

Structural ATR-IR analysis of cellulose fibers prepared from a NaOH complex aqueous solution

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Abstract. In this study, regenerated cellulose fibers were successfully prepared from cellulose/NaOH/thiourea/urea aqueous solution through an efficient extrusion dissolution method. The microstructure of the regenerated cellulose fibers were analysed by using attenuated total reflection infrared (ATR-IR) spectroscopy and the corresponding two-dimensional (2D) correlation spectroscopy. The results showed that the fibers demonstrate a typical crystalline cellulose II and a relatively high crystallinity. Improved crystal structure and tensile strength were obtained in the regenerated cellulose fibers due to improved multi-roller drawing process. The total crystalline index (TCI) and tensile strength of the fibers at different spinning stages were determined in the range of 0.46-0.54 and 1.06-2.30 cN/dtex, respectively. The described cellulose regeneration pathway provided an environmentally friendly and simple method, which could have a significant influence on current cellulose regeneration industries.

1. Introduction

In the past 100 years, the viscose rayon [1] and cuprammonium rayon [2], which was an alternative to the viscose route, were extensively done. As well as known, wood or cotton linter pulp were using to produce these fibers, which could regard as an ideal substitution of the natural fibers. However, both the viscose and cuprammonium process resulted in the generation of hazardous byproducts (H₂S, CS₂ and heavy metals) that needed an additional treatment to meet the aqueous and gaseous emission standard. Therefore, the traditional approaches were not used to produce regenerated cellulose fibers in developed countries [3]. Increasing concerns over developing much more environmentally friendly spinning systems as well as using renewable raw materials were thus highly valuable.

Throughout the years, NaOH-based cellulose dissolution systems are regard as one of the alternatives for regenerating cellulose fibers, as the viscose fiber production machine can almost be used to prepare the fiber. For example, cellulose/NaOH [4-5], cellulose/NaOH/ZnO [6-7], cellulose/NaOH/thiourea [8-9], cellulose/NaOH/urea [10-11], and cellulose/NaOH/thiourea/urea [12-13] solutions have already been processed to regenerate fibers during wet-spun process. The advantages can be represented by the low cost and environmentally friendly solvent systems and production essentially non-toxic byproducts. Moreover, the solubility of cellulose can be significantly enhanced by adding urea or thiourea to NaOH aqueous solution. In addition, the physical of properties of regenerated cellulose fibers prepared by NaOH-based method are similar to NMMO-based fibers [8].



Previously, we presented an efficient extrusion dissolution method to prepare cellulose spinning dope in NaOH/thiourea/urea aqueous solution [14]. The shortening of the dissolution time to about 10 s and the increment of the dissolution temperature from $-10\text{ }^{\circ}\text{C}$ [13] to $-2\text{ }^{\circ}\text{C}$ were of great importance in this method. Hence, regenerated cellulose fibers can achieve a relatively better physical properties by the more stable cellulose spinning dope prepared by this new higher efficiency extrusion dissolution approach. In this work, we focus on regenerated cellulose fibers prepared from 7 wt% cellulose/NaOH/thiourea/urea aqueous solution which dissolved by twin-screw extruder at $-2\text{ }^{\circ}\text{C}$. Thereafter, we present attenuated total reflection infrared (ATR-IR) spectroscopy and two-dimensional (2D) correlation spectroscopy (2DCOS) analysis to investigate the effects of the staged spinning process on the structure of regenerated cellulose fibers.

2. Materials and methods

2.1. Materials

Cotton linter, with degree of polymerization (DP) of 350, was supplied by Longma Corporation (Jiangsu Province, China). All the chemical reagents were of analytic grade and used without further purification.

