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Ma, Yibo; You, Xiang; Rissanen, Marja; Schlapp-Hackl, Inge; Sixta, Herbert

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Sustainable Cross-Linking of Man-Made Cellulosic Fibers with Poly(carboxylic acids) for Fibrillation Control

Yibo Ma,* Xiang You, Marja Rissanen, Inge Schlapp-Hackl, and Herbert Sixta*

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ABSTRACT: Lyocell-type fibers often exhibit a high tendency to fibrillate under wet abrasion conditions, and fibrillation must be diminished for a better quality of the textile product. In this study, we propose a green route for cross-linking regenerated cellulose fibers using citric acid (CA) and 1,2,3,4-butanetetracarboxylic acid (BTCA) to prevent the fibers from fibrillation. We investigated the influence of process conditions and additives on the fibrillation tendency and fiber properties. The fibrillation tendency of the cross-linked fibers highly depended on the concentration of cross-linker solution, curing temperature, and curing time. BTCA showed better cross-linking performance in comparison to CA. CA cross-linked fibers also suffer from yellowing issues due to the formation of unsaturated side products during curing. Thus, glycerol and xylitol were added during cross-linking to avoid the



reaction that led to the unsaturated compound. Washing fastness tests confirmed that the cross-linking has high stability when the cross-linker concentration is 100 g/L and fibers are cured at 180 $^{\circ}$ C for 5 min. The disadvantage of the CA and BTCA cross-linked fibers was a relatively low mechanical performance. The study demonstrated that adding softener in the cross-linker solution enhanced the mechanical properties and was also able to reduce the curing temperature without deteriorating the fibrillation index of the cross-linked fibers.

KEYWORDS: Fibrillation, Cross-link, Cellulose, Ioncell fiber, Citric acid, BTCA

INTRODUCTION

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Cross-linking is a critical process for the chemical treatment of cellulosic fiber and textile production to improve its properties against fibrillation and poor wrinkle recovery.¹⁻⁴ For lyocell-type regenerated cellulosic fibers, the fibers are prone to form microfibrils on the fiber surface under high shear force in a wet or swollen state due to their highly orientated molecular structure.⁵⁻⁸ The so-called fibrillation occurs due to a weak lateral cohesion between crystalline sheets in the oriented structure that eventually leads to the delamination of the fibril structure on the axial of the fiber surface.^{9,10} Therefore, postspinning chemical treatment with cross-linkers (during the spin finish) is often required to prevent the fiber from fibrillation.

Currently, the most dominating cross-linkers for cellulosic fibers are amino-based chemicals, including triazines, amides, and ureas. Among these substances, the most typical cross-linkers are 1,3,5-triacryloylhexahydro-1,3,5-triazine (TAHT) and dimethyloldihydroxyethyleneurea (DMDHEU).^{3,11–14} Both cross-linkers have been reported to efficiently reduce the formation of fibrillations after the fiber is subjected to mechanical abrasion in the wet state. TAHT has been developed by Lenzing AG and has been commercially applied

to produce fibrillation-free Tencel fiber Lenzing A100.¹⁵ TAHT has proven to be also applicable to other types of lyocell fibers. In our previous study, this animo-triazine is able to cross-link Ioncell fiber that is produced by dry-jet wet spinning of a dope prepared from a solution of wood pulp.³ The study confirmed the cross-linking of TAHT with the hydroxyl group on the lyocell-type fiber and altogether ceased the fibrillation under high shear force. Cross-linking with TAHT has several advantages such as relatively low curing temperature and outstanding tensile property retention. DMDHEU is generally a mixture of formaldehyde, glyoxal, and urea, and it is also an efficient commercial cross-linker for enhancing the performance of cellulose-based fibers and textiles.^{13,16} However, the curing process requires a higher temperature (typically 160 °C) and the fiber/textile suffers from severe strength loss after the cross-linking.^{11,13} In

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addition, both cross-linkers are highly toxic. DMDHEU contains formaldehyde, which is dangerous to human health. Even in the formaldehyde-free version of DMDHEU, traces of formaldehyde can still be monitored.¹⁶ TAHT has also been identified as a toxic chemical. Furthermore, commercial TAHT synthesis involves a reaction between ammonia and formaldehyde.¹⁷ As a result, a minor amount of formaldehyde has also been traced from the commercial TAHT.

