

Basic research about corncob residue as Lyocell spinning material

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REZUMAT – ABSTRACT

Cercetare de bază asupra reziduurilor de știuleți de porumb ca material de filare al fibrei Lyocell

Au fost utilizate reziduurile de știuleți de porumb ca material sursă nou, mai ieftin pentru tehnologia de filare a fibrei Lyocell. În această lucrare au fost investigate proprietățile chimice ale reziduurilor de știuleți de porumb după extracția hemicelulozei și ligninei. Compoziția principală a reziduurilor de știuleți de porumb este celuloza, însoțită de o ușoară hemiceluloză și o cantitate foarte mică de component insolubile pentru filare. În comparație cu pulpa de lemn, reziduu de știuleți de porumb are o masă moleculară a numărului mediu similară, o masă molecular medie ușor mai mare, o masă molecular relativă mai mică și o polidispersie mai mare. Toate aceste proprietăți sugerează că acest tip de reziduu de știuleți de porumb are un potențial mare de utilizare ca material de filare pentru fibrele celulozice regenerare. A fost produs un nou tip de fibră din reziduu de știuleți de porumb, utilizând tehnologia de filare a fibrei Lyocell. Au fost analizate proprietățile mecanice ale fibrelor din reziduuri de știuleți de porumb. Fibrele din reziduuri de știuleți de porumb au o valoare a rezistenței la tracțiune între cea a fibrei de viscoză și cea a fibrei Lyocell, indicând perspectivele sale bune de aplicare. Cu toate acestea, fibrele din reziduuri de știuleți de porumb au o cristalinitate ridicată și o valoare de orientare cu o densitate liniară mare de fibră, ceea ce sugerează că tehnologia de filare trebuie îmbunătățită în continuare.

Cuvinte-cheie: reziduuri din știuleți de porumb, tehnologia de filare a fibrei Lyocell, fibră din reziduuri de știuleți de porumb, fibră Lyocell

Basic research about corncob residue as Lyocell spinning material

Using the corncob residue as a new cheaper source material for Lyocell spinning technology. Chemical properties of the corncob residue after extraction of hemicellulose and lignin were investigated in this paper. It was found that the main composition of corncob residue is cellulose, accompanied by slight hemicellulose and very tiny amount of spinning insoluble components. Compared to wood pulp, corncob residue has a similar number-average molecular weight, a slightly larger weight-average molecular weight, a lower peak-relative molecular weight, and a larger polydispersity. All those properties suggest that this kind of corncob residue has big potential to be used as spinning material for regenerated cellulose fiber. A new type corncob residue made fiber was produced, using the Lyocell spinning technology. Mechanical properties of the corncob residue fiber were analyzed. The corncob residue fiber has a tensile strength value between that of viscose fiber and Lyocell fiber, indicating its good application prospects. However, the corncob residue fiber has a high crystallinity and the orientation value with large fiber linear density, suggesting that the spinning technology needs to be further improved.

Keywords: corncob residue, Lyocell spinning technology, corncob residue fiber, Lyocell fiber

INTRODUCTION

Corn cob is the central core of an ear of maize, whose weight accounting for 20%~30% of the maize. Corn cob contains 32%~36% cellulose, 35%~40% hemicellulose, 25% lignin and very little amount of insoluble ash [1]. Usually, Corn cob is considered an agricultural waste with an annual production of approximately 40 million tons in China [2]. Corn cob is rich in nutrients and easy to collect. However, only small amount of the corn cobs are utilized for furfural xylitol production. Most of them are burned directly, causing environmental pollution and a waste of their economic value [3]. After extraction of hemicellulose and delignification processes, the main composition of the corncob residue should be cellulose. If using the corncob residue produces something, it will benefit not only the economy but also the society. The development of viscose products is limited because of the by-products produced during the

production process which may cause environmental pollution. In the 1980s, a new type of green environmental process, Lyocell process was invented. In the Lyocell process, a solution named N-methyl morpholine oxide (NMMO) is used to dissolve wood-pulp cellulose. Then, the mixed solution is spun to form a filament. Finally the solvent extracted during the washing process of the fibers. The Lyocell manufacturing process is simple and environmentally friendly, using a non-toxic solvent with a 99% recycle rate. Fibers, produced using Lyocell process, have superior mechanical properties comparing with viscose fibers [4].