2.2. Preparation of cellulose fibers

Dried cotton linter pulp was dispersed into NaOH/thiourea/urea (9:6.5:6) aqueous solution at room temperature. This mixture was vigorously stirred for 5 min to form a cellulose suspension. Then the suspension was immersed immediately into a co-rotating twin-screw extruder ($L/D = 40$) precooled at $-2\text{ }^{\circ}\text{C}$. Subsequently, the complete dissolution occurred within about 10 s. Finally, the transparent cellulose extrudate was filtered and further deaerated at room temperature before wet spinning.

Wet-spinning equipment was used to produce regenerated cellulose fibers at room temperature (Figure 1). The cellulose spinning dope was extruded through a spinneret (the diameter is 0.08 mm) under a pressure of 0.1 MPa. Thereafter regenerated cellulose fibers was obtained by a multi-roller drawing bath: the coagulation bath (7.6 wt% H_2SO_4 /15.2 wt% Na_2SO_4 /1.25 wt% ZnSO_4 aqueous solution, $15\text{ }^{\circ}\text{C}$), second bath (water, $45\text{ }^{\circ}\text{C}$) and third bath (water, $98\text{ }^{\circ}\text{C}$), respectively. All samples were dried to constant weight before tests under vacuum at $60\text{ }^{\circ}\text{C}$.

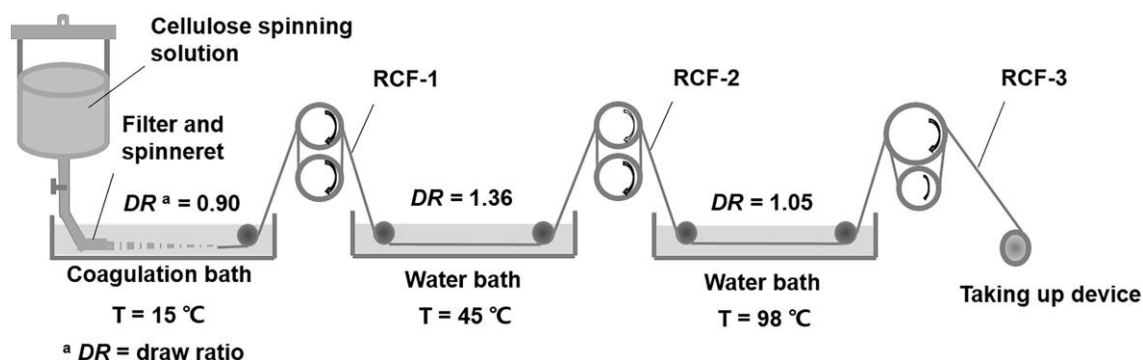


Figure 1. Schematic diagram of the wet-spun process of regenerated cellulose fibers.

2.3. Characterization

A universal tensile tester (XQ-1C, Donghua University, China) was used to calculate the tensile strength of the dried fibers with a gauge length of 20 mm according to GBT14337. At least 15 samples were tested for each sample and the tensile strength was calculated averagely. ATR-IR spectra were recorded by using a Nicolet 6700 FT-IR spectrometer (Thermo Fisher Scientific, America). Sixteen scans were averaged to obtain each spectrum at a resolution of 4 cm^{-1} . The spectra were subject to ATR correction, smoothing and baseline correction and being normalized. The two-dimensional

correlation spectroscopy (2DCOS) was performed using the SpectraCorr software (Thermo Electron Corporation, 2004).

