



Low temperature modification for natural cellulose fibers

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Abstract: Although natural cellulose fibers play an important role in the textile industry due to their merits in many properties, the complicated compositions and high crystallinities reduce their hygroscopicity, dyeability, color fastness and color brightness, and some of the fibers are thick resulting in a tingling hand feeling. Conventional modifications suffer from problems, such as high in energy consumption, low in efficiency and the potential to elicit water pollution. In this research, a low-temperature alkalic treatment was developed to improve the hygroscopicity, dyeability and hand filling of various natural cellulose fibers via a single process. This modification, reduced initial moduli of all fibers about 23 % to 75.4 % except cotton, and the reductions in crystallinities of ramie and flax (38.8% and 50.5 %) are more obvious than cotton and hemp (19.3 % and 19.11 %,) resulting in more elevations in moisture regains and color depth. This modification method has the potential to provide high quality products from natural cellulose fibers with an economic and environmentally friendly process.

Key words: Low temperature modification, Mechanical properties, Cellulose fibers, Moisture regain, Color depth

1 Introduction

Natural cellulose fibers occupy around 30 % of fiber consumption in the textile industry because of their inherent hydrophilicity, dyeability and low cost^[1,2,3]. The main types of nature cellulose fibers for apparels are cotton, ramie, flax and hemp fibers. The major composition of these fibers is cellulose, but they also contain other components, such as hemicellulose, lignin, pectin and wax etc. as shown in Table 1^[4,5], which lowered their hygroscopicity, dyeability, color fastness and color brightness. Besides, most natural cellulose fibers possess high crystallinities that also prevents the infiltration of water or dye molecules. Some natural cellulose fibers are thick in diameter and high in bending stiffness resulting in tingling sensation to reduce the comfortness of the produced fabrics^[6,7].

To overcome these weaknesses of natural cellulose fibers, modifications are required. Mercerization is the conventional modification for cotton products, which carried out in an alkalic environment at high temperatures (40 – 60 ° C). This approach provides cotton fibers with elevated glossiness, hygroscopicity, dyeability and color depth^[8]. However, this process has a high energy consumption with a low efficiency^[9,10]. To improve the dyeability of these fibers, a large amount of electrolyte is required, which not only increases the dyeing cost but also produces wastewater containing a large amount of salt to elicit water pollution^[11]. Similarly, by applying mechanical,



physical, chemical or combined techniques to improve hand feeling, likewise by means of chemical technique, high addition of softener is employed to improve the hand of products made from thick natural cellulose fibers ^[12,13,14], and has the potential to induce water pollution and raise the cost for processing. Therefore, these conventional modification approaches for natural cellulose fibers can no longer meet the requirements to establish a sustainable green textile industry. A desired modification can improve the hygroscopicity, dyeability, color fastness, color brightness of natural cellulose fibers and reduce the tingling sensation via a single process which requires for a low energy consumption and discharges limited and environmentally friendly wastewater.

In our previous study, a low temperature treatment in an alkalic environment was developed to strengthen cotton fibers and provide sizing effects ^[15]. This approach exhibited the ability to provide cotton yarns with higher hygroscopicity, improved dyeability and lower crystallinity. More importantly, this method involved no chemical reaction and thus had limited agent consumption. The treatment bath could be recovered and reused. To confirm the application of these approach to modify various natural cellulosic fibers, in this study, cotton, ramie, flax and hemp fibers were subjected to this modification and their mechanical properties, crystallinities, moisture regains and dyeabilities were investigated.

2 Experimental

2.1 Material

Cotton fibers were provided by the 29th Corp. Ginning Factory of Korla, Xinjiang Uygur Autonomous Region. Ramie fibers were offered by the Hunan Dongting Ramie Textiles Factory. Flax fibers were bought from the Ningbo Xuyi Textiles Co., Ltd. Hemp fibers were purchased from the Nanjing Xinhe Textiles Co., Ltd. Sodium hydroxide (NaOH), urea and glycerol were bought from the Shanghai Lingfeng Chemical Reagent Co., Ltd.

2.2 Fiber treatment

Fibers were lie on a holding frame with a mesh in the form of a thin layer and immersed in the aqueous treatment bath containing 7 wt.% of NaOH, 12 wt.% of urea and 10 wt.% of glycerol. The treatment baths were pre-cooled to the optimized temperatures according to the results of preliminary experiments (0 °C for cotton, -10 °C for ramie, 0 °C for flax, 5 °C for hemp). All the treatments were performed for 10 min. The treated fibers were rinsed by distilled water to neutral, dried for 24 h at 60 °C.

