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# Physico-Mechanical Properties of Chemically Modified Sisal Fibre Reinforced Unsaturated Polyester Composites

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***Abstract*—**Sisal leaves were subjected to enzymatic retting method to extract the sisal fibre. A portion of the fibre was pre-treated with alkali (NaOH), and further treated with benzoyl chloride and silane treatment reagents. Both the treated and untreated Sisal fibre composites were used to fabricate the composite by hand lay-up technique using unsaturated polyester resin. Tensile, flexural, water absorption, density, thickness swelling and chemical resistant tests were conducted and evaluated on the composites. Results obtained for all the parameters showed an increase in the treated fibre compared to untreated fibre. FT-IR spectra results ascertained the inclusion of benzoyl and silane groups on the fibre surface. Scanning electron microscopy (SEM) result obtained showed variation in the morphology of the treated and untreated fibre. Chemical modification was found to improve adhesion of the fibre to the matrix, as well as physico-mechanical properties of the composites.

***Keywords*—**Chemical resistance, density test, Sisal fibre, polymer matrix, thickness swelling.

## I. Introduction

A composite consists of two or more distinct materials, having different chemical and physical properties, merged together to give a well define structure (matrix and reinforcement) [1]. In the olden days, bricks made up of straw and mud are very good examples of composites. Composites in form of wood, teeth, bones, muscle tissue also have their importance in nature. Earlier reported matrices used were high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), poly ether ketone (PEEK) among others. Fibre reinforced composites earlier used various types of glass, carbon and aluminium oxide and many others like flax, hemp, jute as reinforcement for composites [2]. Environmental awareness, increasing concern with green-house effect and also bio-degradation have urged so many industries to look forward to sustainable materials with least impact on the existing surroundings, however, natural fibre reinforced composites seem to be a good alternative due to their renewable nature, hence they attract materials for their application in diverse fields [3].

Natural fibres such as sisal, flax and jute possess good reinforcing capability with polymers, they are relatively inexpensive, originate from renewable resources and possess favourable value of specific strength and specific modulus. Many studies on mechanical properties of natural fibres and how they interact with various polymers have been attempted [4]. All these studies laid emphasis on the properties of the fibre; hence, properties of the composites are governed by the properties of the fibre, aspect ratio of the fibre, thermal stability of the fibre and fibre-matrix interface.

The surface adhesion between the fibre and the polymer plays vital roles in transmitting stress from the matrix to the fibre and thus, contributes towards the performance of the composite. However, in thermoplastic composites, the thermal stability of the fibre plays a crucial role because the process involves the use of high temperature, hence dispersion of the fibre in thermoplastic composites must be considered [5].

In this research, sisal fibre was used as reinforcing agent and unsaturated polyester resin as the matrix. The effect of chemical treatment on the physico-mechanical properties of the sisal fibre reinforced unsaturated polyester composites were investigated. The results obtained shall give the possibility of evaluating the composites for use in many domestic and industrial applications.

## II. Material and Methods

### A. Materials

Sisal leaves was obtained from Gurin-gawa of kumbotso local government, Kano state, Nigeria. Hydrochloric acid (HCl) and Tetraoxosulphate(vi) acid ($H_2SO_4$) (Sigma Aldrich) Potassium hydroxide (KOH) and Sodium hydroxide (NaOH) (Analar), Benzoyl Chloride ($C_6H_5OCl$) and Silane ($C_6H_5Si(C_2H_5O)_3$) coupling agents (Merck). Scanning Electron Microscope (Phenom ProX Super) at Ahmadu Bello University, Zaria, Kaduna, state, Nigeria was used to observe the surface morphologies of the sisal fibre and the composites. The tensile and flexural tests were conducted using Ultimate testing machine (UTM), Shimadzu (MODEL AG-1), while Cary 630 FTIR machine of Agilant Technology, was used to conduct FTIR analysis and also Mass of composite was obtained using Mettler Toledo (Model XP603S) precision balance, all at the Department of Pure and Industrial Chemistry, Bayero University, Kano state.