3. Results and discussion

3.1. Spectral behaviour of regenerated cellulose fibers

It is well known that the Fourier transform infrared spectroscopy technique was one of the well-defined tools to study the structure of polymers[15-16]. For cellulose-based polymers, a comparative study was applied to characterise the structural changes of cellulose in the 1500-850 cm^{-1} region by O'Connor and co-worker[17]. Figure 2 shows the infrared spectra characteristic of the cellulose pulp and regenerated cellulose fibers at different spinning stages in the region of 4000-600 cm^{-1} . The structural changes can be identified by the main infrared spectral differences of the cellulose pulp and regenerated cellulose fibers. The 896, 1107, 1161 and 1430 cm^{-1} absorption bands, which are assigned to group C₁ frequency, ring asymmetric stretching, C-O-C asymmetric stretching, and CH₂ symmetric bending vibration in cellulose I respectively, can be study the type of crystallinity changes[18]. These bands in the crystalline cellulose I spectrum disappear from the spectrum of the regenerated cellulose fibers, which indicates crystalline cellulose II, with amorphous cellulose, occupies the main content in the regenerated cellulose fibers. Furthermore, the 1261, 1313 and 1366 cm^{-1} absorption bands, which are assigned to CH bending vibration in cellulose II, CH₂ wagging vibration in cellulose II, and CH bending vibration in cellulose I and cellulose II respectively, show a predominance of crystalline cellulose II in the regenerated cellulose fibers[19]. Moreover, the 893 cm^{-1} absorption band also corroborate crystalline cellulose I can be almost negligible in the regenerated cellulose fibers. Owing to the 893 cm^{-1} is assigned to group C₁ frequency in cellulose II[20].

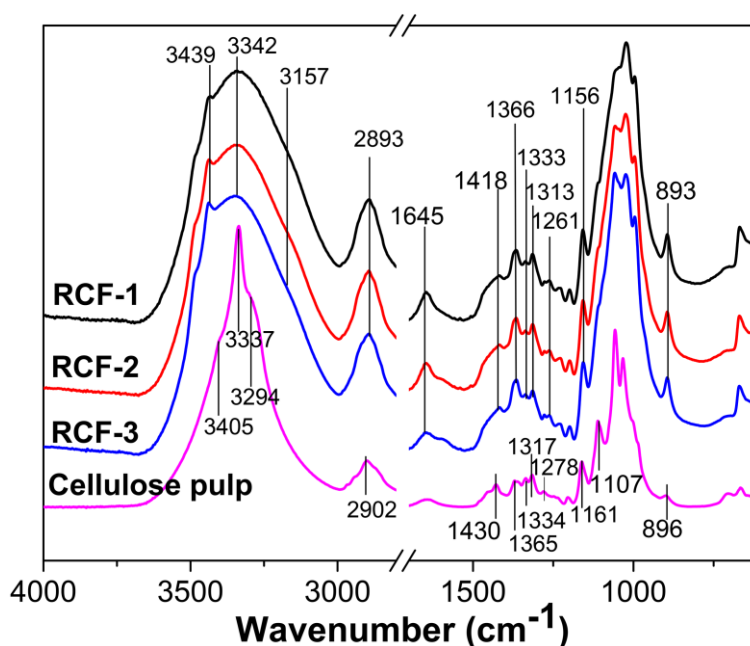


Figure 2. Comparative ATR-IR spectra of cellulose pulp and regenerated cellulose fibers at different spinning stages.

3.2. 2D correlation spectroscopy analysis of regenerated cellulose fibers

The generalized two-dimensional correlation spectroscopy (2DCOS), which is applied to represent spectroscopic intensity fluctuations, proposed by Noda[21]. The information of the spectral intensity changes, as well as the improvement of the apparent spectral resolution can be analysed by the 2DCOS. As shown in figure 2, the 3439, 3342, and 3175 cm^{-1} absorption band (–OH stretching

hydrogen bonds) in the spectra of the regenerated cellulose fibers are typically presented in the crystalline cellulose II but not observed in the crystalline I spectra[20]. Synchronous 2DCOS in the 3600 - 3100 cm^{-1} (the O-H stretching vibration regions) of four samples are shown in figure 3. The intensities of bands in the region 3600 – 3100 cm^{-1} of the regenerated cellulose fibers decrease, while the peak area variations increase as compared to the cellulose pulp. This results indicate that the hydrogen bond interaction reduce and the broad peaks occur, leading to the lower crystallinity in the regenerated cellulose fibers than the cellulose pulp. Moreover, the changes in the peak shape and position of intermolecular and intramolecular hydrogen bonds demonstrate the regenerated cellulose fibers are changed into crystalline cellulose II during the regeneration process. Furthermore, the intensities of the whole broad O-H stretching vibration regions in the regenerated cellulose fibers increase, resulting in the crystallinity increase along the spinning line. Figure 4 shows synchronous 2DCOS in the 910 - 800 cm^{-1} of four samples. The group C_1 frequency vibration, 896 cm^{-1} in crystalline cellulose I, shift to 893 cm^{-1} in cellulose II. Meanwhile, the peak area and intensity variations in the regenerated cellulose fibers increase along the spinning line. This peak behavior is in well agreement with the above conclusions mentioned in the 3600 – 3100 cm^{-1} absorption band.