The production of the Lyocell, using wood pulp cellulose as raw materials, has realized industrialization [5]. Large numbers of wood were cut for producing pulp material, leading to the increasing environmental problems. Usually, a tree has a growth cycle ranging from a few years to decades. Consequently, the

cost of producing the pulp material is relatively high, which limits the production and development of regenerated cellulose fibers [6]. As a result, much attention has recently been paid to find a cheaper, renewable, abundantly available resource. Compared to woods, bamboo has a shorter growth cycle and the production of bamboo pulp material carries a lower cost. Yang investigated the bamboo Lyocell fiber and found that this kind of fiber has better mechanical properties than those of bamboo viscose fiber, obvious negative ion effects, and antimicrobial activities [7]. Uddin produced a new cheaper regenerated cellulose fiber, the bagasse fiber, using the Lyocell process [8]. They studied effects of different coagulants on the fiber properties and found that the bagasse fiber has similar physical properties with commercial Lyocell fiber.

The main objective of our research is to find a cheaper source of material for regenerated cellulose fiber production. This paper innovates in using corncob residue as raw materials for spinning. Corncob residue fibers were produced through a conventional Lyocell spinning process by using corncob residue. In this study, the main components of corncob residue were first detected. Internal structure, mechanical properties, and application value of corncob residue fibers were analyzed.

MATERIALS AND METHODS

Materials

I) Corncob residue

The corncob residue after extraction of hemicelluloses (used for xylitol production) and lignin was provided by Shandong Yingli Industrial Co. Ltd, China as shown in figure 1.



Fig. 1. Corncob residue

II) Corncob residue fiber

Corncob residue fiber is a new regenerated cellulose fiber. Corncob residue fibers analyzed in this research are manufactured by Shandong Yingli

Industrial Company, China, using Corncob residue as materials by Lyocell spinning technology and equipments.

III) Contrast samples

The contrast samples are shown in table 1. The data of structural properties of Lenzing fibers and Tencel A100 were collected from others' studies [9–12]. The chemical structure and mechanical properties of other fibers and the raw materials are tested using the same methods.

Table 1

Sample	Manufacturer
Raw material for Incell fiber	Shandong Yingli Company
Incell fiber	
Viscose fiber	Lenzing Company
Lyocell fiber	
Tencel A100	Courtaulds Company

Methods

Fourier transform infrared spectroscopy measurements (FT-IR)

The FTIR spectra were obtained using the U.S. Nicolet Nexus 670 Fourier Transform Infrared-Raman Spectrometer. The wavelength range is $4000\text{ cm}^{-1} \sim 600\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} , and each spectrum has 128 scans.

Gel permeation chromatography measurements (GPC)

The molecular weight and molecular weight distribution of corncob residues and corncob residue fibers were determined using gel permeation chromatography (GPC). The large numbers of intramolecular and intermolecular hydrogen bonds in crystalline cellulose make it difficult to be dissolved in general solvent, which led to the limited application of GPC in cellulose than in polymer [13]. In 1979, McCormick found cellulose could be dissolved in a Dimethylacetamide (DMAc) solution containing 5%~10% LiCl without any degradation [14]. Since then, the GPC method using LiCl/DMAc as solvent and mobile phase becomes widely used for characterizing molecular weight of cellulose [15].

After preparation of cellulose solution [16], a Waters 1525 liquid chromatograph equipped with GPC was used to measure the relative molecular weight distribution of cellulose in the fiber.

X-ray diffraction measurements (XRD)

The crystallinity (X_c) and crystal orientation (f_c) of corncob residue fibers, Incell fibers, viscose fibers, Lyocell fibers and Tencel A100 were analyzed using an X-ray diffractometer (Rigaku D/max-2550 PC, Rigaku Corporation, Japan). The powder samples were scanned using Cu-K α radiation operated at 40 kV and 200 mA, in a 2θ range from 5° to 60° at a speed of $10^\circ/\text{min}$.

The crystallinity (X_C) of all fibers were calculated from the following equation:

$$X_C = \frac{I_C}{I_C + I_A} \quad (1)$$

Where I_C is the intensity of the crystalline peak, and I_A is the intensity of amorphous peak.

