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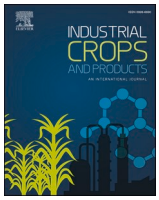

Short communication

Mechanenzymatic production of natural fibre from harakeke (New Zealand flax) and its characterization for potential use in composites for building and construction applications

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ABSTRACT

Mechanical processing of natural fibres can be used to produce large quantities of clean and refined fibres. However, this often results in fibre damage when used alone, thereby affecting the quality of fibres produced, and it generally makes them of insufficient quality for high-performance composite applications. In contrast, the use of biological agents such as enzymes have become a rapidly expanding area of research for producing high quality fibres, but this is still limited to pilot scales. This paper reports the effect of synergizing the salient features of mechanical processing (using a super masscolloider) and enzymatic treatment, on the structure and properties of harakeke (indigenous New Zealand flax) fibre. The cellulose fibres produced are characterized for their potential use as reinforcement in composites. Results show that the combination of mechanical processing with enzymatic treatment could help to overcome the limitations of both processes.

1. Introduction

Polymer matrix based composite materials used in high performance applications are generally developed to combine the salient properties of different components into one material. Generally, it is highly desirable for the dispersed phase, otherwise known as the reinforcing component, to have good interfacial interaction with the continuous polymer matrix phase (Sanjay et al., 2019; Awais et al., 2021). This would help to facilitate effective and efficient stress transfer within the system. Natural fibres exhibit certain properties that make them an attractive alternative to glass fibre, as documented in various research and review articles. For example, they have low density, high specific mechanical properties, wide availability as well as being non-abrasive, and offering cost efficiencies in production (Dixit et al., 2017; Syduzzaman et al., 2020; Huda et al., 2006). In addition, natural fibres are less damaging to health, are renewable and biodegradable, and helps to reduce CO_2 emissions (De Prez et al., 2018). Despite these positive aspects, the use of natural fibres in high-performance composites and their industrial implementation is often limited by their hydrophilic surface character, in direct contrast to the innate hydrophobic character of polymeric matrices. This constitutes a major incompatibility issue which necessitates the use of different approaches to provide good interfacial bonding (Awais et al., 2021; Syduzzaman et al., 2020; Akindoyo et al., 2020).

The conventional strategies for improving the compatibility and interfacial interaction between natural fibres and polymeric matrices are broadly grouped into chemical and physical treatment methods (Sanjay et al., 2019; Senthamaraikannan and Kathiresan, 2018; Saravanakumar et al., 2014; Akindoyo et al., 2015). These methods are applicable in industrial production lines. However, environmental concerns have necessitated the need for alternative methods. Besides chemical and physical methods, mechanical extraction procedures can also be used to process natural fibres intended for use as reinforcement in polymeric composites (Bourmaud et al., 2018). Mechanical extraction generally involves a series of procedures which help to clean and refine the fibre. However, this is a lengthy process which often leads to production costs higher, or on a par with synthetic fibres such as glass fibre (De Prez et al., 2018). In addition, mechanical extraction often induces fibre damage, and when used alone, the quality of fibres produced is generally not sufficient for high-performance applications such as the production of composites for building applications.

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To overcome the challenges associated with chemical, physical and mechanical approaches to natural fibre processing, the use of biological agents such as enzymes (De Prez et al., 2018) has become a rapidly expanding area of research. Enzymes are agents produced by biological organisms including fungi, bacteria, protozoans, termites, plants, and animals (Summerscales, 2021). Generally, enzymatic modification of natural fibres requires lower water and energy input compared to chemical and physical methods. This is because they are reaction-specific, and they catalyse chemical processes or decomposition under mild conditions even at low concentrations (Summerscales, 2021). In addition, there is the possibility for recycling and reuse of enzymes for subsequent treatment sessions because they are not consumed by the reactions they facilitate (Li and Pickering, 2008). Different levels of success have been reported for enzymatically modified natural fibres, such as increased surface roughness which helped to facilitate mechanical interlocking with polymer resins (Yao et al., 2023). Likewise, it has been reported that the mechanical properties of thermoplastic composites were improved when enzyme treated hemp fibres were used as reinforcement (Saleem et al., 2008). Other properties that can be improved through enzymatic treatment of natural fibres are the crystallinity and thermal properties. Despite these interesting reports, and possibilities with enzymatic treatment of natural fibres, most of the available studies are limited to pilot scale (Boey et al., 2022; Sindhu et al., 2016). The high scale industrial implementation of enzymatically modified natural fibres for composite production is still limited by the high cost of enzymes, equipment, and wastewater treatment plants (Summerscales, 2021).

