THE UNIVERSITY OF WAIKATO
Te Whare Wānanga o Waikato
Research Commons

https://researchcommons.waikato.ac.nz/

Research Commons at the University of Waikato

Copyright Statement:

The digital copy of this thesis is protected by the Copyright Act 1994 (New Zealand).

The thesis may be consulted by you, provided you comply with the provisions of the Act and the following conditions of use:

- Any use you make of these documents or images must be for research or private study purposes only, and you may not make them available to any other person.
- Authors control the copyright of their thesis. You will recognise the author's right to be identified as the author of the thesis, and due acknowledgement will be made to the author where appropriate.
- You will obtain the author's permission before publishing any material from the thesis.

Development of sustainable composites from treated harakeke (New Zealand flax) fibre and poly(lactic) acid

A thesis submitted in fulfillment of the requirements
for the award of the degree of
Doctor of Philosophy in Materials and processing Engineering

by

John Olabode Akindoyo

The University of Waikato, Hamilton, New Zealand
January 2025

ABSTRACT

The building and construction sector consumes large volume of materials, it generates enormous amounts of solid wastes, and it is responsible for about 40% of annual global CO_2 emissions. So, sustainable biodegradable, recyclable or renewable materials such as polymer-based materials are seen as potential substitutes to their non-renewable, non-environmentally friendly counterparts. Poly (lactic acid) (PLA) is a polymer produced from renewable sources, thereby supporting sustainability. The use of PLA is sometimes limited by its inherent brittleness, and insufficient mechanical strength when used alone. The brittleness of PLA may be reduced by toughening it with rubbery additives, while its strength can be improved through reinforcement with materials such as natural fibres.

In this thesis, fibres extracted from harakeke (*Phormium tenax*), otherwise called New Zealand flax is used as reinforcement in PLA composites. The fibre properties were modified to facilitate processability, improve its compatibility with PLA, and to enhance its reinforcing ability by removing components such as lignin and hemicellulose which are detrimental to the mechanical and thermal performance of the composite. Different methods such as chemical treatment with alkali solutions, mechanical processing, and enzymatic treatment were explored to modify the harakeke fibre. In addition, polybutylene succinate (PBS) was blended with PLA, followed by reactive compatibilization of the reinforced PLA/PBS blend with dicumyl peroxide (DCP), with the aim of improving the toughness of the composite.

The results show that harakeke fibre is a good reinforcement for PLA, as it increased the composite strength from 62±1.02 MPa to 82±0.98 MPa. In addition, it was found that PLA/PBS blends can be reactively compatibilized and reinforced concurrently, thereby supporting the production of composites with improved mechanical, thermal, and thermomechanical performance. Generally, the results show that enzymatic treatment could serve as a more sustainable environmentally friendly route to fibre treatment as it obviates a chemical processing route and supports recyclability and reusability. Likewise, the combination of mechanical processing with enzymatic treatment has great potential for producing large scale environmentally friendly and good quality fibres, suitable for composites.

DEDICATED

To

My beloved wife and lovely daughter

ACKNOWLEDGEMENTS

I thank the Almighty God, the giver of life for the grace and strength to complete this study. My profound gratitude also goes to my amiable academic supervisors Professor Kim Pickering (chief supervisor), Associate Professor Michael Mucalo (co-supervisor), Dr. Donna Campbell (co-supervisor) and Dr Muhammad Dalour Hossen Beg (unofficial supervisor) for their unceasing support throughout the period of my research.

I appreciate every member of the polymer and composites research group for the good working atmosphere we shared, particularly Christian Gauss for the valuable intellectual discussions we had. I also thank the members of the technical staff at the Large-Scale Laboratory (LSL), particularly Jonathan Van Harselaar and Sophia Rodrigues.

This thesis would not have been possible without the support of my friends and family. My appreciation goes to my parents and siblings. I particularly appreciate my dear wife who sacrificed her career to support my ambition of completing a second PhD. Thanks to my lovely daughter who was born during the period of this research but whose birth brough inexplicable joy to me. I thank everyone who was there for me in one way or the other during the period of this research, both far and near. I am particularly grateful to the friends I made during this research as well. You are all appreciated.

Lastly, I acknowledge the funding from the New Zealand Ministry of Business, Innovation and Employment, under the Āmiomio Aotearoa project hosted by The University of Waikato (UOWX2004). I also appreciate the financial support through a Research & Enterprise Award (108023) provided by the University of Waikato.

