

A Study on Ligno-Cellulosic Fabric *Hardwickia binata*

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ABSTRACT: A naturally occurring fabric belonging to the species *Hardwickia binata* was extracted from the sheath of stem, bark, and branches of the tree. The fabric specimens were treated with sodium hydroxide and poly (vinyl alcohol). The morphology of the fabric specimens before and after NaOH treatment was studied using scanning electron microscopy technique. Ligno-cellulosic properties of fabric were analyzed by XRD, FTIR, and thermo gravimetric methods before and after NaOH treatment. Tensile strength and percentage of elongation at break of the fabric were also studied by using a universal testing machine (model AGS-10kNG). The results showed that the poly

(vinyl alcohol)-treated fabric specimens showed higher tensile strength than sodium hydroxide-treated fabric specimens. The Binata fabric has good thermal resistance and was also found to increase by alkali treatment. The FTIR method indicates lowering the hemi cellulose and lignin content by alkali treatment in the fabric. Further, the X-ray diffraction studies revealed an increase in crystallinity of the fabric by alkali treatment. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2806–2812, 2010

Key words: *Hardwickia binata*; FTIR; ligno-cellulose; thermogravimetric; morphology; crystallinity

INTRODUCTION

The nonbiodegradability of most plastics/composites had led to many environmental problems related to their use and disposal. This situation causes the problem of finding available landfill areas for the waste.¹ Most of the composites are made with synthetic polymers. Because synthetic polymers are nondegradable, the disposal of the composites containing them as a reinforcement is a difficult problem. Moreover, synthetic polymers are nonrenewable.² A sufficient solution for this problem could be the development of fully environmentally friendly products/composites that consist of biodegradable materials/polymers such as natural ligno-cellulosic fibers. Biodegradable materials constitute a loosely defined family of constituents that are able to degrade through the action of living organisms.³

In the present study, the authors selected *Hardwickia binata fabric* (HWB); the tree is abundantly available in Talupula and the Kadiri hills of the Anantapur district, Andhra Pradesh, India. A photograph of the tree is shown in Figure 1. The tensile strength of this fabric could be 4 to 7 times higher

than that of sisal and jute.^{4,5} Accordingly, demand for the fabric is increasing day by day. The sheath of the bark and branches are first washed and then beaten using a rod, followed by storing them in water for about 25 days for “mercerizing” before they are again washed and dried.⁶ The fabric content is about 5–15%, and the balance is mucilage, which can be used as an organic fertilizer. Currently, the fabric is used to make pot-supporting, ropes for cot manufacturing, and for packaging. It is used in the domestic sector for hammocks, fishing lines, and as nets for sleeping.

Very limited studies on the characterization of this fabric have been made so far. The physical and typical chemical compositions of the fabric are reported as 22.4% of cellulose, 17.7% of hemicellulose, 7.01% of lignin, 20–22% of water soluble matters, and the remains residue and ash.⁷ The chemical modifications on some ligno-cellulosic fibers and their further use in polymer composites have been reported.^{8–12} Rout et al.¹³ studied the scanning electron microscopy characteristics of coir fibers by chemical modification. They reported the filling of the void regions of the fibers by chemical treatments. In this way, the authors selected NaOH and PVA for chemical treatment of fabric. Considering the growing demand for the fabric and limited study on its unique strength properties as mentioned above, in this paper a comprehensive systematic study on the characterization

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Figure 1 Photograph of the *Hardwickia binata* tree. [Color figure can be viewed in the online issue, available at www.interscience.wiley.com.]

of the fabric as a function of its dimensions and surface treatment is presented for the first time for its future use in composite production.

The aim of this study was to find biodegradable materials for the production of green composites reinforced with different ligno-cellulosic fibers such as flax, hemp, sisal, kapok, Hilde Guardia, and jute fibers. In this study, the effects of fabric surface treatments on the mechanical and ligno-cellulosic properties of fabric were investigated by using FTIR and thermogravimetric (TGA) methods before and after NaOH treatment. Also, X-ray diffraction and scanning electron microscopy studies of the fabric have been conducted to understand the observed properties of fabric. Also, this type of characterization helps in assessing appropriate dimensions of the fabrics for their use in composites for different applications.