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*B. Methodology*

1. Fibre Surface Treatments

Sisal fibre was extracted from the dried leaves sisal plant by enzymatic retting method for seven days. Mechanical process involving gently squashing the leaves with hand followed by scraping and carding with soft nylon brush was used to obtain the fibre. Surplus wastes on the fibre such as chlorophyll, leaf juices and adhesive solids were washed up using clean water. The clean extracted fibre was then dried under shade for two days, and finally combing was done to give fine sisal fibre strands [6].

2. Alkali Treatment

5% NaOH solution was used to treat the fibre for 1hour. It was then rinsed with distilled water. Washing of the fibre was done with dilute hydrochloric acid (HCl) solution to neutralize the alkali. The fibres were made alkali-free by rinsing with water and finally with distilled water. The washed fibres were dried under shadow at room temperature [7].

3. Benzoyl Treatment

Portion of the alkali pre-treated fibre was suspended in 10% NaOH and benzoyl Chloride ($C_6H_5OCl$) solution for 15mins, the fibre was then removed and soaked in ethanol for 1 hour to remove excess benzoyl Chloride. It was finally rinsed with distilled water and dried in an oven at $80^0$ C [8], [9].

4. Silane Treatment

1% phenyltriethoxysilane solution in acetone was prepared. Acetone was used in preference to water to promote hyd21rolysis to take place in presence of moisture on the surface of the fibre rather than with the carrier. Acetic acid was added to the solution to maintain a pH of 4 and stirred for 10mins. Portion of the dried alkali pre-treated fibres were soaked in the solution for 1hour. The silane treated fibres were removed from the solution and dried in hot air oven at $60^0$C [4].

5. Composite Fabrication

Fabrication of the composite was done using a $16cm^3$ hand lay-up mold. A matrix made up of 100ml unsaturated polyester cured with 1.6% cobalt naphthenate and 2.7% methyl ethyl ketone peroxide (MEKP) was poured on 1.0g of the fibre whose length is 14.0cm in the mold. The composite was cured within 15mins at room temperature and it was then finally removed [10].

6. Mechanical Property Tests

The tensile and flexural tests were conducted on the sample (150X25X4)mm according to ASTM-D 636-03 and ASTM-D 790-97A standard, using Ultimate testing machine (UTM) from Shimadzu (MODEL AG-1) with cross head speed of 20mm/min in each case and also a support of 51mm in the tensile test at room temperature.

7. Water Absorption Test

Water absorption test was carried out on three different composites of each treated and untreated samples in accordance with ASTM D-3010 standard procedure. Samples were weighed designated as ($w_1$), then immersed in distilled water for 24 hours, removed and allowed to dried and, re-weighed after immersion ($w_2$).

8. Density Test

Mass of the composite was obtained using a Mettler Toledo (Model XP603S) precision balance having $\pm 0.001g$ and the dimensions of the samples were obtained using a vernier caliper to give the volume of the composite. The Density of the composites was determined for three different samples each and the average was evaluated.

9. Thickness Swelling Test

Thickness swelling test was conducted according to the ASTM D 570 on five samples of the composite. The test was used to measure the thickness ability of the composites. Thickness of the composites were measured and recorded before immersion ($T_1$) and after immersion and dried ($T_2$) in distilled water for 24 hours, the test was continued for several days until constant thickness was obtained.

10. Chemical Resistance Test

The chemical resistance test was conducted in accordance with ASTM D-543 -87. Three cured composites from each samples were tested using different chemicals and the mean of the results obtained was evaluated using the equation employed as in water absorption test [11], [12].

11. FT-IR Spectra

FT-IR-HATR Technique as conducted by [6] was used to conduct FTIR analysis of the untreated and treated fibre composites using Cary 630 FTIR machine of Agilant Technology.

12. Scanning Electron Microcopy (SEM)

The samples having dimensions of (430X624µm) length and breadth were gold plated by sputtering technique and observed under different magnifications. The composite fractured surface analyses were performed after immersing the material in liquid nitrogen for 10 minutes [13].