Based on these, it is thought that a synergized approach that involves the combination of mechanical processing with enzymatic treatment could help to overcome the limitations of both processes. Mechanical processing of natural fibres does not require the use of hazardous chemicals, the main challenge being the lengthy procedure and high cost involved. In addition, mechanical processing alone is often insufficient to achieve the surface functionalities required for good interfacial bonding of fibres with polymer matrices. The use of enzymes can help to reduce the length of time, water and energy required for mechanical processing of fibre. On the other hand, the mechanical processing will help to separate the fibre bundles, thereby increasing the surface area for enzymatic treatment to improve the fibre quality through the removal of non cellulose components. These non cellulose components are mainly responsible for poor mechanical and thermal performance of natural fibres in polymeric composites. Therefore, in this study, combined mechanical processing and enzymatic treatment was used to extract natural fibre from harakeke. Harakeke fibre is a natural fibre extracted from harakeke plant (New Zealand flax). The plant itself is an important resource in the Māori culture because of its ancestral link to the Māori heritage. In previous times, the plant was used for applications such as baskets, woven mats, and ropes. Recently, there have been efforts to extract cellulose fibre from harakeke by using different chemicals. However, there are no reports on environmentally friendly treatments of harakeke fibre for potential use in composites, especially for composites intended for use in building applications. In this study, the effect of mechanical processing and enzymatic treatment on the structure, and properties of harakeke fibre is discussed in relation to its potential use as reinforcement in composites. Compared to conventional processes where enzymes are first used to modify fibre surfaces to facilitate mechanical processing, mechanical processing was first used to increase the fibre surface in this study followed by enzymatic treatment to impart surface functionalities. This can help to reduce the energy demands of mechanical processing while ensuring the production of large-scale functionalized fibres.

Table 1
Properties and processing conditions of harakeke fibre processed in the super masscolloider.

Fibre processing conditions (number of times and disc distance)	Diameter (μm)	Length (mm)
Unprocessed	600	5
4 times each @ 400 μm and 300 μm	23	3.5
4 times each @ 400 μm and 300 μm, and 2 times @ 200 μm	13	2.3
4 times each @ 400 μm, 300 μm, and 200 μm	13	0.9

2. Materials and methods

2.1. Materials

The harakeke fibre processed in this study was kindly supplied by Templeton Flax Milling Heritage Trust, New Zealand. Pectinase enzymes from Aspergillus niger, laccase enzymes from Trametes Versicolor, and 2,2′-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) used as a mediator were purchased from Sigma Aldrich. Ethylenediaminetetraacetic acid (EDTA), sodium acetate trihydrate, sulfuric acid, and glacial acetic acid were procured from Merck Millipore.

2.2. Fibre processing and enzymatic treatment

The harakeke fibre supplied was chopped using a guillotine to reduce the length from about 1–1.5 m to about 5 mm, then the fibre was dried at 80 °C for 48 h and stored for further processing. Before the fibre was processed in the super masscolloider (SMC), it was dispersed in water at a ratio of 1:50 (w/v) (fibre: water) for 24 h. The soaked fibre was fed into the hopper of the SMC (Masuko Sangyo Version IV ultrafine friction grinder "super masscolloider") while the motor was running at a speed of 2500 rpm at 15 A current. The SMC is an ultra-fine friction grinding machine which is suitable for refining pulp and grinding samples into finer/smaller dimensions. The grinding compartment of the SMC features two nonporous ceramic grinding stones which are adjustable to desired clearance between the upper and lower plates. The distance between the upper and lower plates, and the number of times fibres are passed through the grinder would determine the dimensions of the processed fibre. In this study, the fibre was passed through the SMC at different number of passes, and at different disc distances (400 μm, 300 μm, and 200 μm) as summarized in Table 1. After processing in the SMC, the fibre was subsequently sieved to drain off excess water and then stored in a 4 °C chiller until further analysis.

The SMC processed fibre was subjected to enzymatic treatment by dispersing the fibre in a 50 mM sodium acetate buffer (2.5% EDTA) at a ratio of 1:40 (fibre:buffer). Then, the pectinase enzyme (85 U/g of fibre) was added. The fibre, dispersed in the buffer-enzyme solution was incubated for 20 h at 40 °C in a New Brunswick Scientific innova 4300 incubator shaker. After this, one half of the pectinase treated fibre was further treated with laccase enzyme at 75 U/g of fibre in the presence of ABTS mediator (1% with respect to buffer solution). This was further incubated for 3 h at 60 °C. The treated fibres were washed severally under water flow, sieved, and stored in a 4 °C chiller for further analysis.