EXPERIMENTAL

Materials

Natural fibers were procured from the branches of the tree called *Hardwickia binata*, which is available locally in Talupula mandal and Kadiri taluku, Anantapur district, Andhra Pradesh, India. These fibers were extracted in the form of knitted fabric of 0.21-mm thickness, with length and width of 25 to 30 and 10 cm, respectively. The fabric was washed thoroughly with distilled water and allowed to dry in the sunlight for about 1 week. Poly (vinyl alcohol)

and sodium hydroxide were purchased from SD Fine Chemicals, Mumbai, India.

Treatment of the fabric

Fabric specimens were treated with 2% alkali solution for 1 h. Fabric specimens obtained after the alkali treatment were washed several times in warm water and finally in dilute acetic acid (10% w/w) solution to remove the dissolved substances and dried under ambient conditions. Also, the fabric specimens were treated with 4% poly (vinyl alcohol) solution for half an hour. After this, the excess PVA solution on the fabric was removed by placing them vertically and drying before analysis.

Methods

Tensile testing

The tensile strength and percentage of elongation at break of the fabric specimens, with and without treatments, was determined using SHIMADZU (UK) (AGS-10kNG model) Universal testing machine. Fabric specimens with dimensions of 100 mm 15 mm were used; a gauge length of 20 mm was maintained for all the samples, and the tests were conducted at a crosshead speed of 1 mm/min. The temperature and humidity for these tests were maintained at 22°C and 50%, respectively. The tensile stress was applied in the direction of fiber axis (longitudinal axis). Ten specimens were tested in each case, and the average value reported.

FTIR spectral analysis

Infrared spectra were obtained using a Perkin Elmer (USA) FTIR spectrometer in the range of 400–4000 cm^{-1} . About 5 mg of fabric was crushed into small particles in liquid nitrogen. The powdered fabric particles were then mixed with KBr and pressed into a small disc about 1 mm in thickness.

Thermogravimetric analysis

The thermo gravimetric analysis (TGA) of *Hardwickia binata* fabric with and without treatment was carried out using Mettler Toledo (Switzerland) TGA/SDTA 851e (Switzerland) in nitrogen atmosphere at a heating rate of 10°C/min. The micrograms were recorded at the Indian Institute of Chemical Technology (IICT), Hyderabad, Andhra Pradesh, India.

XRD analysis

The fabric specimens were subjected to X-ray diffraction studies using a Rigaku (Japan) Dmax-A X-ray diffractometer with Ni-filtered Cu $K\alpha$ radiation of

wave length of 1.5418 Å at 40 kV, 20 mA, and with scanning at 2°/min for determining their crystallinity. The degree of crystallinity of the fabric was calculated from X-ray diffractograms recorded on samples, which were analyzed in the powder form and using the computer program.

Scanning electron microscopy analysis

The morphology of fabric and fractured specimens was observed using scanning electron microscopy [Hitachi 5S 520] at different magnifications. The fabric specimens were gold-coated before subjecting it to scanning electron microscopy analysis. The scanning electron micrograms of the fabric specimens before and after alkali treatment were also recorded and studied.

RESULTS AND DISCUSSION

Tensile properties

Tensile strength and percentage of elongation at break of the *Hardwickia binata* fabric specimens with and without treatments are shown in Table I. All values shown are averages. From the data in Table I, it is shown that the values of tensile strength show that untreated fabric specimens are the strongest, followed by PVA-treated fabric. It is also observed that NaOH-treated fabric specimens show the lowest tensile strength value. Varada Rajulu et al.¹⁴ reported that the tensile strength of the alkali-treated fabric has low strength compared with untreated in the case of Hilde Guardia. The tensile strength of untreated fabric is 771.3 MPa, which is one of the highest values of strength compared with other fibers such as kapok, Hilde Guardia, hemp, jute, flax, and cotton. Therefore, we conclude that this fabric is useful for fabrication of composites.

