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Structural Characteristics, Thermal Degradation Behaviour and Tensile Properties of Hand Extracted *Entada mannii* Fibres

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ABSTRACT: *The influences of different fibre extraction methods and chemical treatment on the structural textures, thermal degradation patterns and tensile properties of Entada mannii (Olive Tisserant) plant stem fibres were investigated. The fibres were extracted manually from the plant stem using two conventional methods, hand stripping (HS) and hand beating (HB). After drying, the fibres were either left untreated or were treated with potassium hydroxide (KOH) and then characterised using chemical analysis, scanning electron microscopy (SEM), thermogravimetry analysis and tensile analysis. The results showed that chemical treatment with KOH enhances the removal of lignins and hemicelluloses in the fibres. The KOH treated fibres were also more thermally stable when compared with untreated fibres. SEM analysis revealed exposed surfaces composed of a continuous network of micro fibrils for the KOH treated fibres. In contrast, the untreated fibres had smooth surfaces, suggesting the sub-cell structure is covered by lignins and hemicelluloses. The tensile property results demonstrated a significant improvement in tensile strengths, elastic moduli, and resiliencies for the chemically treated fibres. It was also noted that the best combination of tensile and thermal properties was achieved with the hand stripped, KOH treated fibres.*

Keywords: *Entada mannii* (Olive Tisserant); chemical treatment; natural fibres; fibre micro constituents; extraction methods

1. INTRODUCTION

Composite materials have emerged as the dominant engineered materials over the last 30 years.[1] They constitute a significant proportion of the engineered materials market and are incorporated into a wide variety of products, ranging from everyday products to high technology products used for sophisticated applications. Although composites offer outstanding weight-saving capabilities, high production costs have been an issue that have continued to confront

manufacturers.[2,3] The drive to produce economically attractive composite components has resulted in the innovation of several novel processing and manufacturing techniques by composite materials researchers.[4]

The use of plant fibres as reinforcements for polymer based composites has been a major focal point in the search for cost-effective composite materials.[5] Natural fibres from a variety of plants such as sisal, banana, jute, oil palm, kenaf and coir have been used to reinforce thermoplastic composite materials for applications in aerospace structures, marine materials, boat bodies, automotive body panels, leaf springs and biomedical devices, with promising results.[6] In addition to being cost effective, plant based fibres are also widely available and environmentally friendly, being both biodegradable and from renewable sources. Many plant-based fibres have specific strengths and stiffness that are comparable to most synthetic fibres, such as fibreglass.[7]

The possibility of replacing the more costly synthetic fibres with natural fibres has continued to propel researchers to investigate further natural fibre sources with a view to characterise their properties and assess their suitability as reinforcing materials. *Entada mannii* plant stem fibre is a natural fibre that has not received much attention to date from researchers. *Entada mannii* is a liana plant that belongs to the family (Olive) Tisserant leguminous mermosaesae.[8] This plant is a 2 to 3 m high semi-climber which grows in the tropical forests of Nigeria, Gabon and Madagascar.[9] Prior to the widespread availability of synthetic ropes in Nigeria, *Entada mannii* was used by local farmers to make ropes because of the strength and stiffness of the stems. This historical use of the plant was the basis for its consideration as reinforcing material in the current study.

The investigative work reported here focused on the effects of the fibre extraction methods and chemical treatment methods on the structure, thermal stability and tensile properties of *Entada mannii* fibres.

2. EXPERIMENTAL

2.1 Materials

The materials utilised for this research include the following: *Entada mannii* fibres obtained from Ikare Akoko, Ondo state, Nigeria, and Potassium hydroxide (KOH) used as an alkali reagent to separate the cellulose, hemicellulose, and lignin constituents from the fibres.

2.2 Methods

2.2.1 Extraction of fibres

The *Entada mannii* fibres were obtained from the plant stem bark as shown in Figure 1, 2 and 3. The fibres were extracted from the bark bundles by two convectional processes, referred to as hand beating (HB) and hand stripping (HS). The stem stalk was beaten with a wooden mallet to allow the separation and easy removal of the fibres from the bark stem bundles. The stripped and beaten fibres were then washed with distilled water to separate them from undesirable foreign matter, prior to being dried in an oven at 65°C for 2 days.

