

Comparison of Harakeke with Hemp Fibre as a Potential Reinforcement in Composites

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ABSTRACT

The objective of this study was to characterize the performance of untreated and chemically treated harakeke fibre (a leaf fibre from a plant native to New Zealand) and compare with hemp fibre to assess its use as potential reinforcement in composites. Alkali treatment is among the most popular treatments used to remove unwanted fibre constituents such as pectin, hemicellulose and waxes; it can enhance fibre properties, fibre separation, interfacial bonding and fibre dispersion within a composite. Physical and mechanical properties of untreated and alkali treated fibres were assessed using single fibre tensile testing, X-ray diffraction (XRD), scanning electron microscopy (SEM) and thermal analysis using thermogravimetric analysis (TGA). Untreated harakeke fibre was found to be lower in tensile strength compared to untreated hemp fibre. It was also found that the tensile strength of harakeke and hemp fibres treated with 5wt% NaOH/2wt% Na₂SO₃ and 5wt% NaOH was not significantly affected and these fibres had good fibre separation. However, alkali treatment was found to lead to higher crystallinity index (I_c) and better thermal stability for harakeke as well as hemp fibres.

KEYWORDS:

A. Discontinuous reinforcement; B. Mechanical properties; D. Mechanical testing;
E. Surface treatment

INTRODUCTION

Increased environmental awareness has led to growing interest in the use of more sustainable materials. Typical construction materials have large ecological footprints; production of synthetic composites is generally energy intensive and construction and demolition debris constitute a large percentage of landfill volume [1]. Natural-fibre-reinforced bio-derived polymer matrix composites, commonly referred to as bio-composites have gained renewed interest over the past few decades because of their low material costs, low densities, high specific moduli and environmentally friendly appeal, as well as their low production energy requirements [2]. The natural fibres used are renewable, nonabrasive, can be incinerated for energy recovery and they give less concern regarding health and safety during handling than synthetic fibres. Their excellent price-performance ratios at low weight in combination with their low environmental impact has resulted in increasing uptake by engineering markets such as the automotive and construction industries [3].

Many studies have been carried out internationally to assess the possibility of using natural fibre-composites for non-structural and structural applications [4-8]. However, development of such low cost materials with elevated durability and high mechanical performance is still a real challenge faced by engineers of the 21st century to enable natural fibre to be put on a par with synthetic fibre. Important factors regarding composite performance are:

- the fibre, including fibre type, alignment and length,
- the matrix used and

- the interfacial bonding which enables transfer of the applied load to the fibres

Weak interfacial bonding between the reinforcing agent and the matrix in natural reinforced composites is a major drawback which limits their application. Interfacial strength plays a vital role in determining the mechanical properties of composite materials. A strong interface provides composites that display good strength and stiffness but tend to be brittle. A weaker interface on the other hand, may reduce the stress transfer from matrix to the fibre, hence the composite may display lower strength and stiffness but may in contrast have increased toughness. Depending on the application, interfacial strength can be engineered by modifying the fibre surface using physical and chemical treatment and modifying the matrix by addition of coupling agent. The literature shows that these methods increase compatibility and potential reactivity between fibre and matrix and hence increase the interfacial strength between matrix and reinforcing agent [9].

The present work is a preliminary study of the mechanical and physical properties of harakeke fibre compared to hemp fibre including the effect of alkali treatment. Harakeke is a monocotyledonous plant endemic to New Zealand and is renowned for its fibre which was used by early European settlers in New Zealand as a replacement for European flax and here is commonly called 'native flax'. Its fibre can be extracted from the upper and lower side of its leaves. However, unlike European flax, from which fibre is extracted from stalk, the fibre from harakeke is extracted from the leaves of this plant. The leaves are stiff and tough and can grow up to 3 m long and 125 mm wide. The favourable strength and stiffness of the fibre and mechanisation of the extraction around the 1920s resulted in an expansion of the harakeke fibre industry with the fibres becoming an important export commodity used in a variety of applications such as clothing, mats, baskets, ropes, fishing lines and nets [10, 11]. The chemical composition

of harakeke fibre is tabulated in Table 1[12]. Two different types of alkali with various concentrations were used in isolation or in combination with the aim of maximising the fibre properties for enhancement of mechanical and physical properties of composites. There are several papers published reporting the improvement of fibre properties when treated with various alkali treatments [10, 13, 14], but only limited papers discussing the mechanical behaviour of single fibres, with none for harakeke that have been found by the authors. This work was aimed at acquiring a better understanding of the potential of these fibres for reinforcement in composites. Together with mechanical and physical assessments, this paper also includes analysis of fibre strength using Weibull statistics.

EXPERIMENTAL

Materials

Harakeke fibre was obtained from the Templeton Flax mill, Riverton. It was mechanically prepared and supplied in bundle form. Hemp fibre was locally grown from October 2012 and harvested in February 2013 after 120 days and donated by the Hemp Farm NZ Ltd. Green hemp stalks were dried exposed to air for two weeks and then the bast fibre was hand separated from the stalks.

Methods

Alkali Fibre Treatment

Alkali treatment was carried out using a laboratory scale pulp digester (normally used for paper making) at different temperatures and for different durations. Three alkali formulations were used in this investigation: 5wt% sodium hydroxide (NaOH), 10wt% NaOH and 5wt% NaOH with 2wt% sodium sulphite (Na_2SO_3). The chemicals used (purchased from Scharlau Chemie S.A.) were analytical grade Na_2SO_3 pellets and NaOH powder, both with 98% purity level. The abbreviations used for the fibres and treatments are shown in Table 2.

The three alkali solutions were used with a fibre (harakeke or hemp) to solution ratio of 1:8 by weight. Predetermined amounts of harakeke and hemp fibres were placed in stainless steel canisters with pre-mixed NaOH and Na₂SO₃ solutions. The canisters were then placed into a small lab-scale pulp digester with the treatment cycles, controlled by a 4-step controlled programme, chosen based on preliminary screening trials. Trials had previously been conducted raising the temperature from ambient to a maximum temperature over 90 minutes. It had been demonstrated that treatment conducted for longer than 30 minutes at a temperature for more than 160°C reduced the tensile strength of hemp fibre considerably. However, with treatment conducted at less than 160°C the fibre tensile strength was maintained, but the separation of the fibre was very poor. Therefore, treatment at 160°C for 30 minutes was chosen for hemp fibre. For harakeke, it was found that in order to get fibre separation, treatment was required to be conducted at 170°C for at least 40 minutes, however, harakeke fibre treated at higher than 170°C was slightly degraded even though the fibre separation was improved. This is supported by research conducted elsewhere, such that treatment at 170°C was found to give the optimum fibre separation for harakeke [15]. Therefore, treatment at 170°C for 40 minutes was chosen for harakeke fibre.

