EFFECT OF ALKALI TREATMENT ON WATER ABSORPTION OF SINGLE CELLULOSIC ABACA FIBER

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Environmentally beneficial composites can be made by replacing synthetic fibers with various types of cellulosic fibers. Fibers from pine wood, coir, sisal, abaca, coir, *etc*. are all good candidates. The most important factor in finding good fiber reinforcement in the composites is the strength of adhesion between matrix polymer and fiber. Due to the presence of hydroxyl groups and other polar groups in various constituents of abaca, the moisture absorption is high, which leads to poor wettability and weak interfacial bonding between fibers and the more hydrophobic matrices. Therefore, it is necessary to impart a hydrophobic nature to the fibers by suitable chemical treatments in order to develop composites with better mechanical properties. In the present work, the effect of alkali treatment on the moisture absorption tendency of single abaca fiber was investigated. The results shown that the alkali treated fiber absorbs less moisture than the untreated raw fiber.

Keywords: *Natural fibers; Abaca fibers; Moisture absorption; Chemical treatment; Hydrophobic nature*

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INTRODUCTION

Plant waste fibers can be described as lignocellulosic. Lignocellulosic materials include wood, agricultural residue, water plants, grasses, and other plant substances. Plant waste fibers have the composition, properties, and structure that make them suitable for uses such as composites, textiles, and pulp for paper manufacture. In addition, plant fibers can also be used to produce fuel, chemicals, enzymes, and food. The current major uses of hard cellulosic fibers such as flax, jute, banana, sisal, and pineapple leaf fiber are in textile, packaging, low-cost housing, paper manufacturing industries, and other general applications. These fibers are considered as hard cellulose fibers because of their high tensile modulus and low elongation at break. Many attempts have been made by scientists and technologists to utilize natural fibers in the fabrication of composites. It has been found that these natural fiber-reinforced composites possess good electrical resistance, chemical resistance, good thermal and acoustic insulating properties, and high resistance to fracture. The increasing interest in introducing degradable, renewable, and inexpensive reinforcement materials which have been environmentally friendly has stimulated the use

of cellulose fibers. The low cost, less weight, and density makes the natural fibers an attractive alternative to inorganic or petrochemical-based fibers.

Among all the natural fiber-reinforcing materials, abaca appears to be a promising material because it is inexpensive and abundantly available. Abaca or banana fibers, the cellulosic fibers obtained from the pseudo-stem of banana plant (*Musa textilis*) are bast fibers with relatively good mechanical properties (Joseph *et al.* 2002).

In tropical countries, fibrous plants are available in abundance, and some of them like abaca are agricultural crops. Abaca fiber at present is a waste product of banana cultivation. Hence the input of abaca fiber can be obtained for industrial purposes without any additional cost.

Nowadays abaca fiber reinforced composites are coming into interest due to the innovative application of abaca fiber in under-floor protection of passenger cars by Daimler Chrysler (Bledzki *et al.* 2006; Huang 2009). It is described that abaca fiber has a high tensile strength, resistant to rotting, and its specific flexural strength is nearer to that of glass fiber (Hintermann 2005). However, several considerations have to be taken into account in the design of natural fibers composites. One of the most important issues is the degrading behavior of the composites exposed to environmental conditions such as humidity, sunlight, or microorganisms. The poor resistance of the fibers to water absorption can have undesirable effects on the effective stress transfer from the matrix to the fiber (Srinivasa *et al*. 2011) in addition to the dimensional stability of the composites. Therefore, it is important to study in detail the water absorption behaviour in order to estimate not only the consequences that the water absorbed may have, but also the durability of natural fibers composites aged under water.

Low interfacial adhesion properties between fiber and polymer matrix often reduce their potential as reinforcing agents due to the hydrophilic nature of natural fibers; chemical modifications are considered to optimize the interface of fibers. The moisture absorbed by the fibers can be reduced by chemical modifications of fibers such as alkali treatment, acetylation, methylation, cyanoethylation, benzoylation, permanganate treatment, acrylation *etc*. (Joseph *et al.* 1997; Mishra *et al.* 2001; Sreekala and Thomas 2003; Seena *et al.* 2005; Mishra and Luyt 2008; Dhanalakshmi *et al*. 2012).