## III. Results and Discussion

*A. Fibre Surface Treatments*

Chemical treatment of the fibre usually changes the surface characteristics of the fibre. Alkali (NaOH), benzoyl Chloride and Phenyltriethoxysilane were used to modify the Sisal fibre. Alkali treatment of the fibre activate the O-H groups on the cellulose and further replaced by $Na^+$ of the alkali, resulting in the modification of the fibre [7]. Alkali treatment changes the behaviour of natural fibre chemical constituents; alkali causes the cellulose of fibre to swell, during which the natural crystalline structure of cellulose relaxes. The degree of swelling is determined by the type of alkali and its concentration, the method has lasting effect on the mechanical behaviour of natural fibres especially, on their strength and stiffness [1], as indicated in the reaction in Fig. 1.


Fig. 1 Reaction between cellulosic fibre and alkali [2]

Benzoylation reaction (Fig. 2) was to introduce benzoyl group on to the fibre by. There was observable decrease in the hydrophilic nature of the treated fibre and an improvement on the interaction of the fibre with the hydrophobic polymer resin. There was also improvement on the fibre-matrix adhesion, thereby increasing the strength of the composite, decreases water absorption and also improves thermal stability of the composite as reported by [14].

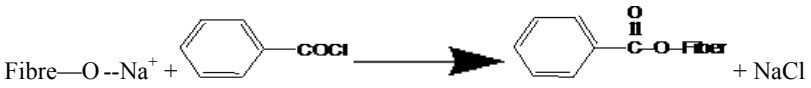



Fig. 2 Reaction between alkali treated fibre and benzoyl chloride [8], [15]

Silane coupling agent allows natural fibres to easily adhere to polymer matrix. It may reduce the number of cellulose hydroxyl groups in the fibre matrix, and can also be hydrolysed into silanol on reaction with moisture present on the fibre [8]. Silynation proceeds via two stages as shown in the reaction as in Fig. 3.

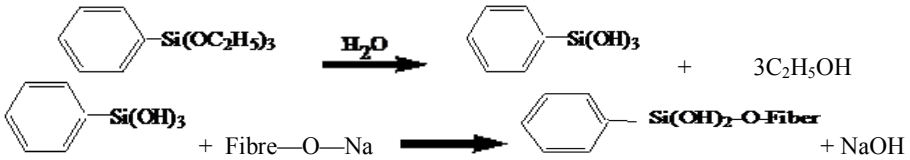



Fig. 3 Reaction between alkali (NaOH) pre-treated fibre with silane coupling reagent [10]

1. Mechanical Properties of the Composites

The tensile and flexural strengths of the sisal fibre composites are shown in Fig. 4 The tensile strength of the treated fibre composites is higher than the untreated composites.

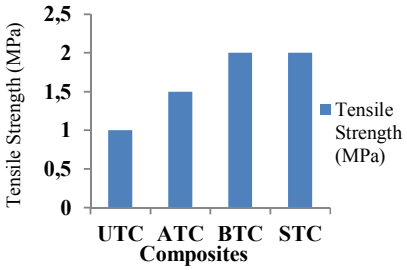



Fig. 4 Effects of chemical treatment on the tensile and flexural strength of the composites: UTC = Untreated sisal fibre reinforced composite. ATC = Alkali treated sisal fibre reinforced composite, BTC = Benzoyl treated sisal fibre reinforced composite, STC = Silane treated sisal fibre reinforced composite

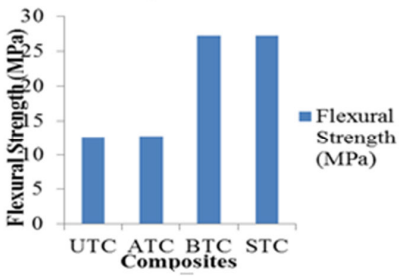



Fig. 5 Effect of chemical treatment on water absorption of the composites

The silane treated fibre composite demonstrated the highest tensile and flexural strength values while, the untreated fibre composites showed the least values. However, the trends of the tensile strengths of the composites are similar to the flexural strength (Fig. 5). The untreated sisal fibre showed the least tensile and flexural properties which, might be due to weak compatibility between the fibre and the matrix because hemicellulose, lignin and pectin are present as revealed by SEM analyses. The properties changing to higher values in the alkali treated fibre composites, might be attributed to the fact that mercerization increases fibre-matrix interaction due to removal of some portion of lignin, hemicellulose and cellulose, thereby destructing the structure of the fibre filaments and also resulting in increased surface area available for contact with the matrix [6], [8].

