Investigating the Effect of Alkaline-Peroxide Treatment on the Chemical Composition and Mechanical Properties of Sisal Fiber

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ABSTRACT

Studies on the use of biofibers as a substitute to man-made fibers in the area of fiber-reinforced composites have continued to open up further industrial applications and possibilities. This is not unconnected with the enormous advantages of natural fibers. However, the poor interfacial bonding between fiber and matrix as well as the hydrophilic characteristics of natural fibers has always remained a concern, hence the need to modify fibers. In this study, sisal fibers are chemically modified using the Alkaline-Peroxide treatment method at the same concentration and at room temperature but different time intervals (2, 4, 6, 8, and10 hours). The chemical constituents and mechanical properties were determined using the TAPPI T222 methods and Instron tensile analyzer, respectively. Spectral analysis was also carried out.

The results show that the chemical treatment enhances the removal of lignin and hemicelluloses which are detrimental to the interfacial bonding in the composite. The treatment time seems to have a great influence on the percentage of cellulosic content. The result for the tensile properties equally shows that sample S8 (8 hours) gave the best tensile properties; therefore, could be suggested to give the optimal process conditions for this type of treatment.

(Keywords: alkaline treatment, mechanical properties, sisal fiber, FTIR, biofibers)

INTRODUCTION

The necessity for balance between the brisk upturn in industrial and technological yield as well as high pollution levels chiefly from non-degradable polymeric materials (such as glass-fiber composite) has raised much interest in research and development of composites from renewable and sustainable resources (Svennerstedt, 2002). The skyrocketing cost of energy, especially which of petroleum has made even, manmade reinforcing fibers more expensive. The excellent properties at the same time low cost of biofibers are increasingly exploring new areas of applications of composite by the day.

Biofibers (also called natural fibers) from sustainable and renewable resources are now increasingly used as reinforcements in polymer matrix as they provide benefits to the environment such as the utilization of natural resources and their biodegradability (Kabir et al, 2012). The successful use of these fibers is highly dependent on their well-defined mechanical as well as structural properties which are influenced by the fiber plant, variety and growing conditions, climate conditions, plant's age, as well as the fibre's extraction method (Kabir et al., 2012). The beneficial engineering properties of biofibers include specific strength, low density/light weight, toughness and high specific modulus, good thermal properties as compared to most of the synthetic polymers, non-respiratory/toxic irritation, reduced tool wear, and ease of processing and absorbing CO_2 during their growth cycle (Asokan, 2012 and Kabiretal, 2012).

Effects of chemical treatments on surface morphology, thermal behavior and structure of natural fibers was reported by various authors. Chemical treatments remove the lignin from surface of natural fibers and fiber surface becomes rough. Chemical treatments also reduce the number of free hydroxyl groups of the cellulose, which results in the reduction of the polarity of the cellulose molecules and enhance the compatibility with hydrophobic polymer matrices. Pre-treatments of the fiber can clean the fiber surface, chemically modify the surface, stop the moisture absorption process and increase the surface roughness.

As the natural fibers bear hydroxyl groups from cellulose and lignin, therefore, they are amenable to modification. The hydroxyl groups may be involved in the hydrogen bonding within the cellulose molecules there by reducing the activity towards the matrix. Chemical modifications may activate these groups or can introduce new moieties that can effectively interlock with the matrix.

Cellulosic fibers are hygroscopic in nature; moisture absorption can result in swelling of the fibers which may lead to micro-cracking of the composite and degradation of mechanical properties. This problem can be overcome by treating these fibers with suitable chemicals to decrease the hydroxyl groups which may be involved in the hydrogen bonding within the cellulose molecules. A number of fiber surface treatments like silane treatment, benzoylation and peroxide treatment were carried out which may result in improved mechanical performance of the fiber and composite. This work was carried out to investigate the effect of Alkaline-Peroxide treatment on the chemical constituents and the tensile properties of sisal fiber.

MATERIALSANDMETHODS

Materials

The major materials used in this work included sisal fibers extracted at the National Research Institute of Chemical Technology (NARICT), Distilled water, Sodium Hydroxide, Hydrogen Peroxide, Acetic acid.

Equipment

Weighing balance, shaker water bath, beakers, furnace, crucible, Instron universal tensile testing machine, FTIR Analyzer.