The crystal orientation (f_c) of all fibers was calculated according to Herman's crystal orientation functions with equations below:

$$I_C = \frac{3 \langle \cos^2 \theta \rangle - 1}{2} \quad (2)$$

where

$$\langle \cos^2 \theta \rangle = \frac{\int_0^{\frac{\pi}{2}} I(\phi) \cos^2 \phi \sin \phi \, d\phi}{\int_0^{\frac{\pi}{2}} I(\phi) \sin \phi \, d\phi}$$

Where ϕ is azimuthal angle and $I(\phi)$ is the relational expression between the intensity of diffraction peak and azimuthal angle.

Mechanical properties

The linear density of the fibers was measured following the China National Standard GB/T 14335-2008. The moisture regain of the fibers was tested according to the China National Standard GB/T 6503-2008. All samples were tested in duplicate.

Tensile properties of the fibers were tested following the China National Standard GB/T14337-2008. All measurements were repeated 50 times.

RESULTS AND DISCUSSION

FTIR analysis

The infrared spectra of corncob residue fiber, corncob residue, and cotton fiber are shown in figure 2. All spectra show the same characteristic absorption bands of cellulose, such as O–H stretching vibration absorption band near 3335 cm^{-1} , peaks around 1060 cm^{-1} in the fingerprint region, C–H stretching vibration absorption band in a wave number of 2895 cm^{-1} .

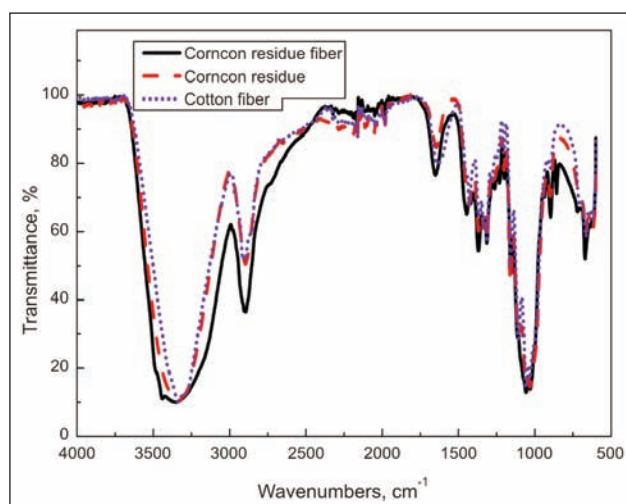


Fig. 2. The infrared spectra of corncob residue fiber, corncob residue, and cotton fiber

There were no obvious characteristic absorbency peaks of lignin for all spectra, such as the peak of carbonyl group of carboxyl and ester group near 1740 cm^{-1} , the peak of C=C aromatic ring around 1600 cm^{-1} , the peak of aromatic ring in a wave number of 1510 cm^{-1} , the peak of C–O stretching of lignin near 1240 cm^{-1} . Those all demonstrate that the composition of corncob fiber is cellulose but no lignin.

Infrared spectra of cotton fiber and corncob residue are similar, which illustrates the similar main components and content of each component in these two samples. However, infrared spectra of corncob residue fiber and corncob residue show a little difference in intensity at the same absorption peak, due to the content change of functional groups of cellulose in the spinning process.

GPC analysis

Molecular weight and its polydispersity of corncob residues and raw material for Incell fibers are shown in table 2. There is no difference in number average molecular weight (M_n) between corncob residues and raw material for Incell fibers. The peak relative molecular weight (M_p) of the corncob residue is slightly lower than that of raw material for Incell fiber. Polydispersity is the ratio of the average molecular weight to the number average molecular weight. The values of weight average molecular weight (M_w) and polydispersity for the corncob residue are slightly higher.

Table 2

Sample	M_n	M_w	M_p	Polydispersity
Raw material for Incell fiber	58331	203471	167858	3.49
Corncob residue	58287	215920	159856	3.70

Figure 3 shows the GPC curves of corncob residue and raw material for Incell fiber. Both curves are asymmetrical. It is mainly because both of them contain a small amount of hemicellulose, resulting in the relative molecular weight distribution curve is skewed, and has poor symmetry, large polydispersity [17]. The hemicellulose acts as a plasticizer, making it easy to improve the spinnability [18]. But the main peak of GPC curve of corncob residue is lower than that of wood pulp raw material for Incell fiber, indicating that the corncob residue has a larger polydispersity.

