – College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, PR China

Xia Dong – College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, PR China; National Engineering Research Center for Dyeing and Finishing of Textiles, Donghua University, Shanghai 201620, PR China; orcid.org/0000-0003-0888-7534

Qiangqiang Zhao – College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, PR China; orcid.org/0000-0001-9192-2921

Rongliang Wu – State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, PR China

Chen Meng – College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, PR China

Jiani Xu – College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, PR China

Tingwei Cai – College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, PR China; orcid.org/0000-0001-7039-9238

Xin Wang – College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, PR China

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsomega.2c03131>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by the National Key Research and Development Program of China (2017YFB0309600) and the Fundamental Research Funds for Central Universities and Graduate Student Innovation Fund of Donghua University (no. CUSF-DH-D-2020064). Also, we are grateful for the support offered by Jiangsu Lianfa Textile Co., Ltd., Nantong, China.

REFERENCES

- (1) Welch, C. M. Tetracarboxylic Acids as Formaldehyde-Free Durable Press Finishing Agents. *Text. Res. J.* **1988**, *58*, 480–486.
- (2) Yang, C. Q.; Mao, Z.; Lickfield, G. C. Ester crosslinking of cotton cellulose by polycarboxylic acids: ph-dependency. *Text. Chem. Color. Am. Dyest. Rep.* **2000**, *32*, 43–46.
- (3) Yang, C. Q.; Andrews, B. K. Infrared spectroscopic studies of the nonformaldehyde durable press finishing of cotton fabrics by use of polycarboxylic acids. *J. Appl. Polym. Sci.* **1991**, *43*, 1609–1616.
- (4) Yang, C. Q. Infrared spectroscopy studies of the cyclic anhydride as the intermediate for the ester crosslinking of cotton cellulose by polycarboxylic acids. I. Identification of the cyclic anhydride intermediate. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1187–1193.
- (5) Xiaohong, G.; Yang, C. Q. FTIR spectroscopy study of the formation of cyclic anhydride intermediates of polycarboxylic acids catalyzed by sodium hypophosphite. *Text. Res. J.* **2000**, *70*, 64–70.
- (6) Choi, H.-M.; Welch, C. M.; Morris, N. Nonphosphorus catalysts for formaldehyde-free dp finishing of cotton with 1,2,3,4-butanetetracarboxylic acid. I. aromatic n-hetero-cyclic compounds. *Text. Res. J.* **1993**, *63*, 650.
- (7) Choi, H. M.; Welch, C. M.; Morris, N. M. Nonphosphorus Catalysts for Formaldehyde-Free DP Finishing of Cotton with 1,2,3,4-Butanetetracarboxylic Acid. *Text. Res. J.* **1994**, *64*, 501–507.
- (8) Hu, H.; Xu, H.; Dong, X.; Zhao, Q.; Wu, J.; Meng, C.; Cai, T.; He, J. Novel kinetics model for the crosslinking reaction of 1,2,3,4-butanetetracarboxylic acid with cellulose within cotton fabrics. *Cellulose* **2021**, *28*, 5071–5085.
- (9) Ji, B.; Qi, H.; Yan, K.; Sun, G. Catalytic actions of alkaline salts in reactions between 1,2,3,4-butanetetracarboxylic acid and cellulose: I. Anhydride formation. *Cellulose* **2015**, *23*, 259–267.
- (10) Priscilla, J.; Dhas, D. A.; Joe, I. H.; Balachandran, S. Spectroscopic, quantum chemical, hydrogen bonding, reduced density gradient analysis and anti-inflammatory activity study on piper amide alkaloid piperine and wisanine. *J. Mol. Struct.* **2021**, *1225*, 129146.
- (11) Xiao, H.; Kelu, Y.; Bolin, J. Improvement of anti-wrinkle properties of cotton fabrics treated with additives of neutral salts. *Fibers Polym.* **2018**, *19*, 1576–1583.
