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Chemical composition and structural characterization of Napier grass fibers

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ABSTRACT

Napier grass fibers were analyzed by chemical, FTIR and solid-state ^{13}C NMR methods. These fibers were also treated with 2% and 5% aq. NaOH solutions and the effect of alkali treatment on the composition and structure of the fibers was studied. Alkali treatment eliminated the amorphous hemicellulose component of the fibers to a larger extent. The morphology of the fibers before and after alkali treatment was observed with a scanning electron microscope. The fibers became thin with a rough surface and the cell structure collapsed after alkali treatment and showed enhanced tensile properties.

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1. Introduction

Concern for the environment, rising oil prices, and the finite nature of oil reserves is driving research into ways to replace petrochemical products with biobased materials. Targets include bioplastics, films, packaging and building materials, and a range of other products [1,2]. Developing biobased alternatives for even a portion of this offers the potential of significant environmental benefits. Manufacturing of high performance engineering materials from renewable resources is one of the ambitious goals currently being pursued by researchers all over the world. Natural fibers have already established a record of accomplishment as reinforcing materials in automotive parts and spreading up with high growth rate to packaging, construction and household utility-based small industries because of their lightweight, low cost, and environmental friendly and renewable nature [1–4]. There has been a tremendous growth in polymer matrix composites containing many natural fibers [2]. Today, the use of natural fibers as reinforcements in technical applications is taking place mainly in the engineering industry. It is thus essential to look for new plants that enable easy and cost-effective extraction that does not impair the properties of the fibers. The new fibers thus identified must be analyzed in order to determine their physical, chemical and mechanical (tensile) properties and morphology. This knowledge is essential to evaluate or simulate efficiently the properties of the fibers [5,6].

Napier grass (also called elephant grass) belongs to the Poaceae family of *Pennisetum purpureum schum* species and requires very little supplement of nutrients for growth. It can be harvested 3–4 months after planting and can continue at an interval of 6–8 weeks for up to 5 years with a dry biomass yield per hectare per annum of 40 tons [7]. The yield of fiber from each plant is around 40%. Although preliminary studies on Napier grass fibers were reported in the literature [8], a complete and thorough study of them is relatively underexplored. The unique high modulus of these fibers has been one of the prime reasons for the choice of these fibers [8]. The prime objective of this study was to explore the possibility of using Napier grass fibers as a green composite reinforcement. The work involved extraction of fibers from the internodes of the Napier grass stems, alkali treatment, and their structural characterization using chemical analysis, FTIR and solid-state NMR methods. The morphology of these fibers was probed with scanning electron microscopy and tensile properties were investigated.

2. Materials and methods

2.1. Materials

Extracted Napier grass fibers [8], commercial grade sodium hydroxide pellets, benzene, sodium chlorite, acetic acid, sodium bisulphate, and ethanol were used as received.

2.2. Fiber extraction and alkali treatment

The Napier grass fibers were collected from Anantapur district in Andhra Pradesh state of India and extracted from the grass internodes

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by the usual retting process. Extracted Napier grass fibers were treated with 2% and 5% aqueous sodium hydroxide (aq. NaOH) solutions at room temperature for 30 min, maintaining a liquor ratio of 20:1 to remove the hemicellulose and other greasy materials. Finally, the fibers were washed with tap water, distilled water many times, and dried at 100 °C.

2.3. Physical properties

The length of 100 individual fibers was determined using a standard ruler scale. The diameter of fibers was determined using a micrometer caliper (Mitutoyo, accuracy = ±0.001 mm). Five determinations were made on each fiber and the average values were reported.

2.4. Chemical analysis

The chemical composition of the fibers was estimated by chemical analysis as reported in literature [9]. In this analysis, the percent values of α-cellulose, hemicellulose, and lignin were determined. In each case, five samples were used and the average values were reported.

2.5. Fourier transform infrared (FTIR) spectral analysis

The FTIR spectra of all the samples were run on an ABB-BOMEM FLATA-2000 model spectrophotometer using KBr pellets.

2.6. ^{13}C NMR (CP-MAS) spectroscopy

^{13}C CP-MAS NMR of all the samples was run on Bruker DSX 300 MHz solid-state NMR spectrometer. The operating frequency for ^{13}C nuclei was 75.46 MHz. The samples were spun with filled 5 mm rotor at a spinning rate of 7.5 kHz at room temperature.