Figure 2 shows the tensile strength of fabric specimens with and without treatments. This figure clarifies that alkali-treated fabric has lower strength than other two values. This poor strength is due to the removal of lignin and hemi-cellulose from fabric by NaOH treatment. We consider, however, after making the composite with this fabric, that the alkali treatment does not affect the fabric alignment and strength. For this reason, we can strongly recom-

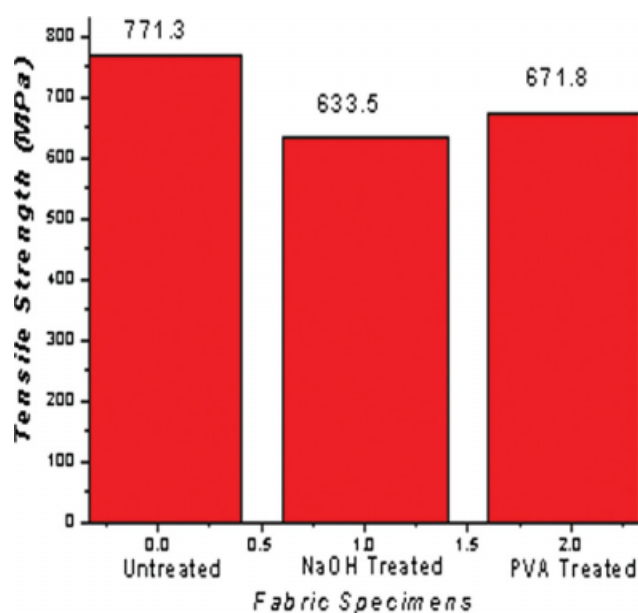


Figure 2 Effect of different treatments on the tensile strength of *Hardwickia binata* fabric with and without treatment. [Color figure can be viewed in the online issue, available at www.interscience.wiley.com.]

mend this fabric for developing well-oriented fiber green composites.

Figure 3 shows tensile properties of *Hardwickia binata* fabric with and without treatments. All values are shown as averages. The tensile strength of alkali- and PVA-treated fabrics were 633.5 and 671.8 MPa, respectively. These values are nearer to that of each other. On the other hand, the elongation at break of alkali-treated fabric is larger than those of untreated

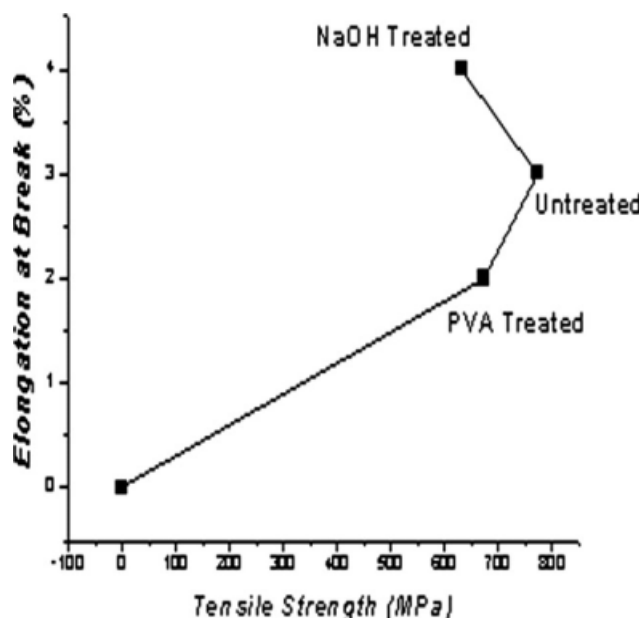


Figure 3 Tensile strength versus elongation at break of *Hardwickia binata* fabric with and without treatment.

TABLE I
Tensile Strength and Elongation at Break of *Hardwickia binata* Fabric with and without Treatments

<i>Hardwickia binata</i> fabric	Tensile strength (MPa)	Elongation at break (%)
Untreated	771.3	1–3
Alkali treated	633.5	1–4
Poly vinyl alcohol treated	671.8	1–2

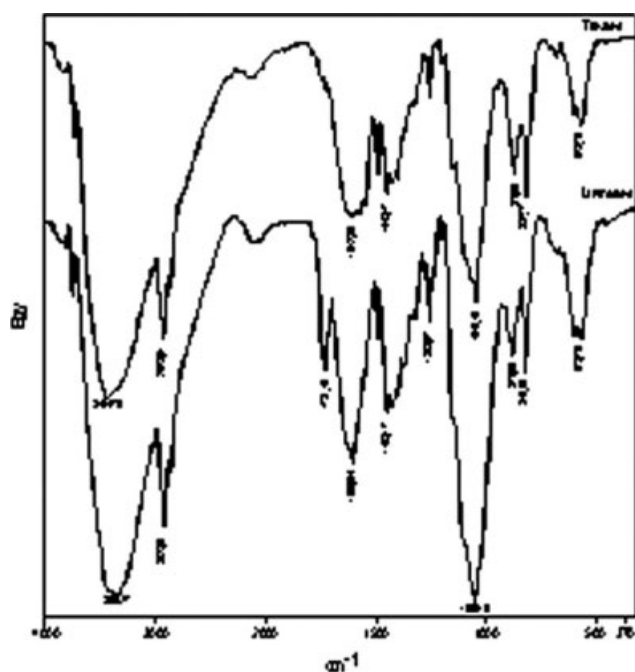


Figure 4 FTIR spectra of untreated (lower) and NaOH treated (upper) *Hardwickia binata* fabric.