Scanning Electron Microscopy

SEM micrographs of untreated and treated fibres were taken using a Hitachi S-4100 field emission scanning electron microscope (SEM). Prior to SEM observation, the samples were mounted on aluminium stubs using carbon tape and then coated with plasma sputtering to avoid the sample becoming charged under the electron beam. SEM observation was carried out at 5 kV.

Single Fibre Tensile Testing

The tensile strength and Young's modulus of untreated, NaOH and NaOH/Na₂SO₃ treated harakeke and hemp fibres were tested according to the ASTM

D3379-75: Standard Test Method for Tensile Strength and Young's Modulus for High-Modulus Single Filament Materials. Single fibres were mounted on 2mm thick cardboard mounting-cards with a 2mm gauge length as schematically shown in Figure 1. PVA glue was applied to hold the fibres to the cardboard and define the gauge length. Harakeke and hemp fibres, similar to other cellulosic fibres generally have variable cross-sectional areas and diameters along their length. To account for this, the diameter of the fibres was measured at five different points along the fibres length by means of an Olympus BX60F5 optical microscope. Typical single harakeke and hemp fibres observed under optical microscope are shown in Figure 2 and 3 respectively. It can be seen that harakeke fibre is finer than hemp fibre, but otherwise looked similar.

The apparent cross-sectional area of each fibre was then calculated using the mean fibre diameter and assuming a circular cross-section. The measured and mounted fibres were then placed in the grips of an Instron-4204 universal testing machine and the supporting sides of the mounting cards were cut using a hot-wire cutter. The fibres were then tensile tested to failure at a rate of 0.5mm/min using a 10N-load cell. 30 replicate samples were tested for each batch and average tensile strength (TS) and Young's moduli (YM) were obtained using the results from all specimens. As an extensometer cannot be used on such thin specimens, elongation of single fibres was determined through the displacement of the testing machine cross head. The crosshead displacement, however, is actually a combination of the fibre elongation as well as the crosshead deformation, specimen grips, and the cardboard mounting card. For accurate measurement of fibre elongation and Young's modulus, system compliance is required and was determined experimentally using related procedures described in ASTM D3375-75 [16]. In this study, specimens of different gauge lengths of 5, 10 and 15 mm of hemp and harakeke were prepared using similar set up used in single fibre testing. From the corresponding load-displacement curves for each specimen, the inverse of the

slope of the initial linear region of the force versus cross-head displacement curve representing the apparent compliance was determined. By plotting indicated compliance against gauge length and extrapolating this function to zero gauge length, leads to the testing device compliance which was then used to calculate Young's modulus.

The data obtained for the tensile properties were statistically analysed using the two-parameter Weibull equation, which expresses the cumulative density function of the strength of the fibres as [17]:

$$P_{f(L)} = 1 - \exp \left[-L \left(\frac{\sigma}{\sigma_0} \right)^w \right] \quad (1)$$

where $P_{f(L)}$ is the probability of failure of a fibre of length L at a stress less than or equal to σ , σ_0 is the Weibull scale parameter or characteristic stress, and w is the shape parameter or Weibull modulus which describes the variability of the failure strength. Weibull parameters were estimated through the linear regression method, using the following estimator [18]:

$$P = \frac{i}{n+1} \quad (2)$$

where n is the number of data points and i the rank of the i -th data point.

Rearrangement of the two-parameter Weibull cumulative distribution expression (Equation 1) gives the following [19]:

$$\ln \ln \left(\frac{1}{1-P_f} \right) = w \ln \sigma - w \ln \sigma_0 + \ln L \quad (3)$$

The scale and shape parameters can be obtained from a plot of $\ln \ln(1/1-P_f)$ versus $\ln \sigma$ (commonly referred to as a Weibull plot) which should produce a straight line, with gradient w and intercept σ_0 at $\ln \ln(1/1-P_f) = 0$.

Wide Angle X-ray Diffraction

A Philips X'Pert diffractometer fitted with a ceramic X-ray diffraction tube was used to assess the influence of alkali treatment on fibre crystallinity. Prior to the

analysis, untreated and treated harakeke and hemp fibres were cut by hand into fine particles and compressed into disks using a cylindrical steel mould with appropriate amount of pressure. The diffracted intensity of CuK α radiation ($\lambda = 1.54\text{nm}$) was recorded between 12° and 30° (2θ -angle range) using a current and voltage of 40 mA and 40 mV with scanning speed of 0.02 degrees/second. The percentage crystallinity index (I_c) was then determined using the Segal empirical method according to the following equation [20, 21]:

$$I_c = \frac{(I_{002} - I_{am})}{I_{002}} \times 100 \quad (4)$$

where I_{002} is the maximum intensity of diffraction of the lattice peak at a 2θ -angle of between 22° and 23° and I_{am} is the intensity of diffraction of the amorphous material, which is taken at a 2θ -angle between 18° and 19° where the intensity is at a minimum [22, 23].

Thermal Analysis

Untreated and treated fibre samples weighing between 8 and 12 mg were analysed using an SDT 2960 Simultaneous DTA-TGA analyser. The analysis was operated in a dynamic mode, heating from ambient temperature to 500°C at $10^\circ\text{C}/\text{min}$ in air purged at 150 ml/min with an empty pan used as a reference. Differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) curves were obtained at the end of the operation.

Results and Discussion

Scanning Electron Microscopy

SEM micrographs of harakeke fibres are shown in Figure 4 to Figure 6 and hemp in Figures 7 and 8. As can be seen in Figure 4a, untreated harakeke fibre bundles were composed of many single fibres attached to each other and coated with substances known to include hemicellulose, pectin, lignin, and other non-strengthening components

[21]. In contrast, alkali treated harakeke fibres (shown Figure 5 and 6) were separated from each other and appeared to have undergone removal of surface coating revealing less rounded sides and a rougher texture with a large numbers of grooves, believed to be cellulose rich as seen for treatment of other cellulosic fibres [24-26]. The fibre separation resulting from the removal of non-strengthening components along with the exposure of rougher texture would have increased contact area for bonding and could therefore be expected to improve fibre-matrix interfacial bonding. The improvement of fibre-matrix adhesion is also expected due to the exposure of more cellulose OH groups, which could bond with reactive sites on the matrix [24]. Likewise for hemp, all treated fibre was well separated and surfaces appeared to have increased overall rugosity compared to the untreated fibre as shown in Figure 7(b) and Figure 8.