Alkali treatment of natural fibers is known to improve the stiffness, strength, and dynamic flexural moduli of the composites, indicating an increased interfacial bond strength and adhesion between the matrix and the fibers (Aziz and Ansell 2004; Baley *et al.* 2006; Stocchi *et al.* 2007). Lignin, pectin, and other impurities within the natural fibers are considered harmful for its adhesion with the matrix during the composite fabrication. The natural fibers are usually treated in order to improve resin-fiber interfacial bonding. Among the methods in improving the adhesive character of natural fiber, alkaline treatment may be considered to be the most economical technique, the main disadvantage of which is the deterioration in the fiber strength during treatment.

Currently, there is no information on the water absorption studies of single abaca fiber. Therefore, the present study seeks to determine the moisture absorption of single abaca fiber. A better understanding of moisture absorption property of fibers will help to develop a productive use of fibers in composite materials. In the present work, a detailed investigation on moisture absorption of single abaca fiber and the effect of alkali treatment on its moisture absorption property were carried out.

EXPERIMENTAL

Materials

Abaca fibers were obtained from the Maruti Peach Finishing Company, Tirupur, Chennai, India, and analytical grade reagents were purchased from Qualigens Company and used as received.

Methods

Fiber characterization

Extractable content: 5 g of air dried abaca fiber was placed in a Soxhlet extraction unit. A mixture of ethanol and toluene was used as solvent and the extraction process continued for a period of five hours. After extraction, the sample was rinsed with ethanol and hot water and dried up to constant weight at the temperature of 60 ^{o}C. The extractables were calculated as a percentage of the oven-dried test sample.

Lignin content: 2 g of extracted sample was placed in a flask, and 15 mL of 72% sulphuric acid was added. The mixture was stirred frequently for three hours at 25 ^{o}C, and 200 mL of distilled water was added to the mixture. Then the mixture was boiled for two hours and cooled. After 24 hours, the lignin was transferred to the crucible and washed with hot water repeatedly until becoming acid-free. The collected lignin was dried at 105 ^{o}C and cooled down in a desiccator and weighed. The drying and weighing were repeated until constant weight was obtained.

Holocellulose content: 3 g of air dried abaca fiber was weighed and placed in an Erlenmeyer flask, and then 160 mL of distilled water, 0.5 mL of glacial acetic acid, and 1.5 g of sodium chloride were added, successively. The flask was placed in a water bath and heated up to 75 ^{o}C for an hour, and then an additional 0.5 mL of glacial acetic acid and 1.5 g of sodium chloride were added. The additions of acetic acid and sodium chloride were repeated two times hourly. The flask was placed in an ice bath and cooled to below 10 ^{o}C. The holocellulose was filtered and washed with acetone, ethanol, and water respectively. After the washings, the sample was dried in an oven at 105 ^{o}C before weighing.

α-cellulose content: 2 g of holocellulose was placed in a beaker, and 10 mL of 17.5% sodium hydroxide solution was added. The fibers were stirred by glass rod so that they could be soaked with sodium hydroxide solution vigorously. Then the sodium hydroxide solution was added to the mixture periodically (once every five minutes) for half an hour, and the mixture temperature was kept at 20 ^{o}C. About 33 mL of distilled water was added to the beaker and kept in it for an hour. The holocellulose residue was filtered and transferred to the crucible and washed with 100 mL of 8.3% sodium hydroxide, 200 mL of distilled water, 15 mL of 10% acetic acid, and with water, successively. The crucible with α-celluloses was dried and weighed.

Hemicellulose content: The hemicellulose content of abaca fiber was determined by calculating the difference between holocellulose and α-cellulose (Bledzki *et al.* 2008).

Fourier-Transform Infrared Spectroscopy (FTIR)

Fourier-transform infrared spectroscopy, model Perkin Elmer System 2000 was used to analyze the possible chemical bonding existing in the untreated and alkali treated

abaca fibers. FTIR spectra were analyzed with an IR spectrophotometer in the range 500 cm^{-1} to 4000 cm^{-1}.