The Author.

TABLE OF CONTENT

CHAPTER 2 EFFECTS OF CHEMICAL TREATMENT ON HARAKEKE FIBRE AND ITS COMPOSITES WITH POLY (LACTIC ACID) 20

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ATBC	Acetyl tributyl citrate
AIR	Acid insoluble residue
BF	Bleached fibre
DF	Digested fibre
DCP	Dicumyl peroxide
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
DTG	Differential thermal gravimetry
FTIR	Fourier transforms infrared
FM	Flexural modulus
FS	Flexural strength
FWHM	Full width at half maximum
GMA	Glycidyl methacrylate
GPa	Giga pascal
IFSS	Interfacial shear strength
IR	infrared
ISE	Isosorbide diester
MCC	Micro crystalline cellulose
MFC	Microfibrillated cellulose
MFR	Melt flow rate
MPa	Mega Pascal
PBAT	Polybutylene adipate terephthalate
PBS	Polybutylene succinate
PCL	Polycaprolactone
PHB	Polyhydroxy butyrate
PHBV	Polyhydroxy butyrate-co-valerate
PLA	Poly(lactic acid)
PMCs	Polymer matrix composites
SEM	Scanning electron microscope
SMC	Super masscolloider
TAPPI	Technical Association of the Pulp and Paper Industry

TFC	Twice functionalized organoclay
TGA	Thermogravimetric analysis
TM	Tensile modulus
TPE	Thermoplastic elastomers
TS	Tensile strength
UV	Ultraviolet
WPCs	Wood plastic composites
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION AND OVERVIEW OF THESIS

1.1 Introduction

This chapter presents the background of the thesis, literature review, significance and objective of the thesis, and thesis outline.

1.2 Background of the study

Natural fibres are notable for their salient properties such as low cost, renewability, biodegradability, recyclability, low density, high flexural strength, high modulus, and non-abrasiveness [1, 2]. So, there have been series of efforts towards the processing and modification of natural fibres over the past recent decades [3]. Most of the research on natural fibre is aimed at expanding its utilization in different applications, to replace materials such as glass fibre in reinforced polymer composites [4]. One area with wide potential application for natural fibre reinforced composites is building and construction [5]. The suitability of natural fibre reinforced composites for these applications is based on the large volume of materials used for building and construction applications, and the wide availability of natural fibres can help to meet material demands. In addition, the properties of natural fibres mentioned above such as low density, renewability, low cost, and recyclability gives it some preferential advantage over materials like glass fibre.

Polymers are another class of materials that can be used for building and construction applications [6]. Some polymers, called natural polymers are naturally found in plants and animals while the synthetic polymers are man-made. Polymers possess unique physical and chemical properties which affords them usage in everyday life [7]. When used alone, the mechanical properties of polymers are generally not sufficient for load bearing applications. The mechanical properties of polymers can be improved by incorporating high strength and high modulus reinforcement, such as natural fibres. However, production of high-performance natural fibre reinforced polymer composites with high load bearing capacity suitable for engineering and structural applications is an ongoing challenge to material engineers. The limitation to the use of natural fibre reinforced polymer composites is due to poor compatibility and poor interface associated with the difference in properties of natural fibres and polymers which generally generates low mechanical strength in the composite. Interfacial interaction can be improved by modifying the fibre, the matrix, or both and this would be beneficial to the development of building materials.

Therefore, the development of composite building materials by combining the salient properties of natural fibres with the unique properties of a polymer produced from renewable sources, namely poly (lactic acid) (PLA) is explored in this thesis. Modification, through treatment of the fibre will help to improve compatibility and interfacial interaction with the polymer. The matrix, PLA, is produced from renewable sources thereby offering the assurance of sustainability, and its high mechanical strength makes it a suitable candidate for structural applications. In addition, PLA is easily processible, and its properties can be easily tuned towards desired applications. So, the main benefit of developing this composite is the assured sustainability, and the possibility for performance engineering.