and PVA-treated fabric, especially for PVA-treated fabric, which achieves 1–2% elongation at break against 1–3% of their untreated fabric. The fabric covered by PVA as a layer to fill the voided regions after the PVA coating is stronger than NaOH-treated fabric.

FTIR analysis

For characterization of ligno-cellulosic fibers to find infrared characteristic transmittance bands of their constituents, IR spectroscopy is very often used. Accordingly, the *Hardwickia* fabric is characterized by using FTIR spectrometry. Figure 4 shows the spectrum of the fabrics with and without alkali treatment.

In the case of the FTIR spectrum of alkali-treated fabric, some changes are observed. Alkali treatment leads to reduction in hydrogen bonding due to removal of the hydroxyl groups by reacting with sodium hydroxide. These results in the increase of the —OH concentration, evident from the increased intensity of the peak between the 1200 and 1800 cm^{-1} band, compared with the untreated fiber (Fig. 4). Absorbance in this range indicates the presence of hemicellulose. The disappearance of the peak between 1240 and 1258 cm^{-1} after alkalization indicates the complete removal of hemicellulose materials rather than lignin but remains unchanged at around 3400 cm^{-1} in fabric. This implies that hemicelluloses are easily removed by alkalization compared with lignin. The hydroxyl groups are also

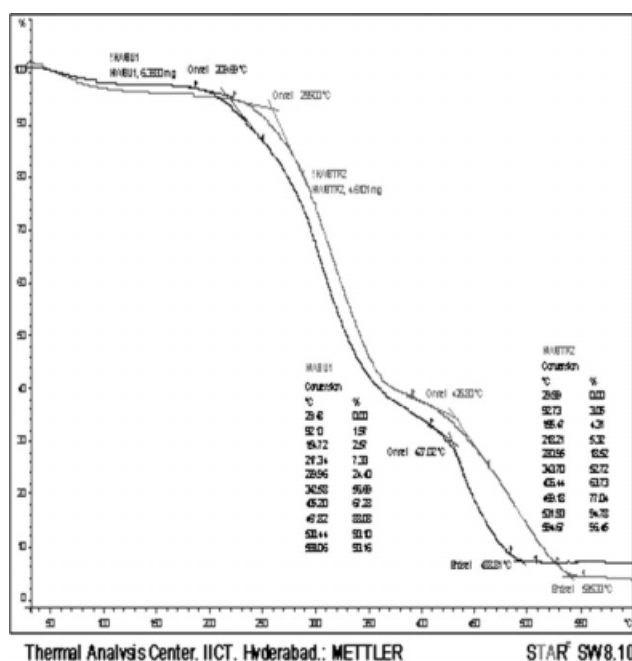


Figure 5 Thermogravimetric analysis of untreated and NaOH-treated *Hardwickia binata* fabric in N_2 atmosphere.

involved in hydrogen bonding with the carboxyl groups, perhaps of the fatty acids, available on the fiber surface of the natural fibers. The peak at 1731 cm^{-1} seen in untreated fabric (Fig. 4) disappears on alkali treatment. This is due to the removal of the carboxylic group (lignin) by alkali treatment by a process called deesterification.