Single Fibre Tensile Testing

Alkali treatment of cellulosic fibres using NaOH and Na₂SO₃ is widely used in the pulp and paper industry to separate single fibres from their bundles and as mentioned previously has also been shown to remove non-reinforcing components and can improve the fibre properties, although overtreatment can decrease fibre properties significantly [27-30]. Ideally alkali treatment should separate fibres, improve fibre dispersion within composites and offer an improvement to the fibre properties [31].

As can be seen in Table 3, the harakeke fibres were a lot finer than hemp fibres (as seen in optical micrographs) and were not quite as strong but stiffer. Alkali treatments resulted in a decrease of fibre diameter for both harakeke and hemp fibres, which can be attributed to the removal of alkali-soluble components from the fibre cell walls. For the treatments using NaOH only, the reduction in diameter for hemp and harakeke fibre was found to correspond to the severity of the treatment used, considered to be simply due to more alkali-soluble components removed from the fibre at higher alkali concentration. The diameter of harakeke reduced by 5.8% and 12.2% and that for

hemp reduced by 16.3% and 16.8% when treated using 5wt% NaOH and 10wt% NaOH solutions respectively. Treatment using 5wt% NaOH/2wt% Na₂SO₃ was found to give maximum reduction in diameter for both fibres. The reductions in fibre diameter for harakeke and hemp treated with this solution were found to be 13.8 and 18.9% respectively. Addition of Na₂SO₃ has been shown elsewhere to assist NaOH in the removal of lignin and shorten treatment times required [32-34]. These effects are facilitated when sulphite groups (SO₂⁻³) in the Na₂SO₃ are introduced into the lignin side chains by means of sulphonation, and enable the lignin to be quickly dissolved into the alkaline solution [12, 35]. Although no specific analysis was conducted to measure the lignin content of treated fibres in this study, it is proven elsewhere that lignin was effectively removed by the application of Na₂SO₃ [28]. It was found that treatment with 10wt% NaOH removed sufficient hemicellulose and pectin from hemp fibre to give good fibre separation, but similar separation was not obtained with 10wt% NaOH for harakeke as harakeke contains greater amount of lignin compared to hemp [12]. However, good separation was achieved for harakeke using 2wt% Na₂SO₃ with 5wt% NaOH at the higher temperature and longer processing time required to remove a greater amount of lignin.

Reduction in average tensile strength was observed for all treated harakeke and hemp fibres. Tensile strength of harakeke and hemp fibres reduced dramatically, up to nearly 30% relative to untreated fibres when treated with 10wt% NaOH solution. The smallest reduction for treated harakeke and hemp fibres were 3 and 15.4% when treated using 5wt% NaOH/2wt% Na₂SO₃ and 5wt% NaOH respectively. However, this reduction was found to be insignificant when the tensile strength data was analysed using a one-tailed Student's t-test and given that fibre separation had occurred, these were considered useful treatments. That different treatment should be required for hemp and harakeke is not surprising given the higher levels of non-cellulosic components

removal in harakeke leading to the requirement of a higher concentration of alkali even when conducted at higher temperature and for a longer time.

Also from Table 3, Young's modulus can be seen to increase or decrease dependent on the treatment used. The average Young's modulus for treated harakeke fibres reduced by *1.54% and 10.0%* when treated with 5wt% NaOH and 10wt% NaOH but increased by *2.36%* when treated with 5wt% NaOH/2wt% Na₂SO₃. Statistical analysis did not support a significant reduction in Young's modulus of treated hemp fibres when compared with those of the untreated fibres, although high variability of data was observed considering experimental errors which at some level have influenced the variability in calculated values [30]. Surprisingly for hemp, the Young's modulus for all treated fibres was improved with treatment; treatment using 10wt% NaOH improved the Young's modulus the most, (by *37.9%*) and was found significant as suggested by the Student's t-test. The increment in Young's modulus could be due to improvement in cellulose rigidity resulting in removal of non-cellulosic components. Taking into consideration the desire for fibre separation as well as strength, harakeke fibre treated with 5wt% NaOH/2wt% Na₂SO₃ was selected along with hemp fibre treated with 5wt% NaOH for further study.

The tensile strength of fibres was further statistically analysed using the Weibull cumulative distribution through linear regression and applying the estimator in equation 2. Weibull characteristic strength and Weibull modulus are tabulated in Table 4. It is worthy of note that the two-parameter Weibull distribution approximated the experimental data relatively well, particularly for alkali treated fibres. As expected, Weibull characteristic strength has the same trend as the average tensile strength. Bearing in mind that natural fibres generally possess much larger property variability than commercially produced synthetic fibres in terms mechanical, physical, and chemical properties, low Weibull modulus representing a high distribution of fibre

strength was expected as is seen here. From Table 4, it can be seen that, Weibull modulus for harakeke fibre varied from 2.43 to 4.88 and from 1.75 to 3.00 for hemp fibre with the lowest Weibull modulus observed in untreated harakeke and hemp fibres. These values are comparable with those from other authors for cellulosic fibres [18, 29, 36-38]. The lower Weibull moduli values for untreated fibre may be explained by the fact that the untreated fibre is larger in diameter having a bigger volume and therefore is more likely to contain more defects.

Wide Angle X-ray Diffraction

For most cellulosic fibres, peaks for crystalline phases are normally observed at around $2\theta = 15, 17$ and 20° (denoted as peaks 1, 2 and 3 respectively as shown in Figure 9) which represent the cellulose crystallographic planes (110), (1 $\bar{1}$ 0) and (002). The amorphous phase peak (denoted as peak 4) was assigned according to the current literature [39] at the lowest point between peaks 2 and 3 (for (002) and (1 $\bar{1}$ 0) planes). Generally, it is found in studies that cellulose crystallographic (002) planes are clearly represented, however, the cellulose crystallographic plane peaks of (110) and (1 $\bar{1}$ 0) are only clearly seen separately when the cellulose content is high [40], but when the fibre contains high amounts of amorphous material, these two peaks overlap and appear as one broad peak [21, 41].

