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Exploring crystalline structural variations of cellulose during pulp beating of tobacco stems

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ABSTRACT

In this work, crystalline structural variations of cellulose during pulp beating of tobacco stems were characterized through X-ray diffraction (XRD) and FT-IR spectroscopy. The results showed that the correlation between the cellulose crystallinity index and the degree of beating was not a linear but an initially upward and then downward trend followed by a repeating fluctuation as a result of the beating action on amorphous regions first and then on crystalline cellulose. It was proposed that the whole beating process might be presumably divided into two phases in the case of the evolution of the crystallinity index. The crystallite sizes of 101 and $10\bar{1}$ lattice planes showed an obvious fluctuation during the beating while the crystallite sizes and *d*-spacings from representative 002 lattice planes exhibited little change. Complementally, FT-IR characterization of cellulose structural properties further proved that the crystallinity index was highly affected by mechanical beating and the intact beating process might be divided into two stages characteristic of a first ascending and then descending tendency.

1. Introduction

The requirement for high quality pulps widely used in the papermaking process and the reconstituted tobacco sheet (RTS) industry has boosted the demands for the pulp beating/refining process (Chen et al., 2014; Gharehkhani et al., 2015). Pulp beating is a mechanical treatment of pulp fibers to develop their optimal paper properties dependent on the products. During the past decades, the view was popularly shared that mechanical refining has three actions that modified the physical properties of pulp fibers: cutting, which reduces fiber length; shearing, which fibrillates fibers on their exterior surface; and compression, which crushes and fibrillates fibers internally (Hartman, 1984). However, the presence of crystallinity in cellulose is one of the most important characteristics contributing to its physical, chemical and mechanical properties (Andersson, Serimaa, Paakkari, Saranpaa, & Pesonen, 2003; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011). As an example, with the increase of crystallinity, tensile strength, dimensional stability and density rise, while properties such as chemical reactivity and swelling are weakened. (Terinte, Ibbett, & Schuster, 2011). Variability in the cellulose crystallinity during mechanical beating is a hypothesis that has been considered in some studies and remains in uncertainty (Gharehkhani et al., 2015).

Crystallinity index (CrI) is a parameter commonly used to quantify the amount of crystalline structure present in cellulosic materials and has also been applied to interpret changes in cellulose crystal structures after physicochemical and biological treatments (Andersson et al., 2003; Lavoine et al., 2012). The analytical methods have also been adopted to measure CrI including X-ray diffraction (XRD), solid-state 13C nuclear magnetic resonance (NMR) spectroscopy, FT-IR spectroscopy and Raman spectroscopy. Among these, XRD is currently employed most (Lee et al., 2016). Based on the XRD spectra, three different methods are commonly applied to calculate the CrI of cellulose. The first is called the peak height method developed by Segal, Creely, Martin, and Conrad (1959), the second the peak deconvolution method based on deconvolution of crystalline and amorphous peaks (Garvey, Parker, & Simon, 2005; Hult, Iversen, & Sugiyama, 2003), and the third the amorphous subtraction method first described by Ruland (1961) and later modified by Vonk (1973). Developments regarding these methods have been reviewed (Ju, Bowden, Brown, & Zhang, 2015; Park, Baker, Himmel, Parilla, & Johnson, 2010; Terinte et al., 2011). Moreover, the CrI calculated in the FT-IR method is usually compared with those in XRD and/or NMR measurements. In addition to the crystallinity index, both crystallite sizes and lattice

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spacings are characteristic parameters of the cellulose crystalline structure.

There are three distinctive viewpoints in terms of changes of cellulose crystallinity resulting from mechanical milling and/or beating. In the first place, a linear decline trend has been generally believed in some cases of ball milling and PFI beating processes. It was reported that the CrI dropped from 59 to 26, 8 and 3% respectively after ball-milling for 10, 20 and 40 min of eucalyptus (Miao, Grift, Hansen, & Ting, 2011), as well as a reduction from 69.6% to 23.7% for raw wheat straw (Gharpuray, Lee, & Fan, 1983). A linear drop relationship between CrI and beating degree was suggested during characterizing the effect of PFI refining of corn stover on enzymatic hydrolysis (Xu et al., 2014). Tonoli et al. (2012) reported that the crystallinity of pulp fibers slid from 69% to 60% after treatment with a Bruno disc refiner to 100 mL CSF. Wertz, Bédué, and Mercier (2010) postulated that mechanical processes might reduce crystallinity and chain cleavage. Similar results showed that the CrI of pulp decreased when the pulp was mechanically fibrillated by a commercial stone grinder or PFI mill (Barakat, Vries, & Rouau, 2013; Gao, Xiang, Chen, Yang, & Yang, 2015). There is one more point that the crystallinity was elevated first and then lowered with increasing degree of beating during PFI refining. Chen, Wan, Zhang, Ma, and Wang (2012), Liu, Wang, Hou, Chen, and Wu (2016) and Ibrahem, Yousef, & EL-Meadawy (1989) agreed that the CrI increased and then decreased with an increase in the degree of beating. An increase in crystallinity in the prior stage of refining was reported for unbleached pulps (Leitner, Seyfriedsberger, & Kandelbauer, 2013). As a result of refining, lignin and hemicellulose were removed partly, which led to an increase in crystallinity. In Leitner's et al. (2013) study, the data was presented only after 2000 revolution PFI mill and no data was available regarding the further refining to monitor the trend of the crystallinity. Also, Saad et al. (1979) stated that beating that caused minor chemical changes presented mainly a gentle climb of DP, crystallinity and resistivity to acid hydrolysis. Last but not the least, there was no significant change in the cellulose crystallinity during PFI mill and/or Valley beater refining. Hai, Park, and Seo (2013) showed that there was little change in the length, viscosity, crystallinity index or alpha cellulose content of bleached wood fibers and cotton fibers subject to PFI mill refining until their freeness levels slumped to around 300 mL CSF for wood fibers and around 100 mL CSF for cotton fibers. So far, although the enhancement of enzymatic saccharification by PFI refining was attributed to the reduction of cellulose crystallinity, and the development of certain fiber properties has also been associated with the change of cellulose crystallinity, the correlation between the cellulose crystal structure and the degree of mechanical beating remains to be elucidated. Therefore, it is essential to explore the effects of mechanical beating on the cellulose crystalline structure.