1.3 Literature review

In the past few decades, there has been an increasing global interest in environmental sustainability due to concerns relating to excessive dependence on petroleum resources and depleting natural resources. Aside from this, a larger percentage of petroleum-based products are not environmentally friendly, and their production, use and recycling often generates toxic substances which pollute the environment [8]. In recent years, technological developments have focused on the use of environmentally benign bio-resources as substitutes for conventional minerals or non-renewable ones [9, 10]. Polymers represent a group of materials that can be found naturally in plants and animals or produced from renewable resources. So, there is growing interest in polymers partly because of their versatility and partly based on their structure-property tunability. However, the limitation to the development of polymer-based materials is how to develop environmentally friendly sustainable, and renewable products with sufficient mechanical performance suitable for broad engineering applications. On this basis, the current trend of research is focused on the utilization of different approaches to enhance the performance of polymer. For example, different fillers are being investigated as reinforcement in polymer matrices and where necessary, modification of the filler, the matrix, or both is being explored as a way of obtaining desirable properties from their composites [11].

1.3.1 Polymer composites

Polymer as a word is the combination of two Greek words “poly” which means “many” and “meres” which is translated as “parts”. So, several smaller chemical units come together to form a polymer. They can be grouped into different classes such as thermosets, thermoplastics, rubber/elastomers, of thermoplastic elastomers (TPE). Although these polymer types can all be used for composite production, the interest of this thesis is on thermoplastics. The thermoplastic composites can be lightweight yet strong and durable and can be reformed and re-shaped. In addition, thermoplastic composites are eco-friendly because they can be recycled at the end of their lifespan.

Polymer composites comprise two or more materials that are mixed to achieve certain performance, with the major constituents being the matrix, and the reinforcement. In addition, to these, some additives can be included in composites to achieve specific properties. The matrix phase in polymer composites helps to ensure that the reinforcement is kept in place, and it helps to facilitate the transfer of stress to the fillers. Although the role of matrices in the entire load-bearing ability of composites is lower compared to the reinforcement, proper selection of matrices is important for the overall performance of the composite [12]. Good selection of matrices will help to ensure that most of the other composite properties including appearance, tolerance to environmental conditions and durability which depends largely on the matrix are not lost.

The polymer matrices used for the development of polymer composites can be categorised as naturally occurring or synthetic. This includes gelatin, starch, polyhydroxy butyrate-co-valerate (PHBV), soy resin, poly-hydroxy butyrate (PHB), and poly(lactic) acid (PLA) [13]. In the past few decades, there have been an increasing interest from scientists, engineers, and industry personnels to replace petroleum based and synthetic polymers with bio polymers obtained from renewable sources. This is largely due to the ecological, safety, and environmental issues associated with the production, use, and recycling of materials produced for non-renewable sources [14]. Among the available bio polymers from renewable sources, PLA has been observed to be an ideal candidate to replace the conventional petroleum based and non-environmentally friendly polymers. Therefore, PLA is used as the matrix in this thesis.

1.3.2 Poly(lactic) acid

Poly(lactic) acid (PLA) is among the most notable thermoplastic biopolymers. It has an aliphatic polyester structure, and it is mainly produced from fully renewable resources such as sugar and corn starch [15]. In addition, PLA possesses considerably high levels of strength and stiffness in contrast to other notable biodegradable polymers as can be seen in Table 1.1. Furthermore, PLA is biocompatible, biodegradable, and it is sufficiently stable against UV radiation [16, 17]. Based on these salient features, PLA is widely accepted in different applications which have resulted in an increased global demand for PLA [18].

Table 1.1 Main properties of the commonly used biodegradable polymer matrices [19]

Polymers	**Properties**				
	Melting temperature (ºC)	**T_g (ºC)**	**Young's modulus (MPa)**	**Tensile strength (MPa)**	**Elongation at break (%)**
PBAT	110-120	-30	20-60	32-36	>600
PLA	173-178	64	350-3500	48-60	<5
PCL	58-63	-60	-	-	-
PBS	114	-32	690	42	230
PHB	177	-	-	43	5

The increasing interest in PLA products has led to the identification of its peculiar shortcoming including its inherently brittle nature, poor thermal resistance, low impact strength, and considerably low long-term use temperature due to its relatively low glass transition temperature [20-22]. It was reported in literature that the semi-crystalline nature of PLA contributes to its poor mechanical performance in terms of toughness and thermal resistance [21]. These shortcomings tend to limit the wide application of PLA, especially in fields where high thermal resistance and toughness are required. Asides the stated shortcomings of PLA, mechanical properties of PLA when used alone is not sufficient for structural application. Based on these, the performance of PLA is often improved through the incorporation of reinforcements [23].