METHODOLOGY

Sourcing and Extraction of Biofibers

Matured sisal plants of average lengths of 100cm and estimated age of 4years was used for this research work. According to literature, researchers employed different percentage concentration of alkali solution, immersion times and solution temperature in treating natural fibers. In this work however, Alkali treatment with 5% NaOH concentration followed by peroxide treatment of 3% H_2O_2 was used. The 5% NaOH solution will be prepared by adding 0.5kg of NaOH to 1.5 liters of distilled water in a beaker. By using a mechanical mixer, the NaOH is dissolved completely. The NaOH solution was then poured into a bigger container containing 8.5 liters of distilled water. The biofibers were then soaked separately in the NaOH solution at room temperature (30^{o}C) maintaining a fiber/solution ratio of 1:15.

The natural fibers were allowed in the alkaline solution for 2, 4, 6, 8, and 10 hrs. The fibers were then removed, washed several times with excess distilled water and further treated with 3w% of H_2O_2 at 45^{o}C and 40rpm for 8hrs. Continued reaction will remove more lignin content and activate the OH groups of the cellulose (Zaabal et al., 2017). The sisal fiber was washed with distilled water and treated with 10w% acetic acid at a room temperature for 30min to neutralize and remove excess NaOH on the fiber. The fibers are then dried at room temperature for 48hrs to remove free water followed by oven drying to remove any trapped moisture at 80^{o}C for 4hrs. Fibers were separated from clamped bundles and kept in covered containers in a conditioning chamber.

The treated and untreated biofibers to be used are subjected to various tests before and after treatments. This was done to ascertain the optimal treatment time. The various tests carried out on the fiber include mechanical tests, chemical composition analysis and spectra analysis.

MECHANICAL TESTING OF FIBRES

The mechanical properties such as maximum tensile strength, Young's modulus, tensile strain, yield stress, maximum load, energy at maximum load, density etc. of the treated and untreated biofibers will be tested. These tests will be carried out on a computer controlled Intsron testing machine with model number 5556. The tests were performed with 20 fibers using a displacement rate of 0.03 $mm.s^{-1}$ with a 5kN load cell and fiber gauge length of 20mm. The fibers were properly selected before testing to ensure that the specimen yields accurate results (Lima et al., 2014, Razali et al., 2015).

Analysis of Chemical Compositions

Analysis such as acid-insoluble lignin content, cellulose content, hemicelluloses content etc. where determined for the untreated and alkaline-peroxide treated sisal fibers.

Determination of Lignin Content

To determine content of acid-insoluble lignin, the TAPPI T222 method will be used. In this method, the pre-hydrolysis of the extracted sample with 72 wt% sulfuric acid at room temperature for 2hrs. Then the concentrated acid is diluted with water, and the sample is hydrolyzed with dilute 3 wt% acid at boiling temperature for 4hrs. After overnight, the acidic dispersion of lignin will be filtered through a glass-filter having average pore diameter of 10 µm. Sediment of lignin will be washed on the filter with hot water up to pH=7 and then dried at 105°C to constant weight. The percentage Lignin will be calculated as follows;

$$AIL = \frac{P - P_t}{P_S} \times 100 \quad (1)$$

Where: AIL = acid insoluble lignin, P = weight of dry acid-insoluble lignin together with PP-tube; P_t = weight of empty PP-tube and Ps = weight of extracted and dried biomass sample.