The spectrum shows many absorption bands, i.e., a very weak and broad band at 3444 cm^{-1}

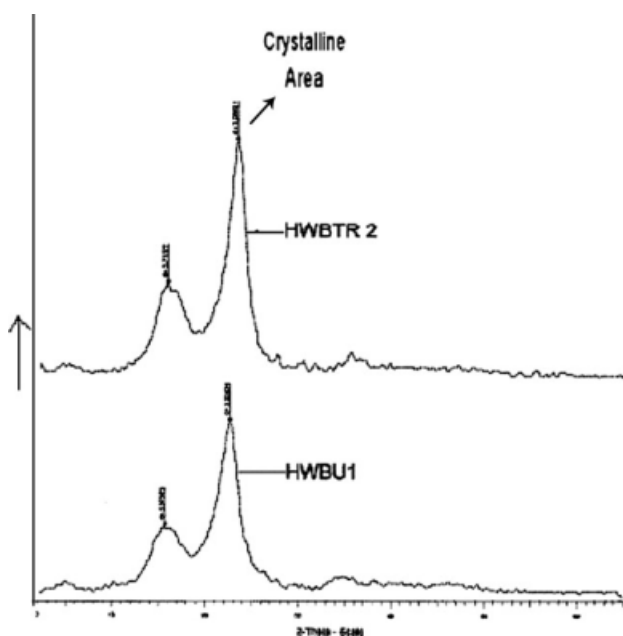


Figure 6 XRD spectrum of untreated (HWBU1) and alkali-treated *Hardwickia binata* fabric (HWBTR2).

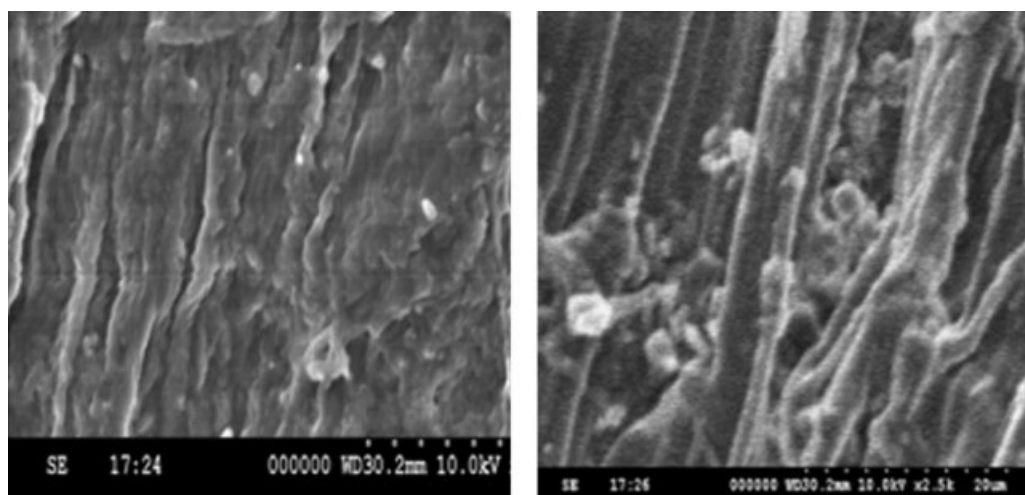


Figure 7 Scanning electron micrographs of the untreated *Hardwickia binata* fabric surface at $\times 2.5k$ magnifications (a) and (b).

representing typical of O—H stretching of cellulose and water, a very strong band at 2923 cm^{-1} typical of C—H stretching, and others in the region of 1800 to 400 cm^{-1} typical of cellulose structural units, which are similar to those reported earlier for other ligno-cellulosic fibers such as sisal, hemp, Hilde Guardia, and kapok.⁵ The peak at 1258 cm^{-1} shows diminishing intensity as the fibers are subjected to alkali treatment. The peaks at 1448 and 1731 cm^{-1} show aliphatic C—H vibration and C=O acidic stretching vibration, respectively. Another important band observed in the region of 1606 to 1731 cm^{-1} is reported to be related to carboxyl band associated with cellulose.⁸ The peak observed at 3359 cm^{-1} in untreated fabric indicates the presence of intermolecular hydrogen bonding and tends to shift to higher absorbency values in alkali treated fabric, e.g., 3444 cm^{-1} in this fabric. In sisal and jute it is completely invisible, indicating that the hemicellulose component in this fabric is easily removed by alkalization and that the hemicellulose in *Hardwickia* fabric is less affected by caustic soda.

Thermogravimetric analysis

The thermal stability of fabric, before and after treatment, was determined by thermogravimetric analysis. Therefore, thermogravimetric analysis was used to determine the high temperature degradation behavior of the fabrics as well as their modifications under nitrogen atmospheres (represented in Fig. 5). It was observed that the thermal degradation of all the samples has taken place within the programmed temperature range. It reveals that (Fig. 5) a mass loss of 3.05% and 1.97% in alkali-treated and untreated fabric, respectively, occurred between room temperature and 600°C due to the elimination of absorbed or

combined water, which was present in the fabric. This is followed by two mass losses of 63.7% at 406°C and of 32.7% peaks at 469 – 594.6°C . These probably are due to the degradation of lignin and cellulose.

