Comparison of Some Key Parameters Contributing to Lignocellulosic Fiber Deformation Behavior by a Mathematical Model

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Deformation behavior is an important fundamental characteristic of lignocellulosic fibers; it affects the application range of fiber materials and the properties of fiber-based products. For instance, the density of a paper sheet depends on the degree to which the wet fibers are able to conform to the shapes of adjacent fibers during pressing and drying. In this study, a model for revealing the contribution of inherent characteristics of lignocellulosic fiber to its deformation behavior was developed and compared with other general models. The response sensitivities of cross-sectional parameters, fiber cell wall composition, and structure to the deformation behavior were determined as 3.26, 0.26, and 0.06, respectively. The results showed that the cross-sectional geometry was the main contributor to the deformation behavior of lignocellulosic fibers, followed by the ratio of different fiber cell wall components, and the fiber cell wall structure. To develop a comprehensive understanding of fiber separation in industrial production, the inherent fiber properties contributing to deformation behavior were investigated. This data could guide manufacturers to manage the treatment of different fiber separation processes to obtain fibers with required deformability, and thereby meet the requirements of fiber-based products.

Keywords: Lignocellulosic fiber; Deformation behavior; Mathematical model; Cross-sectional parameters; Fiber cell wall composition

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INTRODUCTION

Lignocellulosic fiber, derived from natural plant resources, is a natural cylinder-shaped composite mainly consisting of cellulose, lignin, and hemicellulose. In recent years, lignocellulosic fiber has been used more widely in various fields due to its unique characteristics, such as its high availability, cost-effectiveness, low density, renewability, and biodegradability. However, the properties of lignocellulosic fiber limit its application range and have a significant influence on the performance of fiber-based end-uses.

The deformation behavior of lignocellulosic fibers refers to the ability of lignocellulosic fibers to individually deform so that they can conform to one another in the fiber network, which is one of its most significant fiber properties (Lowe *et al.* 2007). Lignocellulosic fiber with proper deformation behavior will respond better to Campbell's forces, and the fiber network will have a greater number and area of the inter-fiber bonds,

resulting in a more compact structure (Paavilainen 1993; Lowe *et al.* 2007). Thus, an increase in tensile strength and decrease in the light scattering coefficient will be obtained. Steadman and Luner (1985) showed that the apparent density of the fiber network increased as the fiber flexibility increased, and for a particular fines-free pulp, the average fiber flexibility could be measured using the sheet apparent density. Paavilainen (1993) reported that the tensile strength of paper produced by softwood pulp fiber without beating was determined by the deformability of lignocellulosic fibers because of the increase in the number and area of inter-fiber bonds. Recent studies of the fiber deformation behavior revealed how the bonding properties of lignocellulosic fiber are influenced by the lignin content (Li *et al.* 2016). The results showed that the lignocellulosic fiber with varied lignin contents differed remarkably in regards to deformation behavior, and further contributed significantly to the bonding properties of the fiber network.

Due to the influence of lignocellulosic fiber deformation behavior on fiber-based products, it is important to clarify the effects of fiber properties on the deformation behavior. Tam Doo and Kerekes (1981) reported that the species, yield, and beating were three major variables that greatly affected fiber deformation behavior. Lignocellulosic fiber derived from different species has various fiber structures, mainly represented as cross-sectional parameters. Pulping or bleaching can result in varied fiber yield, which means different final chemical compositions in the individual fibers. Lignin, as a cross-linker in the cell wall, makes the cell wall a tighter structure and less deformable (Laine and Stenius 1997). The fiber cell wall structure changes during beating and refining, and is mainly represented as variations in the elasticity modulus (Tam Doo and Kerekes 1981; Paavilainen 1993). Therefore, the cross-sectional parameters, chemical composition of the fiber in cell walls, and fiber structure contribute to the fiber deformation behavior. Jang and Seth (1998) developed a relationship between the collapse index (a form of deformation), fiber wall geometry, and physical properties of fiber cell wall material. However, not all factors were quantified, and there is limited literature concerning this issue.