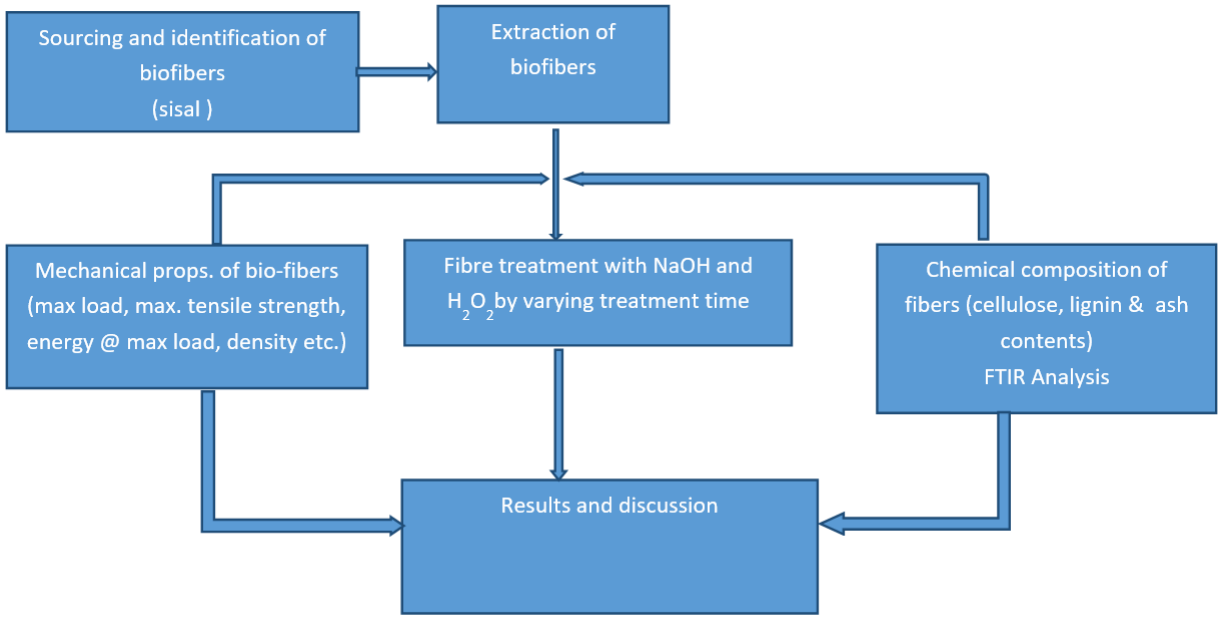


Figure 1: Schematic Representation of the Methodology.

Determination of Cellulose Content

1g of the sample will be weighed and placed inside a beaker where 25ml of 80% acetic acid, 1ml of concentrated nitric acid and 4 glass beads are added and reflux for 20mins on a cellulose refluxing apparatus. The fiber will then be washed into 50ml centrifuge tube with hot 95% ethanol and centrifuge at 18000 r.p.m. for 5 minutes. The liquid is decanted, 95% ethanol is added, stirred and centrifuge for another 5 minutes. Liquid is decanted; sample washed with hot 95% ethanol and filter by suction.

Sample is then washed three times with hot benzene, two times with 95% ethanol and once with ether. The sample will then be placed inside a weighed crucible and later placed in the oven maintained at 105ºC for 1 hour. The crucible will later be cool in desiccators and weighed. The crucible will then be placed inside the furnace that was maintained at 550ºC for 4 hours, cool in desiccators and weigh for ash weight. The percentage cellulose will be calculated as follows:

$$\%cellulose = \frac{W_2 - W_1}{W_s} \times 100 \qquad (2)$$

Where: W_1=weight of crucible + sample after ashing; W_2=weight of crucible + sample after drying and W_S=weight of sample

Determination of Hemicellulose

0.5g of sample will be weighed into two different beakers labelled A and B. 5%KOH will be added to the sample in flask A while 24% KOH will be added to the sample in flask B and both samples are allowed to stand for 2 hours. The mixtures will be filtered with purpling cloth, washed with additional KOH solution of their respective percentages and the filtrate is received into two different beakers (A and B). The hemicelluloses are then quantitatively precipitated by the addition of alcohol (ethanol). The precipitated hemicelluloses will be isolated by centrifuging for 10minutes. The isolated hemicellulose will then be washed with alcohol (ethanol) and ether and finally transferred into two different crucibles (A and B). The samples will be dried in oven for 2 hours at 105ºC. After this, they will be transferred into desiccators and allowed to cool for 30 minutes after which their weights are taken. The samples will also be placed inside the furnace maintained at 550ºC for 3 hours after which they will be cooled inside the desiccators and weighed. The weight of the precipitate A will be calculated (W_A) while the weight of the precipitate B will also be calculated (W_B). Hence the percentage hemicelluloses compositions of the samples will be calculated as follows:

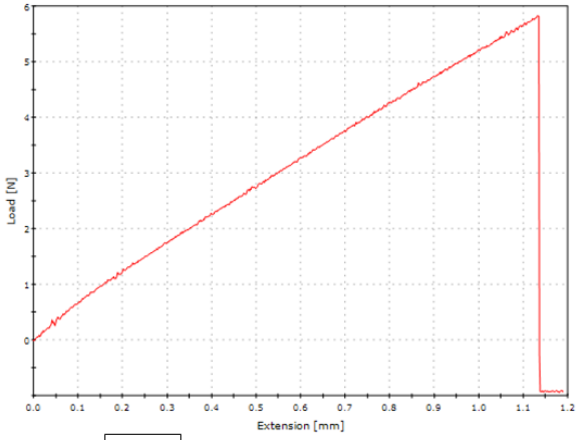
$$\%Hemicelluloses\ (A) = \frac{W_A}{W_2} \times 100 \qquad (3)$$

Where: W_A = dried weight of hemicelluloses precipitate A, W_2 = dried weight of the hemicelluloses sample.