The X-ray diffractograms of untreated, NaOH treated and NaOH/Na₂SO₃ treated harakeke and hemp fibres are shown in Figure 10 and Figure 11. As expected, major crystalline peaks for harakeke and hemp fibres occurred at 2θ around 22° . It can be seen that intensity of the (002) crystallographic plane peak increased significantly as a result of alkali treatment suggesting removal of amorphous material [22, 30]. Other peaks were present on the X-ray diffractograms for harakeke and hemp fibre at 2θ around 15 and 17° , which represent the cellulose crystallographic planes of (110) and (1 $\bar{1}$ 0)

respectively. These peaks can be clearly observed individually for all treated hemp fibre but only with treatment using 10wt% NaOH for harakeke. Although the (002) peak is not the highest for harakeke treated with 10wt% NaOH, it is the peak areas that give most accurate information on crystallinity on which crystallinity index is established. The values of crystallinity index (I_c) for treated and untreated harakeke and hemp fibres are presented in Table 5. The values of crystallinity index (I_c) were calculated using Equation 4 considering the peaks for the crystalline (peak 3) and the amorphous (peak 4) phases as depicted in Figure 9 [39]. It should be noted that the crystallinity index is generally used for comparison rather than to define absolute crystallinity [28]. As can be seen in the presented results, the crystallinity index (I_c) of harakeke and hemp fibres was effectively increased by alkali treatment. The crystallinity index (I_c) of treated fibres was increased up to 20% (using 10wt% NaOH solution) for harakeke and 15% (using 5wt% NaOH solution) for hemp with low variation between treated fibres. Such behaviour is expected, as under the applied treatment, amorphous materials (e.g. lignin, hemicellulose and wax) would be removed from the fibres [20, 29].

Increase in fibre crystallinity with alkali treatment has also been suggested to occur due to better packing and stress relaxation of cellulose chains. However, the removal of excessive amounts of amorphous materials can possibly reduce the tensile strength by loss of adhesion between cellulose microfibrils [22].

Thermal Analysis

The TGA and DTA thermograms for harakeke and hemp fibres are shown in Figure 12 and 13 respectively. The thermal degradation of harakeke and hemp fibre can be identified by reduction in sample weight in TGA themograms and a temperature difference in DTA thermograms. This was evidenced as starting at around 70°C for harakeke and hemp fibre when it is believed there is evolution of adsorbed moisture from the fibres. The fibre weight was then maintained until a reduction at around 250°C

for untreated fibre and around 300°C for treated fibre, which has been associated with the initial thermal depolymerisation traces of hemicellulose and pectin followed by cellulose [42]. This stage was completed when the temperature reached around 345°C for harakeke and 355°C for hemp when the fibres had lost almost 60% for untreated and 80% for treated fibre of their initial weight. The final stage of thermal degradation occurred at temperatures between 400 to 450°C when the fibres had lost almost 95% of their initial weight leaving behind ash and unburnt minerals [28, 43]. The weight loss of untreated and treated fibres at different stages of thermal degradation is presented in Table 6. It can be seen that the degradation temperatures at different stages of thermal degradation for treated fibres were consistently higher than for untreated fibres indicating the heat resistance of fibre was effectively improved by alkali treatment [44].

DTA thermograms (Figure 12(b) and 13(b)) support the different stages of moisture loss and decomposition at the same temperatures as those evaluated by weight lost. Two main peaks were observed for all hemp and harakeke fibres, however, narrower peaks can clearly be observed for treated fibre, representing a more homogeneous cellulose content than for untreated fibre [45].

CONCLUSIONS

Compared to hemp fibre, harakeke fibre was found to be 25% weaker in its untreated state and required a harsher treatment to bring about fibre separation, which is believed to be due to the higher quantity of lignin in its composition. However, with a strength of 782 MPa it would generally be expected to provide significant reinforcement in most common polymer matrices. Treatment with NaOH and Na₂SO₃ was found to improve separation and remove surface constituents for harakeke as well as hemp fibre. As a consequence of constituent removal, fibre diameter, maximum tensile load and tensile strength were found to decrease in most cases. However, it was found that the

tensile strength of hemp fibre treated with 5wt%NaOH and harakeke fibre treated with 5wt%NaOH/2wt% Na₂SO₃ was not significantly affected as confirmed by a Student's t-test, although the average tensile strength suggests a slight reduction. It was also found that the crystallinity index (I_c) for all treated fibres increased significantly compared to untreated fibres. Furthermore, the application of alkali treatment was also found to lead to better thermal stability resulting in more homogeneous cellulose content as indicated with narrower peaks in DTA thermograms.

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FIGURE CAPTIONS

Figure 1: Schematic diagram of cardboard used in testing with mounted single fibre.

Figure 2: Single harakeke fibre as observed under optical microscope.

Figure 3: Single hemp fibre as observed under optical microscope.

Figure 4: Scanning electron micrographs of untreated harakeke: (a) in bundle form, (b) a mechanically separated single fibre.

Figure 5: Scanning electron micrographs of treated harakeke fibre surface using: (a) 5wt% NaOH and (b) 10wt% NaOH.

Figure 6: Scanning electron micrograph of treated harakeke fibre surface using 5wt% NaOH/2wt% Na₂SO₃.

Figure 7: Scanning electron micrographs of (a) untreated hemp and (b) 5wt% NaOH treated fibre surface.

Figure 8: Scanning electron micrographs of treated hemp fibre surface using: (a) 10wt% NaOH and (b) 5wt% NaOH/2wt% Na₂SO₃.

Figure 9: Typical diffraction curves of natural fibres used in calculating crystallinity index by the area method.

Figure 10: X-ray diffraction curves for untreated and treated harakeke fibres.

Figure 11: X-ray diffraction curves for untreated and treated hemp fibres.

Figure 12: (a) TGA thermograms for untreated and treated harakeke fibres

Figure 12: (b) DTA thermograms for untreated and treated harakeke fibres.

Figure 13: (a) TGA thermograms for untreated and treated hemp fibres.

Figure 13: (b) DTA thermograms for untreated and treated hemp fibres.

TABLE CAPTIONS

Table 1: Chemical composition of harakeke fibre Table 2: Abbreviations used for fibre and treatment

Table 3: Mechanical properties of untreated and alkali treated fibres. Standard deviations are included in parenthesis.

Table 4: Experimental tensile strength and Weibull parameters of untreated and alkali treated fibres.

Table 5: Crystallinity index (I_c) of untreated and alkali treated harakeke and hemp fibres

Table 6: Summary of TGA results for untreated and treated harakeke and hemp fibres.

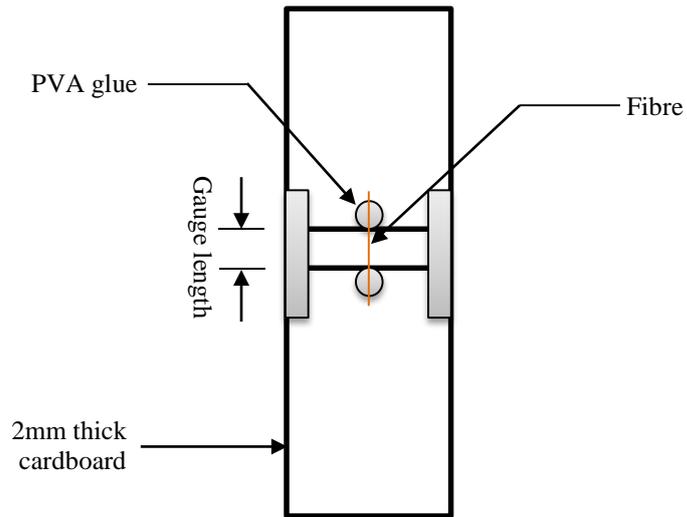


Figure 1: Schematic diagram of cardboard used in testing with mounted single fibre.