On the other hand, in untreated fabric under same atmospheric conditions, the thermal curve represents a water loss of 7.3% at 217°C followed by further mass loss of 67.2% at 405°C and of 26% at 593°C (Fig. 5), representing decomposition processes of the fabric constituents. The initial degradation of fabric in untreated fabric under nitrogen atmosphere occurs at about 209°C and that in treated fabric at 255°C . The first exothermic peak of the fabric in the range of 200 – 425°C indicates degradation of

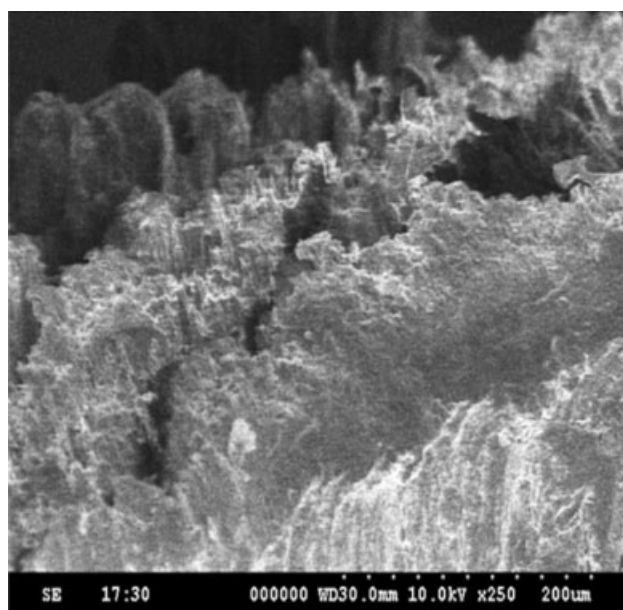


Figure 8 Scanning electron micrographs of the untreated *Hardwickia binata* fabric reverse surface.

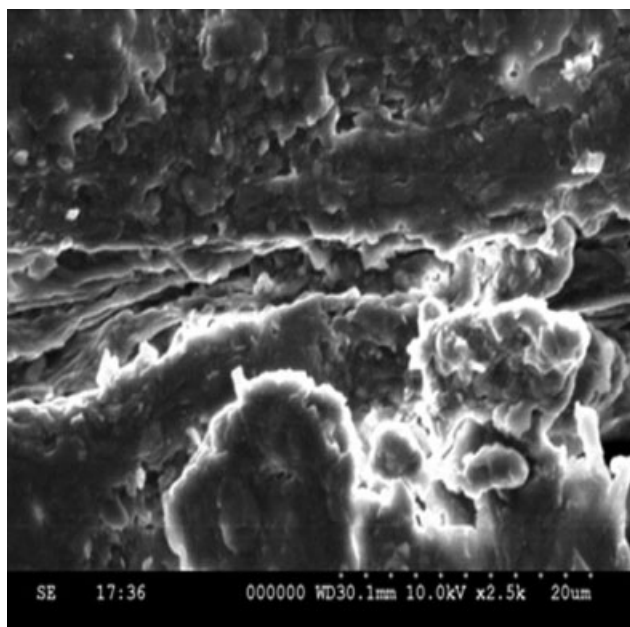


Figure 9 Scanning electron micrographs of the untreated *Hardwickia binata* fabric surface cross section.

hemicellulose and in the range of 427–535°C (giving a branched structure), that of cellulose, and during the second peak lignin degrades between 543 and 594°C, suggesting less branching and consequently producing more resistant material. The thermal stability of the treated fabric was found to be higher than that of untreated fabric in nitrogen (Fig. 5); this is due to the improved crystallinity of the fabric after alkali treatment.