2.3. Characterizations

The SMC processed fibre was observed using a BX53 Olympus optical microscope, equipped with polarized light. To measure the length and diameter of the fibres, a little drop of glycerol was first placed on a glass slide and a small amount of the fibre was placed on the droplet. This was evenly spread on the glass slide, thereby helping to disperse the fibres. A second glass slide was placed on the dispersed fibre before mounting it on the sample holder of the microscope. Then, an OLYMPUS STREAM image analysis software fitted with the microscope was used to measure the length and diameter of the images obtained. About one hundred

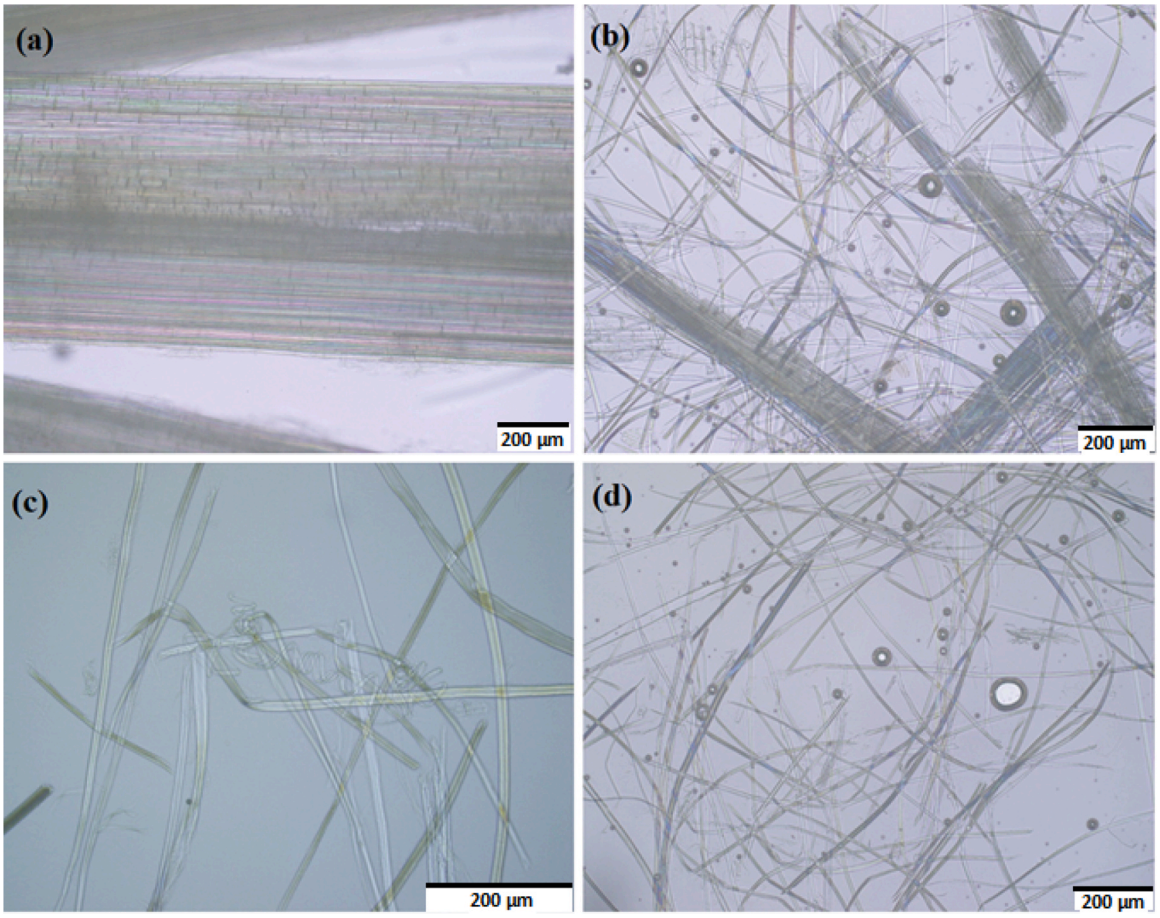

Fig. 1. Optical microscope images of (a) unprocessed harakeke fibre, (b) fibre processed 4 times each at 400 μm and 300 μm disc distance, (c) fibre processed 4 times each at 400 μm and 300 μm, followed by 2 times at 200 μm disc distance, and (d) fibre processed 4 times each at 400 μm, 300 μm, and 200 μm disc distance.