Morphological study

Scanning electron microscopy (SEM) photographs of untreated and alkali-treated abaca fibers were obtained with a JEOL JSM-T330A scanning electron microscope at the accelerating voltage of 20 KV.

Alkali treatment

The fibers were first dewaxed by soaking fibers in 1:2 mixture of ethanol and benzene for 72 h at 50 ^{o}C, followed by washing with deionized water and then air drying. The dewaxed fibers were immersed in NaOH solutions of different concentrations, where the total volume of the solution was 15 times the weight of the fibers. The fibers were kept in alkaline solution for 72 hours at a temperature of 30 ^{o}C; they were thoroughly washed in tap water and then neutralized with 2% acetic acid solution. Lastly, the fibers were washed again in tap water to remove the last traces of acid sticking to it, so that the pH of the fibers was approximately 7. Then, they were dried at room temperature for 48 hours to obtain alkali-treated fibers (Srinivasa *et al*. 2010).

Water absorption

Water absorption studies on untreated and alkali treated fibers were carried out in various sources of water, such as pond water, river water, bore water, and sea water. The pH values of water samples were; bore water: 7.40, pond water: 8.20, river water: 7.74, and sea water: 7.76. Bundles of fibers (2 g) were kept together and placed inside a beaker containing various sources of water at room temperature (25 ^{o}C). The weight of the fibers was measured at different intervals and the MC was calculated by weight difference,

$$\mathrm{MC} = \frac{m_a - m_d}{m_a} \times 100\% \quad (1)$$

where MC is the moisture content, m_a is the mass of the sample after exposure to moisture, and m_d is the mass of the dry sample. More details about the technique can be found in Bismarck *et al*. 2002; Jimenez and Bismarck 2007; and Stana-Kleinschek and Ribitsch 1998.

RESULTS AND DISCUSSION

Chemical Composition of Fiber

The chemical analysis of the major components of abaca fiber is listed in Table 1. Cellulose is the main reinforcement material (Bessadok *et al.* 2007). The cellulose is held together by amorphous hemicelluloses. Fibers are cemented together in the plant by lignin, which is commonly known as plant cell adhesive. The cellulose content in the abaca fibers is comparable with those of flax, jute, sisal, and coir fibers (Rout *et al.* 2001; Saira *et al.* 2007; Majid 2009), and the experimental values are in agreement with the

previous studies (Rowell *et al*. 1997; Indicula *et al*. 2006; Taj *et al*. 2007; Satyanarayana *et al*. 1990).

Table 1. Chemical Composition (wt%) of Abaca Fibre Measured Experimentally and in Comparison with Previous Works

Reference	Cellulose	Hemicellulose	Lignin	Moisture Content	Ash Content
Experimental	68.32	17.32	8.50	0.76	5.10
Indicula *et al.*	63-64	19.00	5.00	10-11	--
Rowell *et al.*	61.50	14.90	9.70	--	4.80
Taj *et al.*	56-63	--	12-13	5-10	--
Satyanarayana *et al.*	66.00	--	5.00	--	--

Fourier-Transform Infrared Spectroscopy (FTIR)

The infrared spectra for single abaca fibers were obtained by using an FTIR spectrometer. Alkali treatment of abaca fibers resulted in significant differences in the infrared spectra (Fig. 1). The obtained peaks are explained in Table 2.