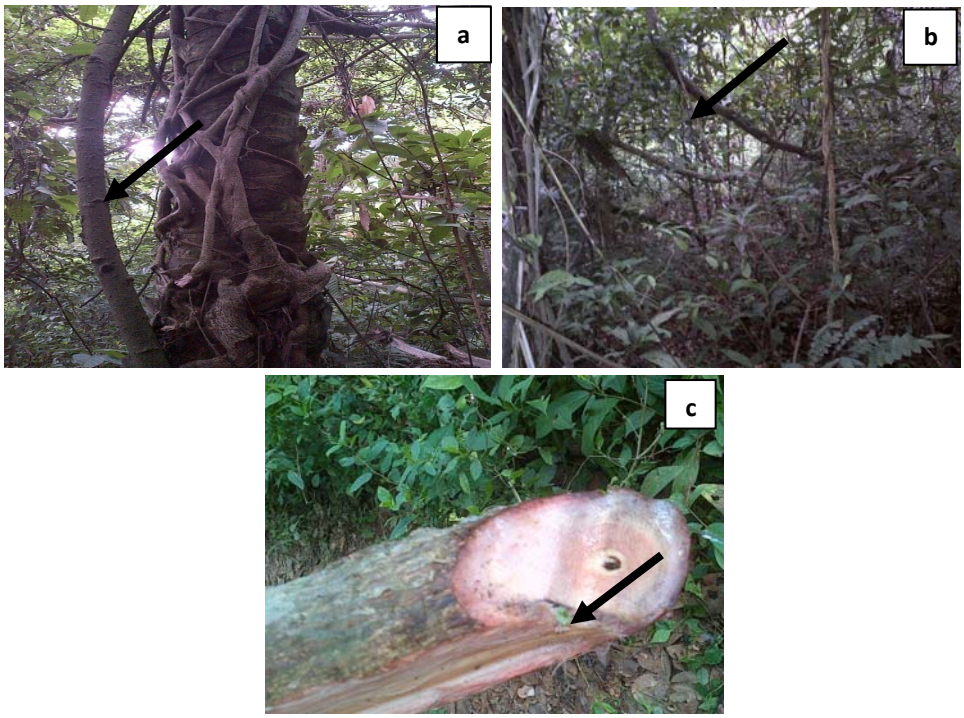

Figure 1: Images showing growth patterns and distribution of the *Entada mannii* plant stem (shown in a and b), and a cross-section of a cut *Entada mannii* plant stem (c).

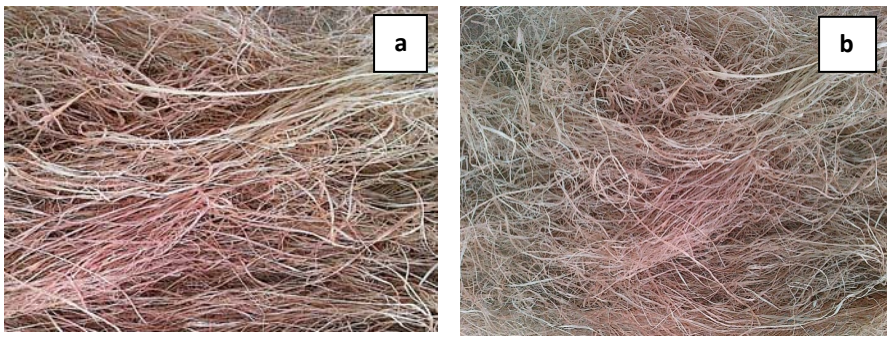

Figure 2: Hand stripped fibres shown (a) before drying and (b) after drying.