Figure 2: Single harakeke fibre as observed under optical microscope.

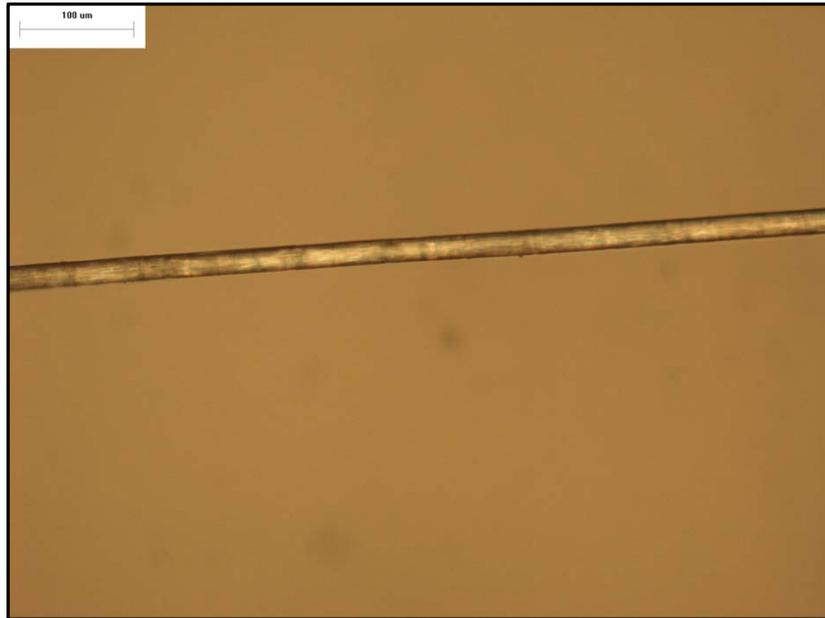


Figure 3: Single hemp fibre as observed under optical microscope.

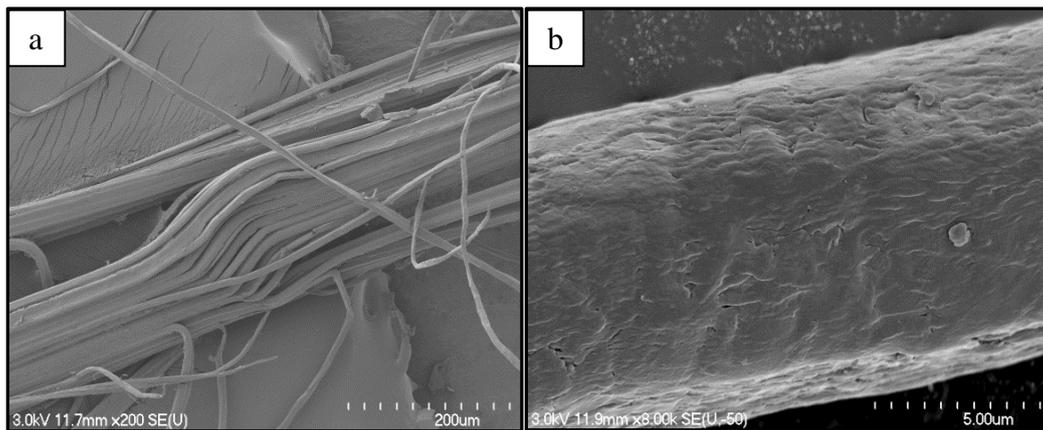


Figure 4: Scanning electron micrographs of untreated harakeke: (a) in bundle form, (b) a mechanically separated single fibre.

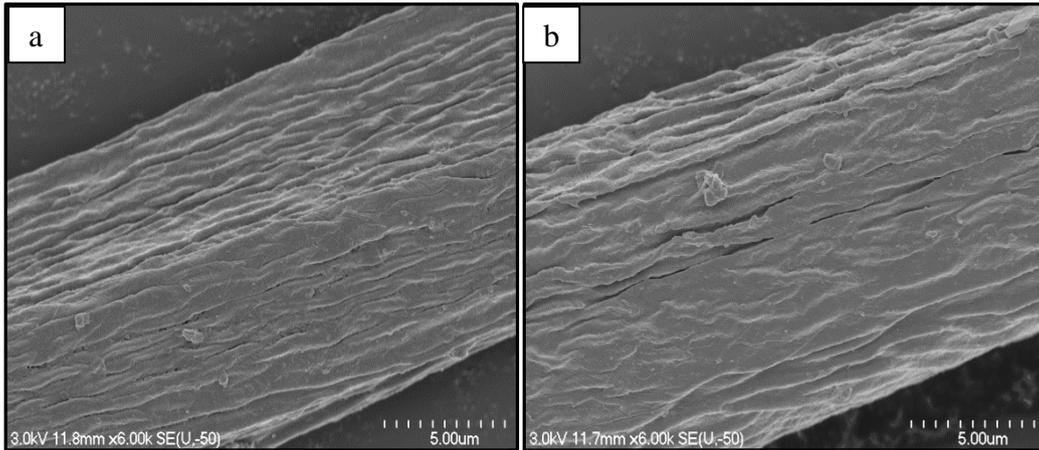


Figure 5: Scanning electron micrographs of treated harakeke fibre surface using: (a) 5wt% NaOH and (b) 10wt% NaOH.

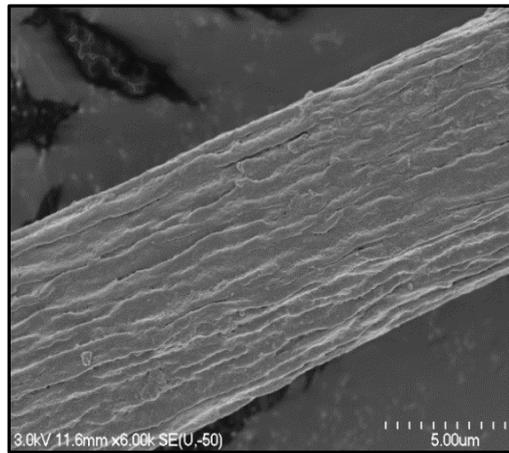


Figure 6: Scanning electron micrograph of treated harakeke fibre surface using 5wt% NaOH/2wt% Na₂SO₃.