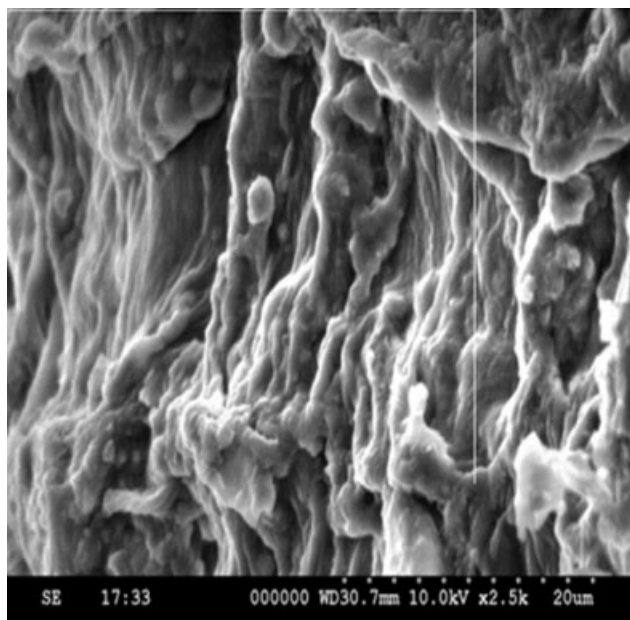


Figure 10 Scanning electron micrographs of the NaOH-treated *Hardwickia binata* fabric surface.

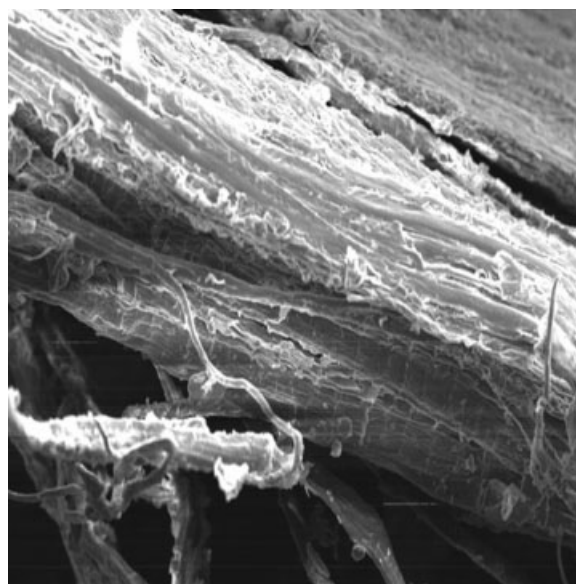


Figure 11 Scanning electron micrographs of the NaOH-treated *Hardwickia binata* fabric surface cross section.

X-ray diffraction studies

The X-ray diffraction spectrums of untreated and alkali treated *Hardwickia binata* fabric samples are shown in Figure 6. It is similar to that observed in other ligno-cellulosic fibers. It shows a peak associated with the crystalline cellulose at $2\theta = 22^\circ$. From Figure 6, it is clearly evident that the crystallinity of the fabric increased on alkali treatment. This is understandable because as the crystalline cellulose content is increased, the amorphous hemicellulose and lignin content decreased on alkali treatment.

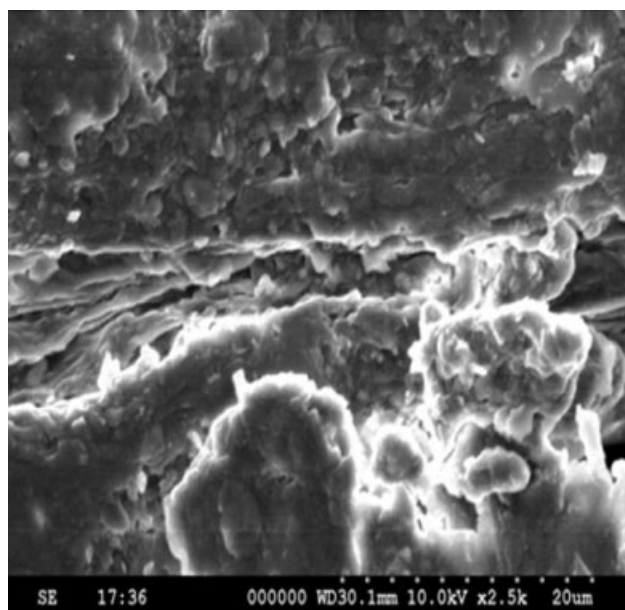


Figure 12 Scanning electron micrographs of the NaOH-treated *Hardwickia binata* fabric reverse surface.