2.3 Characterization

The tensile properties of treated and untreated fibers were tested on a single fiber tensile tester (XQ-2, Shanghai Lipu) with a gauge length of 20 mm and a cross-head speed of 10 mm min⁻¹. The fiber diameters were measured under a light microscope (BEION-M3, Shanghai Beiang Medical Technology Co., Ltd.) and the averages were used for the stress calculation. The fibers before and after treatments were scanned under an X-ray diffractometer (D/Max-2550 PC, Japan RIGAKU) and their crystallinities were calculated from their X-ray diffractograms. The



samples were balanced under the standard conditions ($20 \pm 3^\circ \text{C}$, $65 \pm 5\% \text{RH}$) for 24 h and their weights were recorded. Then, the fibers were dried at 110°C for 1.5h and their dry weights were recorded. The moisture regains of samples were calculated according to equation 1;

$$M.R = \frac{M_w}{M_d} \times 100\% \quad (1)$$

Where M.R is the moisture regain, M_w is the weight of fibers balanced under the standard conditions, M_d is the weight of dry fibers. The dyeing bath for reactive dyeing of cellulose fibers (1.6 mM/L, C.I. reactive red 2) has bath ratio of 1:30^[16], and the dyeing bath temperature kept at 25°C , after dyeing for 5 and 10 minutes, Na_2SO_4 (30 g/L, 30 mL) was added to promote dyeing, later 35 min, Na_2CO_3 (15 g/L, 30 mL) was added for fixation. Afterwards the samples were fixed in the dyeing bath for 30 minutes, the dyed fibers were squeezed dry, rinsed with distilled water, and dried for 24 h at 60°C . The color shades of fibers were represented by the K/S values which were measured on a spectrophotometer (Datacolor SF60, America Datacolor Company).

3 Result and Discussion

3.1 Effect of treatment on the mechanical properties

Fig.1 indicates the breaking stress and initial moduli of the treated and untreated fibers. After the low temperature treatment, the stress of the cotton fibers was enhanced 22.3 %, while all the other fibers showed a declination in their breaking stresses. The ramie fibers treated at -10°C presented a remarkable decline in the breaking stress up to 50.4 %. The decrease in stress of flax and hemp fibers were about 36% and 42 %, but were not statistically significant. The changes in the initial moduli of fibers were similar with the trends of stresses. The initial modulus of the cotton fibers was elevated 27.4 % and the initial moduli of the ramie, flax and hemp fibers were reduced 58.8%, 75.4 and 23 %, respectively.

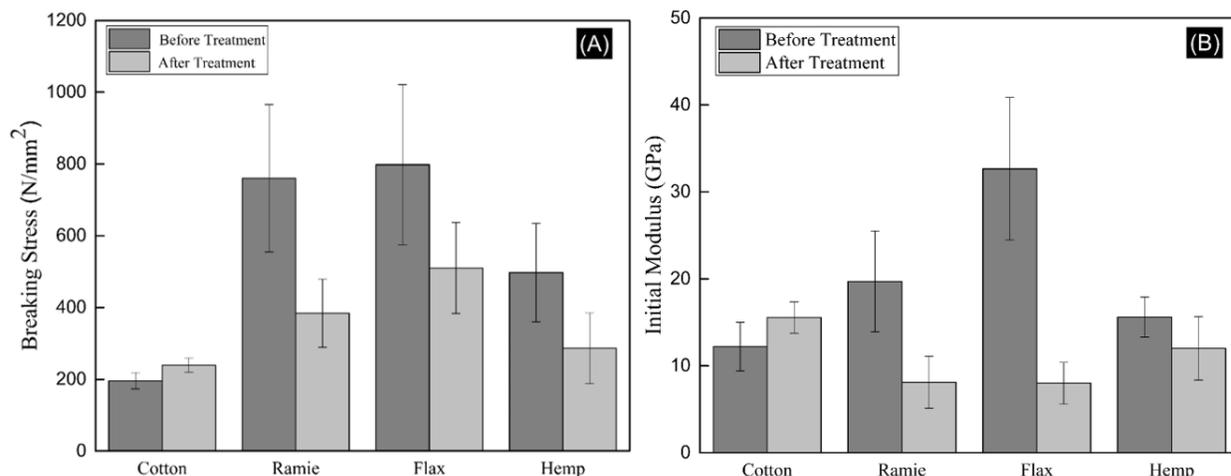


Fig.1 Effects of the low temperature treatment on the breaking stresses (A) and the initial moduli (B) of fibers



