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Properties of High-Quality Long Natural Cellulose Fibers from Rice Straw

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This paper reports the structure and properties of novel long natural cellulose fibers obtained from rice straw. Rice straw fibers have 64% cellulose with 63% crystalline cellulose, strength of 3.5 g/denier (450 MPa), elongation of 2.2%, and modulus of 200 g/denier (26 GPa), similar to that of linen fibers. The rice straw fibers reported here have better properties than any other natural cellulose fiber obtained from an agricultural byproduct. With a worldwide annual availability of 580 million tons, rice straw is an annually renewable, abundant, and cheap source for natural cellulose fibers. Using rice straw for high-value fibrous applications will help to add value to the rice crops, provide a sustainable resource for fibers, and also benefit the environment.

KEYWORDS: Cellulose; biofibers; rice straw; value addition

INTRODUCTION

With an availability of more than 580 million tons every year, rice straw is one of the most common sources of biomass available in the world (*1*, *2*). Currently, there is very limited use of rice straw in construction, agriculture, paper, packing, fuel, and energy industries (*3*, *4*). Most of the rice straw available after harvest is either left on the ground or burnt (*3*). Tilling the straw left on the ground into the soil is expensive and costs about $40 per acre. In addition, rice straw has slow degradation rates, clogs field implements, and is reported to harbor rice diseases (*3*). Although burning of rice straw is fast and economical and kills the disease-causing bacteria, the pollution caused due to the burning of rice straw is of concern to the environment (*3*). There are several pieces of legislations that restrict the burning of rice straw (*5*).

Industries using fibers are seeking a cheap and environmentally friendly alternative to the natural and synthetic fibers in current use due to several disadvantages associated with the production and use of these fibers. Natural fibers such as cotton need land, water, and other natural resources to grow. Growing cotton is environmentally unfriendly because it consumes >25% of the total insecticide used in the world (*6*). Synthetic fibers are from nonrenewable petroleum resources and consume more energy than that required to produce fibers from a renewable resources (*7*). The process of synthetic fiber production may be environmentally unfriendly, and products made from synthetic fibers are difficult to dispose of after use. Therefore, several attempts have been made to find alternative sources for fibers, especially from annually renewable resources.

Agricultural byproducts such as cornhusks, corn stalks, pineapple and banana leaves, and coconut husks (coir fibers) have been used to extract natural cellulose fibers (*8*−*11*). Although rice and wheat straw are cheap and abundant sources available throughout the world, no reports are available on the production of high-quality natural cellulose fibers from rice or wheat straw. However, both rice straw and wheat straw have been used to obtain regenerated cellulose fibers (*12*). For the first time, we have developed a process to produce high-quality natural cellulose fibers from rice straw with properties similar to those of linen. This paper reports the method used to obtain high-quality fibers from rice straw and the structure and properties of the fibers produced. Producing fibers from rice straw would not only mean an environmentally friendly alternative to the natural and synthetic fibers currently in use but will also add value to the rice straw and benefit the farmers economically.

EXPERIMENTAL PROCEDURES

Materials. Rice straw in whole form was supplied by courtesy of the California Rice Commission. Reagent grade sodium hydroxide, acetic acid, sulfuric acid, nitric acid, and chromic oxide used in this study were obtained from VWR International, Bristol, CT. Pulpzyme and cellulase (Cellubrix L) were obtained from Novozymes, Franklinton, NC.

Fiber Extraction. Fibers were produced from rice straw using a combined chemical and enzymatic extraction. Many trials were conducted by varying the extraction conditions such as concentration of chemicals and time and temperature of treatment. Alkali concentrations of 0.1−3 N, temperatures from ambient to 100 °C, and times from 20 min to 48 h were considered for the treatments. Although several of the conditions produced fibers, either the fibers obtained were coarse or the fiber yield was low. However, no major differences were observed in the mechanical properties, such as breaking tenacity and breaking elongation, of the fibers obtained from the different