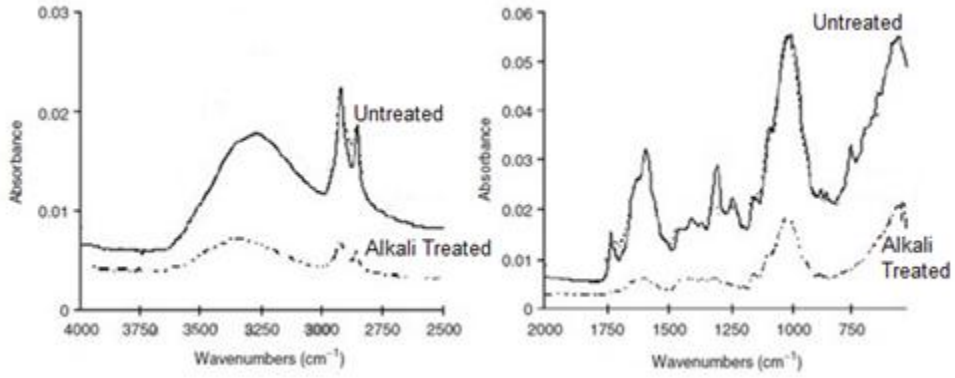

Fig. 1. IR spectra of untreated and alkali treated abaca fiber

A large band at 3400 cm^{-1} is mainly related to the hydroxyl groups and the bonded O-H stretching vibrations present in carbohydrate (cellulose + hemicellulose) (Roger 1997). As for alkali-treated abaca fibers, the 3347 cm^{-1} band assigned to the alcohol group was reduced due to the removal of the hemicellulose component. Another peak due to the alcohol group of cellulose OH deformation that appeared at 1310 cm^{-1} was also reduced by alkali treatment. The untreated abaca fibers show the absorption band of carbonyl stretching at 1732 cm^{-1}, corresponding to hemicellulose; these can no longer be observed in alkali-treated fiber (Herrera-Franco and Valdez-Gonzalez 2005). The large peaks at 1593 and 778 cm^{-1} shown in untreated fiber spectra could be due to the presence of lignin, and they seem to be removed by alkali treatment. It can be observed that the peak at 1245 cm^{-1} disappears for alkali treated fibers. Alkali treatment removes waxy epidermal tissue, adhesive pectins, and hemicellulose that bind fiber bundles to

each other. The C-O-C symmetric glycosidic stretch at 1100 cm^{-1} arose from the polysaccharide component that was largely cellulose and appeared for both untreated and treated abaca fibers (Jannah *et al*. 2009) It can be summarized that treatment with alkali had removed most of the lignin and hemicellulose component. Further, the treatment had changed the hydrophilic nature of the fibers to hydrophobic nature.

Table 2. FTIR Peaks Position of Original Abaca Fibers

Wave number (cm^{-1})	*FTIR peak origin*
3200-3500	Hydroxyl group and bonded OH stretching
1732	C=O stretching vibrations (carboxylic group and ester groups)
1593	Lignin components
1310	Alcohol group
1245	Hemicellulose and pectin
1100	C-O-C symmetric glycosidic stretch
777	Lignin components

Morphological Study

SEM micrographs of untreated and alkali-treated abaca fibers are represented in Figs. 2 and 3, respectively. From Fig. 2, it can be observed that untreated abaca fiber presents a network structure in which the fibrils are bound together by hemicellulose and lignin. The alkali-treatment of fibers results in a higher degree of roughness as indicated in Fig. 3 due to the partial removal of hemicellulose and lignin (Srinivasa *et al.* 2010).