The toxicity and the unsustainability of commercial crosslinkers promote the development of green substitutes. Poly(carboxylic acids) have been considered as promising cross-linkers to replace the toxic cross-linkers for cellulose-based fiber and textile materials.^{16,18–22} Citric acid (CA) is one of the most common and green poly(carboxylic acids) and has been utilized in a wide range of chemical applications, including cross-linking. CA is a nature-based organic chemical that is usually produced by the fermentation of citrus. It is nontoxic, except that irritation may occur if it is directly contacted with the skin and eye.^{16,23} The possible cross-linking of CA with cellulose starts with the dehydration of CA to form a cyclic anhydride followed by esterification with the hydroxyl groups of the cellulose.^{21,23,24} Cross-linking with CA provides cellulose with unique properties such as flame retardance, high swelling ratio, enhanced wrinkle resistance, and antifibrillation. These outstanding properties give the CA cross-linked cellulose many potential applications such as textile fiber finishing, biomedical utilization, special paper production, and filler applications.^{16,23-28} In the textile industry, CA is considered a sustainable cross-linker, replacing formaldehydebased cross-linkers to improve wrinkle resistance and water retention. However, the commercial application of CA in the textile area is still negligible, primarily due to the discoloration caused by the decomposed byproducts after heating.^{21,29,30} 1,2,3,4-butanetetracarboxylic acid (BTCA) is an alternative poly(carboxylic acid) cross-linker. Unlike CA, BTCA is a synthetic chemical with an additional carboxylic functional group.^{22,31,32} A study has shown that BTCA is water-soluble and also considered as a nontoxic substance (only eye and skin irritation) unless a large amount is swollen³³ (the toxicity NOAEL is $\geq 1000 \text{ mg/(kg day)}$). It has been reported to be a more effective cross-linker than CA for improving textile performance, providing no yellowing issues.^{2,22,24,31,34} The BTCA cross-links cellulose by first the formation of cyclic anhydride with two adjacent carboxylic groups. Subsequently, esterification of the anhydride with the hydroxyl group of cellulose takes place.^{24,28,35} The only drawback of BTCA is the relatively high cost because of the limited applications.^{16,24} For both CA and BTCA, sodium hypophosphite (SHP) can be used as an effective catalyst. It promotes the formation of cyclic anhydrate intermediates and accelerates the reactions between the intermediates and the hydroxyl groups of cellulose.¹⁹ In the case of CA, SHP can enhance the decomposition of CA under thermal conditions and reduce the unsaturated intermediates to a methylsuccinic acid, which can eventually convert to cyclic anhydrate and link the hydroxyl groups of cellulose by esterification.^{19,21} SHP has been proposed to suppress the inter and intra hydrogen bonding between the carboxylic groups of the crystallized BTCA that ease the formation of the cyclic anhydrate. The proposed cross-linking reaction scheme between cellulose and CA and BTCA with the presence of SHP is shown in Figures S1 and S2 in the Supporting Information. Other poly(carboxylic acids) such as maleic and succinic acids have also been suggested for the cross-linking of cellulose. However, these acids may not be favorable cross-linkers for cellulose due to the lower number of functional groups.^{18,20,36}

As one of the most promising new-generation fiber technologies, the Ioncell fiber technology has a great potential to commercialize and supplement the current cellulose-based textile fiber market.³⁷ However, the Ioncell fiber's performance in the postspinning chemical process has not yet been fully revealed. Cross-linking is an efficient process to reduce the fibrillation of regenerated cellulose fibers. The cross-linking can enhance the lateral cohesion of the cellulose chains, which potentially improves its resistance to wet abrasion.^{3,38} It is already well-known that CA and BTCA are suitable crosslinkers for cellulose and have the potential to control the fibrillation of cellulose fibers. However, currently, limited works have been established to investigate the cross-linking of CA and BTCA with regenerated cellulose fibers for fibrillation prevention. Fang et al. studied the esterification of lyocell fibers with the BTCA and depicted the successful reduction of the fibrillation tendency on lyocell fibers.³⁸ Cheng et al. reached a similar approach using a mixture of maleic acid and citric acid on lyocell fibers for fibrillation prevention.³⁹ It was found that the swelling ratio of the lyocell fibers in a wet state is significantly reduced as a result of the cross-linking, which indirectly proves the effect of poly(carboxylic acid) crosslinking on the fibrillation control of regenerated cellulose fibers.

This work focuses on developing a green and sustainable cross-linking route using these carboxylic acids for the Ioncell fibers. The effect of CA and BTCA cross-linking and the influence of the treatment conditions on the fibrillation tendency and mechanical properties of Ioncell fibers are investigated. Furthermore, the method of improving the fiber whiteness and mechanical properties and the effect of the washing fastness on the cross-linking are also investigated to reveal the potential of Ioncell fibers for large-scale applications.