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Table 1. Composition, Structure, and Properties of Rice Straw Fibers

composition		structure		properties	
cellulose, %	64	% crystallinity	62.8	denier	27 ± 14
lignin, %	8	CI	57	length, cm	2.5–8.0
ash, %	5	Crystal size, nm	3.75	strength, g/denier[b]	3.45 ± 0.6
others[a], %	23	MFA, deg	19.4	elongation, %	2.19 ± 0.3
		unit cell dimensions		modulus, g/denier[b]	200 ± 26.5
		a, Å	7.56 ± 0.3	work of rupture, g/denier[b]	0.038
		b, Å	10.26 ± 0.17	moisture regain, %	9.8
		c, Å	8.03 ± 0.03		
		β, deg	85.2 ± 2.4		
		single-cell length, mm	0.6 ± 0.15		
		single-cell width, μm	8.1 ± 1.35		

[a] Others are mostly hemicellulose. [b] One gram per denier is approximately 130 MPa.

conditions. In the optimized condition, rice straw was treated with 1 N sodium hydroxide solution for 40 min at boil with 5% of straw by weight in the alkali solution. The treated fibers were washed in water to remove the dissolved substances, and the fibers formed were dried under ambient conditions. The coarse fibers obtained after the alkali treatments were treated with 1% (based on weight of the fiber) each of Pulpzyme and cellulase. A mild concentration of cellulase was used to clean the surface of cellulose fibers. This treatment resulted in finer fibers with better luster and a softer hand. The enzyme treatment was carried out at 55 °C for 40 min with 5% of the fibers in the enzyme solution at a pH of 6.0 adjusted using a buffer. Fibers obtained after the enzyme treatment were thoroughly washed in water and dried under ambient conditions. These fibers are multicellular; several single cells are bonded together by lignin and other materials. The bundle of single cells now called fibers was macerated to separate the single cells from the fibers (*13*). Maceration was done by using equal volumes of 10% chromic (w/w) and 10% (w/w) nitric acid solution with a fiber to acid ratio of 1:15. Fibers were dipped in the maceration solution, heated to 60 °C, and then allowed to stay in the solution at room temperature for 24 h. After the treatment, the single cells formed were washed thoroughly in hot water and dried using acetone. These single cells are typically referred to as fibers in the pulp and paper industry.

Fiber Composition. Fibers obtained after the alkali and enzyme treatments were analyzed for their cellulose and lignin contents. The amount of cellulose in the fibers was determined as acid detergent fiber (ADF) using AOAC method 973.18 (*14*). Lignin in the crude fibers was determined as acid-insoluble (Klason) lignin according to ASTM standard method D1106-96 (*15*). The percent ash in the fibers was determined by burning the fibers at 550 °C for 16 h. The percent difference in weight before and after burning the fibers was taken as the percent ash in the samples. Two replications were done for each compositional analysis, and the average is reported.

Morphological Structure. A Hitachi model S3000N scanning electron microscope (SEM) was used to study the morphological features of the fiber strands mechanically extracted from the untreated rice straw, alkali- and enzyme-extracted fibers, and also the single cells in the fibers obtained by maceration. Samples to be observed under the SEM were laid on an aluminum stub using a conductive adhesive tape and were sputter-coated with gold palladium prior to observations at a voltage of 15 kV. The length and width of the single cells were measured from the SEM pictures, and the mean and standard deviations are reported.

Physical Structure. The physical structure of the fibers in terms of the percent crystallinity, crystal size, dimensions of unit cells, and orientation of the cellulose crystals and microfibrils to the fiber axis was determined using X-ray diffraction. A Rigaku D-max/BΘ/2Θ X-ray diffractometer with Bragg−Brentano parafocusing geometry, a diffracted beam monochromator, and a copper target X-ray tube set to 40 kV and 30 mA was used to determine the percent crystallinity, crystal size, unit cell dimensions, and crystallinity index (CI). Apparent crystal size at the 002 plane was calculated using Scherrer's equation (*16*). A peak resolution program TOPAZ was used to determine the peak positions and intensities for calculating the dimensions of the unit cell. Dimensions of the unit cells in terms of *a*, *b*, and *c* values and the β angle were determined from the diffraction intensities using the equations reported in the literature (*17*). CI was determined from the intensity differences in the peak positions at 18° and 22° (*18*). A Bruker D8 Discover model diffractometer was used to record the X-ray diffraction patterns, which are visual indicators of the orientation of the cellulose crystals in the fibers to the fiber axis. The arrangement of the microfibrils in the fiber in terms of the microfibrillar angle (MFA) was also determined from the diffraction patterns. A bundle of fibers was mounted on a specially designed sample holder with the axis of the fiber perpendicular to the X-ray beam. The 002 peak intensities in the diffraction patterns were fit into two Gaussian curves using a nonlinear least-squares algorithm with the software program Microcal ORIGIN to obtain the MFA.