In this study, a model for the contribution of inherent characteristics of lignocellulosic fiber to deformation behavior was developed. The model was determined based on a basic formula, and all major factors contributing to fiber deformation behavior were considered, including cross-sectional parameters, the composition of the fiber cell wall, the structure of lignocellulosic fiber (characterized as the ratio of fiber perimeter to product of 2π and cell wall thickness), the ratio of carbohydrate and lignin content, and change rate of the elastic modulus. The deformation degree of unbleached softwood mechanical pulp was varied using delignification treatment. The response sensitivities of the cross-sectional parameter, fiber cell wall composition, and structure to the deformation behavior were determined by a series of mathematical operations and data from fiber with different parameters. And further, a deep understanding was investigated on how the fiber separation processes in the papermaking industry affected the deformation behavior. Therefore, paper manufacturers can manage the fiber separation process to obtain fibers with required deformability, thereby improving the high-value applications of lignocellulosic fiber.

EXPERIMENTAL

Materials

An unbleached, never-dried pine thermo-mechanical pulp (TMP) was used, provided by a pulp mill in China. The TMP fiber was performed with hot disintegration (800-1, Lab tech, Laval, Canada) according to TAPPI method T262 sp-96 (1996) to remove the latency (fiber twists, rolls, and nodules). This was conducted prior to fractionating pulp fibers using a Bauer-McNett fiber classifier (TMI 8901-5, New Castle, DE, USA) according to TAPPI method T233 cm-95 (1995). The fiber fraction R30 was used.

The lignin removal was performed on 20 g (oven dry weight) of pulp fibers with a pulp consistency of 3% using a 2 L conical flask at 75 °C with a pH ranging from 3.5 to 4. The fibers were left in a water bath for 1 h with 1% sodium chlorite added to obtain the chlorine dioxide. This was the only delignification cycle, and one more cycle was done for pulp fibers marked as "Sample A."

The pulp fibers delignified with four cycles and six cycles (mentioned above) were marked as "Sample B" and "Sample C", respectively. By using this chlorine dioxide delignification method, lignin was removed selectively, and carbohydrates received little damage. Totally, four lignocellulosic fiber samples with different lignin contents were obtained in this study, including the control sample. For each sample, three or more parallel measurements were done for all related indices.

Methods

Determination of lignin content and water retention value (WRV)

The total lignin content of each pulp sample was determined according to TAPPI T222 om-88 (1988), including the Klason lignin content and the acid-soluble lignin content.

The water retention value (WRV) measurement was based on ISO 23714 (2014). Approximately 0.15 g (o.d. weight) of fiber sample at 0.1% consistency was drained onto a 100-mesh screen in a cylinder, which was placed in a centrifuge (3–16 PK, Sigma, Osterode, Germany) at 2500 rpm for 20 min to remove the free water. After centrifuging, the sample was weighed to produce the wet weight, and then it was oven dried at 105 °C for 8 h and weighed again to produce the dry weight. The WRV was calculated as the ratio of moisture loss (the difference between wet and dry fiber) to the weight of dry fiber.

Elastic modulus of individual fibers

The elastic modulus of each fiber sample was determined by microtensile tests on individual fibers, which were performed with a custom-made microtension tester (SF-Microtester, Beijing, China) developed by Yu *et al.* (2011). Four different levels of deformability pulps (0.05 g, o.d.) were dispersed into single fibers using a bottle containing little glass beads and drained onto a filter mat by a TAPPI standard handsheet former. The dispersed fibers on the mat were dried at the room condition for 24 h. Two droplets of a 2-component epoxy resin adhesive (cold setting adhesive, HY-914, Tianjin, China) was placed using super fine tweezers on both ends of each fiber. The fibers selected exhibited minimal damage and a straight state. More details on fiber preparation for microtensile test can be found in Yu *et al.* (2011).

Determination of cross-sectional parameters

The cross-section images of fibers were obtained by a scanning electron microscope (SEM, JEOL-IT300, Tokyo, Japan). Only the complete cross-sections were used to calculate the cross-sectional parameters with the image processing toolbox in Image-Pro Plus 6.0 (Media Cybernetics, Inc., Rockville, MD, USA).