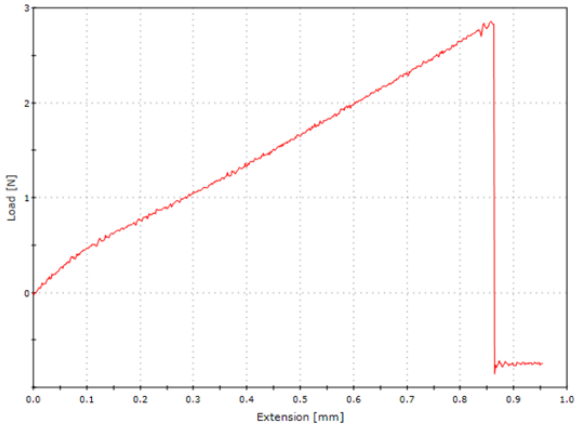
$$\%Hemicelluloses\ (B) = \frac{W_B}{W_2} \times 100 \qquad (4)$$

Where: W_B = dried weight of hemicelluloses precipitate B, W_2 = dried weight of the hemicelluloses sample.

RESULTS AND DISCUSSION



a



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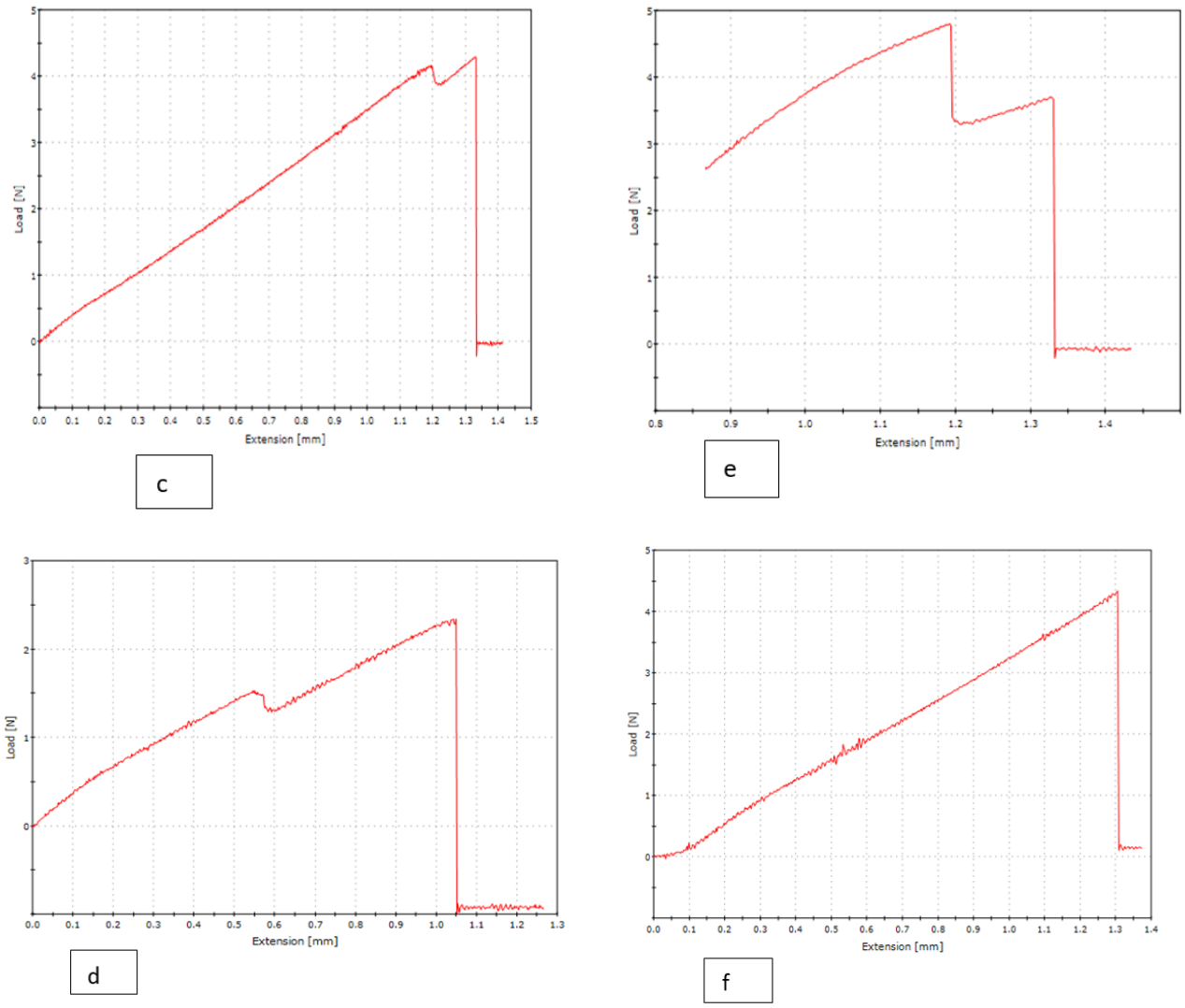