EXPERIMENTAL METHODS

Materials. Ioncell fiber was spun using method described previously.⁴⁰ The raw material for standard Ioncell is prehydrolyzed kraft birch pulp (Enocell, Stora Enso, Finland). Citric acid, 1,2,3,4-butanetetracarboxylic acid, sodium hypophosphite, xylitol, and polyethylene glycol (PEG, molecular weight 600) were purchased from Sigma-Aldrich, Finland. Glycerol was provided by Merck KGaA, Germany. A polysiloxane-based softener (Solusoft Nup Liq) was kindly supplied by Archroma, Switzerland.

Cross-Linking Procedure. The cross-linker CA or BTCA and catalyst SHP were first dissolved in deionized water at a designated concentration in a 100 mL VWR borosilicate 3.3 glass bottle. The fibers were then added to the cross-linker solutions with a fiber to liquor ratio of 1:50. Subsequently, the mixture was gently shaken for 5 min. The treated fibers were then dewatered by pressing to give a wet pickup of ~150% and subjected to drying at 85 °C for 5 min and curing at varying temperatures and durations. Following the crosslinking treatment, the fibers were collected and washed with water until the filtrate was neutral. For whiteness improvement, polyols, including glycerol, xylitol, and PEG, were added to the cross-linking solution in varying mole ratios to CA and the curing temperature was kept at 180 °C for 5 min. To improve the mechanical properties of the cross-linked fibers, a softener was added to the cross-linker solution prior to the reaction with the fibers. TAHT cross-linked fibers were used for comparison. The cross-linking procedure of TAHT on Ioncell fiber has been described in our previous work.³ In general, the TAHT cross-linked fiber was prepared by mixing the fiber

in an alkaline solution containing 10 g/L TAHT for 15 min at 85 $^\circ \rm C.$ No further curing step was carried out.

Fibrillation Test. The creation of microfibrils on the regenerated fibers was carried out using a Metos HotmixPro blender. A 500 mg portion of air-dried cross-linked fibers was cut into \sim 5 mm short fibers and diluted with 500 mL of water in a blender. The fiber suspension was then mixed in an ambient environment with a rotation speed of the blade of 3000 rpm. Subsequent to the mixing, the suspension was filtered, and the fibers were washed and dried at 60 °C for 2 h.

After fibrillation treatment, the dried fibers were cut into an even shorter length ($\sim 2 \text{ mm}$) and diluted with water to a concentration of 1 g/L. The suspension was mixed well with 2% gelatin solution (as a fixation media) in a ratio of 1:1. Two drops of the fiber suspension were dropped onto an objective glass from a height in order to keep the fibrils open. A cover slide was placed, and then the fibrillation of the fibers was examined using an optical microscope.

The microfibrils on the fiber surface were assessed using ImageJ software. The length of the fiber stem and the fibrils can be sketched by importing the microscope images of the fibrillated fiber into the software and evaluated employing the Simple neurite tracer function. For each fiber sample, 10 individual fibers were assessed to give an average value of the fibrillation index. The fibrillation index was calculated as

$$I_{\rm f} = \frac{\sum_L l}{L}$$

where $I_{\rm f}$ is the fibrillation index and l is the length of the fibrils over the length of the fiber L.

Fourier Transform Infrared (FTIR) Spectrometry. The crosslinked fibers were cut into short pieces and treated with 0.1 M NaOH for 5 min. At a wavelength of ~1730 cm⁻¹ of the FTIR spectrum of cross-linked cellulose, the carbonyl ester and carboxylic acid bands overlapped. Therefore, the mild alkaline treatment aimed to convert the free carboxylic acids to carboxylate, which revealed the actual band intensity of the ester carbonyl.^{24,35,41} The treated samples were dried overnight at 50 °C prior to the test. The FTIR analyses were carried out with a PerkinElmer Spectrum TWO FTIR spectrometer. The FTIR results were demonstrated in absorption mode with a spectral resolution of 4 cm⁻¹ and 10 scans for each spectrum. The ester carbonyl intensities (at a wavelength of ~1730 cm⁻¹) of the fibers were presented as a ratio against the cellulose C–H band at a wavelength of around 1313 cm^{-1.41}

Tensile Properties. The tensile properties of the untreated and cross-linked fibers were analyzed using the an automatic single-fiber-tester Favigraph instrument (Textechno H. Stein GmbH & Co., Germany). The tenacity and elongation of the fibers were measured in a conditioned state. Twenty fibers from each sample were tested at 23 °C and 60% RH. The gauge length was 10 mm and the speed 10 mm/ min.

Washing Fastness. The washing fastness test was carried out with a Linitest Original Banau machine. The test was done according to the standard EN ISO 105-C06. A 1 g portion of cross-linked fibers was inserted into the multifiber adjacent fabric and placed in a metal pot with a volume of 500 mL together with 150 mL of makeup liquor (4 g/L of detergent, pH ~10.5). The test was performed at 40 °C for 30 min. The fiber was then washed twice with 100 mL of 40 °C water for 1 min.