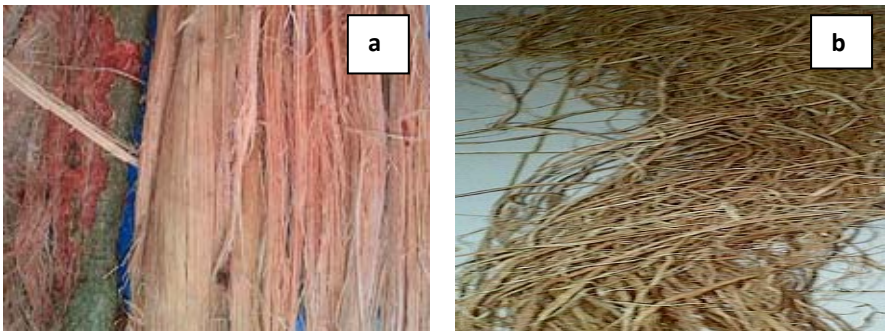

Figure 3: Hand beaten fibres shown (a) before drying and (b) after drying

2.2.2 Fibre surface treatments

The hand stripped fibres were treated with a solution of 0.1 M KOH (500 ml) in a shaker water bath at 50°C for 4 h. The insoluble residues were delignified at pH 3, washed with distilled water to remove mineral traces, and dried in an oven at 65°C for 2 days. The hand beaten fibres were treated with a solution of 0.1 M KOH solution (500 ml) in a shaker water bath at 50°C for 4 h. The insoluble residues were washed with distilled water to remove foreign matter and dried in an oven at 65°C for 2 days. The untreated samples were used as controls for all experiments.

Previous studies have demonstrated that chemical treatment is effective in the removal of fibre constituents that affect the bonding strength between the fibres and the polymer matrices, such as lignins, hemicelluloses and ashes.[10] Additionally, chemical pre-treatment of the fibres improves binding between the fibres and composite matrices by increasing surface roughness, improves the strength of the fibres, and reduces moisture adsorption by the fibres.[10–12]

2.2.3 Determination of the fibre constituents

In general, natural fibres are hygroscopic in nature and absorb or release moisture depending on environmental conditions. Amorphous cellulose and hemicellulose that are present in the natural fibres are principally responsible for the high moisture absorption, as they contain numerous accessible hydroxyl groups that confer a strong hydrophilic character to the fibres.[13] To characterise the content of the fibre constituents lignin, hemicellulose, and cellulose in the *Entada mannii* fibres, the following procedures were performed as previously described.[10,14]

Lignin content

Entada mannii fibres (2.5 g) were weighed and mixed with 75% concentrated sulphuric acid and the mixture was incubated in an ice bath with constant stirring for 12 h. The mixtures were then diluted with 4% acid and refluxed for 5 h. On cooling, the mixtures were filtered and washed continuously until the acid was removed. The residues were then dried at 105°C for 5 h prior to cooling in desiccators and weighing. The weight percentage of the lignin content was calculated by the weight difference.

Cellulose content

Treated *Entada mannii* fibres (2 g) were crushed and dried in an oven at 100°C for 3 h. Distilled water (25 ml) was added, and the mixtures were heated in an 80°C thermostated water bath with constant stirring. Sodium chlorite and acetic acid were added to the mixtures prior to cooling in an ice bath at 7°C. The residues were collected by filtration and washed with distilled water prior to drying in an oven at 105°C for 20 h, cooling in desiccators, and weighing. The percentage of cellulose was calculated by the weight difference.

Hemicelluloses Content

Entada mannii samples (0.5 g) were weighed in a beaker prior to adding 24% KOH solution and stirring continuously for 2 h. The sample mixtures were filtered with purpling cloth and washed with additional KOH solution prior to collecting the filtrate into another beaker. Alcohol was added to the samples to initiate precipitation, and the precipitates were isolated by centrifugation for 10 min. The samples were dried in an oven for 2 h at 105°C prior to transferring to desiccators and allowing cooling for 30 min before weighing. The weight of the precipitate was recorded, and the percentage was calculated.

2.3 Thermogravimetry Analysis (TGA)

Thermo gravimetric analysis was performed on the fibres to measure weight loss as a function of increasing temperature under a nitrogen atmosphere. Weight loss in fibres occurs due to the decomposition of the cellulose, hemicellulose and lignin constituents during heating.[14] The samples were heated from room temperature to 600°C at a heating rate of 10°C min^{-1} and a nitrogen gas flow rate of 60 ml min^{-1}.