2.7. Morphology

The scanning electron micrographs of the cross section of fibers were recorded on a JEOL JSM 820 microscope. The fiber samples were gold coated before recording the micrographs.

2.8. Tensile properties

The tensile properties (maximum stress, modulus and % elongation) of the fibers were determined using an INSTRON 3369 Universal testing machine at a crosshead speed of 5 mm/min maintaining a gauge length of 50 mm. In each case, ten samples were tested and the average value was reported.

3. Results and discussion

The prime work involved in the methodology was to extract fibers from grass internodes, study the chemical composition, and investigate the influence of the alkali treatment on the fibers. Fig. 1 presents the photographs of Napier grass and extracted fibers. The average fiber length was found to be 142 mm. The average diameters of untreated and with 2% and 5% alkali treated fibers were found to be 0.225, 0.193 and 0.158 mm respectively. The differences between the untreated and alkali treated fibers can be attributed to shrinking of the fibers due to the removal of soluble components by alkali treatment. The length and diameter of the fibers and their corresponding aspect ratio (L/D) values are presented in Table 1. From the table, it is evident that due to the thinning of the fibers, the aspect ratio of the alkali treated fibers was increased.

The estimated chemical composition of both untreated and alkali-treated fibers is presented in Table 1. The chemical analysis of untreated fibers (Table 1) indicated the presence of α-cellulose, hemicellulose, and lignin. Usually, natural fibers are treated with alkali to remove weak amorphous components so that the fiber retains crystalline components thus enhancing the strength of the fiber. Hence, in the present case, the fibers were accordingly treated with alkali. A close examination of the results indicates that alkali treatment reduced hemicellulose fraction considerably. Further, the reduction in hemicellulose content was more for 5% alkali treated fibers.

To confirm the changes in the composition on alkali treatment of the Napier grass fibers, FTIR technique was used. The FTIR spectra of the untreated and alkali treated fibers are presented in Fig. 2. From Fig. 2, it can be observed that for alkali treated and native fibers, well defined bands at around 3430, 2923, 1727, 1634, 1514, 1457, 1428, 1377, 1319, 1260, 1164, 1110, 1054 and 897 cm^{-1}, were present in the spectra. However, in the case of native fibers, additional bands at around 1727 and 1260 cm^{-1} were also present which correspond to hemicellulose [6]. On alkali treatment, these bands were found to be almost absent indicating the elimination of the hemicellulose to a larger extent. The bands at around 3430 cm^{-1} and 2923 cm^{-1} corresponded to α-cellulose whereas the remaining bands belonged to lignin. Thus, the FTIR studies suggested the reduction of the hemicellulose content upon alkali treatment of the fibers. This was in support of the chemical analysis data of the alkali treated fibers as shown in Table 1.

To further confirm the changes on alkali treatment of the fiber, high-resolution ^{13}C NMR (CP-MAS) spectroscopy was used. Fig. 3 shows the ^{13}C CP-MAS NMR of the untreated and alkali treated fibers. In the spectrum of untreated fibers, a sharp peak at 22.7 ppm was observed that was assigned to CH_3 carbons of the hemicellulose acetyl group. All noticeable signals of the carbohydrate moiety carbon atoms occurred between 60 and 110 ppm. The peaks in 72–75 ppm

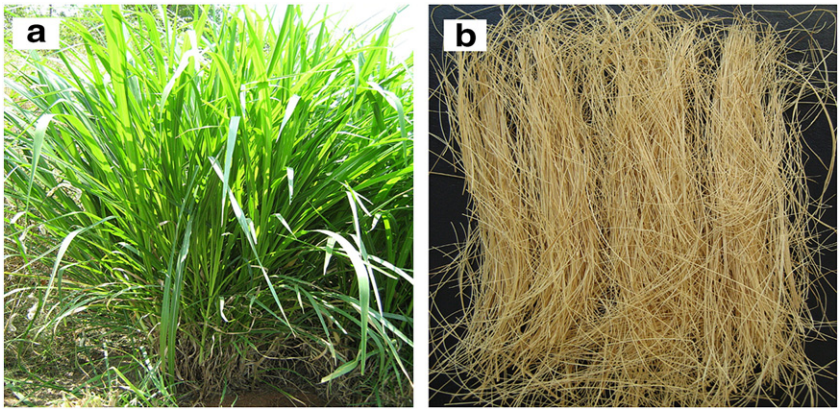


Fig. 1. Photographs of (a) Napier grass and (b) extracted grass fibers.