RESULTS AND DISCUSSION

Modeling of Lignocellulosic Fiber Deformation Behavior

Fundamentally, the deformation behavior of lignocellulosic fiber depends on fiber cross-sectional parameters, chemical compositions in the fiber cell wall, and fiber structure. The deformability of fiber will have a significant effect on the inter-fiber bonding properties of fiber networks, further influencing the performance of lignocellulosic fiber-based materials.

Determination of the Integrated Multifactor Mathematical Model

The deformability of lignocellulosic fibers, characterizing the ability of fiber morphology to be conformed within the fiber network (Lowe *et al.* 2007), can be expanded by the definition from Jang and Seth's (1998) expression of the collapse index on the fractional loss in lumen volume (induced by mechanical or chemical treatment) with respect to the original lumen volume. The deformation index, DI, is defined in Eq. 1,

$$DI = 1 - \frac{A}{A_0} \quad (1)$$

where A is the lumen area obtained from the cross-sectional image of a fiber after mechanical or chemical treatment, and A_0 is the original lumen cross-sectional area of the same fiber when it had not been subjected to any treatment. If a fiber is more deformable, it has a higher DI value; otherwise, the DI value is lower. As Jang and Seth (1998) proposed (Eq. 2),

$$\frac{A}{A_0} = \exp\left[- \alpha(\varepsilon, F) \cdot \left(\frac{P_L}{2\pi T} \right)^{\beta} \right] \quad (2)$$

where α depends on the inherent properties of fiber cell wall material, which can be determined by the fiber wall structure, the chemical composition of the fiber wall, and the environment conditions including the moisture content and the external force applied to a fiber; P_L is the lumen perimeter; and T is the fiber wall thickness. The fiber wall cross dimension can be determined by $(P_L/2\pi T)^{\beta}$.

In this study a specific expression is proposed to characterize the conformability of lignocellulosic fibers based on fundamental principles. The expression is given explicitly as Eq. 3),

$$DI = 1 - \frac{A}{A_0} = 1 - \exp\left[- H \cdot CL^{\alpha} \cdot (\Delta E)^{\beta} \cdot \left(\frac{P_L}{2\pi T} \right)^{\gamma} \right] \quad (3)$$

where H is the environment factor (H could be 1 when there is no external force and the relative humidity is 50%), CL is the ratio of carbohydrate and lignin contents, ΔE is the

change rate of elastic modulus compared with the untreated sample, P_L is the fiber wall lumen perimeter, and T is the fiber wall thickness. The parameters α, β, and γ are used to characterize the response sensitivity of chemical compositions in fiber cell wall, fiber wall structure, and fiber cross-section dimension to the fiber deformation, respectively.

Table 1. Fiber Parameter Data for Modeling Fiber Deformation Behavior

Samples	1-A/A_0	Lignin Content (%)	E (×10^{9}Pa)	P_L(μm)	T(μm)
Control	0.329	24.28	4.012	32.730	7.442
A	0.387	13.57	3.837	36.777	7.810
B	0.543	7.19	3.528	35.732	7.164
C	0.792	2.67	3.357	39.354	6.955

Next, a series of mathematical operations were done based on Eq. 3 (H is set to 1).

$$\frac{A}{A_0} = \exp\left[- CL^{\alpha} \cdot (\Delta E)^{\beta} \cdot \left(\frac{P}{2\pi T}\right)^{\gamma} \right] \quad (4)$$

$$Ln\left(\frac{A_0}{A}\right) = CL^{\alpha} \cdot (\Delta E)^{\beta} \cdot \left(\frac{P}{2\pi T}\right)^{\gamma} \quad (5)$$

$$Ln\left(Ln\left(\frac{A_0}{A}\right)\right) = \alpha Ln(CL) + \beta Ln(\Delta E) + \lambda Ln\left(\frac{P}{2\pi T}\right) \quad (6)$$

$$m = \alpha x + \beta y + \gamma z \quad (7)$$

where, $m = Ln\left(Ln\left(\frac{A_0}{A}\right)\right)$, $x = Ln(CL)$, $y = Ln(\Delta E)$, $z = Ln\left(\frac{P}{2\pi T}\right)$.