This is in conformity with FTIR. X-ray diffraction results for alkali-treated fabric, which shows an overall increase in the “crystallinity” index and indicates the improvement in the order of the crystallites as the cell wall thickens on alkali treatment. Alkali treatment is reported to increase the proportion of crystalline material present in plant fibers, as observed by several researchers.¹⁵

Scanning electron microscopy studies

Figures 7–12 demonstrate scanning electron micrographs of fabric surfaces of untreated and alkali-treated (NaOH) with different magnifications, respectively. It clearly indicates that the differences in microstructure of the various fabric specimens are significant. The fabric surface fully covered by hemicellulose and lignin as layers and individual cells were bound together. The presence of lignin and the bonding material can be seen as the top of the layers on the individual fibers (Figs. 7 and 8).

From Figure 11, it is clearly evident that the covering layer having probably hemicellulose and lignin is considerably removed by alkali treatment in layers. Further, it is evident that the surface of the fabric becomes rough on alkali treatment. Higher roughness was observed for the fabric surface after chemical modification with higher concentrations. Similar observation was made in the case of some ligno-cellulosic fibers.^{3–16} Overall morphology of the fabric could be favorable for making green composites with fabric reinforcement.

CONCLUSIONS

1. In this work, a systematic study has been carried out on tensile and ligno-cellulosic properties of *Hardwickia* fabric as a function of its treatments. This fabric has highest tensile strength when compared with other fibers.
2. FTIR studies reveal the structural features such as stretching of O—H, C=O, and C—H bond characteristics of chemical constituents of the fiber, such as cellulose, hemicellulose, and region of the lignin in the fabric as well as presence of some acids.
3. Both untreated and alkali-treated fibers of *Hardwickia* are thermally stable, and, as such, can be effectively used for reinforcements. TGA analysis indicates that the fabric of *Hardwickia* can be used as reinforcement in thermosets as well as in thermoplastics with a melting temperature less than 250°C.
4. X-ray diffraction studies reveal that the crystallinity of the fabric increased by alkali treatment due to fiber rough cellular structure, which also explains the observed FTIR and scanning electron micrograms.
5. All the scanning electron micrograms showed that the fabric has a favorable morphology for making the composites with supporting superior mechanical properties.

References

1. Wu, C. S. *Polym Degrad Stab* 2003, 80, 127.
2. Rajulu, A. V.; Rao, G. B.; Rao, B. R. P.; Reddy, A. M. S.; He, J.; Zhang, J. *J Appl Polym Sci* 2002, 84, 2216.
3. Fábio, T.; Thais Helena Demetrio, S.; Gundappa Satyanarayana, K. *Compos A* 2007, 38, 1710.
4. Mwaikambo, L. Y.; Ansell, M. P. *Die Angew Makromol Chem* 1999, 272, 108.
5. Mwaikambo, L. Y.; Ansell, M. P. *J Appl Polym Sci* 2002, 84, 2222.
6. Satyanarayana, K. G.; Guimaraes, J. L.; Wypych, F. *Compos A* 2007, 38, 1694.
7. Praveen, K.; Jagadish, C.; Tarafdar, J. C.; Jitendra, P.; Shyam, K. *J Plant Nutr Soil Sci* 2003, 166, 662.
8. Fábio, T.; Gundappa Satyanarayana, K.; Thais Helena Demetrio, S. *Compos A* 2007, 38, 2227.
9. Thi-Thu-Loan, D.; Hanna, B.; Edith, M. *Compos Sci Technol* 2007, 67, 2707.
10. Yan, L.; Yiu-Wing, M.; Lin, Y. *Compos Sci Technol* 2000, 60, 2037.
11. Nabi Saheb, D.; Jog, J. P. *Adv Polym Technol* 1999, 18, 351.
12. Debasish, D.; Debapriya, D.; Basudam, A. *Polym Adv Technol* 2004, 15, 708.
13. Rout, J.; Tripathy, S. S.; Nayak, S. K.; Misra, M.; Mohanthy, A. K. *J Appl Polym Sci* 2001, 79, 1169.
14. Varada Rajulu, A.; Babu Rao, G.; Ganga Devi, L.; Li, X. H.; Meng, Y. Z. *J Reinforced Plast Compos* 2004, 23, 216.
15. Bisanda, E. T. N.; Ansell, M. P. *Compos Sci Technol* 1991, 41, 165.
16. Varada Rajulu, A.; Venu Nadhan, A.; Rama Devi, R. *J Appl Polym Sci* 2006, 102, 2338.