2.4 Microstructural characterisation

The surface morphology of the chemically treated and untreated *Entada mannii* fibres were examined using a JEOL JSM-7600F model scanning electron microscope. The samples were cleaned thoroughly, air-dried, and coated with a 100 Å thick layer of irradium in a JEOL sputter ion coater prior to analysing via SEM at 15 kV.

2.5 Tensile Testing

Tensile testing of a single fibre pull out was performed on both chemically treated and untreated samples in accordance with ASTM-638D standards.[15] The mounted fibres were placed in the grips of an Instron-4204 tensile testing machine, and the supporting sides of the mounting cards were carefully cut using a hot-wire cutter. The fibres were then subjected to tensile loading until failure at a strain rate of 0.5 mm min^{-1} using a 10 N-load cell. Average fibre tensile strengths were obtained using the results from 6 independent specimens.

3. RESULTS AND DISCUSSION

3.1. Chemical Analysis

Figure 4 illustrates the compositional analysis of *Entada mannii* fibres for: (1) hand stripped, treated; (2) hand stripped, untreated; (3) hand beaten, treated; and (4) hand beaten, untreated. The authors observed that both the hemicellulose and lignin contents of the *Entada mannii* fibres decrease with KOH treatment when compared to the untreated fibres. As a result of the decrease of these constituents, the percentage of cellulose was increased in the treated fibres when compared with the untreated fibres. The cellulose content increased after treatment from 41.18% to 67.87% and from 41.32% to 63.72% for the hand stripped and hand beaten fibres, respectively. Previous reports indicate that chemical treatment decreases the hydroxyl groups present in the amorphous region, removes the

lignin and hemicellulose coverings from the fibre surfaces, and exposes the cellulose structure to react with binder materials.[14–16]

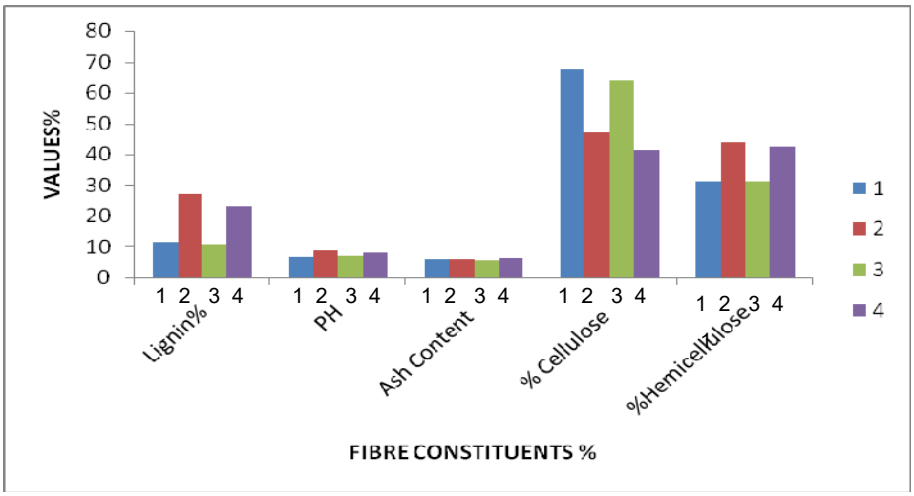

Figure 4: Plots of the *Entada mannii* constituents and PH values for both treated and untreated fibres.

A greater reduction in cellulose content was observed during the chemical treatment of the hand beaten fibres (3). Most likely this is due to the reduction in the strength following removal of the surface lignin and hemicellulose constituents when compared to the hand stripped fibres (1). In addition, the applied stress effect and superficial fibrillation resulting from hand beating decreases the strength and length of the fibres.[17]