Three sets of data, as shown in Table 1, were used in Eq. 7, and the related numbers for solving the derivative equations are listed in Table 2. Finally, three response sensitivity factors (α, β, and γ) could be obtained, α = 0.26, β = 0.06, and γ = 3.26. The complete equation of the deformation index is given as Eq. 8.

Table 2. Data for Solving the System of Ternary Linear Equations

No.	m	x	y	z
1	-0.715	1.852	-3.133	-0.288
2	-0.270	2.558	-2.115	-0.230
3	0.451	3.596	-1.812	-0.104

$$DI = 1 - \exp\left[- (CL)^{0.26} \cdot (\Delta E)^{0.06} \left(\frac{P_L}{2\pi T}\right)^{3.26} \right] \quad (8)$$

Comparison of Deformation Index with General Evaluation Models of Lignocellulosic Fiber Deformation Behavior

Due to its special structure (cylinder-like structure) and chemical components (cellulose, hemicellulose, and lignin), lignocellulosic fiber shows deformations including

fiber bending and lumen collapse during the formation of fiber networks (Paavilainen 1993; Li *et al.* 2016). Hence, the deformation behavior of lignocellulosic fibers is usually characterized by wet fiber flexibility and collapsibility.

Fiber flexibility is defined as the reciprocal of the elastic modulus (E) and moment of inertia (I) of lignocellulosic fibers by assuming that the fibers are subjected to only pure bending (Waterhouse and Page 2004; Yan and Li 2008) as follows (Eq. 9),

$$Fiber\ Flexibility = \frac{1}{E \times I} \tag{9}$$

where, E and I are the longitudinal modulus and the inertia moment of the cross-section of fiber cell wall, respectively.

The collapsibility of lignocellulosic fibers refers to the part or full collapse behavior of fibers when subjected to pressing during the fiber network formation, which is usually determined by the aspect ratio (Jang and Seth 1998; Yan and Li 2008) as follows (Eq. 10),

$$Aspect\ ratio\left(AR\right) = \frac{D_{\max}}{D_{\min}} \tag{10}$$

where D_{max} and D_{min} are the longest diameter and the shortest diameter of the fiber cross-section, respectively.

Obviously, using flexibility and aspect ratio (AR) to characterize the deformability of lignocellulosic fibers only takes the fiber wall structure and fiber cross-section into consideration, neglecting the chemical compositions in fiber cell wall. Therefore, the deformation index (DI) of lignocellulosic fibers, which involves the factors of chemical compositions, fiber wall structure, and cross-section parameters, is more comprehensive to evaluate the deformation behavior of lignocellulosic fibers during the formation of fiber matrix.

Comparison of Different Factors Responding to the Fiber Deformation Behavior

Lignocellulosic fiber, a material with a hollow lumen and a solid fiber wall, is mainly composed of lignin and carbohydrates (cellulose and hemicellulose). Cellulose is mainly organized in microfibrils embedded in a matrix with soft lignin and hemicellulose, which are helically wound along the hollow fiber lumen axis (Dicker *et al.* 2014). Therefore, the deformation behavior of lignocellulosic fibers mainly depends on three inherent properties: chemical compositions in the fiber cell walls, fiber wall structure, and geometry dimension of the fiber cross-section, apart from other external conditions, such as applied force (Paavilainen 1993; Jang and Seth 1998).

According to Eq. 4, the DI value increases with increases in the three aspects, $(CL)^{0.26}$, $(\Delta E)^{0.06}$, and $(P_L/2\pi T)^{3.26}$. The results indicate that the increases in the ratio of carbohydrate to lignin contents, changing rate of elastic modulus, and $(P_L/2\pi T)$ had positive effects on the deformation behavior of lignocellulosic fibers; however, the response sensitivities were quite different.