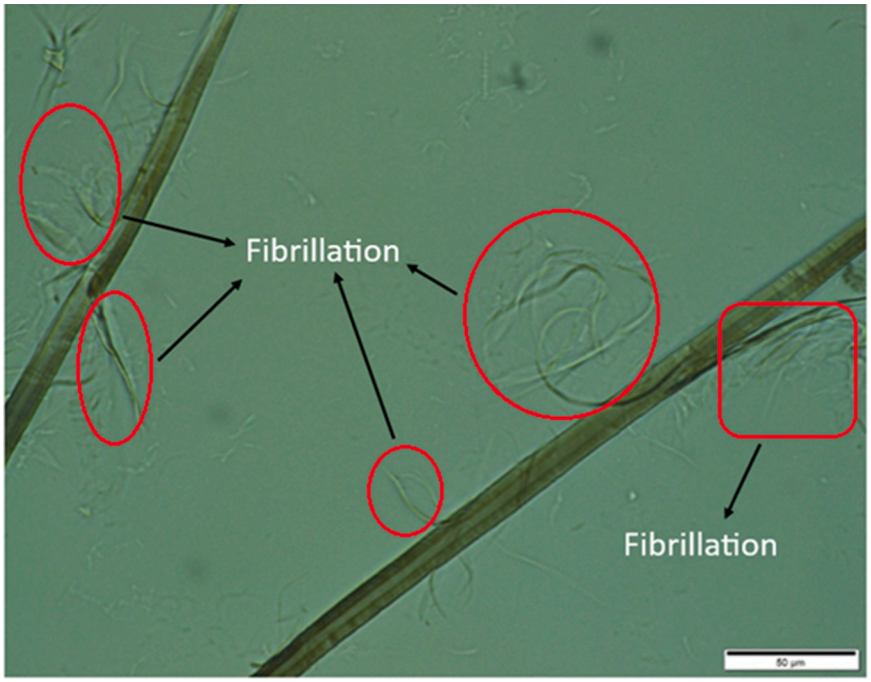

Fig. 2. Optical microscope image showing fibrillated harakeke fibre after processing 4 times each at 400 μm and 300 μm, followed by 2 times at 200 μm disc distance in the SMC.

measurements were taken for each fibre type and the average values was recorded. Spectroscopic analysis was performed in a Perkin Elmer® Spectrum 100 FTIR spectrometer. The FTIR data were recorded over a wavelength range of 4000–400 cm^{-1} using the standard KBr pellet technique. Thermogravimetric analysis (TGA) was performed using a Perkin Elmer STA 8000 thermal analyzer. About 10–20 mg sample was placed in a crucible and heated at 10 °C/min from 30 °C to 600 °C under an argon atmosphere flowing at 40 mL min^{-1}.

The residual lignin in the fibres was determined using the method described in the Technical Association of the Pulp and Paper Industry (TAPPI) T 222 om-02 test methods. The dry fibre was weighed and digested in a 72% (w/w) H_2SO_4 solution inside a test tube. This was placed in a water bath for 1 h at 30 °C, while being stirred at regular intervals. The mixture was then transferred into a beaker and diluted with distilled water to ~ 3% (w/w) H_2SO_4 and kept in an autoclave set at 121 °C for 1 h. After cooling to about 80 °C, a vacuum filter was used to filter the mixture and the acid insoluble residue (AIR) was dried in an oven set at 105 °C. After 24 h, the AIR (Klason lignin) was determined using the following equation:

$$Acid \quad insoluble \quad residue \quad (AIR) = \frac{m}{M} \quad x1000$$

where, m is the dry weight of residue after acid hydrolysis, in g, while M is the oven-dry weight of fibre (100% dry matter) before acid hydrolysis, in g.

3. Results and discussion

The effect of processing cycles (number of passes) in the super masscolloider (SMC), on the morphology of harakeke fibre was assessed by viewing the fibre under an optical microscope. Fig. 1 shows the optical microscope images of raw harakeke fibre and the processed fibres, while the average length and diameter of the fibres are presented in Table 1. It is generally evident from Fig. 1 that processing with the SMC helped to produce unitary (single) fibres. Fig. 1b (fibre processed 4 times each at 400 μm and 300 μm disc distance) shows several unitary fibres, but with some fibre bundles which suggests that additional processing was needed. In contrast, there are no obvious fibre bundles in Fig. 1c (fibre processed 4 times each at 400 μm and 300 μm, and 2 times at 200 μm disc distance), and Fig. 1d (fibre processed 4 times each at 400 μm, 300 μm, and 200 μm disc distance). This indicates that harakeke fibre bundles can be effectively reduced to consistent unitary fibres in the SMC at a disc distance of 200 μm.