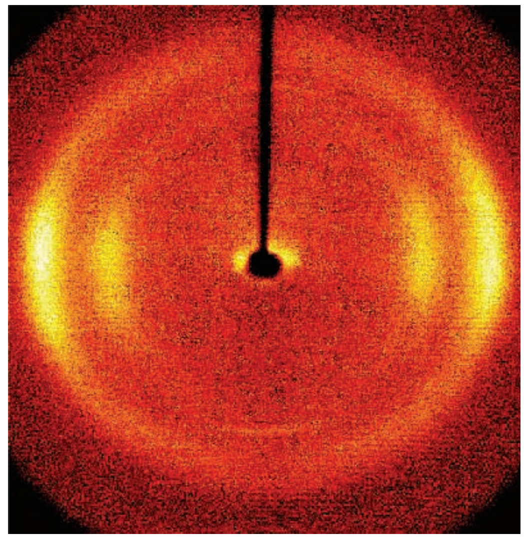

Figure 1. Diffraction pattern of a rice straw fiber bundle showing bright and short diffraction arcs indicative of oriented cellulose in the fibers.

Fiber Properties. The fineness of the fibers was measured in terms of denier (weight in grams per 9000 m of the fibers) by weighing a known length of the fibers. Mechanical properties of the fibers were measured using an Instron tensile testing machine. A gauge length of 25 mm with a crosshead speed of 18 mm/min was used for the tensile tests. Four sets of 10 fibers each were tested to determine the fiber properties. The average ± one standard deviation of fiber properties is reported. Moisture regain of the fibers was determined by drying the fibers at 105 °C in a hot air oven and later allowing the fibers to regain moisture under standard testing conditions of 65% relative humidity and 21 °C.

RESULTS AND DISCUSSION

Fiber Composition. Rice straw contains about 40% cellulose, 30% hemicellulose, 15% silica, and about 15% lignin (*2*). About 50% of the cellulose in rice straw is obtained as high-quality fibers after the alkali and enzyme treatment. Rice straw fibers