Literature has shown that PLA can be effectively strengthened through fibre reinforcements and its toughness can be improved through the incorporation of rubbery additives [24]. However, it is still a challenge to concurrently enhance the toughness and strength of PLA to develop materials suitable for structural applications. This notwithstanding, the growing global interest in a circular economy suggests that the property tunability and recyclability of PLA and its composites can offer immense benefit. Particularly, the production, usage and recyclability of PLA and its composites can offer significant energy savings and drastically reduce greenhouse gas emissions. These are critical factors towards achieving sustainable or circular environments [25].

Currently, the use of PLA in building materials is low compared to the volume used in packaging, medical and biomedical applications [26]. The limited application of PLA in building and construction is due to the low impact strength and high brittleness of PLA which generally limits its suitability for structural applications where high load bearing properties is required. Nevertheless, PLA can be potentially used to produce different building materials such as sheet walls, corner guards, handrails, crash rails, lighting products, wallpapers, for floorings, and in floor pads [27-30].

1.3.3 Natural fibres

The reinforcements used to produce polymer composites can be grouped into synthetic and natural fillers. The natural fillers are obtained from natural and renewable sources, while the synthetic ones are mostly obtained from non-renewable sources. So, the use of natural fillers such as natural fibres as reinforcement have been reported to offer significant environmental benefit over their synthetic counterparts [31, 32]. For instance, the substitution of 50% glass fibre by natural fibre to produce reinforced composites in North American automobiles was reported to reduce CO_2 emissions by about 3.07 million tons while reducing the consumption of crude oil by about 1.19 million m^3 [33]. Therefore, the focus of this thesis is on the use of natural fibres as reinforcement in PLA composites. Natural fibres are broadly classified into mineral, plant, and animal fibres [34, 35]. Among the natural fibres, plant fibres are more commonly used to reinforce polymer matrices to develop environmentally friendly composites [36-38].

Natural fibres can be extracted from different parts of a plant including seed, leaves, fruits, and stems. These are among the most intriguing renewable materials that are currently being widely investigated for various polymeric applications [39-41]. As a reinforcement for polymers, natural fibres generally present significant enhancement in mechanical and thermal properties, while modifying the crystalline behaviour of the matrix [42]. This have particularly facilitated their wider acceptance in applications where sustainability is of high interest. Particularly, natural fibres exhibit some salient features including wide availability, biocompatibility, excellent biodegradability and tuneable properties [43]. Generally, the incorporation of natural fibres in polymer matrices often require surface treatment to facilitate good interfacial interactions between the fibre and the matrix.

1.3.4 Harakeke fibre

New Zealand has a wide array of natural fibres which can be potentially used as reinforcement in polymer composites. The production of reinforcing fibres from these natural fibres which are mainly from non-food sources ensures that there is no competition with food resources. When combined with suitable polymers, these fibres hold great potential for the development of novel high-performance bio-based composite for building applications. Among the available plants that may be used to produce natural fibres, the interest of this thesis is on harakeke (*Phormium tenax*), otherwise called New Zealand flax, based on the high strength and modulus of harakeke fibre, and the historical use of harakeke fibre which suggests that it has great potential as reinforcement in composites.

In early Māori subsistence economy, fibres were either extracted from the leaves of harakeke, or by directly plaiting the leaf strips. These were used for mats, garments, basket and other containers (due to the absence of pottery), medicines, and cordage (such as fishing and hunting gear) [44]. During this time, different unique weaving cultivars of harakeke were identified through oral tradition. However, most of the known weaving cultivars of harakeke have been lost over time, such that most of the previously known specie names cannot be identified with presently growing plants [45]. Over the past recent decades, traditional and contemporary crafts and arts that involve the use of harakeke and other weaving plants have been revitalised but the status of harakeke as a treasured plant remains [44]. After the second World War, young Māoris migrated from rural to urban areas due to job demands. This led to reduced interest in the use of harakeke for weaving purposes and a concurrent decline in the resource availability partly due to land modification, and partly due to destruction of resources in unused bushes [44].

