Novel Regenerated Cellulose Fibers from Rice Straw

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ABSTRACT: Regenerated cellulose fibers from rice straws with a diameter of 10 to 25 μm and initial modulus of 11 to 13 GPa were prepared by wet spinning in rice straw/*N*-methylmorpholine-*N*-oxide (MMNO) solution. X-ray diffraction analysis indicates that the rice straw regenerated fibers are classified as cellulose (II). This observation indicates a potential utility of rice straw as an alternative to wood pulp as a cellulose-based fiber material. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1705–1708, 2001

Key words: rice straw; regenerated fiber; cellulose; cellulose-based fiber

INTRODUCTION

Rice is one of the major crops in the world. Global rice production in 1999/2000 was projected at a record 395.9 million tons.[1] Associated with rice production is a corresponding annual production of rice straw. In round numbers, on a dry basis, rice straw contains 43 to 49% cellulose, 25 to 28% hemicellulose, 15.8% lignin, and 12 to 15% silica. Resins, gums, proteins, and mineral compounds are also present.[2] The straw has been removed by the practice of open-field burning or used as fodder. Recently, low-cost lignocellulosic biomass, such as rice straw, has become attractive as a renewable resource because it is available in large quantities and routinely cultivated. There have been some efforts to study the effective treatment techniques for efficient utilization of lignocellulosic biomass.

One way to utilize rice straw is to hydrolyze it enzymatically into fermentable sugars, which can then be converted to ethanol.[3,4] Another way is to use it in the pulp and paper industry.[5] Straw paper has been available for centuries and has been used in a wide variety of commercial applications.

There are several studies on the process for making regenerated cellulose articles, such as fibers and films, from wood pulp.[6,7] Researchers have used several solvent systems for cellulose such as *N*-methylmorpholine-*N*-oxide (MMNO)/H_2O, trifluoroacetic acid (TFA)/1,2-dichloroethane, LiCl/dimethylacetamide (DMAc) solution, and so forth.[8] The most appropriate solvent for cellulose from among these solvents is MMNO. The ecological safety of this compound and its high activity of interaction with cellulose stimulated extensive investigations into the process of cellulose dissolution in MMNO and the properties of solutions, which were necessary to develop the optimum technology of obtaining cellulose-based fibers and films.[9]

The process for making regenerated cellulose fibers from rice straw has only rarely been reported in the literature. The twofold objective of this work was (1) to use low-value agricultural waste to prepare environmentally friendly regenerated rice straw fibers and (2) to evaluate rice

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straw as a new source of fiber materials by spinning the rice straw dissolved in a tertiary amine N-oxide solvent. Straw fibers have some advantages, both economically and environmentally, because rice straw is a low-value agricultural residue and can be obtained in large quantities after cultivation. It is expected that rice straw can be an important alternative to wood as a source of cellulose-based materials.

EXPERIMENTAL

Materials

Pure MMNO (97%) and propyl gallate (97%) were obtained from Aldrich Chemicals (Milwaukee, WI). Both were used without any further treatment. The raw material used in this study was Korean rice straw (obtained locally), which had been reduced to about 10 cm by chopping and then used in the investigation. The materials were treated under an alkali condition (20% sodium hydroxide) to break down hemicellulose, lignin, and other soluble materials in the biomass and to obtain purer cellulose for various testing times (12 h to 5 days) at room temperature, giving rise to the yield of about 50%. The alkali-treated rice straw was washed to remove the remaining alkali.

Preparation of Fibers

A mixture of 78 g of MMNO and 11.3 mL distilled water was stirred at 50°C until dissolved. Then alkali-treated rice straw (12 g) was added, together with 0.05 wt % of propyl gallate, which was used to prevent reduction of polymerization degree caused by oxidation of cellulose.[10] The mixture was stirred at 100°C until clear. The dark honey-colored solution was poured into a spinning vessel. A nitrogen gas supply was then used to force the solution through a single 0.15-mm spinneret orifice. Spinning dope made from rice straw solution in MMNO was extruded at 100°C from the spinning nozzle into the air. After running for 50 mm in the air, it entered into the coagulant bath (water). The fiber was elongated in the coagulant bath (25°C) to some extent by the tension applied by a take-up roller, then removed from the coagulation bath at a velocity of 10 m/min. After winding, the filaments on the bobbins were immersed in the distilled water for 24 h to extract the remaining solvent. Finally, the fibers were dried in the oven at 50°C for 6 h.