Combined with infrared spectrum analysis, it can be found that corncob residue has the same main components with the wood pulp raw material for Incell fiber, which is consist of are cellulose and a small amount of hemicellulose. What's more, relative molecular weight distribution curves of both materials above are similar, suggesting that the corncob residue in this study has potential to be used as the material for spinning instead of wood pulp.

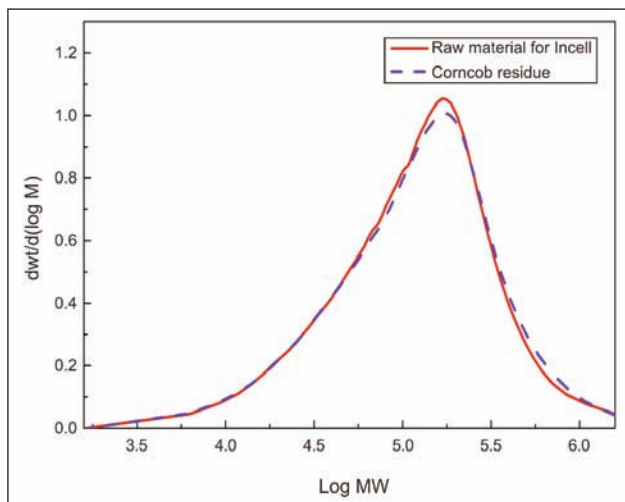


Fig. 3. The relative molecular weight distribution curve measured using GPC

When the solution was preparing in GPC method, the corncob residue is not completely dissolved and there is a tiny amount of undissolved flocculent substance at the bottom of the container. The substance could probably be the very tiny amount of ash impurities, which suggests the corncob residue need to be filtrated and purified before the spinning process.

XRD analysis

The crystallinity (X_c) and crystal orientation (f_c) of all fibers were measured by Wide-angle X-ray diffraction (WAXD) measurements. The X_c and f_c of all fibers are listed in table 3.

The crystallinity degree of corncob residue fiber is higher than that of any other fibers in this study, shown in table 3. The crystal orientation degree of corncob residue fiber is higher than that of Viscose fiber and Lyocell fiber, however, a litter bit lower than that of Incell fiber. Those all directly suggest that draft ratio of corncob residue fiber is relatively high during the spinning process. In order to obtain flexible fibers, the draft ratio should be reduced when manufacturing corncob residue fibers.

Linear density analysis

The average linear density of the corncob residue fiber is 10.33 dtex, which is too high if the fiber is

Table 3

Sample	Degree of crystallinity, X_c (%)	Degree of crystal orientation, f_c (%)
Corncob residue fiber ^a	61.9	79.5
Incell fiber ^a	51.7	80.4
Viscose fiber ^a	27.0	58.0
Lyocell fiber ^b	44.0	71.0
Tencel A100 ^c	53.6	—

^a New data in this study; ^b Data collected from Carrillo's research [9]; ^c Data collected from Wu's study [10].

used for textile. For further industry application, the linear density of the fiber must be reduced.

Moisture regain analysis

The moisture regains of the corncob residue fiber measured by oven method is 9.31%, which is slightly higher than moisture regains of cotton and much greater than that of synthetic fiber, such as polyester. But the moisture regains of corncob residue fiber are lower than moisture regain of regular viscose fiber (12%~14%) and Lyocell fiber (11%~13%) [19], which is possible because of that the degree of crystallinity and crystal orientation of corncob residue fiber is relatively high.

Mechanical properties analysis

The mechanical properties of corncob fibers, Incell fibers, viscose fiber, Lyocell fiber and Tencel A100 are listed in table 4. The load-elongation curve of Corncob residue fiber Incell fiber and Viscose fiber are shown in figure 4.

The tensile strength of corncob residue fiber was significantly higher than that of viscose fiber, suggesting that corncob residue fiber has broad application prospects and will play an important role in reducing the cost of production, effective utilizing of industrial and agricultural waste, and reducing of environmental pollution.

The tensile strength of four kinds of fibers produced by Lyocell spinning technology is generally higher than that of viscose fiber, which due to the Lyocell process technology. Except for viscose fiber, other fibers have the same spinning technology principle, but different parameters and raw materials. The

Table 4

Sample	Tensile strength		Elongation at break		Initial Modulus	
	average (cN/dtex)	CV (%)	average (%)	CV (%)	average (cN/dtex)	CV (%)
Corncob fiber ^a	2.72	6.54	8.01	28.7	112	8.90
Incell fiber ^a	3.75	11.9	11.9	16.8	72.4	28.9
Viscose fiber ^a	1.82	13.2	19.6	10.5	22.3	31.2
Lyocell fiber ^d	3.17	—	12.5	—	35.4	—
Tencel A100 ^e	3.97	—	12.6	—	41.4	—

^a New data in this study; ^d Data collected from Kreze's research [11]; ^e Data collected from Lou's study [12].