Silane and benzoyl treated fibre composites had the highest tensile and flexural strengths. Silane used as a coupling agents allow natural fibres to adhere to polymer matrix. It reduces the number of cellulose hydroxyl groups in the fibre, which was also hydrolysed into silanol when it reacts with moisture on the fibre [11].

The silanol formed is capable of condensing with adjacent silanol group (Si-O-Si), to form a cross-linked network of covalent bonds between the matrix and the fibre, hence the fibre can adhere to the matrix and improve interfacial strength. Benzoylation also include benzoyl group on the fibre leading to high fibre matrix interaction as well as increased mechanical properties [4], [12]. This explanation was supported by the SEM observation in Fig. 5 which shows fibre fibrillation in the fractured surface of the composites.

*B. Water Absorption Results*

The percentage gain/loss water was evaluated according to the following equation [11]:

$$\%\ weight\ gain/\ loss\ = \frac{W_2 - W_1}{W_1} \times 100\%$$

where, $W_1$ = Initial weight of the composite sample and $W_2$ = Final weight of the composite sample.

The result obtained on water absorption test is shown in Fig. 6 which indicated the highest value of 0.45% weight gain for the untreated fibre composite due to hemicellulose and lignin contents.

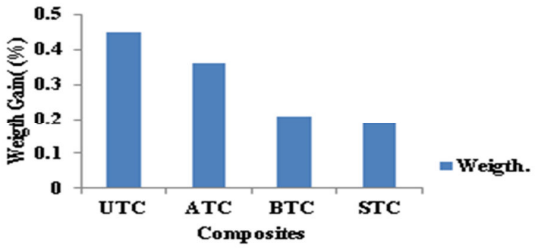



Fig. 6 Effect of chemical treatment on water absorption of the composites

Alkali treated fibre gave 0.36% due to partial removal of lignin and hemicellulose and partial modification of OH on the fibre as revealed by FT-IR and SEM observations. Benzoylated fibre gave 0.21% due to presence of benzoyl group on alkali pre-treated fibre while, silane treated fibre composite showed the least value of 0.19%. The hydrophobic nature and less water absorption are believed to be due to high fibre-matrix interaction resulting from benzoyl and silane treatment. These results are in accordance with the findings of [3] on the effect of chemical modification on the water repellence and mechanical properties of natural fibre where increase in water repellence and mechanical properties were found to increase in the treated fibres [10] and also found a decrease in water absorption of chemically modified coconut fibre treated with silane and alkali [10], [13] also found a decrease in water absorption and thickness swelling of the oil palm empty fruit bunches (EFB)/woven jute fibre ($J_w$) reinforced epoxy hybrid composite compared to EFB.

*C. The Density of the Composites*

The Density of the composites was determined for three different samples each and the average was evaluated, using the expression [16]:

$$\text{Density} = \text{Mass (g)/Volume(cm}^3\text{)} = M/V.$$

where, M = Mass of the composite; V = volume of the composite.

The result of the chemical treatment on the density of the composites is represented graphically in Fig. 7. The density measurement showed the highest value of 0.80g/cm$^3$ for untreated fibre composite, which might be attributed to presence of lignin and hemicellulose which makes the composite absorbs moisture resulting in the increase in its density. Benzoylated fiber composite had 0.71g/cm$^3$, alkali treatment gave 0.68g/cm$^3$ while silane treatment showed least value of 0.52g/cm$^3$.

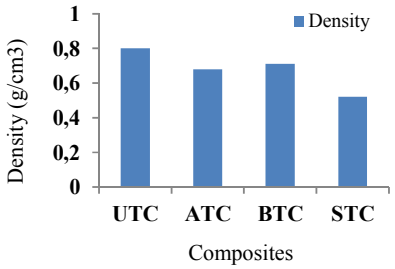



Fig. 7 Effects of alkali treatment, benzoylation and silylation on density of composites

The decrease in the density of the treated fibre composites might be attributed to partial removal of lignin and hemicellulose in the alkali treated fibre and the subsequent introduction of benzoyl and silane groups in to the fibre respectively [10], [11].