Further analysis of the fibres revealed that the diameter and length of the fibres generally decreased as the number of passes increased, and as the disc distance became smaller. It is significant, as seen in Table 1, that an increase in the number of passes from 2 times to 4 times (200 μm disc distance) did not affect the average fibre diameter. Instead, the fibre length was shortened, thereby reducing the fibre aspect ratio from about 170 for the fibres processed twice at 200 μm disc distance to 69, for the fibres processed 4 times at the same disc distance. This indicates that extraction of unitary fibres was already achieved during the 2 times pass through the SMC at a disc distance of 200 μm. In fact, as seen in Fig. 2, fibrillation of the fibre had occurred after 2 times pass through the SMC at a disc distance of 200 μm. So, further passes (from 2 to 4 times) are believed to have resulted in fibre breakage instead of additional fibrillation. This was supported by visual inspection which showed that the number of fines produced during processing is in the order of Fig. 1b < Fig. 1c < Fig. 1d. Undoubtedly, the reinforcing properties of the fibre when used in composites will be influenced by this because the presence of fines is generally not desirable in fibre reinforced polymer composites.

Preliminary studies on the use of these processed fibres as reinforcement in poly (lactic acid) (PLA) composites (not included in this article) have indicated that the interfacial bonding between the fibre and matrix appears very low. Therefore, since unitary fibres and fibrillation

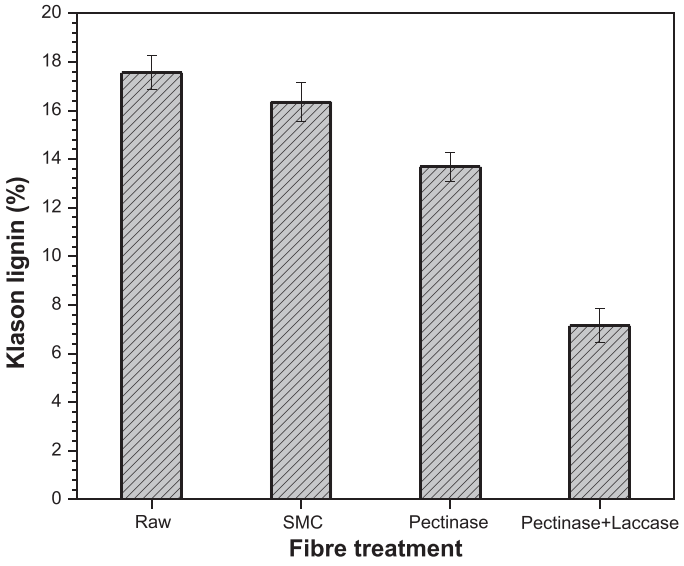

Fig. 3. Lignin content of unprocessed (raw), SMC processed (SMC), SMC processed-pectinase treated (pectinase), and SMC processed-combined pectin and laccase treated (pectinase+laccase) harakeke fibres.

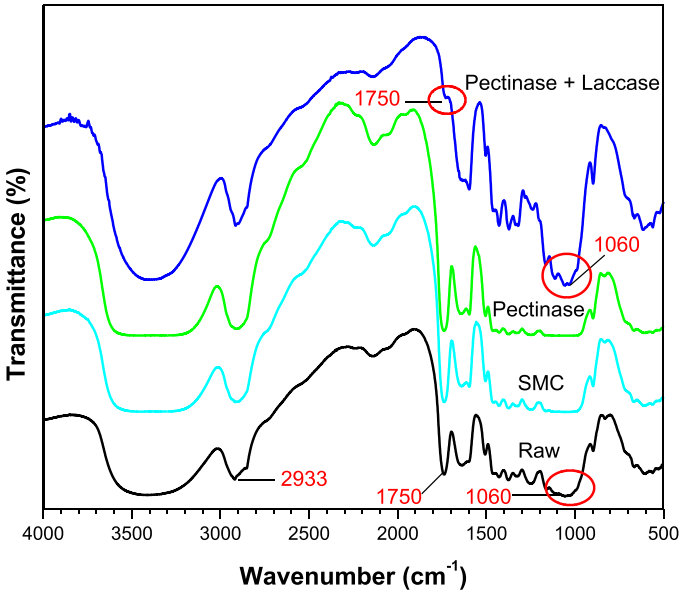

Fig. 4. FTIR spectra of unprocessed (raw), SMC processed (SMC), SMC processed-pectinase treated (pectinase), and SMC processed-combined pectin and laccase treated (pectinase+laccase) harakeke fibres.

were achieved from 2 times pass through the SMC at a disc distance of 200 μm, this material was subjected to enzymatic treatment with the intention of modifying the fibre surface, potentially to facilitate compatibility with the polymer matrices and thereby improve interfacial interactions. Enzymatic treatment was selected because it is an environmentally friendly approach to fibre processing and it helps to minimize fibre damage (De Prez et al., 2018; Boey et al., 2022).