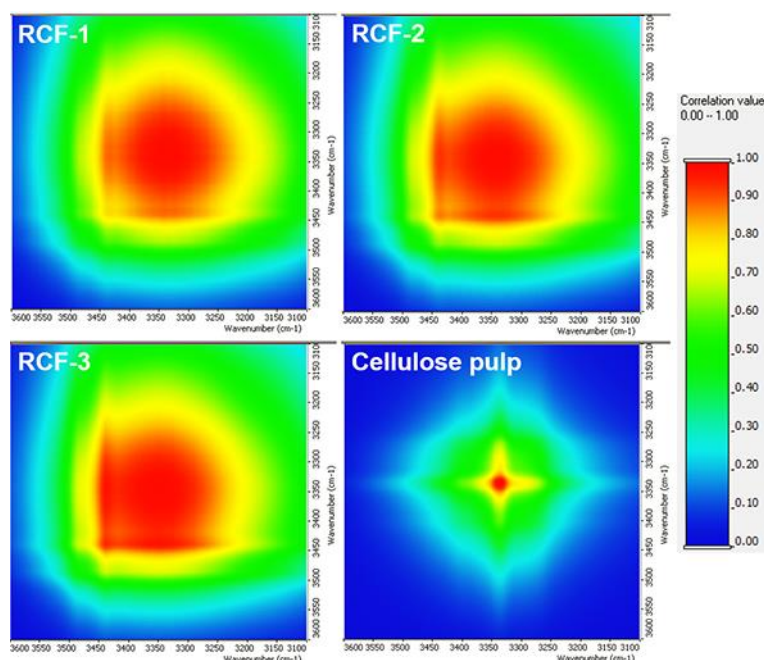


Figure 3. Synchronous 2DCOS in the range 3600 – 3100 cm^{-1} of cellulose pulp and regenerated cellulose fibers at different spinning stages.

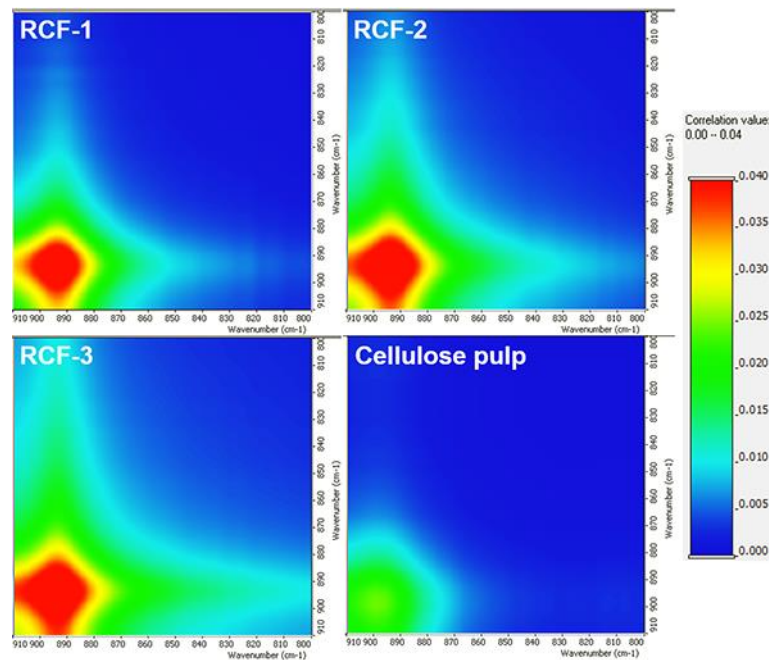


Figure 4. Synchronous 2DCOS in the range $910 - 800 \text{ cm}^{-1}$ of cellulose pulp and regenerated cellulose fibers at different spinning stages.