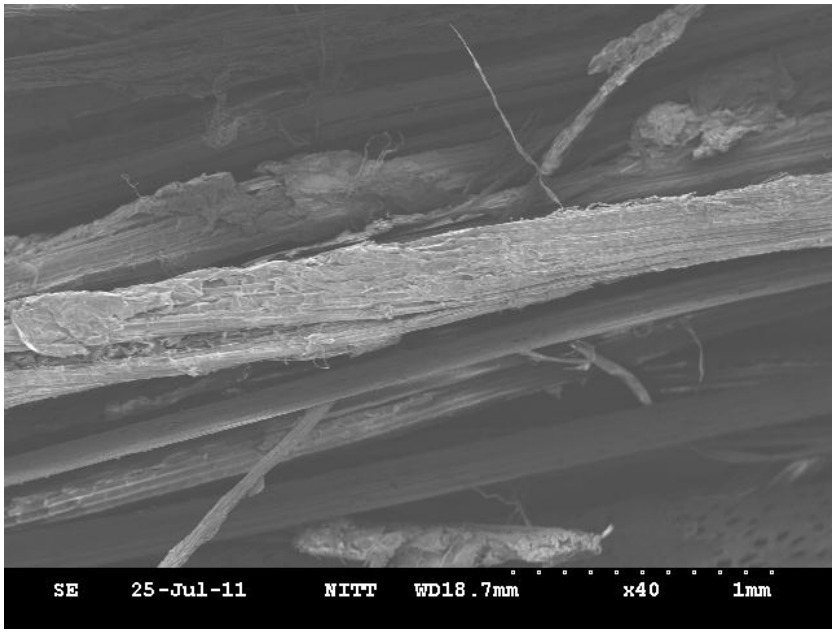

Fig. 2. SEM photograph of untreated abaca fiber

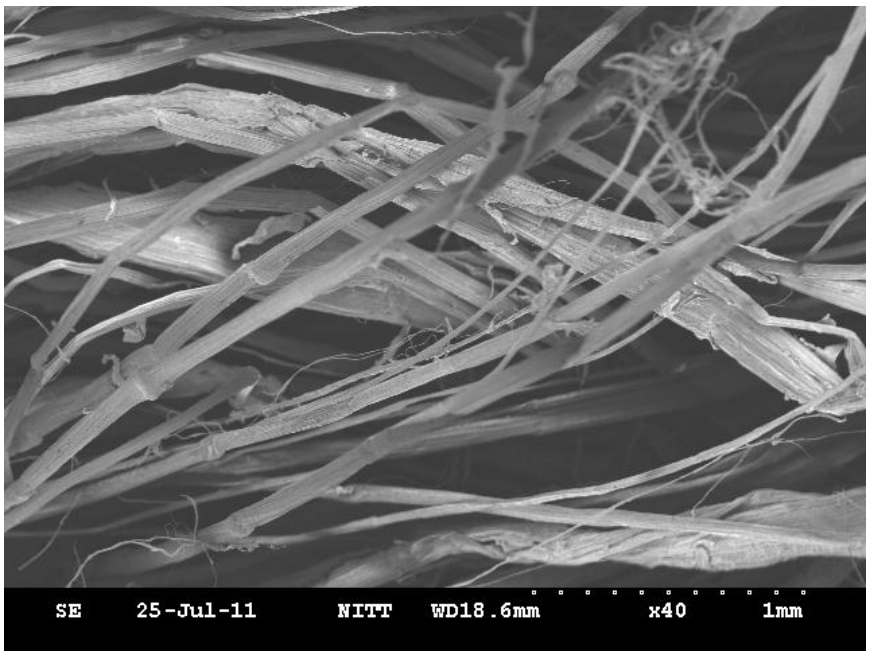

Fig. 3. SEM photograph of 5% NaOH treated abaca fiber

Water Absorption

To measure the moisture content of the abaca fiber, the fiber was immersed in a beaker containing water from various sources at room temperature. After every 24 hours, the fiber was taken out, and excess water on the fiber surface was removed before weighing. Three replicates were tested, and the results were presented as an average of three. The untreated abaca fiber was used as a control in this study. It was observed that moisture absorption of fiber was reduced drastically upon alkali treatment, which agrees with previous reports (Bismarck *et al*. 2002; Jimenez and Bismarck 2007; Stana-Kleinschek and Ribitsch 1998). Comparison of moisture absorption studies of untreated and alkali-treated abaca fiber in sea water, pond water, river water, and borewell water (Fig. 4) reveals that the moisture absorption capability of abaca fiber was reduced by alkali treatment. Also, the moisture absorption of the treated fiber decreased with an increase in alkali concentration. From Fig. 4, it can also be seen that alkali treated fiber absorbed less moisture in pond water (pH = 8.2) than in the other water samples.

To summarize, abaca fiber treated with 20% alkali showed about 38.27, 52.94, 62.50, and 63.50% lower moisture absorption properties than the untreated abaca fiber in river water, borewell water, sea water, and pond water, respectively after immersing the fiber in a water sample for about 624 hours. This may be due to removal of lignin and hemicellulose component of fiber by alkali treatment (Srinivasa *et al.* 2010; Jannah *et al*. 2009; Dhanalakshmi *et al*. 2012). Further, the hydrophilic nature of fiber had changed into a more hydrophobic nature by alkali treatment.