The lignin content of the fibres is illustrated in Fig. 3. As seen in the figure, the unprocessed fibre (Raw) has higher lignin content than the processed and treated fibres. Among the processed and treated fibres, the fibre subjected to combined pectinase and laccase treatment has the lowest lignin content. Compared to the unprocessed fibre, the combined pectinase and laccase treatment reduced the lignin content of the fibre by about 60%. This is desirable for composite production because it will

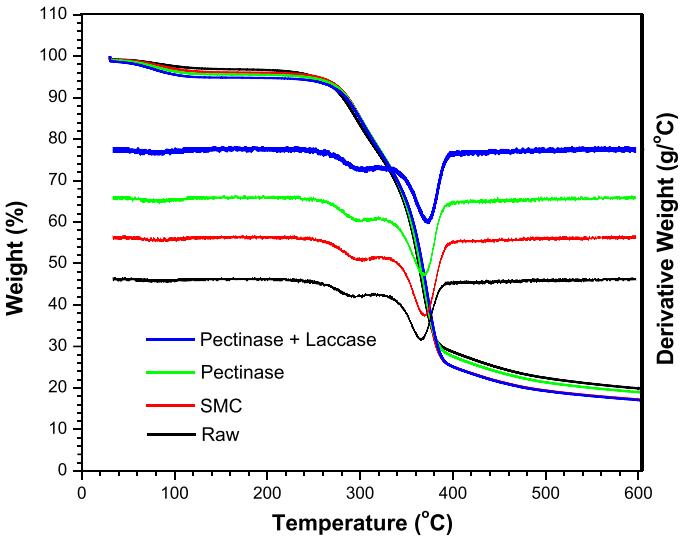

Fig. 5. TGA and DTG curves of unprocessed harakeke fibre (Raw), harakeke fibre processed with the super masscolloider (SMC), harakeke fibre treated with pectinase enzyme (Pectinase), and harakeke fibre treated with combined pectinase and laccase enzymes (Pectinase + Laccase).

undoubtedly influence the compatibility of the fibre with polymer matrices. In addition, it will help to improve interfacial interactions that would normally enhance good stress transfer within the composite.

The FTIR spectra of unprocessed (raw), SMC processed (SMC) and SMC processed enzyme treated harakeke fibres are illustrated in Fig. 4. The important peaks as shown in the figure include the −OH stretching vibrational peaks around 3200–3600 cm^{-1}, the C−H stretching vibrational peaks of cellulose and hemicellulose around 2850–2950 cm^{-1}, and the peak at 1750 cm^{-1} which represents the C═O stretching peak of methyl ester and carboxylic components in pectin, hemicellulose, and lignin components in the fibres (Sisti et al., 2016; Akindoyo et al., 2023). In addition, the peak at 1647 cm^{-1} represents the =CH vibration of the aromatic skeletal vibration in lignin, while the peak at 1422 cm^{-1} is attributed to the $-CH_3$ asymmetric, and C−H symmetric deformational modes in aromatic rings (Sisti et al., 2016). Furthermore, the peak at 1060 cm^{-1} represents the in-plane deformational mode of the easily cleavable C−O−C linkage in pectin, lignin, and hemicellulose (Sisti et al., 2016).

Generally, modification of natural fibres intended for use in polymer composites is often aimed at removing, or at least to reduce the hemicellulose and lignin components, thereby making the cellulose hydroxyl groups available for bonding with the polymer matrix. This can be confirmed through FTIR analysis mainly be observing the C═O stretching peak at 1750 cm^{-1}. As seen in Fig. 4, there is no significant difference in the C═O stretching peak at 1750 cm^{-1} of the raw, SMC processed, and SMC processed-pectinase treated fibre. This is not surprising for the SMC processed fibre since SMC mainly helps to refine, rather than removal of components. And this explains the reason for not obtaining the desired improvement in the properties of the preliminary composites as stated earlier. In the case of the enzyme treated fibres, it is evident that the use of pectinase and laccase enzymes is more efficient than pectinase enzyme alone which aligns with the lignin content result presented in Fig. 3. This is because laccase enzymes help to break down lignin structure in natural fibres while pectinase mainly helps to facilitate fibre separation into fibrils through removal of pectin and other water-soluble constituents (Ponnusamy et al., 2023). Therefore, the significant reduction in the C═O stretching peak at 1750 cm^{-1} for the combined pectinase and laccase treated fibre indicates the dissolution of hemicellulose, and removal of large amounts of lignin from the fibre which is highly desirable for ensuring good fibre/matrix interactions. This is further confirmed by the split in the aromatic C−H in-plane deformation peak around 1060 cm^{-1} and supported by the Klason lignin in the fibres which is presented in Fig. 3. Therefore, it can be inferred that enzymatic treatment of harakeke fibre using combined pectinase and laccase enzymes can help to remove some of the non cellulose components from the fibre, thereby improving the reinforcing ability of the fibre. It is noteworthy that removal of non cellulose components is not the only factor responsible for development of fibre-matrix interface in composites. Other factors include mechanical interlocking and molecular entanglement among others. However, removal of non cellulose components will help to ensure that components such as lignin and hemicellulose which may be detrimental to the mechanical and thermal performance of the composite are removed, or at least significantly reduced. In addition, removal of these components can help to enhance other mechanisms required for strong interface due to increased interfacial interactions between the fibre and the matrix. This is because the cellulose hydroxyl groups of the fibre would become more exposed to interact with the functional groups of the polymers.