3.3. Crystallinity analysis

The crystallinity FTIR index is a significant and well defined tool to analyse the crystallinity of cellulose-based polymers, because the index is proportional to the degree of crystallization[20]. Consequently, the absorbance ratios A_{1366}/A_{2902} and A_{1366}/A_{2893} focus on determining the total crystalline index (TCI) of the cellulose pulp and regenerated cellulose pulp respectively. The results of the cellulose pulp and regenerated cellulose fibers at different spinning stages are shown in Table 1. Meanwhile, Figure 5 shows the TCI of the regenerated cellulose fibers, and the tensile strength is also depicted for comparison. The tensile strength increases as the TCI increases. Furthermore, the sample RCF-3 has the highest TCI and tensile strength, where the values are 0.54 and 2.30 cN/dtex, respectively. This phenomenon corroborates that the multi-roller drawing spinning process plays an important role in crystal structure and tensile strength of the regenerated cellulose fibers, and the crystal structure appears to have a significant impact on the tensile strength.

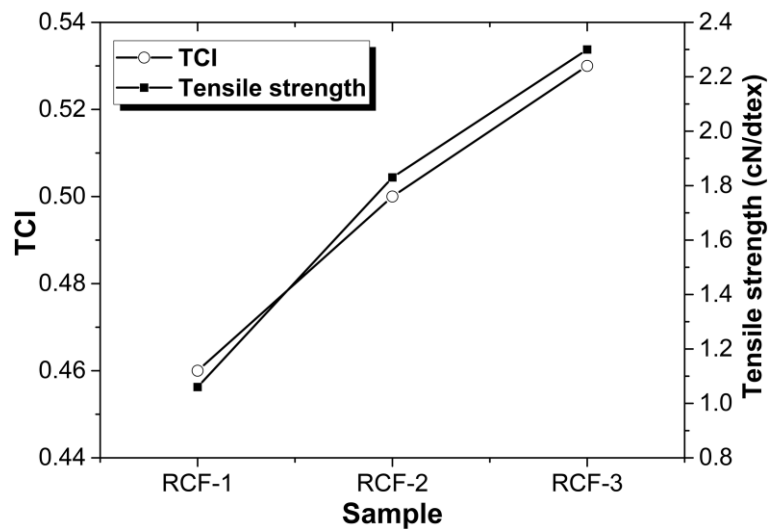


Figure 5. TCI of regenerated cellulose fibers at different spinning stages.

Table 1. Total crystalline index (TCI) and tensile strength of cellulose pulp and regenerated cellulose fibers.

Samples	A_{1366}	A_{2893}^a/A_{2902}^b	TCI	Tensile strength (cN/dtex)
RCF-1	0.243	0.532	0.46	1.06
RCF-2	0.267	0.530	0.50	1.83
RCF-3	0.268	0.500	0.54	2.30
Cellulose pulp	0.096	0.166	0.58	

^a A_{2893} is the absorbance of 2893 cm^{-1} band from regenerated cellulose fibers.

^b A_{2902} is the absorbance of 2902 cm^{-1} band from cellulose pulp.

4. Conclusions

Attenuated total reflection infrared (ATR-IR) spectroscopy and the two-dimensional correlation spectroscopy (2DCOS) were applied to characterize the regenerated cellulose fibers. The qualitative analysis of the ATR-IR spectra showed that the regenerated cellulose fibers was mainly composed of crystalline cellulose II and amorphous cellulose, as the characteristic spectral bands at 1430 , 1161 , 1107 cm^{-1} were not found for the regenerated cellulose fibers. Moreover, the 893 cm^{-1} absorption band, assigned to group C_1 frequency in cellulose II, also corroborate crystalline cellulose I can be negligible in the regenerated cellulose fibers.