The results indicated that, except cotton fibers, the treated fibers were softened efficiently and showed the potential to provide fabrics with lower tingling hand feeling. The reason for these results might be similar to the mercerization effect. Cotton fibers are composed mainly of cellulose. The degree of polymerization of the molecules of cotton fibers is extremely high and the molecular chains go through several crystal cells. Once the cotton fibers were subjected to

Table.1 Comparison of the chemical composition of cellulose fibers

Fiber type	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Pectin (%)	Waxes (%)	Crystallinity (%)	Degree of Polymerization
Cotton	94	0.5-1	0.7-1.6	0.7-1.2	0.7	60-70	8000-13000
Ramie	65-67	14-16	0.8-1.0	4.0-5.0	0.5-1.1	75-85	2200-2600
Flax	70-80	12-15	2.5-5	1.4-5	0.3-1.8	70-80	2190-2420
Hemp	76	9.3	8.3	3.4	1.2	70-80	2000-2300

to the low temperature treatment, the alkali and urea penetrated into the amorphous regions and dissociated the hydrogen bonds between molecule allowing for the rearrangement of molecular chains in amorphous regions and generating higher orientation of molecules. Thus, the mechanical properties of cotton fibers were improved. On the contrary, the cellulose molecules with high degrees of polymerization in other fibers are much lower and the compositions of these fibers include hemicellulose, lignin, pectin and wax etc. as shown in Table.1 with smaller molecular weights. These components serve as the glue to bind the fibrils of fibers. When the hydrogen bonds were dissociated by the treatment bath, those components could be partially dissolved and induce the weakening of fiber.

3.2 Effects of the treatment on the crystallinity

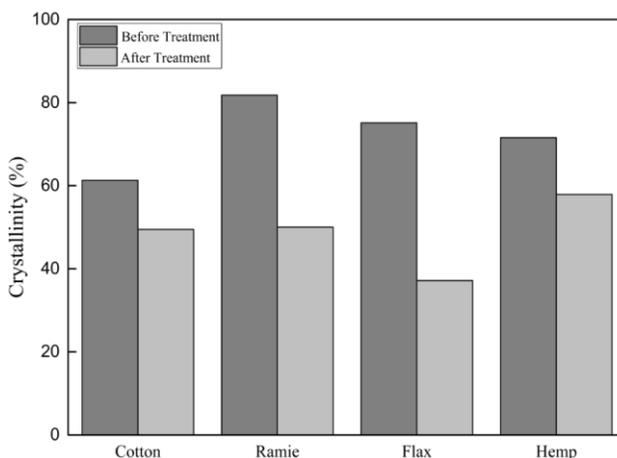


Fig.2 Effects of low temperature treatment on crystallinities of fiber

Fig. 2 displays the crystallinities of the treated and untreated fibers analyzed from the X-ray diffractograms. Cotton fibers possess the lowest original crystallinity around 61.3 %, hemp fibers above 70%, ramie fibers display the



highest original crystallinity about 81.7 %. After the treatment, the crystallinities of the cotton and hemp fibers were reduced 19.3 % and 19.11 %, while the values of the ramie & flax fibers decreased 38.8 % and 50.5 %. The result indicated that the structures of cotton and hemp fibers had higher resistance to the treatment and the ramie and flax fibers were more vulnerable to the alkali/urea system. This trend was in accordance to the changes in the mechanical properties. Table.1 shows chemical composition of different cellulose fibers ^[4,5], during the treatment hemicellulose, lignin, pectin and waxes were degraded to certain extent, and the fiber swells which consequently decreases crystallinity ^[17].