Whiteness Characterization. The optical properties of crosslinked samples were assessed by CIELab coordinates using a 10 °C observer and the standard illuminant D65 (SpectroScan, GretagMacbeth, Germany). CIE tristimulus values X_{10} , Y_{10} , and Z_{10} were determined, from which the chromaticity values x_{10} and y_{10} were calculated. The whiteness index (W_{10}) of the cross-linked fibers was calculated from the equation

$$W_{10} = Y_{10} + 800(0.3138 - x_{10}) + 1700(0.3310 - y_{10})$$

where W_{10} is the whiteness value or index (a higher value indicates a whiter sample), Y_{10} is the tristimulus value of the specimen, x_{10} and

 y_{10} are the chromaticity coordinates of the specimen, and 0.3138 and 0.3310 are the x_{10} and y_{10} chromaticity coordinates for a perfect reflection, respectively.

Scanning Electron Microscopy (SEM). SEM imaging was performed by using a Zeiss Sigma VP instrument with variable pressure. The fibers were attached onto the conductive support and sputtered with gold for 5 nm to ensure electrical conductivity. The images were taken at a 3 kV operating voltage.

RESULTS AND DISCUSSION

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Effect of Cross-Linking on the Fiber Fibrillation Tendency. The cross-linking of the Ioncell fibers was first assessed by varying the cross-linker concentrations and the curing conditions. The fibrillation index of the cross-linked fibers reflects the cross-linking efficiency. In previous studies, cross-linking of CA and BTCA with cotton has been confirmed to be most effective at temperatures from 150 to 180 °C.^{13,16,42} Therefore, the curing temperatures were first set at this range at various cross-linker concentrations (60-100 g/L) to identify the best conditions. The curing time was fixed at 5 min. Table 1 presents the effect of cross-linking temperatures

Table 1. Effect of Cross-Linker Concentrations and Curing Temperatures on the Fibrillation Tendency, Whiteness, and Ester Carbonyl Band Intensity of the Cross-Linked Ioncell Fibers^a

cross- linker	concn (g/L)	curing temp (°C)	fibrillation index	CIE whiteness index	ester carbonyl band intensity
reference	0		1.28	47.94	
TAHT ^b	10	85	0	50.10	
citric acid	100	180	0	26.39	0.597
citric acid	100	170	0.01	29.88	0.534
citric acid	100	160	0.01	36.22	0.548
citric acid	100	150	0.38	36.15	0.502
citric acid	80	180	0.06	37.67	0.535
BTCA	100	180	0	41.88	0.600
BTCA	100	170	0	42.15	0.627
BTCA	100	160	0	41.29	0.561
BTCA	100	150	0.44	45.72	0.534
BTCA	80	180	0	40.77	0.576
BTCA	60	180	0	41.85	0.525

^{*a*}The curing duration was fixed at 5 min. The ester carbonyl band intensity is the FTIR absorption intensity ratio of the bands at 1730 and 1313 cm⁻¹. ^{*b*}The TAHT cross-linked fiber was prepared by mixing the fiber in a 10 g/L TAHT solution for 15 min at 85 °C. No further curing step was carried out.³

and cross-linker concentrations on the fibrillation tendency and the whiteness of the cross-linked fibers. Under these conditions, the fibrillation resistances of both CA and BTCA cross-linked fibers were improved. For CA cross-linked fibers, the fibrillation tendency was reduced when the curing temperature was increased. When they were cured at 180 °C and 100 g/L CA concentration in the cross-linker solution, Ioncell fibers exhibited no fibrillation, indicating that the crosslinking was most effective under these conditions. When the CA concentration was reduced to 80 g/L, fibrils reappeared after a mechanical shear treatment. Thus, the results demonstrated that both the cross-linker concentration and curing temperature have pivot influences on the CA reactivity. On the other hand, BTCA revealed better cross-linking performance in comparison to CA. Despite the partial fibrillation reduction at 150 °C, fibrillation can be completely prevented at curing temperatures of 160–180 °C with a BTCA concentration of 100 g/L, and at a curing temperature of 180 °C with reduced BTCA concentrations of 80 and 60 g/L. In comparison to TAHT cross-linking, the CA and BTCA crosslinking required more energy and chemical input in order to reduce the fibrillation tendency of the Ioncell fibers.