3.2 TGA Analysis for Both Treated and Untreated Fibres

Figure 5 shows the thermogravimetric analysis of the treated and untreated *Entada mannii* fibres. Thermal decomposition of the fibres (measured by weight loss) was observed between 200°C–350°C for both the treated and untreated fibres. The authors also observed increased weight loss in the HS(3) and HB(2) treated fibres as a result of exothermic combustion following thermal degradation as the temperature was increased from 300°C–370°C. In contrast, the untreated fibres HB(4) and HS(1) degraded at lower temperatures in the range of 200°C–300°C, suggesting the presence of hemicellulose and lignin constituents in the fibres resulted in lower thermal stability. Kabir et al.[14] and Beckerman et al.[18] previously reported that untreated fibres degrade at lower temperatures due to the presence of thermally unstable fibre constituents such as hemicelluloses and pectins, whereas the alkali treated fibres were more thermally stable due to the

removal of these constituents. It has also been reported that thermal decomposition occurred principally on cellulose and in turn increased the overall degradation temperature of the treated fibres, which contain higher cellulose levels.[14,19]

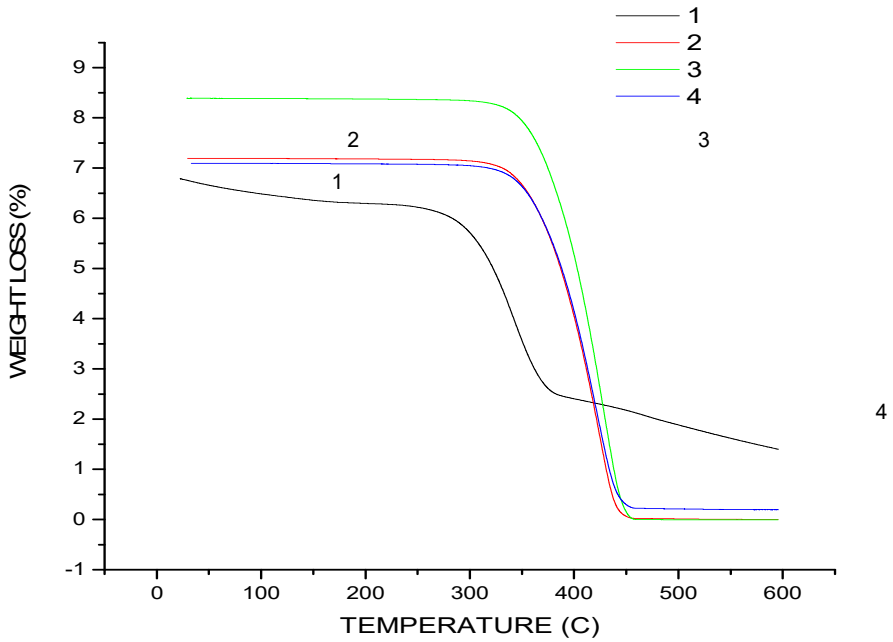

Figure 5: Comparison graphs for treated and untreated, hand stripped and hand beaten fibres.

3.3 SEM Analysis of *Entada mannii* Fibres

The structural features of the treated and untreated *Entada mannii* fibres are shown in the SEM micrographs presented in Figure 6. The authors observed that the surface texture of the untreated fibres appears smoother than that of the KOH treated fibres. This results from the presence of the lignins, hemicelluloses, and waxes, which concealed the sub cells and micro fibrils that form the substructure of the fibres. In the case of the KOH treated fibres, the authors observed that the sub cell networks made up of continuous cellulose micro fibrils were clearly visible once the treatment removed a significant amount of the hemicelluloses and lignins covering the fibres. These results confirm the chemical analysis data indicating that KOH treatment substantially decreases the lignin and hemicellulose contents from the top surface layers of the fibres.[20,21] Previously, the increased surface roughness of the treated fibres has been reported to contribute to improved bonding of the fibre-matrix interface and results in the improved strength of polymer based composites reinforced with the fibres.[22,23]