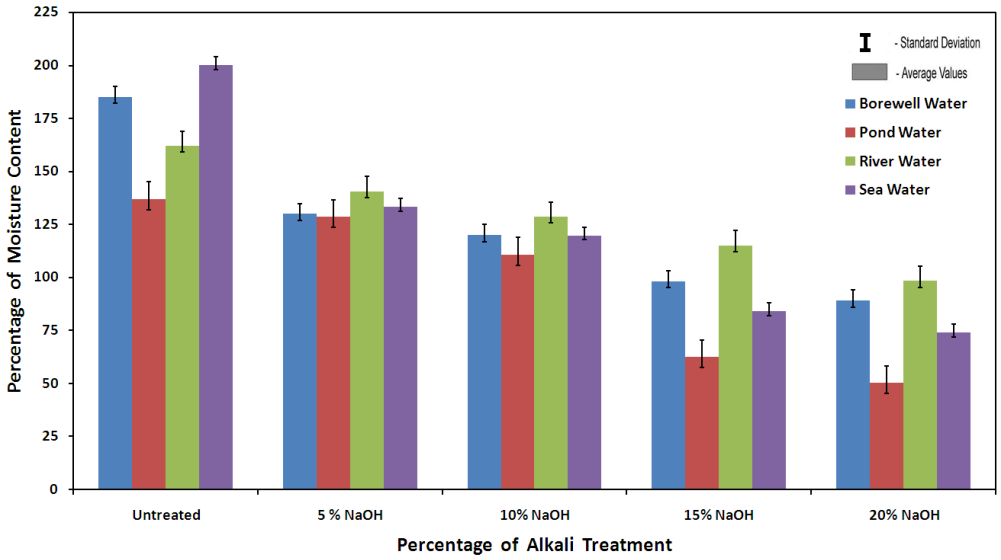

Fig. 4. Comparative study of water absorption of untreated and alkali-treated abaca fiber

CONCLUSIONS

1. Alkali-treated abaca fiber showed lesser absorption of moisture in comparison with untreated fiber.
2. Alkali treatment of abaca fibers resisted up to 67% moisture absorption, depending on the extent of alkali treatment.
3. Abaca fiber morphology significantly changed due to the alkali treatment.

REFERENCES CITED

Aziz, S. H., and Ansell, M. P. (2004). "The effect of alkalization and fiber alignment on the mechanical and thermal properties of kenaf and hemp bast fiber composites: Part I-Polyester resin matrix," *Composites: Science and Technology* 64(9), 1219-1230

Baley, C., Busnel, F., Grohens, Y., and Sire. (2006). "Influence of chemical treatments on surface properties and adhesion of flax fiber-polyester resin," *Composites Part A: Applied Science and Manufacturing* 37(10), 1626-1637.

Bessadok, A., Marias, S., Gouanve, F., Colasse, L., Zimmerlin, I., Roudesli, S., and Metayer, M. (2007). "Effect of chemical treatments of alfa (*Stripatenacissima*) fibers on water-sorption properties," *Composites Science and Technology* 67, 685-797.

Bismarck, A., Askargorta, I.A., Springer, J., Lampke, T., Wielage, B., Stamboulis, A., Shenderovich, I., and Limbach, H. H. (2002). "Surface characterization of flax, hemp and cellulose fibers; Surface properties and the water uptake behavior," *Polymer Composites* 23(5), 872-894.

Bledzki, A. K., Faruk, O., and Sperber, V. E. (2006). "Cars from bio-fibers," *Macromolecular Materials and Engineering* 291, 283-293.

Bledzki, A. K., Mamun, A. A., Lucka-Gabor, M., and Gutowski, V. S. (2008). "The effects of acetylation on properties of flax fiber and its polypropylene composites," *eXPRESS Polymer Letters* 2(6), 413-422.

Dhanalakshmi, S., Ramadevi, P., Basavaraju, B., and Srinivasa, C. V. (2012). "Effect of esterification on moisture absorption of single areca fiber," *International Journal of Agriculture Sciences* 4(4),227-229.

Herrera-Franco, P. J., and Valdez-Gonzalez, A. (2005). "A study of mechanical properties of short natural fiber reinforced composites," *Composites Part B: Engineering* 36(8), 597-608.