The evidence of the cross-linking can be easily monitored by comparing the FTIR spectra between the original and crosslinked Ioncell fibers (Figure S4 in the Supporting Information). Similar to the FTIR spectrum of cellulose, the carbonyl group band of the Ioncell fibers is shown at a wavelength of ~ 1630 cm⁻¹. As the cross-linking took place, the carbonyl band shifted to $\sim 1730 \text{ cm}^{-1}$ and an additional peak at ~ 1580 cm⁻¹ appeared due to the conversion of the carboxylic acids after a mild alkaline treatment. The effect of the treatment conditions on cross-linking and the resulting fibrillation index is also presented as a function of the FTIR band intensity ratios between the ester carbonyl and the C-H banding of cellulose (shown in Table 1). The treatment conditions have pivotal influences on the cross-linking rate. For both CA and BTCA cross-linked fibers, the ester carbonyl band intensity was enhanced with increasing treatment temperatures and crosslinker concentrations. At 150 °C, the carbonyl ester band intensity was relatively low (close to 0.5) for both CA and BTCA cross-linked fibers. When the curing temperature was increased, the carbonyl band intensity increased, which was also indicated by the reduced fibrillation tendency. BTCA was able to be cross-linked more intensively than CA even at relatively lower concentrations. In comparison, the ester carbonyl intensity of CA cross-linked fiber was already at a lower level at 80 g/L, which led to an increased fibrillation tendency. The better cross-linking ability of BTCA over CA is attributed to the additional carboxylic groups that are able to cross-link with multiple cellulose units.

The curing time dependence of the fibrillation tendency of cross-linked fibers is illustrated in Figure 1. The curing



Figure 1. Effect of curing time on the fibrillation tendency, whiteness, and ester carbonyl band intensity of the cross-linked fibers. The curing temperature was fixed at 180 $^{\circ}$ C. The table under the figure indicates the FTIR ester carbonyl band intensity ratio.

temperature was fixed at 180 °C to avoid the potential effect of a lower curing temperature on the fibrillation tendency. After they were heated for 1 min at 180 °C, the fibrillation index of the BTCA cross-linked fibers decreased from 1.28 to 0.23. However, the CA cross-linked fibers still possessed a relatively high fibrillation index (0.89) after 1 min of curing. When the curing duration was extended to 3 min, the fibrillation tendency of the Ioncell fibers was nearly suppressed, leaving only a small number of fibrils on the fiber core after mechanical abrasion. A further extension of the baking temperature to 5 min would completely eliminate the fibrillation on the crosslinked fibers. The carbonyl ester bands from the FTIR spectra also demonstrate the effect of the curing duration on the crosslinking, in which the carbonyl band intensity increased as the curing time was extended.

To further confirm the presence of the cross-linkers CA and BTCA, a solid-state NMR analysis has been carried out. In comparison to untreated Ioncell fibers, both the BTCA- and CA-treated fibers show additional peaks at around 173 and 44 ppm, which visualize the carbonyl (C=O) and methylene groups (CH₂) of the cross-linkers, respectively. In the case of BTCA one more peak is found at 34 ppm, which is ascribed to the tertiary carbons (CH). The quaternary carbon of the citric acid is shifted to higher values and is hidden by the NMR spectrum of an untreated Ioncell fiber. The NMR spectra are shown in Figure S5.

Whiteness of the Cross-Linked Fibers. As demonstrated in Table 1 and Figure 1, the whiteness of the cross-linked fibers is closely dependent on the cross-linking conditions: crosslinker concentration, curing temperature, and curing length. The CA cross-linked fibers suffer from severe discoloration. When the CA concentration, curing temperature, and time were increased to a higher level, the whiteness of the crosslinked fibers dropped, resulting in fibers with a beige color. Under the most effective treatment conditions (100 g/L, 180 °C, and 5 min), the whiteness of the treated fiber was reduced from 47.94 to 26.39. However, the yellowing effect did not appear in the case of BTCA cross-linked fibers; only a minor whiteness loss could be observed.

The yellowing issue of CA cross-linked fibers was caused by the decomposed byproducts of CA at elevated temperatures. It has been reported that the formation of the unsaturated carboxylic acids, *cis*-aconitic acid and *trans*-aconitic acid, can be observed due to the dehydration of the hydroxyl group in the CA on exposure to a relatively high temperature.^{19,21,29,30} The alkene double bonds (C==C) in these side products are the main reasons for the yellowing of the CA cross-linked fibers. The loss of whiteness for BTCA-treated fibers may be due to the impurity of the commercial BTCA, as the cross-linker solution showed a very slightly off-white color.²² Since no such unsaturated products formed on exposure to high temperatures, the BTCA cross-linked fiber remained white.