The response sensitivity for the cross-sectional geometry dimension was 3.26, which was many times higher than of the other two parameters (changing rate of elastic modulus and ratio of carbohydrate to lignin contents), showing that the geometry dimension of the fiber cross-section has a remarkable effect on fiber deformation

behavior. The fiber cross-sectional parameters generally refer to the relationship between the fiber wall and lumen, which is usually expressed using the Runkel ratio (2×fiber wall thickness/lumen diameter) (Ververis *et al.* 2004). Lignocellulosic fibers have a hollow cylinder-like structure, and they are more flexible and easier to deform when they have a relatively larger lumen diameter and lower cell wall thickness (namely Runkel ratio<1). Paavilainen (1993) studied the effect of wood fiber properties on fiber flexibility and collapsibility and found that the fibers with thicker cell walls were less flexible and more difficult to collapse. When the cell wall thickness increased from 5.5 μm to 9.0 μm, the wet fiber flexibility decreased from 80 $N^{-1}•m^{-2}$ to 10 $N^{-1}•m^{-2}$. Thus, lignocellulosic fibers with thicker cell walls are less deformable. As Lowe (2007) pointed out, cell wall thickness is probably the most important wood fiber property with regard to the wet fiber flexibility, which is confirmed by the results of this study.

The chemical composition response sensitivity for lignocellulosic fibers was 0.26, which was much smaller than that of the cross-sectional geometry dimension, but it still had an important effect on the fiber deformation behavior. The main chemical compositions of lignocellulosic fiber are cellulose, hemicellulose, and lignin. During fiber separation and purification, most lignin is removed, and the cellulose backbone remains. The water retention values (WRV) of lignocellulosic fibers with different lignin contents are shown in Fig. 1. As the lignin content decreased from 24.28% to 2.67%, the WRV increased from 135.9% to 219.1%. Lignin removal loosened the micro structure in the fiber cell walls, and more water molecules moved into the microfibrils, resulting in a more easily deformable structure.

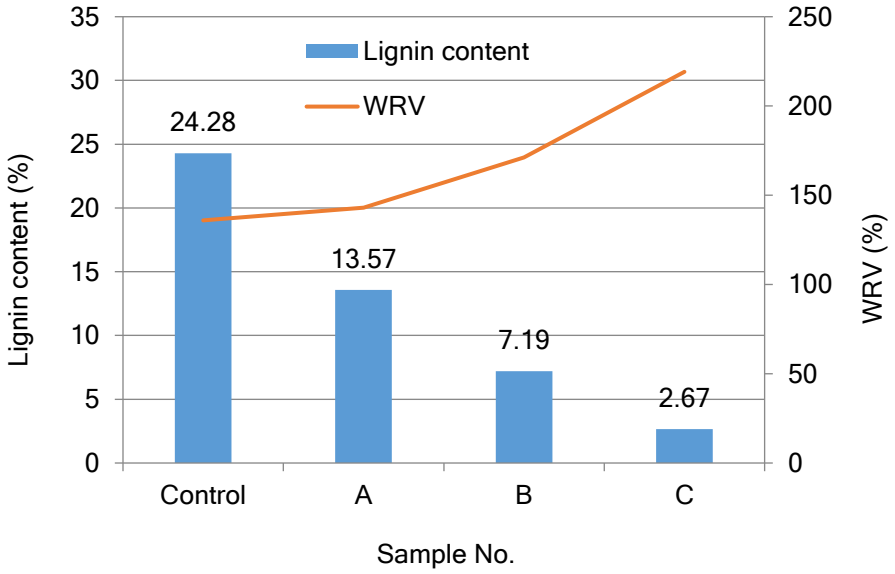

Fig. 1. Relationship between lignin content and water retention value (WRV) of lignocellulosic fibers

The response sensitivity for the lignocellulosic fiber cell wall structure was 0.06, which was the smallest among the three response sensitivities, and had the least effect on the fiber deformation behavior. The microfibrils in the fiber cell wall are spirally arranged around the cell lumen, and the S2 layer of the secondary wall is the main characteristic (Paavilainen 1993). The angle between microfibrils in the S2 layer and radial direction of fiber has an important effect on the elasticity of the fiber cell wall.

When the microfibril angle is small, the elastic modulus of fiber is small, and fiber is easy to deform. Conversely, when the microfibril angle is big, the elastic modulus of fiber is large, and the fiber is difficult to deform (Lowe 2007). Compared with the more macroscopic property of chemical composition and geometrical size of the fiber cross-section, the structural characteristics of wood pulp fiber had little effect on the deformation behavior of fibers.