In the 18th century, the early European settlers arrived New Zealand and they quickly identified harakeke as a substitute for European flax which may be used for commercial enterprise [46, 47]. During this time, harakeke was referred to as native flax. However, unlike the European flax, which was mainly extracted from the stalk, harakeke fibre is mainly obtained from the leaves of the plant [48]. The leaves of harakeke which grows up to about 3 m long, and with a diameter of 125 mm are usually very tough and stiff. These properties, coupled with possible mechanisation of extraction around 1920s extended the industrial importance of harakeke. The fibres went on to become a significant export commodity which was used in different applications including mats, ropes, clothing, baskets, fishing lines, and fishing nets [49, 50]. During this time, products obtained from harakeke accounted for about 20% of the total income generated by New Zealand from export activities [48]. Specifically, harakeke fibres were traditionally used as baby napkin, whereas the tow produced from the dressed fibre may be used as sponge for bathing infants [51]. Juice extracted from the root was used as dyes [52]. Similarly, gums derived from the root were used for sealing letters whereas the fibres were mainly used for construction, fishing and hunting in early times [53]. In addition, the medicinal properties of harakeke were exploited for different medicinal remedies. For instance, decoctions of the exudate at the base of harakeke leaf were used for healing severe wounds, burns, old sores, and rheumatic or sciatic regions. Likewise, tumours and abscesses were often relieved by using roasted pulped bases of the blanched leaf [54], while juices extracted from the root dunks are used as purgatives [47, 54]. Furthermore, good wound dressing fibres were obtained from the harakeke fibre while fresh cuts and ringworms were often treated by the application of warm roots [54]. Over time, there was a gradual decrease in the sales of harakeke products, especially in the 20th century when there was a boom in the market for synthetic fibres. This led to the restriction of harakeke use to craft making [55]. However, there have been a recent renaissance in the potential use of harakeke for different purposes. The applications of interest include traditional, pharmaceutical, cosmetics, ecological use, and fibre extraction [56].

Harakeke plant have strong, and long sword like leaves which grows to heights of about 3 m. Like other natural fibres, the three main components of fibre bundles in harakeke are depicted in Figure 1.1 [57]. These components are cellulose, hemicellulose, and lignin. Cellulose is a crystalline glucose polymer that makes up the fibre itself and it is responsible for the stiffness and strength of the fibre. Cellulose contains high amounts of inter-cellulose hydrogen bonding which makes it chemically stable. The cellulose fibres are surrounded by an amorphous matrix of hemicellulose distributed around and within the fibre bundles. Hemicellulose helps to strengthen the cell wall by bonding with other hemicellulose molecules through hydrogen bonding, thereby promoting uniform strength distribution in the fibre. The lignin component on the other hand binds the hemicellulose thereby helping the plant to be rigid.

