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Excellent oil absorbent kapok [*Ceiba pentandra* (L.) Gaertn.] fiber: fiber structure, chemical characteristics, and application

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Abstract The study focused on kapok [Ceiba pentandra (L.) Gaertn.] fruit as a biomass for effective utilization. Kapok fruits were harvested just before full maturation at the campus of University of the Philippines Los Baños and in southern Vietnam. The kapok fibers are utilized locally as fiberfill in pillows, quilts, and some soft toys. Kapok fiber was isolated and analyzed microscopically, and the physicochemical properties were determined by spectroscopic methods. Some tests were done to determine the effective utilization of kapok fiber. Microscopic analysis of the higher structure of kapok fiber gave quite different results from cotton fiber, which has a significantly homogeneous hollow tube shape and is composed of cellulose (35% dry fiber), xylan (22%), and lignin (21.5%). Kapok fiber is characterized by having a high level of acetyl groups (13.0%). Usually cell walls of plants contain about 1%–2% of acetyl groups attached to noncellulosic polysaccharides. Kapok fiber is significantly hydrophobic and does not get wet with water. Thus, the absorptivity of oil was tested. The fiber selectively absorbed significant amounts of oil (40 g/g of fiber) from an oil suspension in freshwater and seawater. It is suggested that this fiber could be used to recover oil spilled in seawater.

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Introduction

Kapok [*Ceiba pentandra* (L.) Gaertn., Family Bombacaceae] trees, which originated in tropical India, are found widespread in several plantations in Southeast Asia. The kapok fiber in fruits is currently utilized as packing materials for pillows and quilts in Southeast Asian countries. The kapok seeds contain oil similar to cotton oil. The leaves and bark have medicinal values (used by the Chinese), and the trunk has been tested as resources of pulp for papermaking.[1] In this paper, the kapok fruit was harvested just before full maturation, and fibers were isolated. Kapok fiber is significantly hydrophobic (i.e., does not wet by water). The chemical composition was analyzed, and the chemical structures were characterized to understand the high hydrophobicity of the fibers. The absorption property of the fiber was tested using machine oil.

Materials and methods

Kapok fiber

Kapok fruit was harvested just before full maturation at the campus of University of the Philippines Los Baños, and the fibers were isolated from the seeds and fruit cover. Kapok fiber was dried at 40°C in a vacuum oven. Each fruit packed about 13–15 g (dry weight) of fiber. Kapok fiber was also collected from southern Vietnam.

Chemical analyses

Kapok fiber was extracted sequentially by boiling with diethyl ether (three times for 1 h) and alcohol-benzene (1:2) using with a Soxhlet extractor (8 h) then with hot water at

37°C overnight. An extract-free sample was analyzed for lignin content using the Klason procedure including the acid-soluble lignin determination[2] and acetyl bromide procedure.[3] The neutral sugar composition of the cell wall was determined by the alditol acetate procedure.[4] The sample was hydrolyzed with 1M NaOH at 37°C overnight and 4M NaOH for 2h at 170°C to determine the esterified and etherified phenolic compounds.[5] Aromatic constitution of lignin of the samples was characterized by alkaline nitrobenzene oxidation.[6] Acetyl content was determined by the ^{1}H-nuclear magnetic resonance (NMR) procedure after hydrolysis with 25% D_2SO_4/D_2O at 90°C for 90min using ethanol as an internal standard.[7] Klason lignin (which from kapok fiber is significantly different from that of woody plants) was acetylated and characterized by for ^{1}H-NMR and ^{13}C-NMR in $CDCl_3$. The molecular weight distribution was determined by high-performance size-exclusion chromatography (HPSEC) in tetrahydrofuran (THF) using polystyrene standards as markers. The extract-free kapok fiber was treated with $NaClO_2$/acetic acid to obtain holocellulose.