Comprehensive Understanding of the Fiber Separation Process in the Papermaking Industry by Fiber Deformation Behavior

To satisfy the required performance of paper and paperboard products, wood fibers are subjected to a series of treatments during fiber separation and purification before the formation of the fiber network (paper or paperboard), mainly including the species of wood, lignin removal (chemical pulping or bleaching), and mechanical processing (such as refining). The sequence of these three stages is highly consistent with the contribution of response sensitivity based on fiber properties to its deformation properties (α, β, and γ, from the greatest to the least), as shown in Fig. 2.

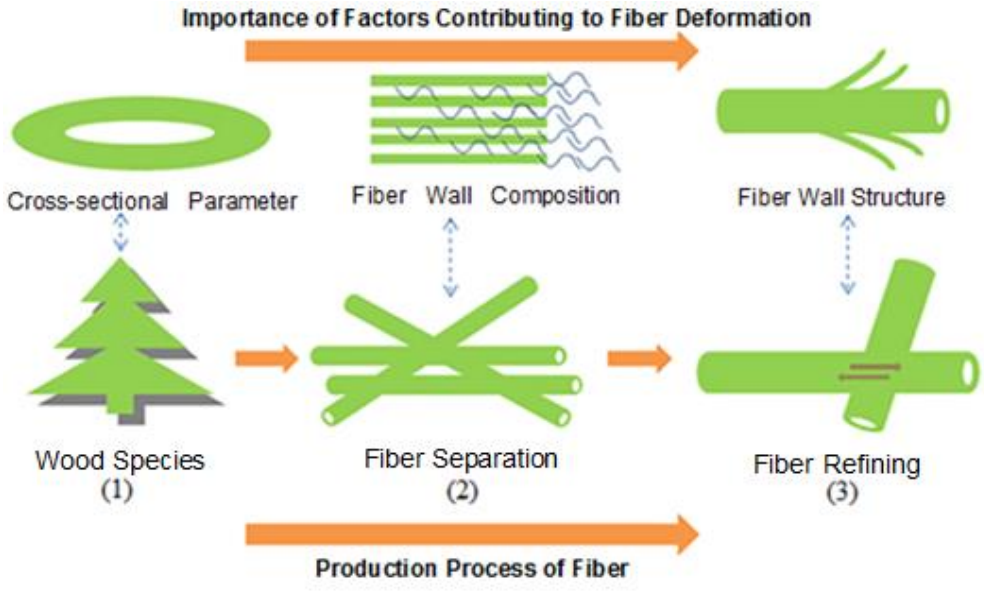

Fig. 2. Schematic of contributions to the fiber deformation during different fiber production stages

The cross-sectional parameters of lignocellulosic fibers are mainly determined at the stage of raw material selection. The ratio of different chemical components in the fiber cell wall can be changed during the combined processes of fiber separation/purification process (pulping and bleaching), and the fiber wall structure (the degree of fibrillation) can be substantially increased by mechanical post-treatment (refining). Different contributions to fiber deformability were obtained during the fiber production process, as shown in Fig. 2. The biggest contribution to fiber deformability is the cross-sectional parameters, and the smallest is the fiber wall structure (the degree of fibrillation). Therefore, the practical implication is that manufacturers can adjust the treatment of different fiber separation processes to obtain fibers with the required deformability, thereby meeting the property requirements of fiber-based products.

CONCLUSIONS

1. An integrated multifactor mathematical model was developed for revealing different contributions of inherent characteristics of lignocellulosic fiber to its deformation behavior. The response sensitivities of cross-sectional parameters, chemical compositions in fiber cell wall, and fiber cell wall structure to the deformation behavior were determined and compared, which were 3.26, 0.26, and 0.06, respectively.
2. The cross-sectional geometry was the main contribution to fiber deformation behavior, followed by the chemical composition in fiber cell wall and finally the fiber wall structure, which was in accordance with the fiber separation process for industrial production. A comprehensive understanding of the fiber separation process by fiber deformation behavior was obtained. Hence, the deformation behavior of lignocellulosic fiber can be adjusted precisely in different fiber separation processes to meet the requirements of fiber-based products.

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