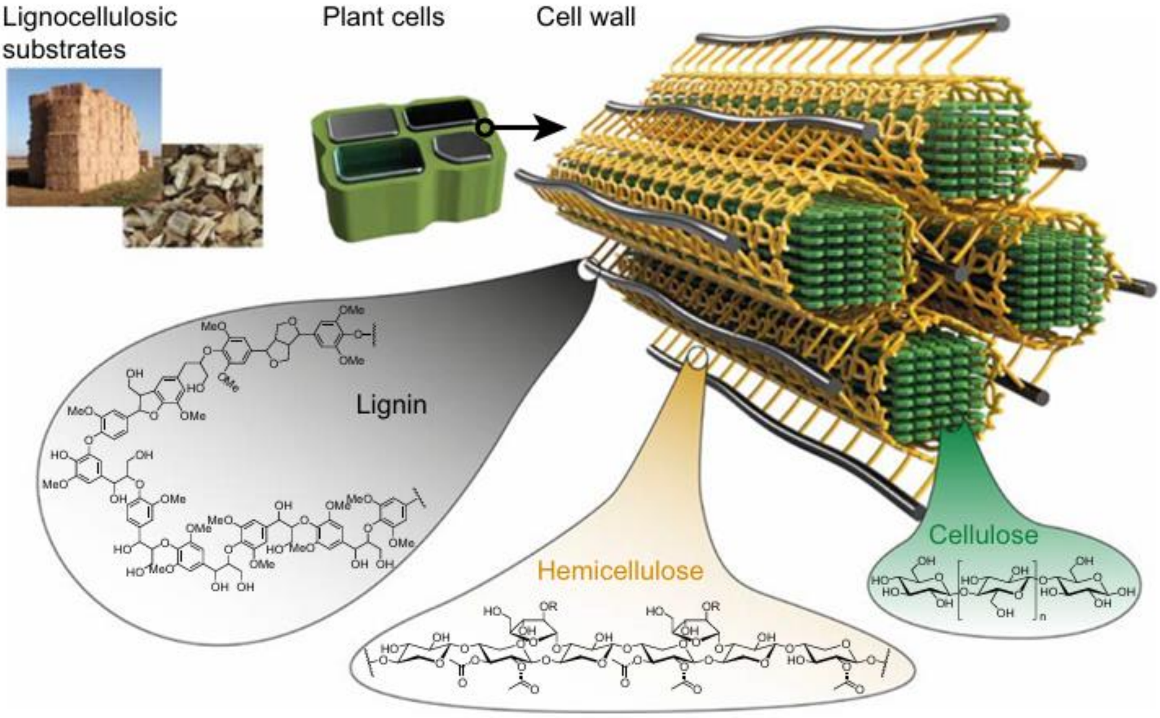


Figure 1.1 Illustration and arrangement of the major chemical components of natural fibres [57].

The relative amount of cellulose, hemicellulose and lignin in harakeke fibre have been estimated and the composition of these components have been found to vary [58]. The variation in the components of natural fibres is attributed to the presence of some other components such as pectin, waxes and water-soluble compounds, in addition, to cellulose, hemicellulose and lignin which are the three main components in natural fibres [59-61]. So, while the cellulose, hemicellulose, lignin, ashes, and total extractives found in harakeke fibre were reported as 44.27%, 13.20%, 15.02%, 23.4%, and 4.11%, respectively, by Furtado et al. [62], Fortunati et al. reported values of 60.9, 27.3%, 7.8%, and 4.0% for cellulose, hemicellulose, lignin, and extractives, respectively [63].

The chemical compositions and structural parameters of some common natural fibres summarized in Table 1.2 confirms the variability of the chemical composition of most natural fibres. The factors responsible for these variations include planting locations, climatic conditions, age of the plant and the type of extraction process. In the case of harakeke fibre, it is evident in Table 1.2 that its cellulose content is low, while its hemicellulose content is high compared to some other common natural fibres, similar to what was reported by Daniels, 1999 [58]. So, while the strength of harakeke fibre is associated with its cellulose component, its toughness is associated with its high hemicellulose content, because the toughness has been reported to increase with growing amounts of hemicellulose and lignin [64].

Table 1.2 Chemical composition harakeke fibre and other common natural fibres [65]

Type of fibre	**Cellulose (wt.%)**	**Hemicellulose (wt.%)**	**Lignin (wt.%)**	**Pectin (wt.%)**	**Moisture content (wt.%)**	**Wax (wt.%)**
Bast fibre						
Flax	64.1-71.9	16.7-20.6	2.0-2.2	1.8-2.3	8-12	1.7
Hemp	70.2-74.4	17.9-22.4	3.7-5.7	0.9	6.2-12	0.8
Jute	61-71.5	12.0-20.4	11.8-13	0.2	12.5-13.7	0.5
Kenaf	31-57	21.5	8-19	3-5	-	-
Ramie	68.6-76.2	13.1-16.7	0.6-0.7	1.9	7.5-17	0.3
Leaf fibre						
Sisal	65.8-78	8-14	10-14	0.8-10	10-22	2
Harakeke	45.1-72.0	30.1	11.2	0.7	10.0	0.7
Henequen	77.6	4-8	13.1	-	-	-
Pineapple	70-82		5-12.7	-	11.8	-
Banana	63.64	10-19	5	-	10-12	-
Seed fibre						
Cotton	82.7-90	5.7	-	0-1	7.85-8.5	0.6
Fruit fibre						
Coir	32-43	0.15-0.25	40-45	3-4	8	-

The fibre extracted from harakeke is known as “MUKA” and its properties are comparable to most natural fibres commonly used as reinforcement in polymer composites as presented in Table 1.2 and Table 1.3. As stated earlier, fibres obtained from harakeke were historically used for producing cloaks, ropes, and for making baskets and fishing nets [66].