Microscopic observation

The original (untreated) kapok fiber, extract-free samples, and holocellulose of kapok fiber were characterized by optical and scanning electron microscopies and X-ray diffraction techniques.

Oil absorptivity

Machine oil (10g) colored by dye to visualize its absorption was suspended in water (100g) in a beaker. The original kapok fiber (0.2g) was added and mixed for 1min at room temperature. The oil was found to be absorbed immediately by the fiber. The fiber was then picked out and weighed. The remaining oil in the beaker was removed by adding fresh kapok fiber, and the weight of water in the beaker was determined to calculate the water absorptivity of the fiber. The extract-free sample and holocellulose of kapok fiber were also tested as above.

Results and discussion

The color of the original kapok fiber is pale yellowish brown for Philippine kapok and pale yellow for Vietnamese kapok. The solvent extraction process with diethyl ether, hexane, chloroform, ethanol, ethanol-benzene (1:2v/v), or ethylacetate could not remove these colors. The fiber was significantly hydrophobic, although the extract with diethylether was quite low for kapok fibers from both the Philippines and Vietnam. Lignin content and neutral sugar composition of cell walls were similar to those of cell walls of typical angiosperm plants (Table 1). The cell walls of kapok fibers are probably composed of cellulose and xylan as wall polysaccharide, with a small amount of arabinosyl residues, suggesting no or fewer middle lamella fragments.[8]

Table 1. Chemical composition of kapok fibers

Substance	Content (% of ODM)	
	Philippines	Vietnam
Ash	0.8	0.5
Extracts		
Diethyl ether	0.6	0.7
Alcohol benzene (1:2)	2.2	1.8
Hot water	1.8	2.0
Total	4.6	4.5
Lignins		
Klason lignin	17.4	15.4
Acid-soluble lignin	4.1	3.8
Total	21.5	19.2
AcBr lignin	20.8	18.8
Neutral sugars		
Rhamnose	0.4	0.5
Arabinose	0.3	0.2
Xylose	21.9	22.8
Mannose	0.8	0.6
Galactose	0.4	0.3
Glucose	35.1	38.5
Total	58.9	62.9
Acetyl group	13.0	12.5

Table 2. Alkaline nitrobenzene oxidation products of kapok cell walls

Product	Philippines	Vietnam
Oxidation product[a]		
p-Hydroxybenzaldehyde	0.3	0.2
Vanillin	5.1	4.8
Syringaldehyde	21.3	22.2
p-Hydroxybenzoic acid	0.0	0.0
Vanillic acid	0.3	0.4
Syringic acid	2.4	2.1
Total yield (% of total lignin)	29.5	29.7
H/V molar ratio	0.06	0.04
S/V molar ratio	3.67	3.90

H/V, *p*-hydroxypheugl/guaiacyl; SV, syringyl/guaiacyl
[a] Percent of sum of Klason lignin and acid-soluble lignin

Esterified or etherified phenolic compounds were not detected by alkaline hydrolyses.

In general, noncellulosic polysaccharides, such as arabinoxylan from the walls of angiosperms and galactomannan from gymnosperms, are substituted by acetyl groups within a range of 2%–4% of cell walls.[7] In contrast, the wall polysaccharides of kapok were substituted with significantly high levels of acetyl groups (Fig. 1, Table 1). The degrees of substitution of acetyl groups on the xylosyl residue were calculated as 1.43 and 1.38 for kapok fibers from the Philippines and Vietnam, respectively, with the assumption that all acetyl groups are attached to xylan molecules of kapok cell walls.