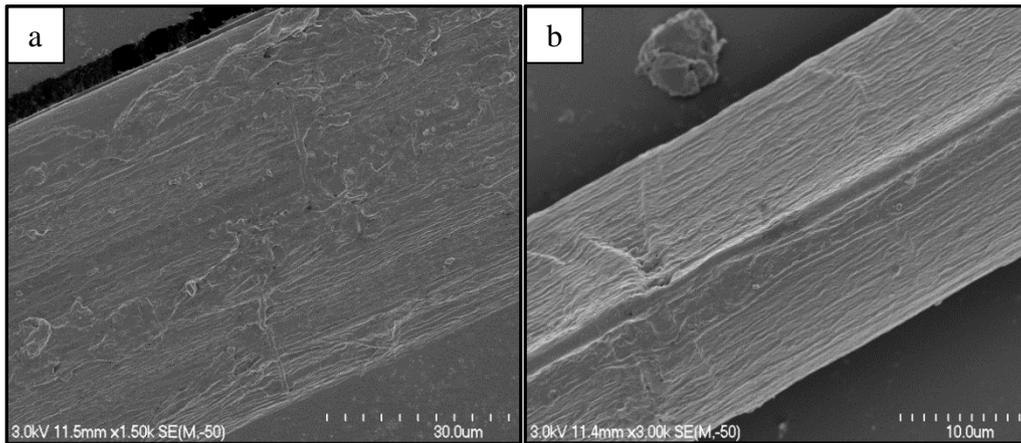


Figure 7: Scanning electron micrographs of (a) untreated hemp and (b) 5wt% NaOH treated fibre surface.

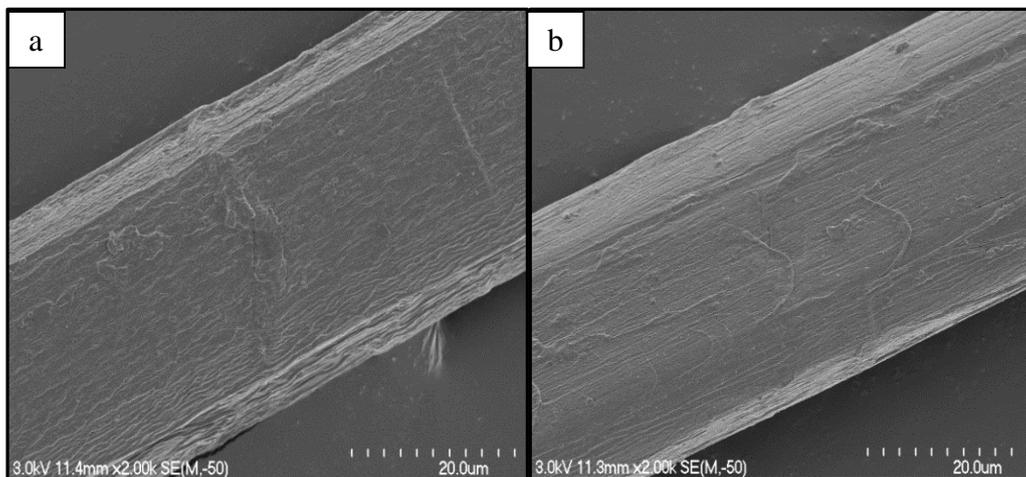


Figure 8: Scanning electron micrographs of treated hemp fibre surface using: (a) 10wt% NaOH and (b) 5wt% NaOH/2wt% Na₂SO₃.

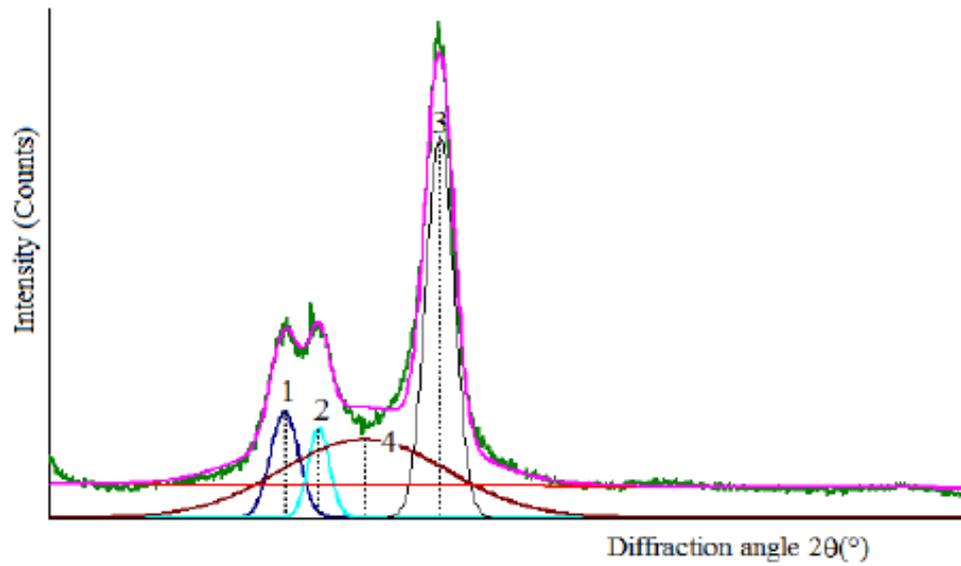


Figure 9: Typical diffraction curves of natural fibres used in calculating crystallinity index by the area method.

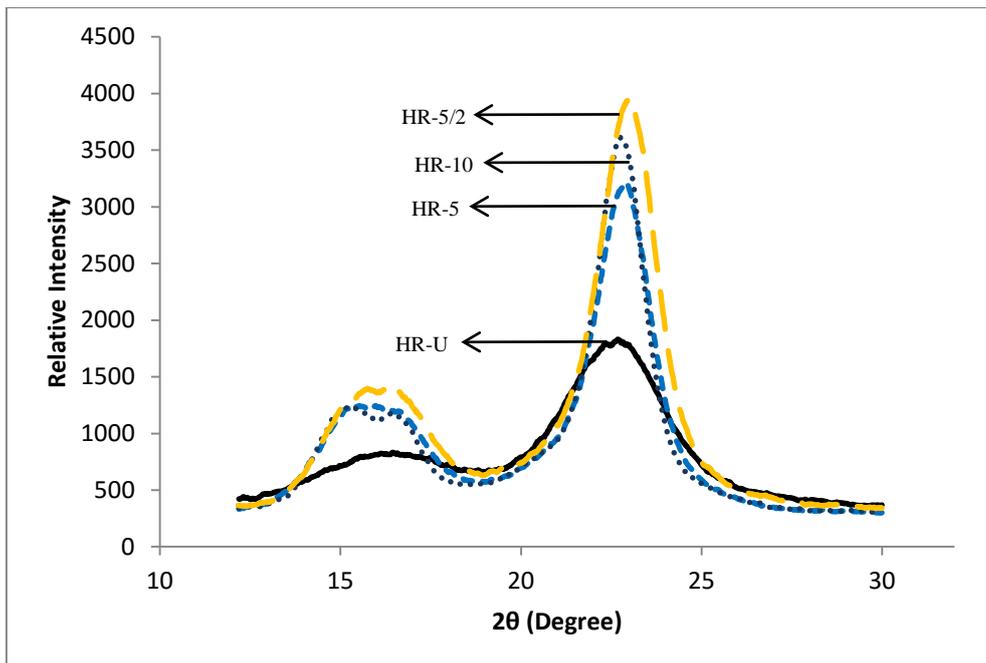


Figure 10: X-ray diffraction curves for untreated and treated harakeke fibres.