Whiteness Improvement through the Addition of Polyols. Research studies have proposed that, as cross-linking extenders, polyols can solve the yellowing problem of the CA cross-linked cellulose.^{19,21,43} When the polyols are present in CA cross-linking, the formation of unsaturated side products due to the dehydration of the hydroxyl in CA can be avoided. The extender tends to bridge the CAs to form oligomeric esters of polyol and CA, which are less prone to decompose and would act as new cross-linkers. As the formations of decomposed byproducts subsided, the whiteness of the fiber could be improved. The chemistry of CA and cellulose cross-

linking in the presence of polyol is illustrated in Figure S3 in the Supporting Information. In this study, we have selected three different polyols with varying molecular weights: glycerol, xylitol, and polyethylene glycol (PEG, $M_w = 600$). All of the chosen polyols have an apparent influence on the whiteness improvement of the CA-treated fibers. The whiteness index of the resulting fibers was closely related to the chemical properties of polyols and their concentration in the cross-linker solution. Table 2 shows the influence of the polyols on

Table 2. Addition of Polyols for Whiteness Improvement and Its Influence on the Fibrillation $Tendency^a$

extender	polyol:CA mol ratio	fibrillation index	CIE whiteness index	ester carbonyl band intensity	
glycerol	1:8	0	27.29	0.628	
glycerol	1:4	0	30.87	0.674	
glycerol	1:1	0	40.56	0.507	
PEG	3:16	0.39	47.14	0.557	
PEG	3:2	1.56	55.35	0.512	
xylitol	3:40	0	52.11	0.564	
xylitol	1:4	0	50.58	0.630	
xylitol	3:2	0.06	51.35	0.528	
^a Fibers were cured at 180 °C for 5 min.					

the fibrillation tendency and whiteness of the CA cross-linked Ioncell fibers. For glycerol, the whiteness index of the crosslinked fibers was gradually enhanced when their mole ratio to CA was increased from 1:8 to 1:1. Meanwhile, the fibrillation index of the glycerol-aided CA cross-linked fibers remained at 0. The cross-linking of the CA with Ioncell fibers performed well with the presence of glycerol and xylitol at a relatively low polyol to CA mole ratio. The ester carbonyl band intensities were even higher than those of fibers cross-linked with neat CA. This can be explained by the lower production of unwanted side products and also the linking of CAs by the polyols, which created more ester bonds. A better whiteness improvement has been observed for PEG- and xylitol-aided cross-linked fibers. The addition of both extenders resulted in cross-linked fibers having a CIE whiteness index similar to that of the original Ioncell fibers.

However, the involvement of PEG and xylitol in crosslinking caused a deterioration of the fibrillation tendency of the resulting fibers. This is in agreement with a previous study done by Ye et al., in which a high polyol concentration suppressed the wrinkle recovery performance of the crosslinked fibers.²¹ With a relatively high concentration of xylitol, the fibrillation index of the cross-linked fibers increased from 0 to 0.06. This adverse effect may be attributed to the competition between xylitol and cellulose for reacting with CA. These phenomena can also be reflected by the ester carbonyl band intensity from the FTIR analysis. At the highest polyol to CA ratio, the ester carbonyl intensity of the crosslinked fibers was significantly reduced in comparison to that at lower polyol concentrations. With a higher polyol concentration, CA may prioritize reacting with polyols, thus hampering the cross-linking with cellulose, especially in the case of PEG and xylitol. The performance of fibrillation prevention was poorest for PEG among the selected extenders. The long bridges between the CAs seem less favorable to withstand the high shear forces during the fibrillation treatment.

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Washing Fastness. The cross-linking efficiencies of CA, CA with extenders, and BTCA were evaluated by a washing fastness test. The aim was to investigate whether the cross-linker on the fiber can withstand the standard washing tests at 40 °C under mildly alkaline conditions (pH ~10.5). For the washing fastness tests, fibers that were cross-linked under different conditions and had a fibrillation index of 0 were used. The fibrillation indexes of the cross-linked fibers before and after the washing fastness test are shown in Table 3. It was not

Table 3. Washing Fastness of the Cross-Linked Fibers Presented as the Fibrillation Index

			fibrillation index	
	extender	curing temp (°C)	before washing	after washing
reference			1.28	2.76
CA		180	0	0
CA	glycerol:CA mole ratio 1:8	180	0	0.24
CA	xylitol:CA mole ratio 3:40	180	0	0
CA		170	0	0.01
BTCA		180	0	0
BTCA ^a		180	0.02	0.09
BTCA		170	0	0.03
^a Curing ti	me 3 min.			

surprising to note that the washed untreated fiber fibrillation tendency was higher than that without washing. It is possible that fibrils were already formed during the washing test under alkaline conditions, which led to swelling of the fibers and eventually facilitated the formation of fibrillation while the fibers were beaten in the rotating metal containers.