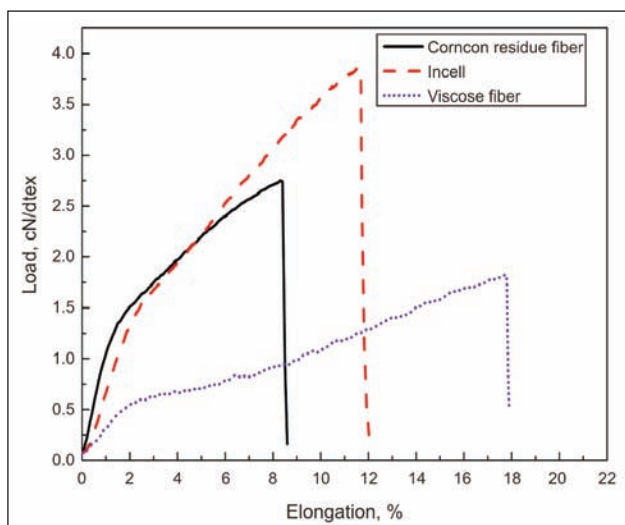


Fig. 4. Load-elongation curve of three kinds of fibers

degree of crystallinity and orientation can reflect differences of the spinning process parameters. Corncob residue fiber has high crystallinity and orientation degree, indicating that it should have high strength and modulus, smaller elongation. However, corncob residue fiber manufactured in this study has high modulus and low elongation characteristics but did not get a high strength, mainly because that the raw material has slightly large dispersion in molecular weight and the tiny amount of impurities. The purification of corncob residue and reduction of its cellulose dispersion inside should be an important research subject to improve fiber strength.

Among these five kinds of fibers, elongation of viscose fiber is the highest, followed by that of Tencel A100, Lyocell fiber, and Incell fiber, and the elongation of corncob residue fiber is the lowest. When draft ratio increases, the breaking elongation will decrease [20]. The initial modulus of corncob residue fiber is the highest, followed by that of Incell fiber and Tencel A100, and initial modulus of viscose fiber is the lowest. This is because of the high crystallization of corncob residue fiber, leading to its high rigid and low flexibility. Those evidences above all suggest that it is necessary to decrease the draft ratio in the future

producing process. The coefficient of variation of extension at break of corncob residue fiber is higher than that of Incell fiber, which may because of the uneven line density of corncob residue fiber.

CONCLUSIONS

Corncob residue fiber is a new regenerated cellulose fiber manufactured by Shandong Yingli Industrial Co. Ltd., China with corncob residue as main raw materials using Lyocell spinning technology. With analysis of chemical properties of corncob residue, mechanical properties of corncob residue fiber, the conclusions are shown as follows:

- (1) Main compositions of corncob residue are cellulose, slight hemicellulose and very tiny amount of spinning insoluble components. These components can be dissolved in the same solvent when dissolving wood pulp. Similar relative molecular weight distribution curves of corncob residue and wood pulp suggest that corncob residue can replace wood pulp as raw material for spinning in a certain extent. Compared to wood pulp, corncob residue has a similar number-average molecular weight, a slightly larger weight-average molecular weight, a lower peak-relative molecular weight, and a larger polydispersity.
- (2) The breaking strength of corncob residue fiber produced by Lyocell technology is 2.72 cN/dtex, which is higher than that of viscose fiber, slightly lower than that of Lyocell fiber and Tencel A100, indicating corncob residue fiber has broad application prospects.
- (3) The line density of corncob residue fiber is 10.33 dtex. The crystallinity of corncob residue fiber is higher than that of viscose fiber, Incell fiber, Lyocell fiber and Tencel A100. The degree of orientation of corncob residue fiber is higher than the other fibers, which lead that the standard moisture regain of corncob residue fiber is lower than that of the other fibers. The initial modulus of corncob residue fiber is higher than that of other fibers. Those all tell that a great effort should be taken in optimizing of manufacturing technology of corncob residue fiber.

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