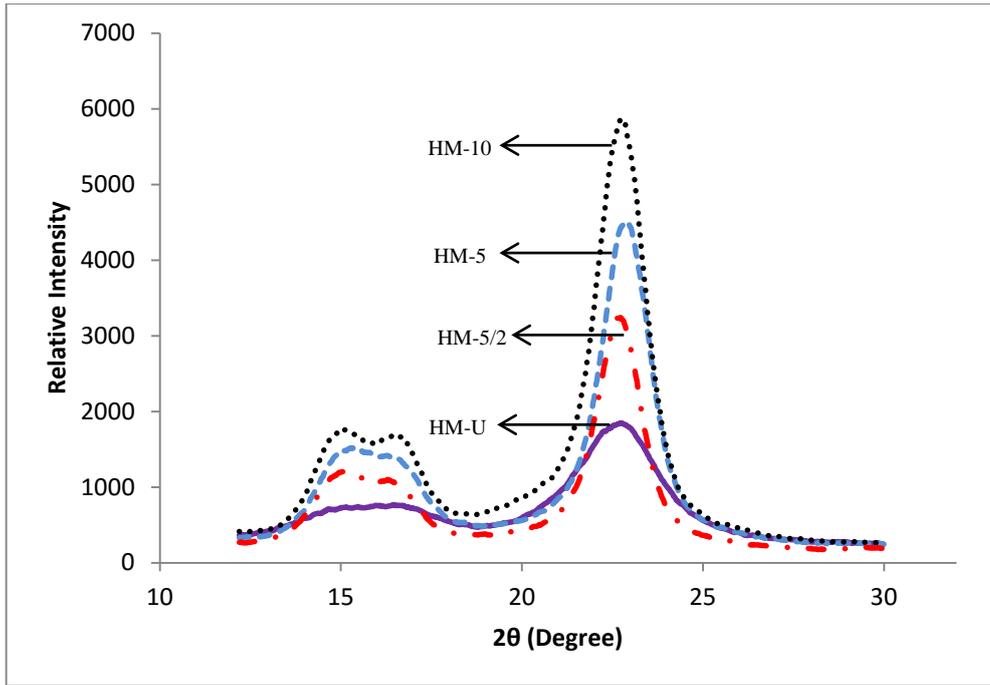


Figure 11: X-ray diffraction curves for untreated and treated hemp fibres.

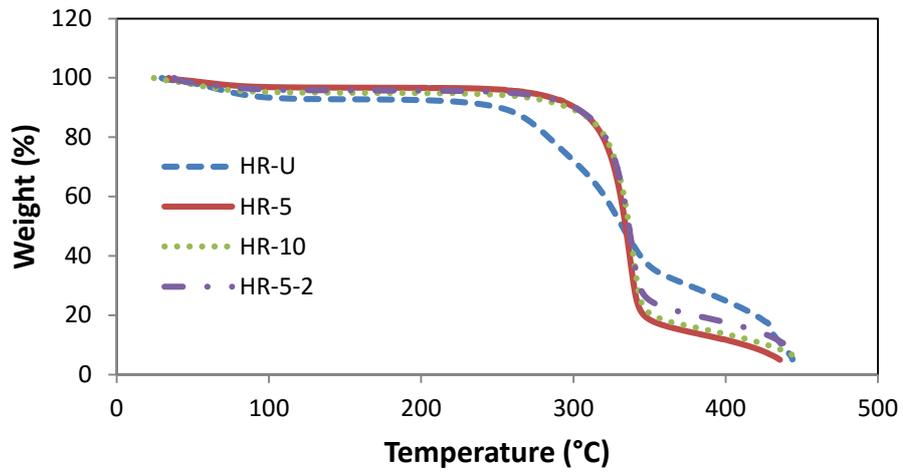


Figure 12: (a) TGA thermograms for untreated and treated harakeke fibres.

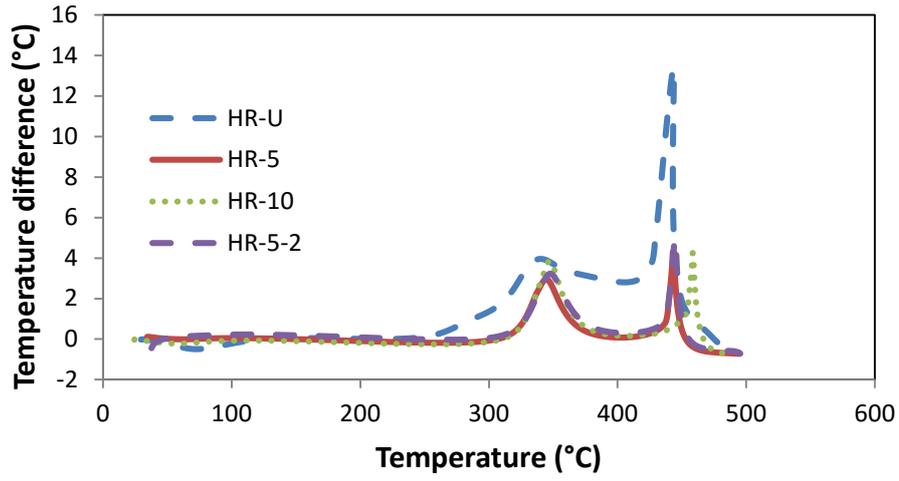


Figure 12: (b) DTA thermograms for untreated and treated harakeke fibres.