Hintermann, M. (2005). "Automotive exterior parts from natural fibers," *RIKO-2005*, Hannover, Germany.

Huang, G. (2009). "Tensile behaviours of the coir fibre and related composites after NaOH treatment," *Materials and Design* 30, 3931-3934.

Indicula, M., Boudene, A., Umadevi, L., Ibos, L., Candau, Y., and Thomas, S. (2006). "Thermophysical properties of natural fiber reinforced polyester composites," *Composite Science and Technology* 66(15), 2719-2725.

Jannah, M., Mariatti, M., Bakkar, A., and Khalil, A. (2009). "Effect of chemical surface modifications on the properties of woven banana reinforced unsaturated polyester composites," *Journal of Reinforced Plastics and Composites* 28(12), 1519-1532.

Jimenez, A., and Bismarck, A. (2007). "Wetting behaviour, moisture up-take and electrokinetic properties of lignocellulosic fibres," *Cellulose* 14, 115-127.

Joseph, K., Paul, A., and Thomas, S. (1997). "Effect of surface treatments on the electrical properties of low-density polyethylene composites reinforced with short sisal fibers," *Composites Science and Technology* 57, 67-79.

Joseph, S., Sreekala, M.S., Oomzen, Z., Koshy, P., and Thomas, S. (2002). "A comparison of the mechanical properties of phenol formaldehyde composites reinforced with banana and glass fibers," *Composites Science and Technology* 62, 1857-1868.

Majid, A. (2009). "Natural fibers as construction materials," *Proceedings of the 11th International Conference on Non-Conventional Materials and Technologies*, Bath, UK.

Mishra, S., Misra, M., Tripathy, S. S., Nayak, S. K., and Mohanty, A. K. (2001). "Graft copolymerization of acrylonitrile on chemical modified sisal fibers," *Macromolecular Materials and Engineering* 286, 107-113.

Mishra, S. B., and Luyt, A. S. (2008). "Effect of organic peroxides on the morphological, thermal and tensile properties of EVA-organoclay nanocomposites," *eXPRESS Polymer Letters* 2, 256-264.

Rowell, R. M., Young, R. A., and Rowell, J. K. (1997). "Chemical composition of fibers, paper and composites from agro-based resources," CRC Press Inc., Boca Raton, Florida, 105-131.

Rout, J., Misra, M., Tripathy, S. S., Nayak, S. K., and Mohanty, A. K. (2001)."The influence of fiber treatment on the performance of coir-polyester composites," *Composites Science and Technology* 61, 1303-1310.

Satyanarayana, K. G., Sukumara, K., Mukherjee, P. S., Pavithran, C., and Pillai, S. G. K. (1990). "Natural fibre-polymer composites," *Cement and Concrete Composites* 12(2), 117-136.

Seena, J., Koshy, P., and Thomas, S. (2005). "The role of interfacial interactions on the mechanical properties of banana fiber reinforced phenol formaldehyde composites," *Composite Interfaces* 12, 581-600.

Sreekala, M. S., and Thomas, S. (2003). "Effect of fiber surface modification on water-sorption characteristics of oil palm fibers," *Composite Science and Technology* 63, 861-869.

Srinivasa, C. V., Basavaraju, B., Mownesh, G. K., and Raghu Patel, G. R. (2010). "Flexural behaviour of areca fibers composites," *BioResources* 5(3), 1845-1858.

Srinivasa, C. V., Suresh, Y. J., and Premakumar, W. P. (2011). "Mechanical behavior of areca fiber reinforced epoxy composites," *Advances in Polymer Technology*, DOI: 10.1002/adv.20255.

Stana-Kleinschek, K., and Ribitsch, V. (1998)." Electrokinetic properties of processed cellulose fibers," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 140, 127-138.

Stocchi, A., Lauke, B., Vazquez, A., and Bernal, C. (2007). "A novel fiber treatment applied to woven jute fabric/vinyl ester laminates," *Composites Part A: Applied Science and Manufacturing* 38(5), 1337-1343.

Taj, S., Munawar, M. A., and Khan, S. (2007). "Natural fiber-reinforced polymer composites," *Proceedings of Pakistan Academy of Science* 44(2), 129-144.

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