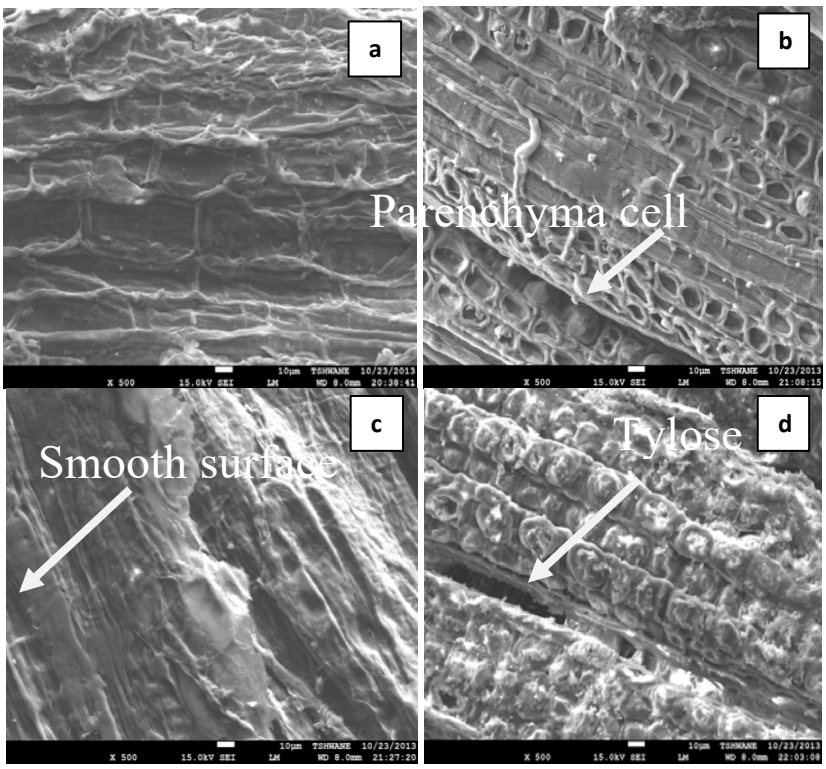

Figure 6: SEM images of (a) hand stripped, untreated fibre; (b) hand stripped, KOH treated fibres; (c) hand beaten, untreated fibre; and (d) hand beaten, KOH treated fibre.

3.4 Variation of the Tensile Properties of the *Entada mannii* Single Fibre Pullout

An example of the variations in the tensile properties of the treated and untreated single *Entada mannii* fibres is presented in Figure 7. In Figure 7, the authors observed that the tensile strength of the fibres increased with chemical treatment, irrespective of the hand extraction method. This finding is attributed to the removal of lignins and hemicelluloses, which are reported to be deleterious to the strength of fibres, from the KOH treated fibres.[24] The presence of lignins and hemicelluloses on the untreated fibres reduce the strength of the fibres when compared with treated fibres. In addition to reducing tensile strength, the presence of lignins, pectins and hemicelluloses result in poor fibre-matrix interactions and poor fibre-matrix interfacial bonding.[25]

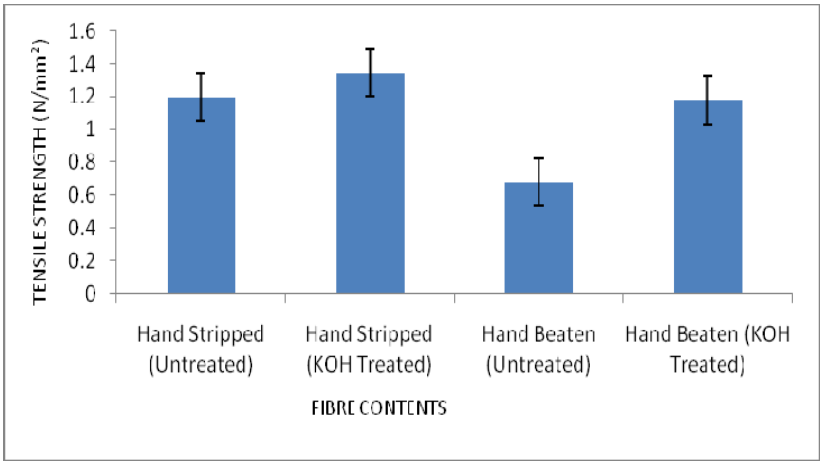

Figure 7: Variation of tensile strength of single fibres resulting from the different extraction and treatment conditions.

The improvement following chemical treatment can also be explained by the SEM micrographs in Figure 6 (b and d). The results show that the removal of fibre constituents, such as hemicellulose and lignin, after chemical treatment resulted in the formation of rough surfaces and pits. Following removal, the tensile properties were improved and the fibre diameters were reduced in treated fibres. Similar results were observed by Mohanty et al.,[3,26] who demonstrated that alkali treatment reduces fibre diameter and leads to the formation of a rough surface with pits, which results in reduced mechanical anchorage and pullout, and gaps between the fibre and matrix.