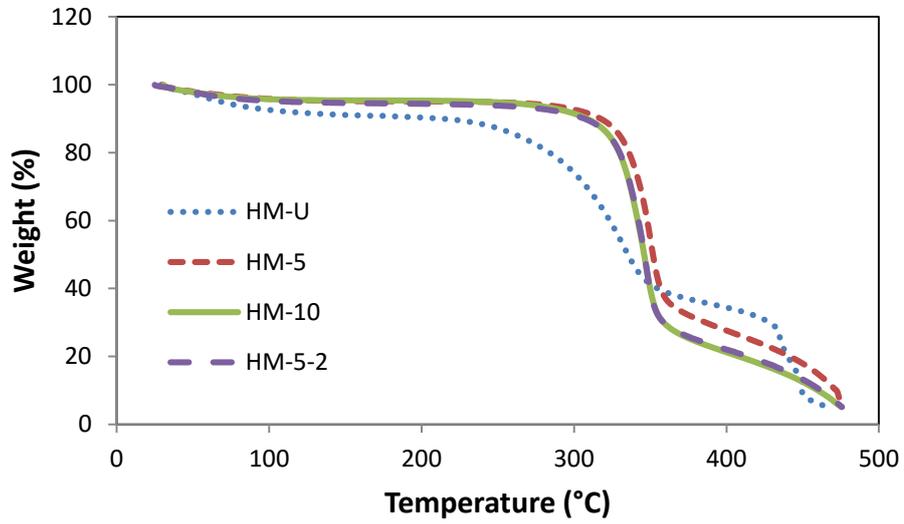


Figure 13: (a) TGA thermograms for untreated and treated hemp fibres.

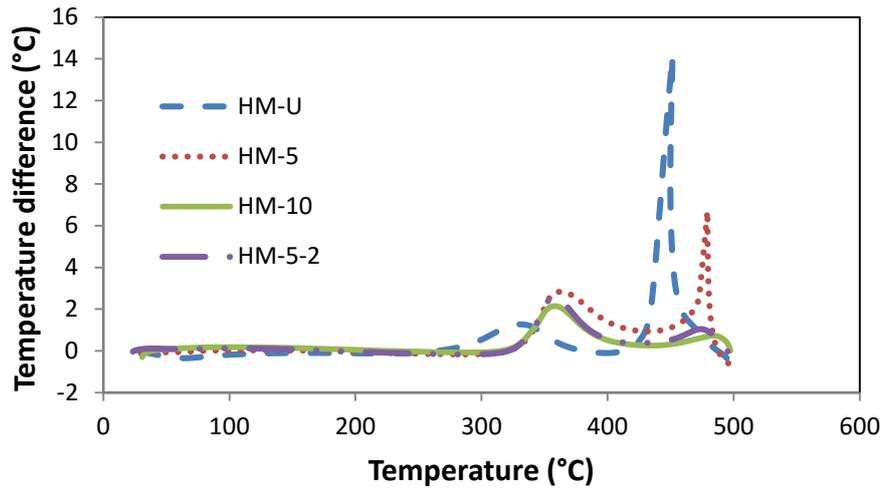


Figure 13: (b) DTA thermograms for untreated and treated hemp fibres.

Table 1: Chemical composition of harakeke fibre

Composition	Content (%)
Cellulose	60.9 ± 4.4
Hemicellulose	27.3 ± 4.1
Lignin	7.8 ± 1.3
Extractives	4.0 ± 0.3

Table 2: Abbreviations used for fibre and treatment

Fibre and Treatments	Abbreviation
Harakeke – Untreated	HR-U
Harakeke – Treated with 5wt%NaOH	HR-5
Harakeke – Treated with 10wt%NaOH	HR-10
Harakeke – Treated with 5% wtNaOH/2wt%Na ₂ SO ₃	HR-5/2
Hemp – Untreated	HM-U
Hemp – Treated with 5wt%NaOH	HM-5
Hemp – Treated with 10wt%NaOH	HM-10
Hemp – Treated with 5wt%NaOH/2wt%Na ₂ SO ₃	HM-5/2

Table 3: Mechanical properties of untreated and alkali treated fibres. Standard deviations are included in parenthesis.

Fibre	Fibre Treatment	Fibre Diameter (mm)	Tensile Strength (MPa)	Young's Modulus (GPa)
Harakeke	HR-U	13.0 (1.7)	804.6 (305.0)	20.76 (8.6)
	HR-5	12.3 (1.7)	641.3 (209.6)	20.4 (6.7)
	HR-10	11.4 (1.5)	540.3 (115.5)	18.7 (5.6)
	HR-5/2	11.2 (1.5)	782.4 (277.2)	21.3 (7.3)
Hemp	HM-U	34.9 (12.9)	1077.6 (663.2)	20.9 (11.8)
	HM-5	29.2 (7.0)	911.3 (315.6)	26.4 (13.3)
	HM-10	29.0 (9.9)	790.2 (350.0)	26.7 (14.07)
	HM-5/2	28.3 (8.3)	866.1 (458.6)	28.9 (13.3)

Table 4: Experimental tensile strength and Weibull parameters of untreated and alkali treated fibres.

Sample	Tensile Strength (MPa)	Characteristic strength, σ_0 (MPa)	Weibull Modulus, w
HR-U	804.6	923.3	2.4
HR-5	641.3	713.4	3.4
HR-10	540.3	588.8	4.9
HR-5/2	782.4	882.7	2.9
HM-U	1077.6	1222.1	1.8
HM-5	911.3	1022.8	3.0
HM-10	790.2	895.3	2.5
HM-5/2	866.1	993.7	1.8

Table 5: Crystallinity index (I_c) of untreated and alkali treated harakeke and hemp fibres

Fibre Treatments	I_{am} ($18^\circ \leq 20 \leq 19^\circ$)	I_{002} ($22^\circ \leq 20 \leq 23^\circ$)	Crystallinity Index (%)
HR-U	603.0	1912.0	68.5
HR-5	543.0	3285.0	83.5
HR-10	504.0	3691.0	86.3
HR-5/2	608.0	4061.0	85.0
HM-U	445.0	1913.0	76.7
HM-5	438.0	4586.0	90.4
HM-10	610.0	6076.0	90.0
HM-5/2	343.0	3331.0	89.7

Table 6: Summary of TGA results for untreated and treated harakeke and hemp fibres.

Fibre Treatments	$T_{10}/^\circ\text{C}$	$T_{50}/^\circ\text{C}$	$T_{90}/^\circ\text{C}$
HR-U	251	330	437
HR-5	301	334	412
HR-10	296	336	427
HR-5/2	300	336	438
HM-U	214	335	450
HM-5	317	351	472
HM-10	309	346	460
HM-5/2	321	347	478

$T_{10}/^\circ\text{C}$, $T_{50}/^\circ\text{C}$ and $T_{90}/^\circ\text{C}$ means temperature at 10, 50 and 90% weight loss.