These uses suggest that harakeke fibre can offer good reinforcement properties. Therefore, some studies have explored the possibility of combining harakeke fibre with different polymers [65, 67, 68], based on earlier report that which confirmed that harakeke fibres have sufficient tensile properties and suitable as reinforcement for polymer composites in semi-structural applications [49]. Particularly, the cellulose content (between 45 and 63%) in harakeke fibres make it quite resistant in tension, thereby affording it tensile strength of over 300 MPa and elongations of about 2% [69]. When compared with other leaf fibres, micro-compressive defects are reportedly present in the individual fibre cells of harakeke. These defects may reduce the fibre strength, but they are important for the development of strong fibre–matrix interface through adhesion, because of wrinkled cell-wall surfaces [68]. Despite the number of studies on the characterization of harakeke fibre and its potential use as reinforcement in polymer matrices, the use of harakeke fibre in composites intended for use in building and construction is limited. Most of the studies on harakeke fibre reinforced polymer composites incorporated it into epoxy resin [67, 68, 70], which is not recyclable or biodegradable. When used as reinforcement in biodegradable or recyclable polymer composites, harakeke fibre could serve as a sustainable way of developing high performance materials with great economic value [71, 72]. The main benefits of this sustainable approach to building and construction includes resource availability, recyclability, no toxicity, biodegradability, low environmental cost, and improved thermal and mechanical performance.

Table 1.3 Properties of common natural and synthetic fibres for PLA composites

Fibre	**Density (g/cm^3)**	**Length (mm)**	**Failure strain (%)**	**Tensile strength (MPa)**	**Stiffness/Young's modulus (GPa)**	**Specific tensile strength (MPa/gcm^{-3})**	**Specific Young's modulus (GPa/gcm^{-3})**
Ramie	1.5	900-1200	2.0-3.8	400-938	44-128	270-620	29-85
Flax	1.5	5-900	1.2-3.2	345-1830	27-80	230-1220	18-53
Hemp	1.5	5-55	1.6	550-1110	58-70	370-740	39-47
Jute	1.3-1.5	1.5-120	1.5-1.8	393-800	10-55	300-610	7.1-39
Harakeke	1.3	4-5	4.2-5.8	440-990	14-33	338-761	11-25
Sisal	1.3-1.5	900	2.0-2.5	507-855	9.4-28	362-610	6.7-20
Alfa	1.4	350	1.5-2.4	188-308	18-25	134-220	13-18
Cotton	1.5-1.6	10-60	3.0-10	287-800	5.5-13	190-530	3.7-8.4
Coir	1.2	20-150	15-30	131-220	4-6	110-180	3.3-5
Silk	1.3	Continuous	15-60	100-1500	5-25	100-1500	4-20
Feather	0.9	10-30	6.9	100-203	3-10	112-226	3.3-11
Wool	1.3	38-152	13.2-35	50-315	2.3-5	38-242	1.8-3.8
E-glass	2.5	Continuous	2.5	2000-3000	70	800-1400	29

1.3.5 Additives

Aside from the matrix, and fillers or reinforcements, other components or additives that may be found in polymer composites include but not limited to coupling agents, coatings, and processing aids.

Additives can be used to improve the performance of polymers and polymer matrix composites. For example, due to the inherent brittle and low impact properties of PLA, incorporation of rubbery additives can help to improve the toughness, or elongation at break of PLA. In addition, other additives such as flame-retardant agents can be used to improve the thermal stability, thermal insulation behaviour and fire resistance/flame retardance properties of the composite, especially if it is intended to be used as building materials.

Generally, the addition of rubbery additives in PLA might lead to the sacrifice of some mechanical strength. However, the use of reinforcement and proper control of additive concentration can help to ensure sufficient enhancement in strength and modulus of the resulting PLA composite [24, 73].

1.3.6 Challenges to natural fibre reinforced polymer composites

A major limitation to the use of natural fibres as reinforcement in polymer composites is the inherent poor adhesion between natural fibres and polymer matrices [74]. Specifically, natural fibres are hydrophilic in nature whereas the polymer matrices are hydrophobic. This often results in poor interfacial interactions and low compatibility between natural fibres and polymer matrices.

Aside from this, natural fibres are susceptible to high moisture absorption and UV degradation [75]. These can affect the mechanical performance of the fibre, and its reinforced composites [76]. So, fibre treatment is often used to remove or at least reduce the components such as lignin and hemicellulose, as well as improve compatibility and interfacial interaction between natural fibres and polymeric matrices [77]. Removal of hemicellulose and lignin helps to facilitate a molecular rearrangement and closer packing of the fibre cellulose which reduces the functional –OH groups on the fibre surface, such that its moisture susceptibility is reduced. In addition, the phenolic hydroxyl groups in lignin are susceptible to UV photochemical breakdown. So, the removal of lignin through fibre treatment helps to reduce the UV degradation tendency of the fibre [78]. Therefore, the components that are targeted for removal or reduction from natural fibres are notably responsible for the poor thermal and mechanical performance, and high UV susceptibility of natural fibres.