In this paper, changes of cellulose crystalline structure in PFI mill beating process were investigated in the XRD and FT-IR methods in a bid to probe into the relationship between the cellulose crystalline structure and the degree of beating. Comparative analyses were performed to better illustrate the variations of cellulose crystalline structure during beating. Supramolecular parameters of cellulose such as the crystallinity index, crystallite size and lattice spacings were measured in the XRD method.

2. Materials and methods

2.1. Materials

Tobacco stem is one fundamental raw material utilized to produce reconstituted tobacco sheet in the papermaking process. Air-dried tobacco stems with the length of 3–6 cm were sourced from Chengdu, China, in the autumn of 2014. The chemical compositions of the raw tobacco stems, determined according to the procedures of NREL/TP-510-42618 and NREL/TP-510-42619, were tested as follows: cellulose 17.94%, acid insoluble lignin 5.34%, acid soluble lignin 2.87%, pentosan 7.12%, hot water extractives 40.23% and ash 14.36% on a dry weight basis, which were comparable with the literatures (Zhao et al., 2016). Before mechanical pulping, the tobacco stem was extracted by water with a solid-to-liquid ratio of 1:6, at 80 °C for 90 min in a water circulation digester. After solid-liquid separation by extrusion, the tobacco stem with a solid content of about 25% was prepared for the following mechanical pulping process.

2.2. Mechanical pulping and PFI beating

Mechanical pulping was performed in a continuous high-consistency disk refiner (No. 2500-II, Kumagai Riki Kogyo Co., Ltd., Japan) with a refining consistency of approximate 25% resulting from the former solid content of extracted tobacco stem. To obtain a high yield mechanical pulp with a rational fiber fraction distribution, the refining process was divided into two steps: in the first step with a disc plate gap of 0.3 mm and then in the second with a plate gap of 0.15 mm (Gao et al., 2012).

The primary mechanical pulp was then beaten by a PFI mill (Mark VI, No. 621, Hamjern Maskin A/S Hamar Company, Norway). PFI beating was operated at a medium-consistency of 10% at a rotational speed of 1450 rpm and with a refining gap of 0.24 mm. The PFI beating revolution numbers used in this paper were 0, 1500, 2500, 3500, 4500, 5500, 7000 and 9000, respectively. Correspondingly, samples with different beating degrees such as SR-16, SR-20, SR-26, SR-31, SR-44, SR-48, SR-52 and SR-61 were obtained, denoted as B0, B1, B2, B3, B4, B5, B6 and B7 respectively.

2.3. X-ray diffraction analysis

The crystalline structures of the cellulose samples (B0-B7) were analyzed by a wide-ranging X-ray diffractometer (X'pert^3 Powder, PANalytical Co., Netherlands). The Ni-filtered Cu K_α radiation (λ = 1.54 Å) was generated at 40 kV and 40 mA. The scattering angle (2θ) ranged from 4° to 60° at a scanning speed of 0.5°/min. The crystallinities of celluloses were calculated from the perspective of the diffraction intensity in two different methods (Segal et al., 1959; Hult et al., 2003; Garvey et al., 2005).

The crystallite sizes (dimension) D_{hkl} from the 101, 10$\bar{1}$, 002 lattice planes were calculated in Scherrer Eq. (1) and the lattice spacings (d-spacing) were calculated in Bragg's Eq. (2).

$$D_{hkl} = \frac{0.94\lambda}{B_{hkl}cos\theta} \quad (1)$$

$$n\lambda = 2d\sin\theta \quad (2)$$

where λ is the X-ray wavelength; B_{hkl} is the angular full width at half maximum intensity (FWHM) in radians of the (hkl) line profile; θ is the scattering Bragg angel; n is an integer; d is the spacing between the planes in the atomic lattice (Park et al., 2010).

2.4. FT-IR spectroscopy

Pellets of about 2 mg tobacco stem samples were prepared by mixing with 200 mg spectroscopic grade KBr. FT-IR spectra of unbeaten and beaten samples were recorded using a Fourier transform infrared spectrometer (Bruker VERTEX 70, Germany). Spectra were collected in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} and 64 scans per sample. The cellulose crystallinity index was evaluated by the absorbance ratios using all the characteristic