Figure 2: Tensile Properties Graphs (a) Untreated Fiber, (b) S2, (c) S4, (d) S6, (e) S8, and (f) S10.

Table 1: Tensile Properties of the Sisal Fiber Samples.

Samples	Max. Tensile strength MPa	Tensile Strain mm/mm	Modulus of Elasticity MPa	Max. Load N	Percentage Elongation	Yield stress (@ 0.1% offset) MPa
Untreated sample (SN)	515.4	0.02	25,770	5.82932	2	456.5
S2	252.8	0.02	12,648	2.85907	2	217.8
S4	709.65	0.24	30,367	4.3274	2	683.716
S6	207.2	0.02	10360	2.34348	2	159.6
S8	754.521	0.024	31,438	4.8	2	652.005
S10	383.6	0.03	12,786	4.3386	3	367.4

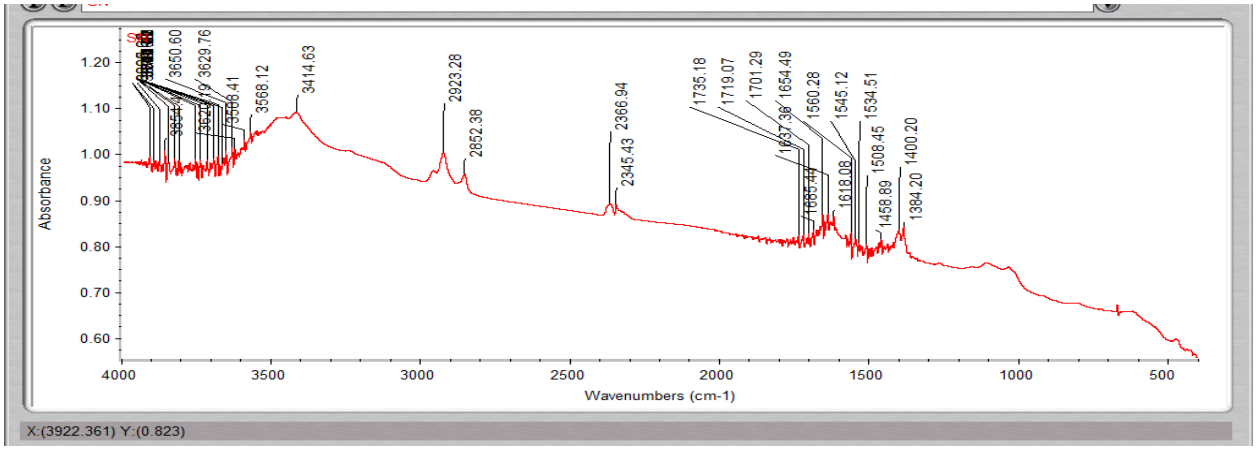

Figure 3: FTIR for Untreated Sample.