Table 2
TGA parameters of unprocessed, SMC processed, and enzyme treated harakeke fibre.

Fibre Type	T_{onset} (°C)	T_d (°C)	Residue@600 °C	E_a (kJ/mol)
Raw	250.75	367.08	22.01	67.85
SMC	253.77	367.38	19.21	73.41
Pectinase	255.33	369.25	18.76	75.98
Pectinase + Laccase	255.98	373.02	16.95	86.18

The TGA and DTG curves of unprocessed harakeke fibre (Raw), SMC processed fibre (SMC), and SMC processed enzyme treated fibres are presented in Fig. 5. Generally, removal of non-cellulose component from natural fibres would lead to an increase in the onset temperature of thermal degradation (T_{onset}), and the thermal degradation temperature (T_d). The T_{onset}, and T_d of the fibres as extracted from the DTG curve are presented in Table 2. As presented in the table, treatment of harakeke fibre with pectinase and laccase enzymes resulted in an increase in the thermal stability of the fibre, confirmed by the higher T_d. It is well known that the thermal stability of natural fibres is directly related to the proportion of cellulose and non-cellulose components in the fibre. Accordingly, it can be inferred that the higher thermal stability of the enzyme treated fibres is due to the removal of some non-cellulose components from the fibre, which would otherwise have resulted in lower thermal stability. In addition, it is significant that the combination of pectinase and laccase enzymes produced higher thermal stability than pectinase enzyme alone. This suggests that the amount of non-cellulose components removed from the fibre is higher when combined enzyme was used and this is supported by the lignin determination analysis, and it aligns with the FTIR analysis discussed in the previous paragraphs.

The DTG data is useful for determining the activation energy associated with thermal degradation of natural fibres (Kathirselvam et al., 2019), the activation energy (E_a) being a good indicator of the energy barrier that hinders molecular chain mobility in the fibre. This energy barrier helps to restrict thermal degradation. Based on this, the thermal stability of the fibres was determined through a kinetic study, using the TGA data as described by Broido (Broido, 1969). The kinetic parameter for thermal decomposition of the fibres was calculated using the following equation:

$$\ln\left(\ln\frac{1}{y}\right) = -\frac{E_a}{RT} + \ln\left(\frac{RZ}{E_a\beta}T^2_{\max}\right)$$

where, y is the fraction of non-volatilized material as yet undecomposed, T_{max} is the temperature of the maximum reaction rate, β is the heating rate, Z is the frequency factor, E_a is the activation energy and R is the gas constant (8.314 J mol^{-1} K^{-1}). The values of y is obtainable from the TGA data, and ln(ln(1/y)) can be calculated accordingly. A plot of 1/T (in Kelvin) against ln(ln (1/y)) would produce a slope (which when multiplied by R) represents the activation energy (E_a) associated with