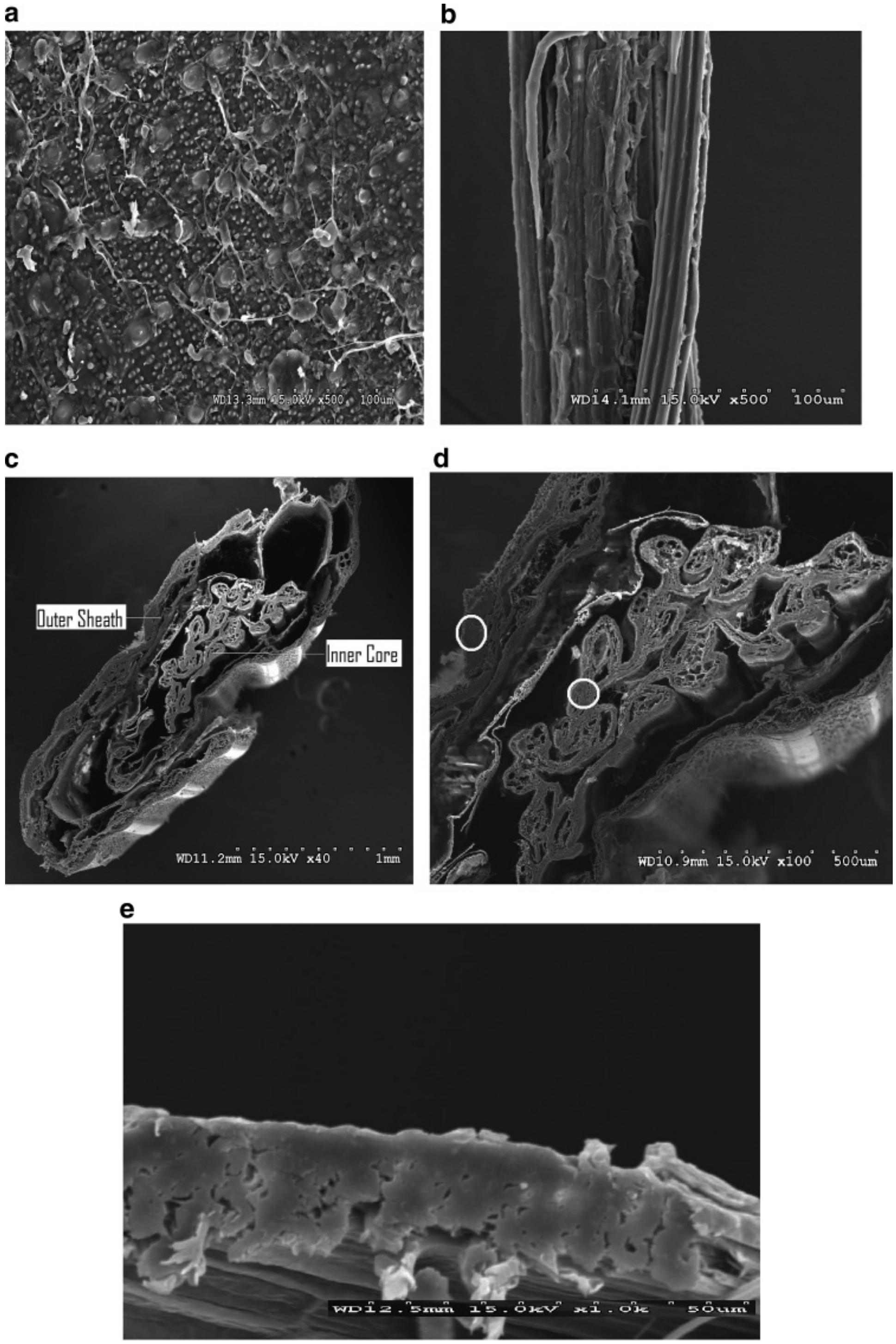

Figure 2. (**a**) SEM picture of the surface of untreated rice straw showing surface deposits; (**b**) SEM picture of the surface of the rice straw fiber bundle obtained after the alkali and enzyme treatments with relatively clean surface; (**c**) cross section of an untreated rice straw showing the inner core wrapped by an outer sheath (bundles of single cells are seen in both the sheath and core); (**d**) higher magnification picture of an untreated rice straw showing the location of fibers (circled) in the sheath and core; (**e**) SEM picture of a cross section of a relatively large fiber bundle selected to show the presence of single cells. The single cells have a small lumen at the center.

obtained after alkali and enzyme extraction are composed of 64% cellulose, 8% lignin, and about 5% ash as given in **Table 1**. Hemicellulose probably is a major component in the remaining constituent of the rice straw fibers. The cellulose content in rice straw fibers is similar to that in linen (64%) but lower than that in cornhusk, cornstalk, and pineapple leaf (PALF) fibers, which have about 80% cellulose (*8−10*). The lignin content in rice straw is higher than that in linen (2%) but similar to that in cornhusk and cornstalk fibers (*8−10*). Although rice straw has about 15−20% silica, most of it is removed during fiber extraction, and the rice straw fibers have <5% silica.

Physical Structure. The crystalline parameters of rice straw fibers in terms of the percent crystallinity, crystal dimensions, and orientation measured as CI are given in **Table 1**. The percent crystallinity of rice straw fibers at about 63% is similar to the percent crystallinity of linen (65%) but higher than that in cornhusk, cornstalk, and PALF fibers, which have about 50% crystallinity (*8−11*). **Table 1** also gives the dimensions of the