The lignin content of kapok fibers from the Philippines and Vietnam were 21.0% and 19.0% respectively. The nitrogen content of Klason lignin was less than 0.1%, suggesting the absence of protein in kapok fiber. A significant amount of Klason lignin was dissolved in acetone and the lignin was then acetylated to measure the NMR spectra and molecular weight distribution. The ^{1}H-NMR spectra of

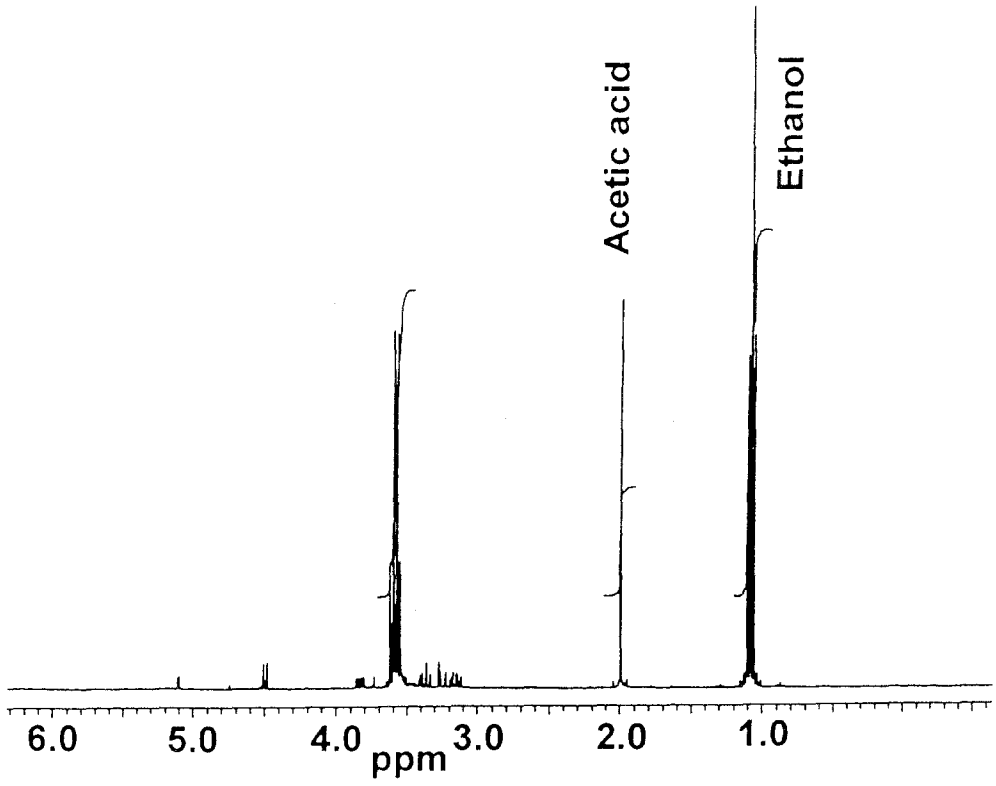

Fig. 1. ^{1}H-NMR (nuclear magnetic resonance) spectrum of hydrolysate of kapok fiber with 25% D_2SO_4/D_2O to determine acetyl substitution to wall polymers. Ethanol was used as an internal standard