Table 1
Physical properties, chemical compositions and tensile properties of Napier grass fibers.

Fiber	Physical properties			Chemical composition			Tensile properties		
	Average length (mm) L	Average diameter (mm) D	Aspect ratio (L/D)	α-Cellulose (%)	Hemicellulose (%)	Lignin (%)	Maximum stress (MPa)	Young's modulus (GPa)	Elongation at break (%)
Untreated	142	0.255	556.8	45.66	33.67	20.60	75	6.8	2.8
2% Alkali treated	142	0.193	735.7	54.66	24.34	21.00	111	8.0	3.1
5% Alkali treated	142	0.158	898.7	55.99	20.01	24.00	136	10.5	3.2

region were assigned to the C-2, C-3, and C-5 carbons of cellulose, and the signal at 109 ppm was assigned to the cellulose C-1. Distinct peaks for amorphous and crystalline carbons could be detected. The peaks at 87.3 and 68.4 ppm were assigned to the more ordered cellulose C-4 and C-6 carbons, respectively, whereas the peaks at 79 and 60.3 ppm were assigned to the less ordered cellulose C-4 and C-6 carbons [10,11]. The peaks at 152.6, 148.5 and 132.8 were assigned to aromatic resonances arising from lignin [12]. The peak at 55.0, however, was due to methoxyl ($-OCH_3$) groups present primarily in the lignin component. The CH_3COO and COOH groups of hemicellulose [6] contributed the broad peak at 172.1 ppm. The chemical shift values and intensity characteristics of the spectra were supportive of presence of cellulose, hemicellulose, and lignin in the untreated fibers. The ^{13}C CP-MAS NMR spectrum of alkali-treated fibers is shown in Fig. 3. The notable features of the spectrum included reduction in the intensity of carbonyl peak and deshielding of its chemical shift. This was also followed by no change of 152.6 ppm peak. Although the other important peaks, i.e. those appearing in the region 60–110 ppm almost remained the same. The methyl group of CH_3COO of hemicellulose component observed in the raw fibers now disappeared and accordingly no signals were noticed at 22.7 and 172.1 ppm. The spectral features indicated that the alkali treatment affected only the hemicellulose component leaving the other two components viz. α-cellulose and lignin unaffected. These observations were very much in consistent with the FTIR spectral data and chemical analysis.

Scanning electron micrographs of the cross section of the alkali treated and untreated fibers are shown in Fig. 4. Fig. 4(a) exhibits the multi cellular structure of the untreated fiber, which indicates the porous structure. According to Reddy et al. [6], in general all natural cellulose fibers are multi cellular, where lignin and hemicellulose bind a bundle of individual cells. The fiber used in this study referred to a bundle of individual cells. The hollow cavity called lumen exists inside the unit cell of the biofibers. The alkali treatments (Fig. 4(b) and (c)) revealed a compressed cellular structure. In other words, the treatment destroyed the cellular structure of the fibers, hence reduced the void content of the fibers and this can lead to lower water absorption.

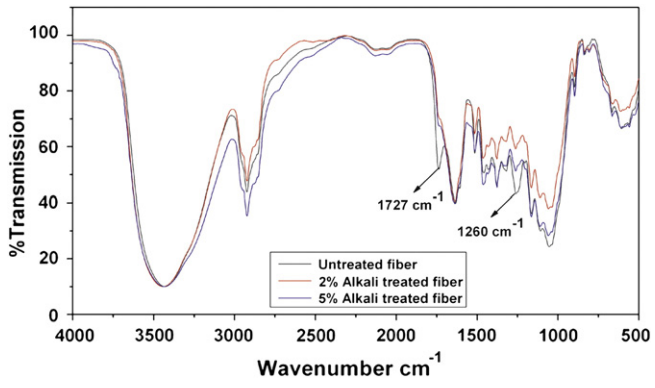


Fig. 2. FTIR spectra of untreated and alkali treated Napier grass fibers.