Measurements

The purity of alkali-treated rice straw cellulose was determined by the method of Goering and Van Soest.[11] Mechanical testing of blend fibers was determined at room temperature using an Instron (4301) tensile tester, equipped with a 2-kgf load cell. The gauge length was 50 mm. The photomicrographs of the starting alkali-treated rice straw and regenerated rice straw fibers were taken by Hitachi SEM S-4200 and optical microscopy (Olympus, Lake Success, NY).

RESULTS AND DISCUSSION

Purity of Alkali-Treated Rice Straw Cellulose

The dissociation of lignin from cellulose is a key step in the utilization of cellulose for the desired purpose.[12] The purity of alkali-treated rice straw cellulose was increased proportionately with

Table I Rice Straw Components After 20% NaOH Treatment

Composition	Rice Straw Composition (Dry Basis) (%)			
Treating Time (h)	Cellulose	Hemicellulose	Lignin	Ash
Untreated rice straw	44.0	26.0	15.8	14.2
6	60.4	18.8	5.1	15.7
12	75.3	11.2	2.2	11.3
18	85.7	7.0	1.7	5.6
24	92.9	3.6	1.4	2.1
30	92.4	3.9	1.5	2.2
36	93.6	3.5	1.4	1.5
42	93.6	3.3	1.2	1.9

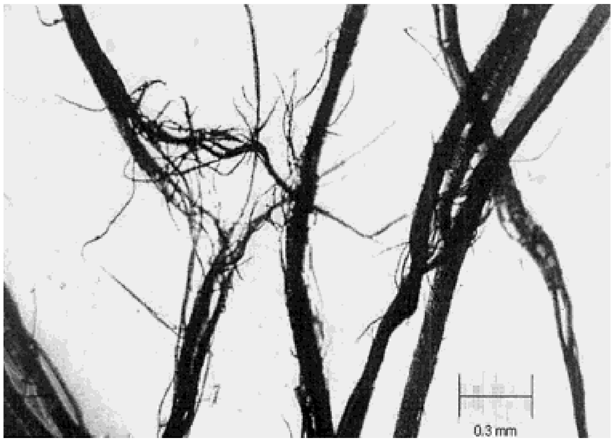

Figure 1 Micrograph of alkali-treated rice straws (magnification ×100).

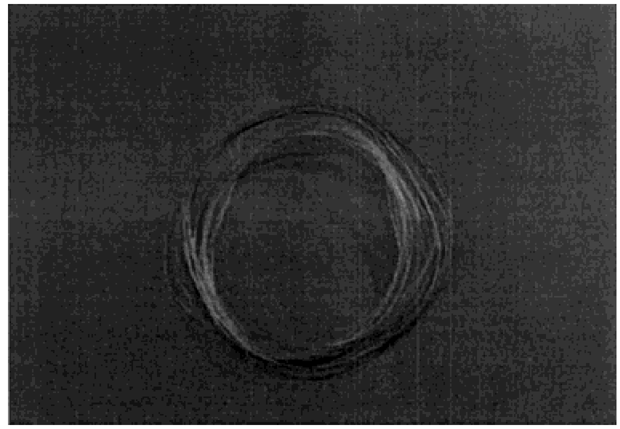

Figure 2 Rice straw regenerated fibers prepared by wet spinning.

treatment time up to 24 h, although thereafter the increment of cellulose purity was slowed. The optimum condition for cellulose extraction from rice straw was to treat rice straw with 20% NaOH for 24 h at room temperature (Table I).

Morphology of Alkali-Treated Rice Straw

The physical characteristics of the alkali-treated rice straw, such as apparent diameter and length of the fibers, were observed by optical microscopy. It is clear that the rice straws were separated into fibrils. The fibrils appeared to have been somewhat distorted by the alkali treatment. The straw fibers formed by alkali treatment had an apparent diameter of 5–10 μm, a round cross section, and an accumulated microfibril structure. The apparent length of the rice straw fibril was 50 to 100 mm (Fig. 1).