*D. Thickness Swelling Results*

The thickness swelling was evaluated from the following expression [14]:

$$Thicknesss\ \ welling\ \ (\%)\ = \frac{T_2 - T_1}{T_1} \times 100\ \%$$

where, $T_1$ = Thickness before soaking, $T_2$ = Thickness after soaking.

The result of the chemical treatment on thickness swelling is shown graphically in Fig. 5. The result obtained showed highest value of 8.91% swelling for untreated fibre, alkali treated fibre had 7.2%, benzoylated fibre had 6.2% and silylated fibre had the least swelling of 5.8%. The reason might be the same as stated in water absorption as presented in the water absorption results.

The test was carried out using acids 10% each HCl and $H_2SO_4$ separately and also using bases 10% each with $NH_4OH$ and KOH. The results obtained are shown graphically in Fig. 8.

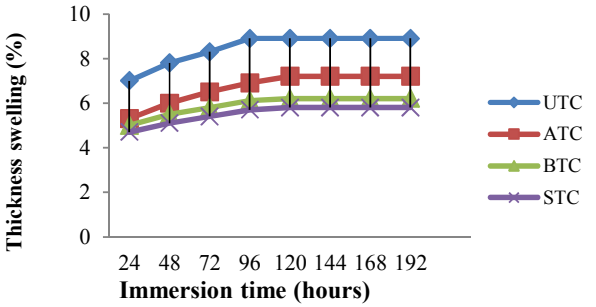



Fig. 8 Effect of Chemical treatment on thickness swelling of the composites

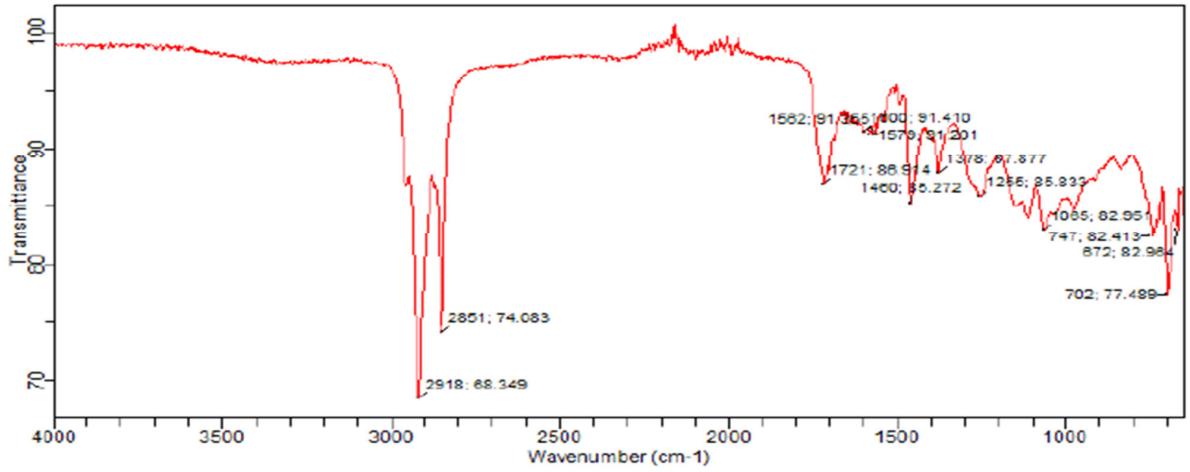
The results obtained in the chemical test showed that the composites are resistant to all the chemicals used, an increase in weight of the composites was observed. This is due to interaction of the composites with the chemicals resulting in gel formation as shown in Fig. 8. These results are in agreement with the work of [12].