The tensile properties of the untreated and alkali treated fibers are presented in Table 1. The data supports that for the alkali treated fibers the maximum stress and Young's modulus increased significantly whereas the % elongation at break increased marginally. In untreated fibers, hemicellulose and lignin remain dispersed in the interfibrillar region separating the cellulose chain from one another. The cellulose chains are, therefore, always in a state of constraint. Removal of hemicellulose after alkali treatment, removed internal constraint and the fibrils became more capable of rearranging themselves in a compact manner. This leads to a closer packing of the cellulose chains, which improved the fiber strength and its tensile properties. These observations were largely consistent with the chemical analysis data and SEM analysis.

4. Conclusions

The composition of the native fibers was determined by chemical analysis, which indicated the presence of α-cellulose, hemicellulose, and lignin in them. The alkali treatment of fibers resulted in solubilization of hemicellulose leading to reduction of its content in the fibers. This was further supported by FTIR and solid-state ^{13}C NMR spectra. The SEM analysis of untreated and treated fibers indicated changes in morphology. The tensile properties of the alkali treated fibers were found to be higher than those of the untreated fibers. This study indicates the feasibility of utilizing the by-product such as Napier grass fibers as reinforcement for composites.

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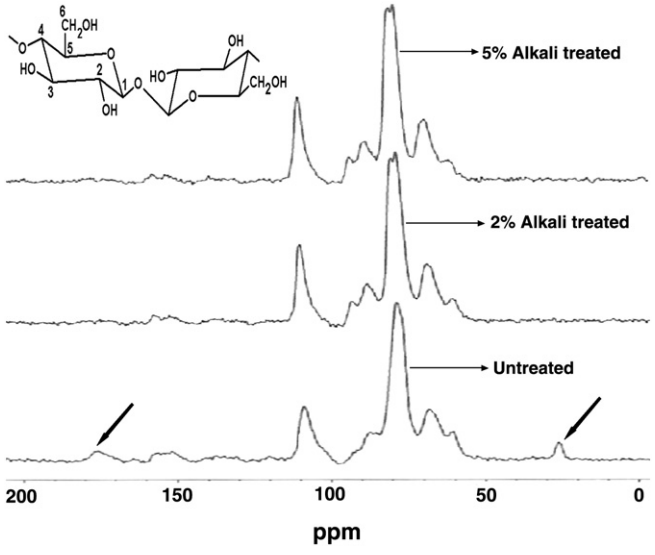


Fig. 3. ^{13}CP-MAS NMR spectra of untreated and alkali treated Napier grass fibers.

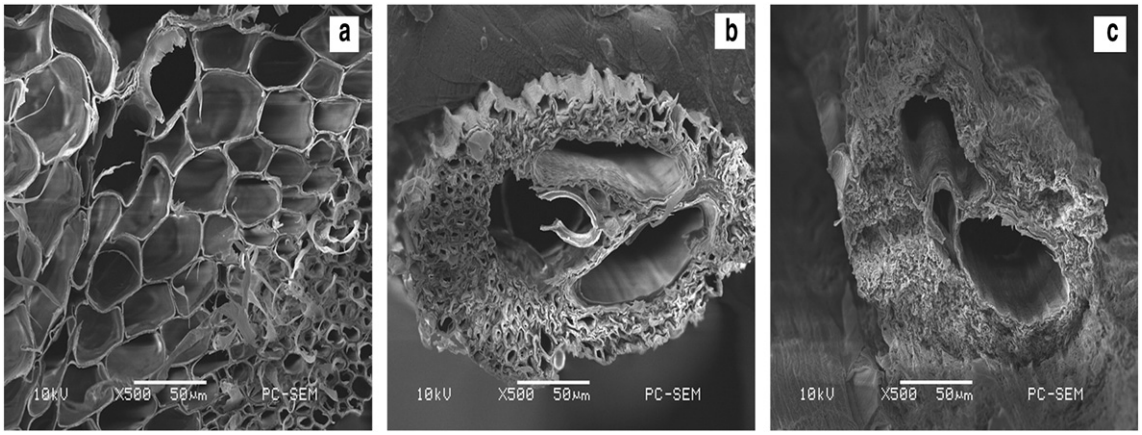


Fig. 4. Scanning electron micrographs of the cross section of Napier grass fibers, (a) untreated, (b) 2% alkali treated and (c) 5% alkali treated.

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