The resilience of the cross-linked fibers to the washing fastness test varied depending on their cross-linking conditions. The CA and BTCA cross-linked at 100 g/L concentration, 180 °C, and 5 min rendered fibers with the best resistance to the washing test; the fibrillation index remained 0 after being washed under alkaline conditions. A decrease in the crosslinker concentration, curing temperature, and time led to an increase in the fibrillation tendency of the cross-linked fibers after washing. However the deterioration of the fibrillation was not pronounced. The performance of washing on the fibrillation for the glycerol- and xylitol-aided CA treated fibers was distinct. Glycerol-aided fibers possessed a higher fibrillation tendency (0.24) in comparison to that from xylitol (0) after washing. The exact reason was not clear. A possible explanation could be the number of hydroxyl groups on the polyols. Glycerol can link to CA to form a dicitrate, which can further cross-link with cellulose. The new cross-linker formation might not be very stable under the washing conditions, which would eventually lead to the breakage of the cross-linker and increase the fibrillation tendency. Despite the similarity of its reaction mechanism to that of glycerol, xylitol contains more hydroxyl groups that can link multiple CA groups. Subsequently, the formation of the oligomer esters cross-links with multiple cellulose units at their ends, forming a more stable linkage.

Mechanical Properties. The mechanical properties of the cross-linked fibers are illustrated in Figure 2. As acid-based cross-linkers, CA and BTCA reduced the mechanical properties of the cross-linked fibers through the acid-catalyst





hydrolysis of cellulose at relatively high temperatures.³⁴ Moreover, the cross-linking of the cellulose chains restricts their elasticity, which makes the fibers stiffer and more brittle.²¹ The mechanical performance was also influenced by the treatment conditions during cross-linking (such as curing temperatures, duration, additives, and cross-linker concentrations), and the trend was opposite to the fibrillation tendency.^{21,38} The fibers generally exhibited low mechanical properties when the fibers had a reduced fibrillation tendency. Fibers cross-linked with CA and BTCA (at 100 g/L concentration, 180 °C, and 5 min) had the best fibrillation resistance. Still, the tenacity of the fibers was halved, and the elongation also dropped dramatically. Less severe cross-linking conditions (reduced curing duration and temperature) allowed enhanced mechanical properties of the fibers, and there is no need to mention that the cross-linking efficiency was also weakened.

Effect of Softener on the Fiber Mechanical Properties. Softeners have long been used to improve the performance of textile fibers (including the mechanical properties). By far, silicon-based softeners have been extensively used for textile applications.^{44–46} Previous studies have shown that the addition of softeners may improve the mechanical performance of the CA and BTCA cross-linked fibers.^{16,21,46} In this study, we have utilized a polysiloxanebased macromolecule emulsion softener to avoid severe strength loss during the cross-linking. This particular softener can attach to cellulose or the residual carboxylic groups of the cross-linker after esterification to the cellulose via its positively charged surface.⁴⁶ Figure 3 demonstrates the SEM images of the original, cross-linked, and softener-aided CA cross-linked fibers. No clear changes could be identified between the



Figure 3. SEM images of original, CA cross-linked, and softener-aided CA cross-linked Ioncell fibers.

untreated and the cross-linked fibers. However, a pastelike surface of the softener-aided cross-linked fibers was obtained, evidencing the softener's presence.

The softener indeed enhanced both the tenacity and the elongation of cross-linked fibers, and the improvements were more pronounced for BTCA cross-linked fibers (Figure 4).



Figure 4. Influence of softener on the mechanical properties of crosslinked fibers. Fibers were cured for 5 min. The optimum conditions with regard to low fibrillation tendency and the preservation of the fiber tenacity are CA and BTCA cured at 150 $^{\circ}$ C with the support of a softener.

The mechanical performance enhancement seemed somehow dependent on the curing temperature. For both CA and BTCA cross-linked fibers, the improvement rate of the mechanical properties was more significant at a lower curing temperature (150 $^{\circ}$ C). Surprisingly, the fibrillation tendency can also be controlled by using a softener. The smooth surface of the softener-aided fibers significantly reduced the abrasion of the fiber during the mechanical fibrillation treatment, thus leading to a lower fibrillation tendency (Table 4). The fibrillation

Table 4. Influence of Softener on the Fibrillation Tendency

		fibrillation index		
	curing temp (°C)	without softener	with softener	after washing fastness
reference	150	1.28	0.68	
CA	180	0	0	0
BTCA	180	0	0	0
CA	150	0.38	0	0
BTCA	150	0.44	0	0

tendency of CA and BTCA cross-linked fibers supported with softener was already suppressed to a lower level on curing at 150 °C. As a result, the curing temperature can be reduced to a lower level (from 180 to 150 °C) to further increase the mechanical performance of the fiber.