*E. Chemical Resistance Results*

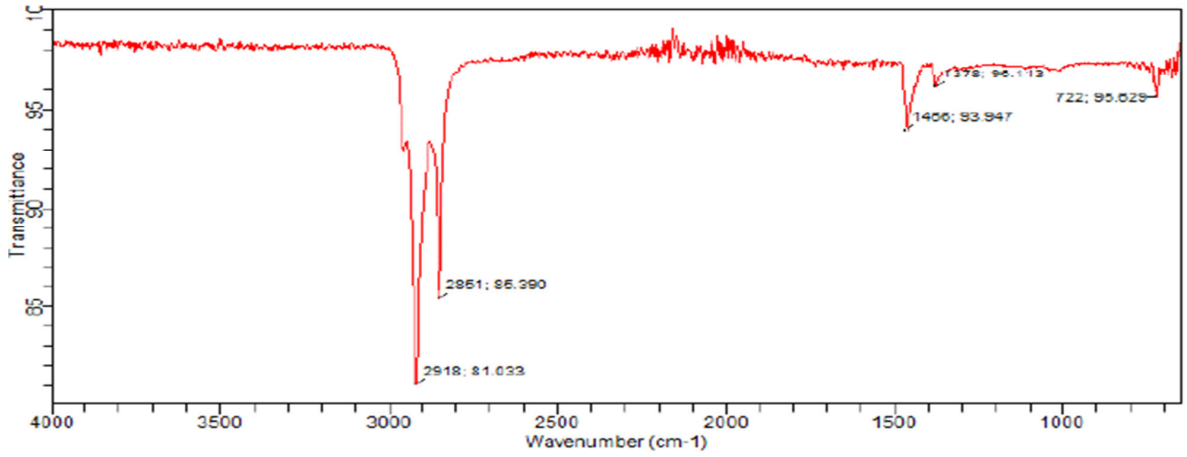
The results obtained in the chemical test showed that the composites are resistant to all the chemicals used, an increase in weight of the composites was observed. This is due to interaction of the composites with the chemicals resulting in gel formation as shown in Fig. 7. These results are in accordance with the work of [15] on chemical resistance, impact, flexural and compressive properties and optimization of natural fibres reinforced epoxy blend where increase in these properties were observed after treatment with alkali and a variation of the content with 0, 10, 20 and 30% fibre content.

*F. FT-IR Analysis*

The FT-IR analysis was conducted to ascertain whether reaction has taken place between the cellulosic fibre and reagents used to modified the surface of the fibre. The functional groups present are shown in representative FT-IR spectra (Figs. 9 (a) and (b)). The untreated fibre shows peak at 1255cm$^{-1}$ corresponding to -C-O stretching of primary alcohol. Important modifications were observed at peaks 1182cm$^{-1}$ indicating -C-O for stretching of primary alcohol in the alkali treated fibre, reduction in the peak compared to that of untreated fibre, indicating the removal of lignin and hemicellulose from the fibre.Also the peak 1460cm$^{-1}$ indicating C-C stretching in aromatic ring and also 1719cm$^{-1}$ for C=O stretching of the benzoyl carbonyl group in the benzoylated fibre. The peak at 1488cm$^{-1}$ is attributed to the stretching of C-C in the aromatic ring of the phenyl triethoxy silane used on the fibre. The results obtained are in accordance with the work of [3], [4].




(a)




(b)

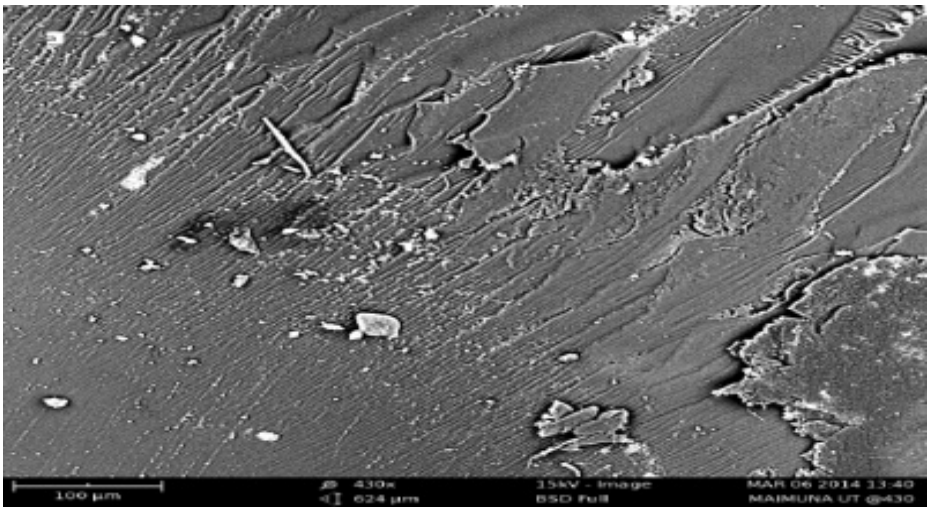
Fig. 9 FTIR Spectra (a) Untreated Sisal fibre (b) Alkali treated Sisal fibre