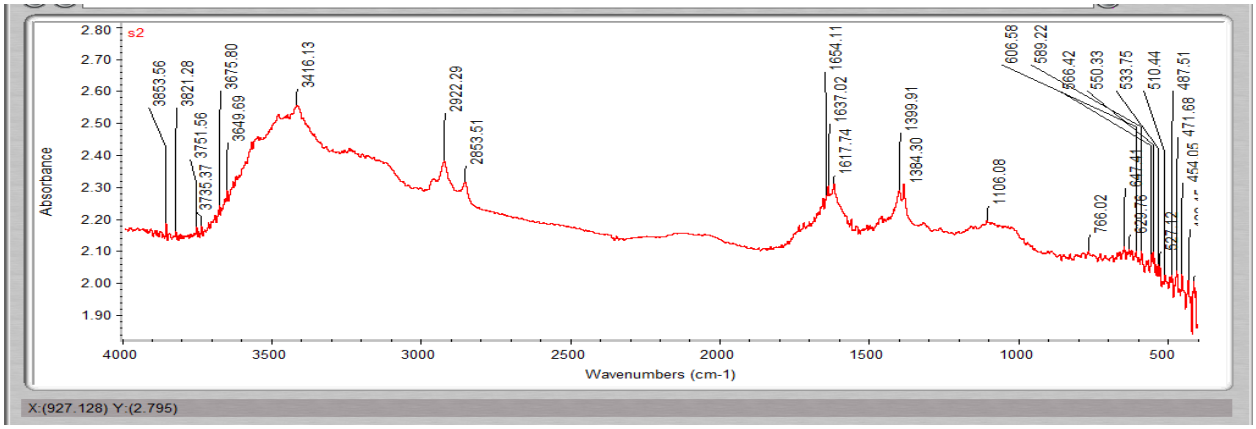

Figure 4: FTIR for Sample S2.

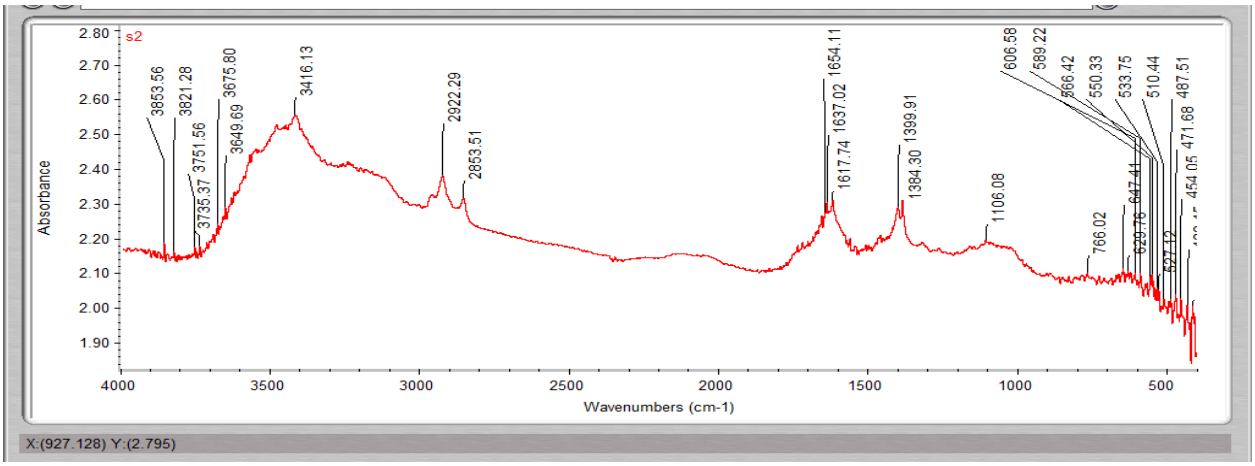

Figure 5: FTIR for Sample S4.