Process Economy. The durability of the cross-linker solution is of utmost importance to evaluate the cost of the cross-linking process. Herein, we have treated our Ioncell fibers in both CA and BTCA solutions five times (concentration 100 g/L, softener 15 g/L, and curing at 180 °C for 5 min), and each cross-linking was done with an interval of 1 day. All of the cross-linked fibers showed fibrillation indexes of 0, which

indicated that the cross-linkers in the solution were stable over time. This is an advantage in comparison to the TAHT used to prepare Tencel A100 cross-linked fibers, which tends to hydrolyze under alkaline conditions (NaOH as the catalyst), leading to inefficient cross-linking over time. Thus, fresh TAHT has to be used, which significantly increases the process cost. After treatment of 1 g of fibers, approximately 2 g of the CA or BTCA cross-linker solution was lost (trapped in the fibers and a minor amount lost during pressing), which equals to the consumption of 0.2 g of CA or BTCA and 0.03 g of softener. However, in an industrial-scale cross-linking process, the loss of the cross-linker solution can be better controlled because of more professional equipment. Thus, the costs of the process can be further diminished.

CONCLUSION

The performance of CA and BTCA cross-linking on the Ioncell fibers and their ability to reduce the fibrillation tendency were investigated. The stability of the cross-linker against fibrillation relied heavily on the cross-linking conditions. Fibers treated in a 100 g/L CA or BTCA solution and subsequently cured at 180 °C for 5 min resulted in best resilience of the fibers to fibrillation. CA cross-linked fibers have serious yellowing problems, which can be overcome by the addition of polyols such as glycerol and xylitol without compromising the fibrillation behavior. The washing fastness of the cross-linked fibers is a decisive factor as to whether or not they can be used for specific textile applications. Under the employed conditions, most of the cross-linked fibers demonstrated strong resistance to washing under alkaline conditions. However, when the fibers were cured at a lower temperature or for a shorter duration, the cross-linker attached to the fiber exhibited less stability. Moreover, employing an extender (e.g., glycerol) in the CA cross-linking might also weaken the performance of the cross-linking. Cross-linking with polycarboxylic acids resulted in a decrease in the mechanical properties of the fibers. Under the optimum cross-linking conditions (100 g/L CA or BTCA, curing at 180 °C for 5 min), the tenacity of the cross-linked fibers was halved. Therefore, a softener must be applied to preserve the loss of mechanical strength. The application of a softener also gave the cross-linked fibers further protection against fibrillation. This gave the process an advantage to cure fibers at a relatively lower temperature of 150 °C and eventually achieve a strength similar to that of a Tencel fiber. However, it is still critical to note that a temperature of 150 °C in the post-treatment process requires the establishment of a pressurized reaction zone, since the reaction can no longer be achieved in an open post-treatment zone as is possible with TAHT cross-linking in the case of the Tencel A100 (which cured can be cured at much lower temperatures of 85-100 °C). This will result in higher investment and also higher energy costs. Therefore, more optimization studies on the CA and BTCA cross-linking have to be carried out prior to commercialization. This work unfolded a green route to cross-link the regenerated cellulose fibers and prevent the fibers from forming microfibrils under wet abrasion. The process can be accomplished by utilizing fully sustainable bio-based raw materials with no or minor toxicity: Ioncell fibers, xylitol, and citric acid manufactured from renewable plant resources and the possibly less toxic synthetic acid BTCA. The method demonstrated the possibility to become a potential alternative to the highly

poisonous cross-linkers to improve fiber fibrillation prevention and textile performance.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.1c06101.

Reaction schemes of the polycarboxylic acids and cellulose, FTIR spectra of the cross-linked fibers, ¹³C CP-MAS NMR spectra of pure Ioncell fibers and CAand BTCA-treated Ioncell fibers, and the experimental setup (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Yibo Ma Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, 00076 Aalto, Finland; • orcid.org/0000-0001-9031-6460; Email: yibo.ma@aalto.fi
- Herbert Sixta Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, 00076 Aalto, Finland; orcid.org/0000-0002-9884-6885; Email: herbert.sixta@aalto.fi

Authors

- Xiang You Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, 00076 Aalto, Finland
- Marja Rissanen Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, 00076 Aalto, Finland
- Inge Schlapp-Hackl Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, 00076 Aalto, Finland

Complete contact information is available at: https://pubs.acs.org/10.1021/acssuschemeng.1c06101

Notes

The authors declare no competing financial interest.

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