*G. Scanning Electron Microscopy (SEM)*

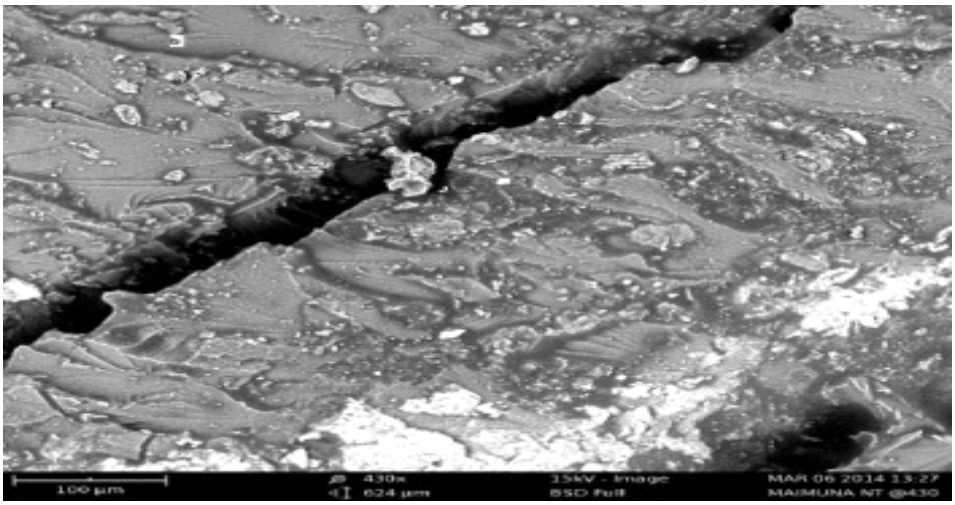
Scanning Electron Microscopic analysis examined the surface morphology of the treated and untreated Sisal fibre. The impurities at the surface of plants play vital roles in fibre-matrix adhesion as it facilitates both mechanical interaction of the bonding reaction. Fig. 7 shows the SEM photomicrographs of fractured Sisal fibre composites before and after modification with alkali (NaOH), Benzoyl Chloride and Silane coupling agents.

Fig. 10 (a) shows the presence of wax, oil and surface impurities which provide a protective layer to the surface of the Sisal fibres, also surface roughness of the lignocelluloses of Sisal fibre was observed indicating presence of lignin. Fig. 10 (b) showed a rougher surface and is more visible compared to the untreated Sisal fibre.

The rough surface topography in the alkali treated fibre was due to removal of hemicelluloses, lignin and amorphous waxy layer in Fig. 10 (c), the surface of the benzoylated Sisal fibre becomes smoother compared to that of untreated and alkali treated fibre. These could be due to the fact that benzoylation increased fibre-matrix interaction resulting in better adhesion. Similar morphology was observed in the Silane treated fibre (Fig. 10 (d)) which could be due to the cross-linked network brought about by covalent bonding formed between the matrix and Silane treated fibre which promotes fibre-matrix interaction as well as increased interfacial strength. The treatments used provide clean surfaces on the fibres which resulted in direct bonding between the cellulose and the matrix. Comparing the photomicrographs of the treated and untreated Sisal fibres, the morphology indicated a separation of the micro-fibrillar of the structure probably due to delignification. The treatment also increased the effective surface area by fibrillation, thereby facilitating interfacial fibre-matrix adhesion. This result is in accordance with the work of [3], [10], [12] on SEM analyses of alkalized, benzoyl and silylated modified natural fibres.