- (12) Ji, B.; Wang, X.; Gong, S.; Zhong, W.; Xie, R. Locating the reaction site of 1,2,3,4-butanetetracarboxylic acid carboxyl and cellulose hydroxyl in the esterification cross-linking. *ACS Omega* **2021**, *6*, 28394–28402.
- (13) Dong, X.; Gu, Z.; Hang, C.; Ke, G.; Jiang, J.; He, J. Study on the salt-free low-alkaline reactive cotton dyeing in high concentration of ethanol in volume. *J. Clean. Prod.* **2019**, *226*, 316–323.
- (14) Madsen, N. J. Hydrophilic coating and a method for the preparation thereof. U.S. Patent 20,080,003,348 A1.2008.
- (15) Chen, L.; Wang, B.; Chen, J.; Ruan, X.; Yang, Y. Comprehensive study on cellulose swelling for completely recyclable nonaqueous reactive dyeing. *Ind. Eng. Chem. Res.* **2015**, *54*, 2439–2446.
- (16) Zhao, J.; Agaba, A.; Sui, X.; Mao, Z.; Xu, H.; Zhong, Y. A heterogeneous binary solvent system for recyclable reactive dyeing of cotton fabrics. *Cellulose* **2018**, *25*, 7381.
- (17) Zaout, S.; Chafaa, S.; Hellal, A.; Boukhemis, O.; Bendjeddou, L. Hydroxyphenylamine phosphonate derivatives: synthesis, x-ray crystallographic analysis, and evaluation of their anti-alzheimer effects and antioxidant activities. *J. Mol. Struct.* **2021**, *1225*, 129121.
- (18) Xu, F.; Zhong, L.; Zhang, C.; Wang, P.; Zhang, F.; Zhang, G. Novel High-Efficiency Casein-Based P-N-Containing Flame Retardants with Multiple Reactive Groups for Cotton Fabrics. *ACS Sustainable Chem. Eng.* **2019**, *7*, 13999–14008.
- (19) Kwiczak-Yiitba, J.; Demir, M.; Ahan, R. E.; Canl, S.; Baytekin, B. Ultrasonication for environmentally friendly preparation of antimicrobial and catalytically active nanocomposites of cellulosic textiles. *ACS Sustainable Chem. Eng.* **2020**, *8*, 18879–18888.
- (20) Zhao, Q.; Sun, J.; Liu, B.; He, J. Novel kinetics model for third-liquid phase-transfer catalysis system of the "complex" carbanion: Competitive role between catalytic cycles. *Chem. Eng. J.* **2015**, *280*, 782–795.
- (21) Roy, J. S. D.; Chowdhury, D.; Hussain Sanfui, M. D.; Hassan, N.; Mahapatra, M.; Ghosh, N. N.; Majumdar, S.; Chattopadhyay, P. K.; Roy, S.; Singha, N. R. Ratiometric pH Sensing, Photophysics, and Cell Imaging of Nonaromatic Light-Emitting Polymers. *ACS Appl. Bio Mater.* **2022**, *5*, 2990.
- (22) Ji, B.; Tang, P.; Hu, C.; Yan, K. Catalytic and ionic cross-linking actions of l-glutamate salt for the modification of cellulose by 1,2,3,4-butanetetracarboxylic acid. *Carbohydr. Polym.* **2019**, *207*, 288–296.
- (23) Qi, H.; Zhao, C.; Qing, F. L.; Yan, K.; Sun, G. Antiwrinkle finishing of cotton fabrics with 5-(carbonyloxy succinic)-benzene-1,2,4-tricarboxylic acid: comparison with other acids. *Ind. Eng. Chem. Res.* **2016**, *55*, 11850.
- (24) Yang, C. Q.; Bakshi, G. D. Quantitative analysis of the nonformaldehyde durable press finish on cotton fabric: acid-base titration and infrared spectroscopy. *Text. Res. J.* **1996**, *66*, 377–384.
- (25) Hou, A.; Sun, G. Multifunctional finishing of cotton fabrics with 3,3',4,4'-benzophenone tetracarboxylic dianhydride: Reaction mechanism. *Carbohydr. Polym.* **2013**, *95*, 768–772.
- (26) Ji, B.; Zhao, C.; Yan, K.; Sun, G. Effects of acid diffusibility and affinity to cellulose on strength loss of polycarboxylic acid crosslinked fabrics. *Carbohydr. Polym.* **2016**, *144*, 282–288.
- (27) Chen, W.; Lickfield, G. C.; Yang, C. Q. Molecular modeling of cellulose in amorphous state part II: effects of rigid and flexible crosslinks on cellulose. *Polymer* **2004**, *45*, 7357–7365.
- (28) Lu, T.; Chen, F. Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012**, *33*, 580–592.