The authors also noted that the tensile strengths of the hand stripped, chemical treated fibres are higher than that of the hand beaten, chemically treated fibres. The hand beating extraction method results in damage to the intra-fibriller binders of the bundles, leading to stress release and molecular relaxation of the cellulose fibre components and a concomitant reduction in the strength of HB fibres. Hand beating also affects the activation of both the fibre networks and fibre segments during extraction and drying, and results in swelling and dislocation within individual fibres.[17,27]

In Figure 8, the authors also observed that the modulus of elasticity of the fibres improves with chemical treatment. This increase may also be attributed to the removal of lignins and hemicelluloses in the fibres. The hand stripped *Entada mannii* fibres treated with KOH were also noted to have a higher modulus of elasticity when compared with the KOH treated hand beaten fibres. This is attributed to the fibre deformation and swelling resulting from the hand beating. The fibre deformation decreased the fibre segments, resulting in decreased tensile

strength and stiffnes.[28] In contrast, the untreated fibres had lower values for the modulus of elasticity due to high moisture content and the presence of fibre constituents such as lignins, hemicelluloses and impurities on the fibres surface. Non cellulose compounds such as waxes, hemicelluloses, and lignins on the surface of the untreated fibres tend to absorb moisture and to create weaknesses in the microfibrils, resulting in easy deformation of the fibres during tensile loading.[16,26,29]

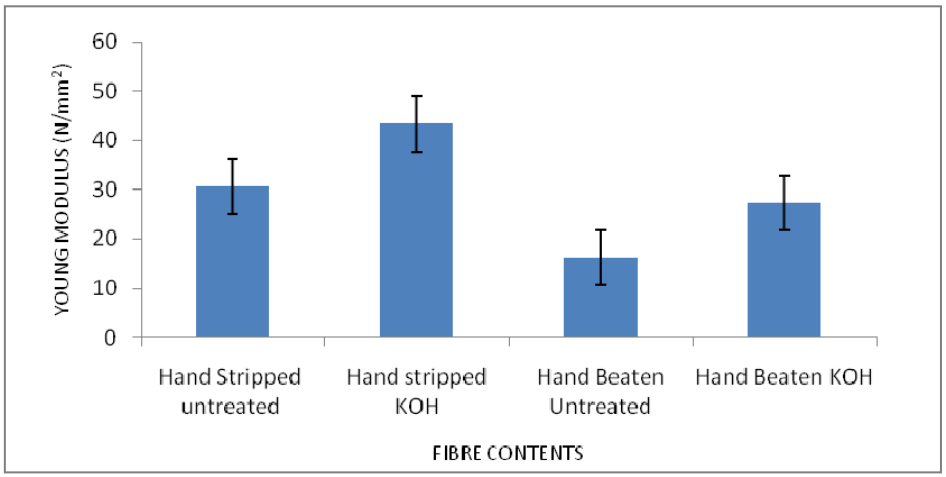

Figure 8: Variation of the modulus of elasticity of single fibres from the different extraction and treatment conditions.

4. CONCLUSION

The influences of fibre extraction methods and chemical treatment on the structural features, thermal degradation patterns, and tensile properties of *Entada mannii* (Olive Tisserant) plant stem fibres were investigated. The results show that chemical treatment with KOH enhances the removal of lignins and hemicelluloses in the fibres. The resulting KOH treated fibres were more thermally stable when compared with the untreated fibres. Additionally, SEM analysis revealed an exposed surface consisting of a continuous network of micro fibrils for the KOH treated fibres. In contrast, untreated fibres had a fairly smooth surface suggesting the covering of its sub-cell structure by lignins and hemicelluloses on the fibre surface. It was also observed that the tensile property results demonstrate a significant improvement in tensile strength, elastic modulus and resilience for the chemically treated fibres. Finally, the hand stripped KOH treated fibres yielded the best combination of tensile and thermal properties.

5. ACKNOWLEDGEMENT

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