The total crystalline index (TCI) results indicated the crystallinity decreased when cellulose pulp was changed into regenerated cellulose fibers. However, the increase in TCI was accompanied by an increase in the tensile strength of the regenerated cellulose fibers along the spinning line. Comparative analysis of the 2DCOS in the range $3600 - 3100\text{ cm}^{-1}$ and $910 - 800\text{ cm}^{-1}$ showed a significant change in the peak area, shape, position and intensity between the cellulose pulp and regenerated cellulose fibers. This behaviour and the trend of TCI values were consistent with the ATR-IR analysis results. Therefore these results corroborated the staged spinning process were in favor of obtaining improved crystal structure, as well as the tensile strength of the regenerated cellulose fibers prepared by the described extrusion dissolution method.

Acknowledgments

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References

- [1] Klemm D, Heublein B, Fink H P and Bohn A 2005 *Angew. Chem. Int. Ed.* **44** 3358-93
- [2] Fink H P, Weigel P and Purz H J 2001 *Prog. Polym. Sci.* **26** 1473-524
- [3] Reddy N and Yang Y Q 2015 *Innovative Biofibers from Renewable Resources* (German: Springer Berlin Heidelberg)
- [4] Yamane C, Mori M, Saito M and Okajima K 1996 *Polym. J.* **28** 1039-47
- [5] Budtova T and Navard P 2016 *Cellulose* **23** 5-55
- [6] Fu F Y, Zhou J P, Zhou X M, Zhang L N, Li D X and Kondo T 2014 *ACS Sustainable Chemistry & Engineering* **2** 2363-70
- [7] Vehviläinen M, Kamppuri T, Grönqvist S, Rissanen M, Maloney T, Honkanen M and Nousiainen P 2015 *Cellulose* **22** 1653-74
- [8] Chen X M, Burger C, Fang D F, Ruan D, Zhang L N, Hsiao B S and Chu B 2006 *Polymer* **47** 2839-48
- [9] Ruan D, Zhang L N, Lue A, Zhou J P, Chen H, Chen X M, Chu B and Kondo T 2006 *Macromol. Rapid Commun.* **27** 1495-500
- [10] Cai J, Liu Y T and Zhang L N 2007 *Adv. Mater.* **19** 821-5
- [11] Luo X G and Zhang L N 2013 *Food Research International* **52** 387-400
- [12] Zhang S, Li F X, Yu J Y and Gu L X 2009 *Fibers and Polymers* **10** 34-9
- [13] Wang W C, Li F X, Yu J Y, Navard P and Budtova T 2015 *Cellulose* **22** 1333-45
- [14] Yang Y P, Zhang Y, Dawelbeit A M and Yu M H 2016 *Proc. Int. Conf. on Polymer and Composite Materials (Hangzhou, China)* vol **137** (UK: IOP Publishing)
- [15] Yang H, Yan R, Chen H, Dong H L and Zheng C 2007 *Fuel* **86** 1781-8
- [16] Kumar R and Sekhon S S 2013 *Ionics* **19** 1627-35
- [17] Nelson M L and O'Connor R T 1964 *J. Appl. Polym. Sci.* **8** 1311-24
- [18] Nelson M L and O'Connor R T 1964 *J. Appl. Polym. Sci.* **8** 1325-41
- [19] Marchessault R H and Liang C Y 1960 *J. Polym. Sci., Part A: Polym. Chem.* **43** 71-84
- [20] Carrillo F, Colom X, Suñol J J and Saurina J 2004 *Eur. Polym. J.* **0** 2229-34
- [21] Noda I 1989 *J. Amer. Chem. Soc.* **111** 8116-18