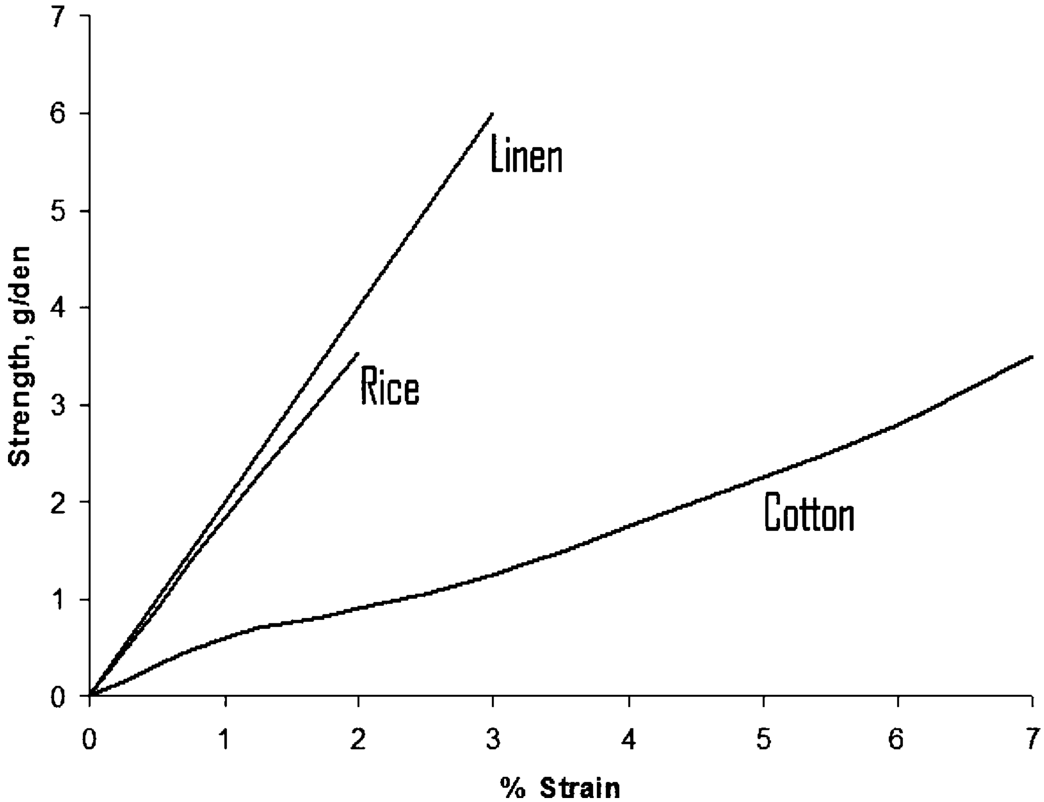

Figure 3. Stress–stain curve of rice fibers compared with cotton and linen.

cellulose crystals in the rice straw fibers. Rice straw fibers have *b* and *c* axes similar to those of cotton cellulose but have a smaller dimension of the *a* axis. The β angle of cellulose crystals in rice straw fibers is close to the 84° recognized for cotton. On the basis of the unit cell dimensions, it is reasonable to believe that the rice straw fibers have cellulose I crystal structure, similar to that found in native cotton and other common cellulose fibers. The size of cellulose crystals in rice straw fibers is about 3.8 nm, larger than that in linen (2.8 nm) but similar to that in cornhusk and cornstalk fibers (3.2 and 3.8 nm, respectively) (*8*, *9*).

CI and MFA indicate the arrangement of cellulose crystals and microfibrils, respectively, in the fibers to the fiber axis. Microfibrils are the smallest fibrous elements in single cells with widths of about 10−20 nm and lengths of several micrometers. A higher CI and a lower MFA indicate more parallel arrangement of the cellulose crystals and the microfibrils to the fiber axis, respectively. Rice straw fibers have lower CI (57) but higher MFA (19.4°) than linen, which has a CI of 70 and a MFA of 6−10° (*19*). In addition to the quantitative determination of the orientation of cellulose crystals in the fibers, the orientation of the crystals can be visually assessed from the patterns of the diffracting arcs in an X-ray diffraction picture. **Figure 1** shows the diffraction pattern of the rice straw fibers. As can be observed from the figure, rice straw fibers have bright and short diffraction arcs, indicating the better orientation of the cellulose crystals to the fiber axis.