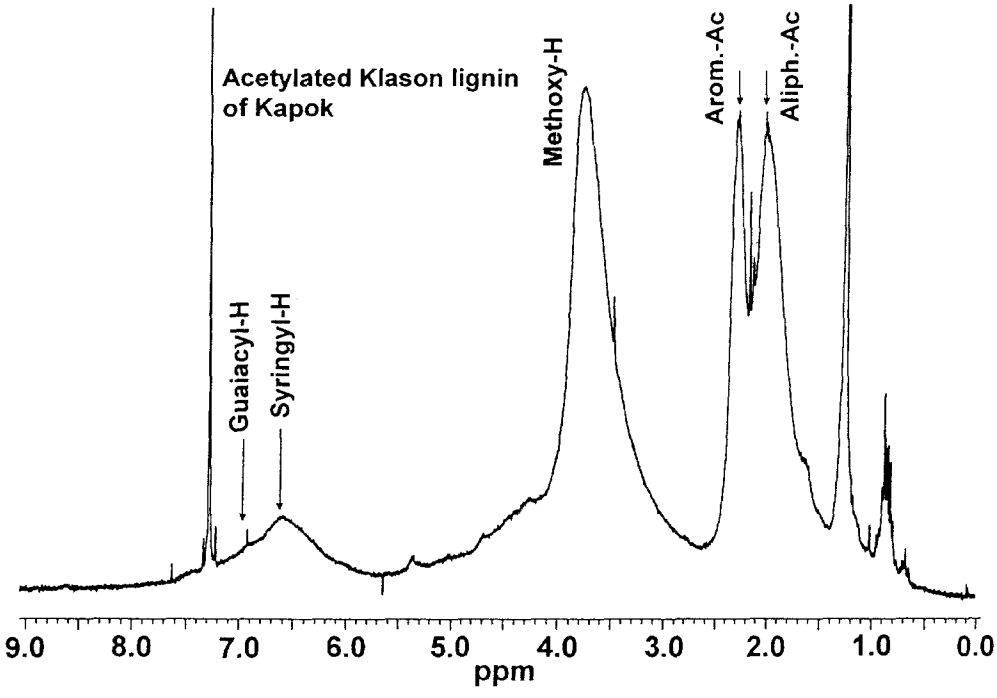

Fig. 2. ^{1}H-NMR spectrum of acetylated Klason lignin of kapok fiber

acetylated Klason lignin (Fig. 2) suggested that Klason lignin is significantly rich in syringyl units and aromatic acetyl, which probably were produced by acid hydrolysis of β-ether linkages during Klason treatment.[9–11] Signals assigned to phenylcoumaran linkages were not detected. The aromatic composition of lignin components was characterized by alkaline nitrobenzene oxidation of kapok cell walls (Table 2). Molar ratios of syringyl nuclei to guaiacyl nuclei (S/V) of kapok lignins collected in the Philippines and Vietnam were 3.67 and 3.90, respectively, and were significantly higher than the lignins in walls of typical angiosperm woods.

The weight average molecular weight (MW) of acetylated Klason lignin determined by HPSEC was 4700 and the

number average molecular weight MN was 1900 (MW/MN 2.47), which were higher than the molecular weight reported for Klason lignin (around tetramer: MN 800–1000).[9–11] X-ray diffraction analysis of original kapok fiber showed a "cellulose II" type with low crystallinity because of the presence of lignin and noncellulosic polysaccharides highly substituted by acetyl groups. However, the holocellulose prepared using $NaClO_2$ showed a clear "cellulose I" type crystal structure with 48% degree of crystallinity.

Kapok fiber is significantly hydrophobic and does not wet with water in the absence of an organic solvent such as ethanol and acetone. The oil absorptivity was examined using machine oil colored by a dye. The colored oil was suspended in water and treated with original, extract-free kapok fibers or holocellulose from the fiber. The machine oil in water was immediately absorbed by the kapok fibers, which do not absorb water. The capacity of oil absorbence of any of the samples was 40 g/g of fiber, which is similar to other, published results.[12] It is suggested that significantly high hydrophobicity and oil absorptivity are not due to the extractable components of the kapok fiber, because the fiber extracted with diethylether followed by alcohol-benzene gave the same results as with the original fiber.

Thus, kapok fiber could be used effectively to recover oil spilled in bodies of water such as in lakes, rivers, and oceans. After oil absorption, kapok fiber was observed by optical microscopy. The fiber is quite fine (ca. 8–10 μm diameter) and has a homogeneous hollow tube shape with a wall thickness of ca. 0.8–1.0 μm. It was observed that a significant amount of oil was diffused in the hollow tubes (ca. 8–10 μm) of the kapok fiber, suggesting that water cannot penetrate the tube because of its high surface tension (7.2×10^{-4} N/cm at 20°C against air[13]). However, it is still not clear how oil is absorbed effectively and quickly by kapok fiber. Further studies to elucidate the mechanism of oil absorption by the fibers are necessary.

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