Properties of Regenerated Rice Straw Fibers

SEM and photo images of regenerated rice straw fibers prepared by wet spinning and the fractured surface of the fibers are shown in Figures 2 and 3. Typical as-spun fibers have a diameter of about 10 to 25 μm. The fibrillate nature of the fibers is obvious and the fibrils are fairly aligned. The cross section of the regenerated fibers is almost a true circle and dense, and the fibers are fractured in a brittle fashion, which can be attributed to high modulus. The specific gravity of the regenerated fibers, determined by the flotation method (tetrachloroethane/n-heptane system at 25°C), was found to be 1.45, which is in good agreement with that of natural cellulose fibers.[13] X-ray diffraction patterns of raw materials and regenerated fibers are shown in Figure 4. Rice straw is crystallographically cellulose (I), revealing typical characteristic peaks, as observed for natural fibers.[14] The regenerated cellulose fibers had double peaks at 19.8° 2θ for the (110) plane, 22.0° 2θ for the (200) plane, and a small broad peak at 12.2° 2θ for the $(1\bar{1}0)$ plane. These X-ray traces

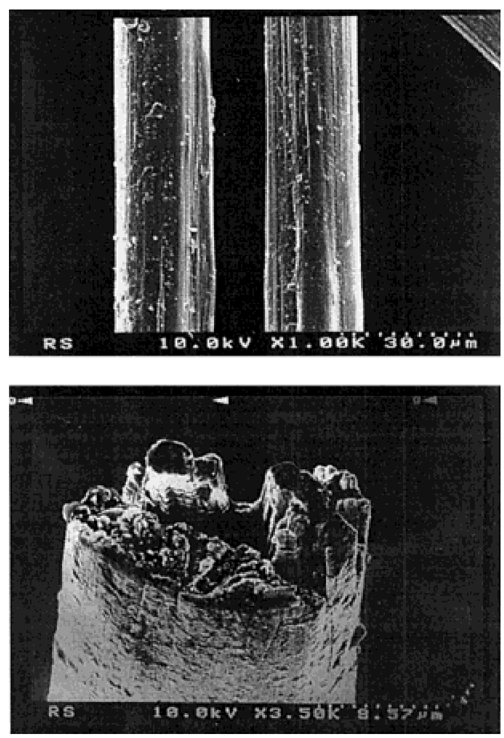

Figure 3 Rice straw regenerated fibers prepared by wet spinning. Top: surface of the fibers; bottom: fractured surface of the fibers.

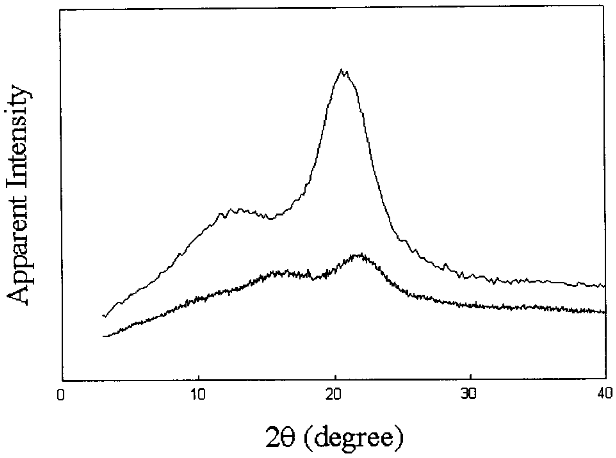

Figure 4 X-ray diffraction patterns of regenerated fibers and raw materials (in descending order).

are in accord with those of commercial regenerated fibers; therefore, rice straw regenerated fibers can be classified as type (II) cellulose fibers.[15]

An Instron tensile tester with a 2-kgf load cell was used to perform a mechanical test on single filaments. The tensile strength of all the as-spun fibers was between 0.28 and 0.40 GPa and the initial modulus was between 11 and 13 GPa. The tensile strength of the rice straw regenerated fibers was in the range similar to that of the commercial fibers. The initial modulus, however, was relatively higher than that of commercial regenerated fibers.[16]

CONCLUSIONS

Novel regenerated cellulose fibers were prepared by wet spinning in MMNO solution. The mechanical properties and structural characteristics of the resulting novel regenerated cellulose fibers were compared with commercial regenerated cellulose fibers and natural fibers. The novel cellulose fiber revealed a cellulose (II) crystal from X-ray analysis. It is expected that rice straw can be an important alternative to wood as a source of cellulose-based fiber materials.

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