3.3 Effect of the treatment on the moisture regain

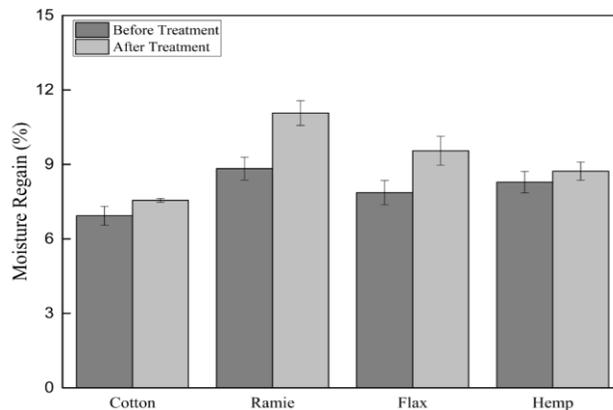


Fig.3 Effect of the treatment on the moisture regains of fibers.

Fig. 3 shows the moisture regains of fibers before and after the treatment. The values of cotton, ramie, flax and hemp fibers have been increased by 8.9 %, 25.3 %, 21.3 % and 5.4 %, respectively. The changes were consistent with the results of crystallinities. Since the crystallinities were reduced, the water molecules could easily penetrate into fibers and the increased amorphous phase allowed for the storage of a higher amount of water. Therefore, the moisture regains of fibers have been elevated.

3.4 Effect of the treatment on the dyeability of fibers

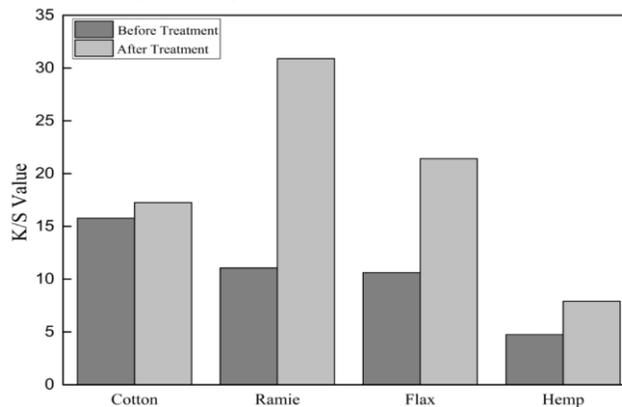


Fig.4 Effect of the treatment on the dyeability of fibers



The K/S values of the treated and untreated fibers stained by the reactive dye are shown in Fig. 4. The color shades of all the fibers have been increased. The reason for this result was similar with the explanation for the changes in the moisture regain. The increase in the amorphous phase allowed for the penetration and adsorption of dye molecules. Besides, the components of hemicellulose, pectin, lignin and wax exist as (shown in Table. 1) in fibers in the form of networks and provide fibers with hydrophobicity and structural hindering of molecular diffusion [18]. Once these components were removed from fibers, the diffusion of dye molecules became more readily. Since the crystallinities of the ramie and flax fibers reduced more obvious than cotton and hemp fibers, the changes of the K/S values of the ramie and flax fibers were higher. The increase ratios of K/S values of cotton and hemp fibers were about 9.45% and 66.12 %, while the elevation percentages were 18.9% and 10.7 %.

4 Conclusions

This work provided a low-temperature treatment for the medication of various natural cellulose fibers with the aim to improve their hygroscopicity, dyeability, hand feeling with acceptable mechanical properties. This modification was able to reduce the crystallinities of fibers, and exhibited higher treatment efficiencies on ramie and flax fibers (38.8 % and 50.5 %) comparing to the effects on cotton and hemp fibers (19.3 % and 19.11 %). The higher reduction in crystallinities of ramie and flax fibers generated more substantial elevation ratios in moisture regains (about 3 to 4 folds of the elevation ratio of cotton) and color depths (about 10 to 18 folds of the elevation ratio of cotton). The initial moduli of all fibers were reduced about 23 % to 75.4 %, which indicated the effective softening of fibers. Except cotton (27.4 % increment), the rest of fibers displayed decreased breaking stress (36 % to 50.4 %), but the fibers still possess sufficient strength for the future processing. Comparing to the conventional mercerization process, this approach could reduce 60 % alkali consumption and shorten 80 % of treatment duration. The treatment bath could be refreshed and reused. Therefore, the high efficiency, low cost and environmentally friendly nature of this approach have the potential to promote the transition of traditional textile processes to sustainable and green ones.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (51503031); the Pujiang Project from Shanghai Science and Technology Committee (15PJ1400300); and the Scientific Research Foundation for the Returned Overseas Scholars from the Ministry of Education (15B10127).

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