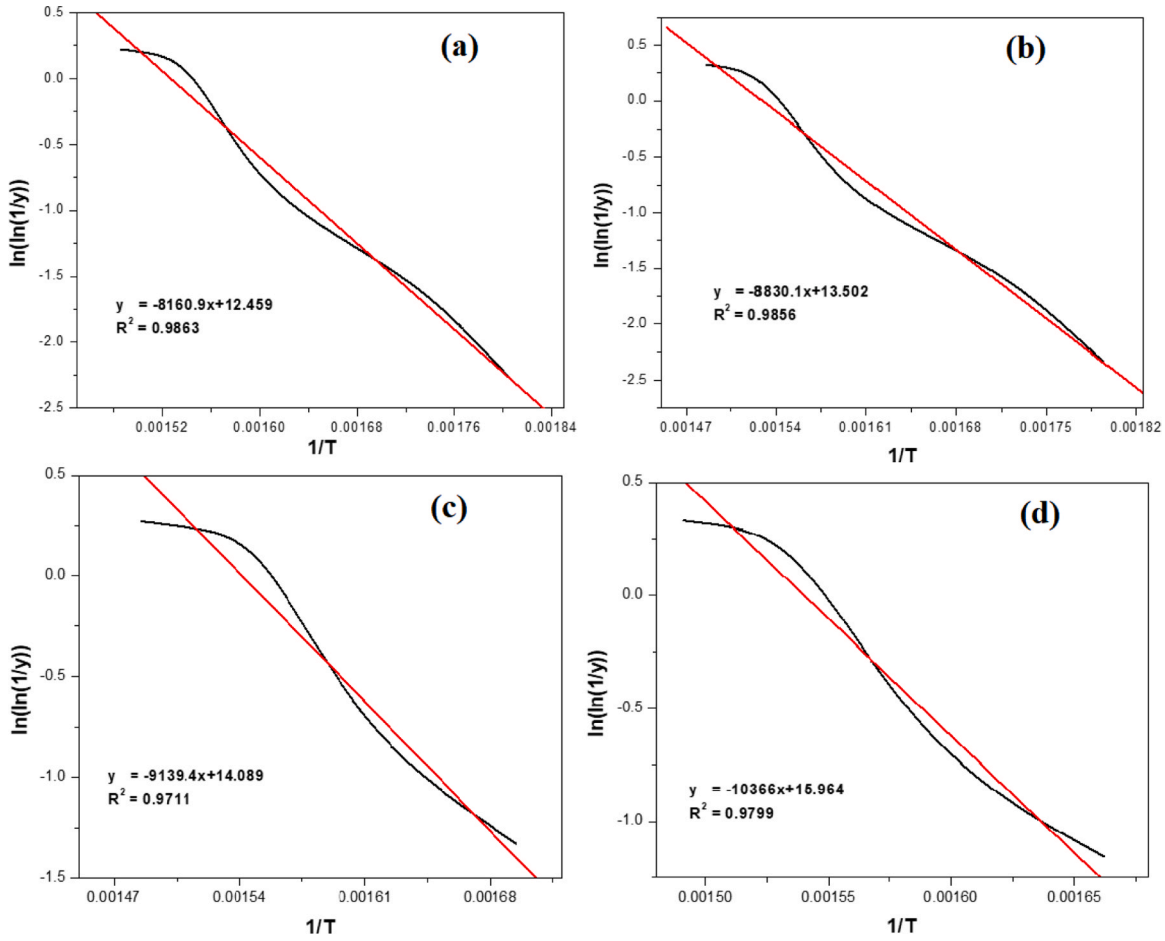

Fig. 6. Broido curves of (a) unprocessed harakeke fibre (Raw), (b) harakeke fibre processed with the super masscolloider (SMC), (c) harakeke fibre treated with pectinase enzyme (pectinase), and (d) harakeke fibre treated with combined pectinase and laccase enzymes (pectinase + laccase).

the thermal decomposition of the fibres (Oza et al., 2014).

As presented in Fig. 6, the R^2 of the 1/T vs ln(ln (1/y)) plots for all the fibres were above 0.9 which indicated good linearity, and agreement with the Broido equation. The E_a of the fibres included in Table 2 confirms the higher thermal stability of the enzyme treated fibres, with the combined pectinase and laccase treated fibre showing the highest thermal stability, which aligns with the TGA result. This confirms that the thermal properties of natural fibres can be improved through enzymatic treatment and this will undoubtedly improve the thermal stability of their reinforced composites.

4. Conclusions

Fibres were produced from harakeke through combined mechanical processing and enzymatic treatment of the fibre. Optical microscopy revealed that mechanical processing with the super masscolloider was able to refine the fibre and produce unitary fibres from harakeke. The removal of non-cellulosic components was achieved to different extents when enzymes were used to modify the mechanically processed fibre. In addition, thermal analysis shows that the thermal stability of the mechanenzymatically treated fibres is higher than the mechanically processed fibre, with the combined laccase and pectinase enzyme treatment showing the better result than the pectinase enzyme alone. The lower thermal stability of the mechanically processed fibre is attributed to the presence of non-cellulosic components. On the other hand, the better properties obtained from the use of combined enzymes is attributed to the removal of portions of lignin by the laccase enzyme, compared to the disruption of pectin structure, generally achieved when the pectinase enzyme was used alone. Generally, it can be inferred based on the results of this study that the combination of mechanical processing with enzymatic treatment has great potential for producing large scale, environmentally friendly and good quality fibres, suitable for composites.

CRediT authorship contribution statement

Mohammad Dalour Beg: Writing – review & editing, Resources. **Joanna Hicks:** Supervision, Methodology, Investigation. **Kim L Pickering:** Writing – review & editing, Supervision, Funding acquisition. **Michael Mucalo:** Writing – review & editing, Supervision. **John Olabode Akindoyo:** Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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