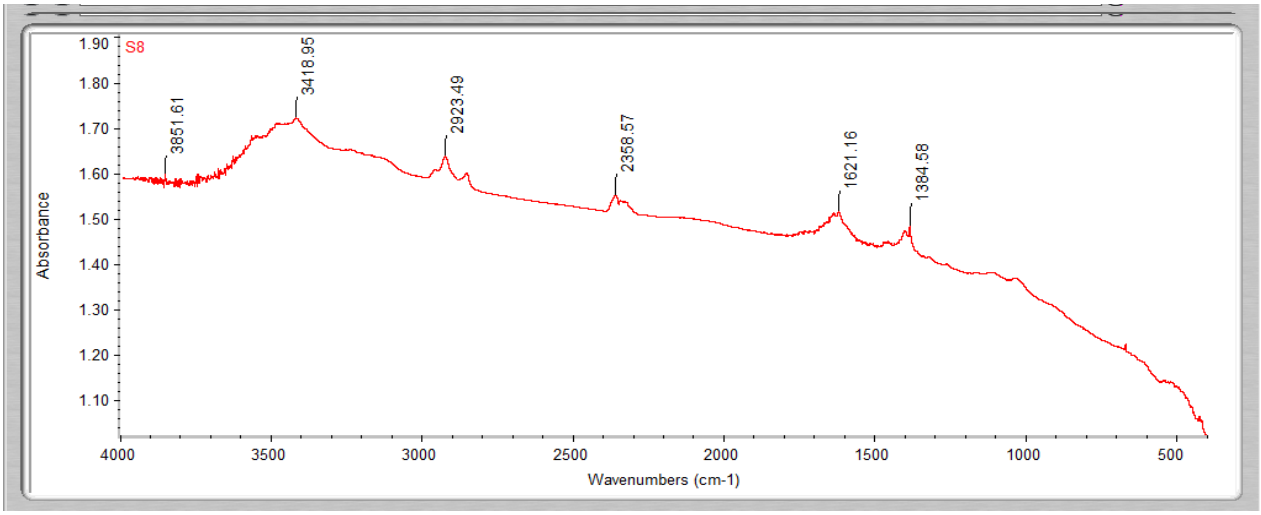

Figure 6: FTIR for Sample S8.

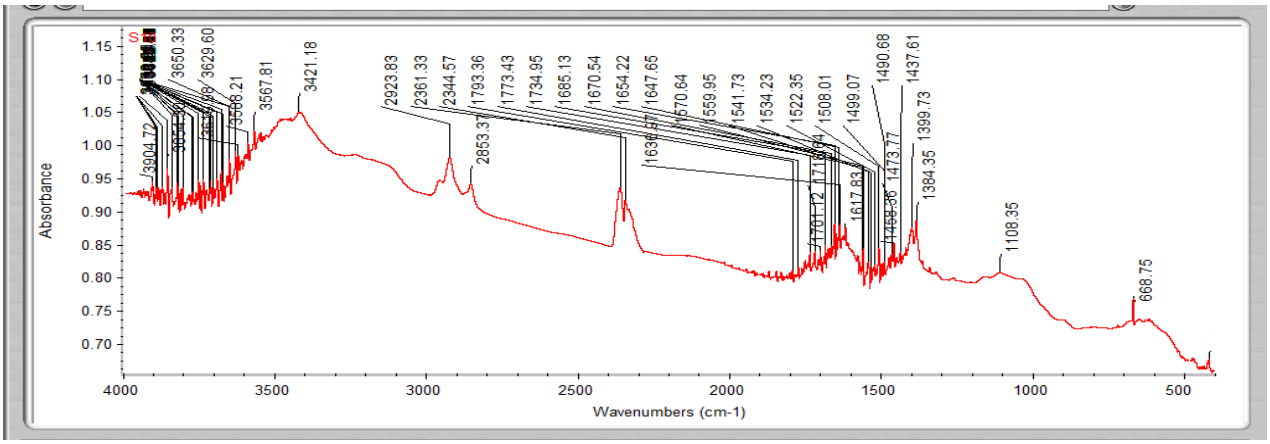

Figure 7: FTIR for Sample S10.

Table 2: FTIR Absorbance Peaks.

Bonding Type	Untreated fiber	S2	S4	S6	S8	S10
OH Stretching	3414.63	3416.13	3416.13	3415.31	3418.95	3421.18
C_H symmetrical stretching	2923.83	2922.29	2928.90	2923.85	2923.49	2923.83
C-H asymmetrical stretching	2852.38	2853.51	--------	----------	---------	-------
C-H vibrational	2366.94	-------	---------	2363.85	2358.57	2344.57
OH bending of absorbed water	1617.74	1617.74	1620.74	----------	1621.16	---------
HCH and OCH in plane bending	1400.20	-------	----------	---------	1384.58	----------