Morphological Structure. Fibers obtained from rice straw are composed of a bundle of single cells held together by lignin and other binding materials. Panels **a**−**d** of **Figure 2** show the morphological features of the untreated rice straw and the fibers obtained after the alkali and enzyme treatments. The untreated rice straw has a layer of substances mostly composed of lignin, silica, and other noncellulosic substances on the outer surface as seen from **Figure 2a**. The alkali and enzyme treatments remove most of the surface substances, resulting in fiber bundles that have a relatively smooth surface as shown in **Figure 2b**. **Figure 2c** shows the cross section of an untreated rice straw in which a distinct inner core wrapped by an outer sheath can be seen. Both the outer sheath and the inner core were used for fiber extraction. The location of fibers in the sheath and core of the straw is shown in **Figure 2d**. The cross section of a rice straw fiber bundle shown in **Figure 2e** has a number of single cells held together by lignin and other binding materials. The single cells have a thick cell wall and a relatively small lumen compared to the lumen in cell walls of cornhusk fibers (*10*). The voids between the single cells probably serve as capillaries for moisture absorption and transportation.

Single cells in the rice straw fibers have lengths of about 0.3−0.8 mm as given in **Table 1** and within the range of single-cell lengths (0.4−3.4 mm) reported earlier (*2*). Also, the length of the single cells in rice straw fibers is similar to those in other sources of biomass such as cornhusk and cornstalks, which have single cells of about 0.5−1.5 mm (*8*, *9*). However, single cells in rice straw fibers are 8−15 μm in width, similar to that reported in the literature but finer than those in cornhusks (10−25 μm) and cornstalks (14−35 μm) (*8*, *9*). The single cells in rice straw fibers are circular and have tapered ends but do not have as many convolutions as seen in cornhusks (*9*).

Fiber Properties. Fibers obtained from rice straw have lengths from 2.5 to 8.0 cm and an average denier of 27 as shown in **Table 1**. Factors such as the length and width of the single cells play a major role in determining the length and fineness of the multicellular fibers obtained. Rice straw fibers have smaller width single cells, which produces finer denier fibers. As seen from **Table 1**, rice straw fibers have good strength and elongation required for textile and other high-value applications. The strength of the rice straw fibers is higher than that of cornhusk, cornstalk, or PALF fibers, which have strengths of about 2.7, 2.2, and 3.0 g/denier, respectively (*8*−*11*). The elongation of the rice straw fibers is similar to that of cornstalk and PALF fibers (2.2%) but lower than that of cornhusk fibers (13−16%) (*8*−*11*). The higher percent crystallinity and better orientation of the cellulose crystals in rice straw fibers contribute to its higher strength and lower elongation, respectively, compared to the other biomass fibers. As seen from **Figure 3**, rice straw fibers have a modulus of about 200 g/denier, similar to that of linen (203 g/denier) but higher than that of cornhusk and cornstalk fibers (36 and 127 g/denier, respectively) (*8*−*10*, *19*). The modulus of a fiber determines the softness and flexibility of the products made from the fibers. A lower modulus means a softer and flexible fiber. Although rice straw fibers have a relatively high modulus and are therefore not as soft and flexible as cornhusk and cornstalk fibers, products made from the rice straw fibers will be durable because of their high work of rupture, which is similar to that of linen fibers. The fineness, length, strength, elongation, and modulus of rice straw fibers indicate that rice straw fibers are closer to linen and would be suitable for most high-value fibrous applications.

Rice straw is a cheap, abundant, and annually renewable source suitable for producing high-quality natural cellulose fibers. For the first time, natural cellulose fibers from rice straw with properties similar to those of linen have been produced using cheap and common chemicals. The composition, structure, and properties of the rice straw fibers indicate that the fibers are suitable for most high-quality fibrous applications. On the basis of the structure and properties of the fibers, we expect that rice straw fibers could be used to produce textiles, composites, and other fibrous products similar to those produced from the common natural and synthetic fibers. Using rice straw for high-quality fibrous applications will add value to the rice crops, mitigate our concerns regarding the burning or disposing of rice straw, and provide us an environmentally friendly alternative to replace at least a part of the environmentally unfriendly natural and synthetic fibers currently in use.

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