(a)

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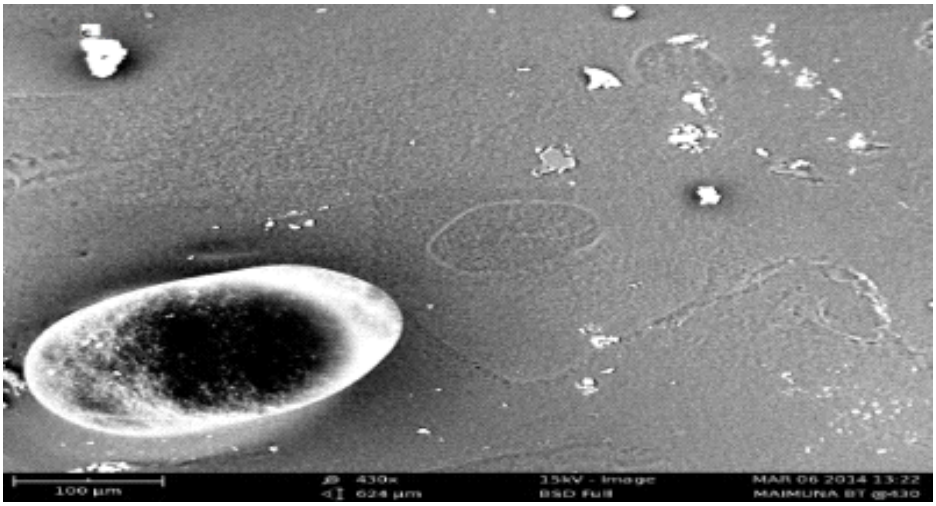
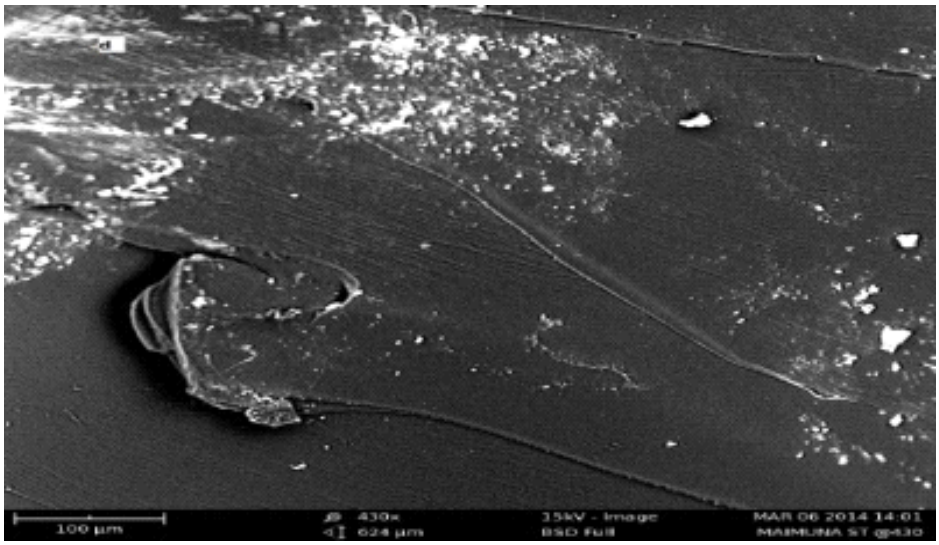



(c)




(d)

Fig. 10 SEM Photomicrographs of the composites (a) Untreated fibre (b) Alkali treated fibre (c) Benzoylated fibre (d) Silane treated fibre

## IV. Conclusion

Treatment of Sisal fibre with alkali, benzoyl and silane coupling reaagents modified the surface of the sisal fibre. The tensile and flexural properties; water absorption and density of the composites were found to increase in the treated fibre composites compared to untreated fibre.

The highest tensile and flexural properties were observed in benzoyl and silane treated fibre composites. Water absorption, density and thickness swelling results showed highest in the untreated fibre composites while, silane treated fibres had the least values. Silane treated fibre composites showed best resistant to acids and alkalis while, least values were observed in untreated fibre composites. FT-IR analysis of the fibre showed that benzoyl and silane groups were covalently bonded onto the fibre as supported by the SEM photomicrograph observations. Further work should be conducted on other mechanical properties such as impact strength, X-RD, DSC and TGA test in order to evaluate the appropriate application of the composite material.

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