DISCUSSION

Chemical Composition

During chemical treatments, constituent like hemicelluloses was hydrolyzed by the action of alkaline solutions, whereas lignin was removed during the addition of hydrogen peroxide. To improve and achieve an acceptable dispersion level in the solution, mechanical homogenization with shaker water bath was also used for all samples. All the treatments contributed to the removal of hemicelluloses and lignin contents as shown in Table1 resistance to extraction with alkaline of the sugars that are the main constituents of hemicelluloses are due to the association between xyloglucan and cellulose that is very strong. Xyloglucan probably binds not only to the surface of cellulose microfibrils, but it can also be entrapped within the micro fibrils. Xylans, xyloglucans and glucomannans are all able to bind onto cellulose fibrils in a manner similar to the interchain bonding of cellulose itself. The results show a linear increase in percentage cellulose content as treatment time was increasing. Conversely, as the treatment time increases, a percentage of lignin and hemicellulose reduces. Also, the results revealed the response of the ash contents of the fibers to the chemical treatments.

The bonding nature between the fiber and the matrix depends on the atomic arrangement, chemical properties of the fiber and the chemical constitution of polymeric matrix. However, in the natural fiber composite, cellulose is the principal coupling agent in the polymer/fiber bonding. On the other hand, lignin acts as an obstruction to the coupling agent diffusion, preventing good adhesion.

Response to Tensile Stress and UTS

Results revealed the response of the fibers (treated and untreated) to tensile stress and UTS. It was observed that samples treated for 8 (S8) gave the highest UTS of 754.521 MPa, closely followed by S4 with 709.65MPa. However, the untreated sample gave higher UTS (515.4MPa) as compared to the other treated samples. The results for the treated fibers are influenced by the percentage cellulose content, where, where higher cellulose structure in the fiber contributed to the high strength properties. This supports the findings of Reddy and Young (2005) that cellulose crystalline structure contributes to stability of the plant.

The study of tensile properties of fibers is important because the load applied to composites will transfer to the fiber first. The fiber helps to sustain the load applied, and once the fiber has failed, then the composite as a whole will have failed. Generally, natural fibers consist of cellulose, lignin and hemicellulose. Usually, the tensile strength and Young's modulus of fibers increase as the cellulose content increases (Ishak *et al* 2011). The ductility of the plant fibers depends on the orientation of microfibrils to the fiber axis. If it is spiral, then it is ductile, while if it is parallel, it is rigid, inflexible, and has high tensile strength. another factor that affects the properties is the fibers' defects. The fiber used as a reinforcement material must have a minimum of defects, where if the defected present in the structure, the failure will start at the weak point (defects). Thus, a detail inspection under microscope needs to be performed in other to determine the quality of a fiber.

Young's Modulus of the Fibers

The results of the Young's modulus of elasticity of the fibers were shown in Figure 2. Samples S8 and S4 again gave the best results of 31,438MPa and 30,367 Mpa, respectively, followed by the untreated fiber (25770MPa). Young's modulus is the slope of the stress-strain curve within the range of proportionality before yield. Yield stress is defined as the stress at which materials experience a major micro structural deformation while the breaking stress is the stress at which materials failed. At the yield stress, a large amount of deformation takes place at constant stress.

FTIR

The absorbance peaks of interest in this study have been identified and shown in Table 2. Alkali treatment reduces hydrogen bonding due to removal of the hydroxyl groups by reacting with sodium hydroxide. This result in the increase of the OOH concentration, evident from the increased intensity of the peak between 1000 and 1500 cm^{-1} bands compared to the untreated

fiber. Absorbance between this ranges are indicative of the hemicelluloses. The hydroxyl groups are also involved in hydrogen bonding with the carboxyl groups, perhaps of the fatty acids, available on the fiber surface of natural fibers. This is indicated by the reduction of the peaks between 3200–3600 cm^{-1}.

The peak between 1736 and 1740 cm^{-1} seen in untreated fiber disappears upon the alkali peroxide treatment. This is due to the removal of the carboxylic group by the hydrogen peroxide. The carboxylic group may also be present in the fiber as traces of fatty acids present in oils. The reduction in the peak intensity found at around 1654 cm^{-1} in sisal completely removed, indicating that the hemicellulose component in these fibers is easily removed by alkali peroxide treatment. The observed peak at 1384 cm^{-1} and between 1245–1259 cm^{-1} indicates the presence of lignin and hemicellulose, respectively. The disappearance of the peak between 1245–1259 cm^{-1} after alkalization indicates the complete removal of hemicellulose materials rather than lignin. This implies that hemicelluloses are easily removed by alkalization compared to lignin.

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