1.3.7 Fibre treatment

The conventional strategies for modifying natural fibres in a bid to improve the compatibility and interfacial interaction between natural fibres and polymeric matrices are broadly grouped into chemical and physical treatment methods [79]. Chemical treatment of natural fibres are the most frequently used methods, and includes mercerization, acetylation, benzoylation, permanganate treatment, peroxide treatment, and silane treatment [79-82]. These can be implemented on an industrial scale and even though they have produced good results, have generally involved the use of hazardous chemicals. This not only exerts undesirable pressure on the environment, but can also result in increased production costs, high energy consumption, and issues relating to waste disposal. Like chemical methods, the physical methods such as plasma treatment, corona treatment, steam explosion, ultraviolet (UV) and electron radiation treatments are applicable in industrial production lines. However, the use of physical methods is also limited by their high energy requirements, high cost and lengthy procedures.

Besides chemical and physical methods, mechanical extraction procedures can also be used to process natural fibres intended for use as reinforcement in polymeric composites [83]. 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 [84]. 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.

To overcome the challenges associated with chemical, physical and mechanical approaches to natural fibre processing, biological agents such as enzymes can be used to treat natural fibres [84], and this has become a rapidly expanding area of research. Enzymes are agents produced by biological organisms including fungi, bacteria, protozoans, termites, plants, and animals [85]. Biological treatment of fibres using enzymes is an eco-friendly and economically feasible alternative approach to fibre treatment [86]. Particularly, the use of enzymes to treat natural fibres intended for use as reinforcement in polymer composites is being explored by several researchers [87-89]. This approach offers certain relative advantages compared to chemical and physical processes, such as mild conditions, reduced energy consumption, selectivity, specificity, and recyclability [90, 91]. There are different classes of enzymes such as pectinases, laccases, proteases, and lipases. These enzymes, being specific in their action, facilitates the removal of specific components from the fibre during treatment. Therefore, selection of suitable enzymes holds great potential as a long-term solution to environmental and economic issues associated with chemical and physical methods of natural fibre treatment. The effects, advantages, and limitations of the highlighted fibre treatment methods are summarized in Table 1.4.

Table 1.4 Comparison of different fibre treatment methods, their effects, benefits and limitations

Methods	Types	Effects	Advantages	Disadvantages	Ref.
Enzymatic treatment	Pectinase, laccase, cellulase, xylanase, hemicellulase, etc	Cleans fibre surface, facilitates fibre separation from nonfibre components, improves fibre-matrix interfacial adhesion	Environmentally friendly, non-toxic processing conditions, supports high product yields, negligible side reaction, lower energy consumption, highly selective and specific, reusable, and recyclable	Prolonged incubation time, dimensional instability, low hydrolysis rate, limited to pilot scale	[92-96]
Chemical treatment	Alkaline treatment, acetylation, peroxide treatment, silanization, graft copolymerization, benzoylation, etc.	Modifies and activates fibre structure and composition, reduces water absorption, roughens fibre surface, facilitates interfacial bonding, improves mechanical strength	More commonly used, can implementable at large scales	Involves the use of hazardous chemicals, requires high cost and energy input, leads to solvent disposal issues	[94, 97-99]
Physical treatment	Corona treatment, plasma treatment, ultraviolet (UV), electron radiation	Modifies the property and structure of fibres, facilitates fibre breakdown from bundles into individual filaments, improves mechanical interfacial properties	No alteration to the chemical composition of fibres, can be incorporated into industrial production line, not limited by reaction conditions	Costly, lengthy process, high energy consumption	[90, 93, 100-102]
Mechanical processing		Facilitates the separation of fibres	Produces high yield of short fibres within a short period	Lower fibre quality and high cost	[103]

1.4 Significance of the topic

The significance of this topic can be described from the performance, economic, and environmental point of view.

Regarding performance, conventional wood plastic composites (WPCs) are mainly suitable for non-load bearing applications. However, the increasing acceptance and interest in polymer composites for building and construction applications necessitates the development of more versatile composites which will result in widened applications of natural fibre reinforced composites in different areas of building and construction.

From an environmental perspective, the materials used to develop composites in this thesis such as PLA, harakeke fibre, and poly (butylene succinate) (PBS) are fully biodegradable. These offers significant reduction in greenhouse gas emission. In addition, the potential biodegradability of PLA and the composites produced in this thesis eliminates potential environmental concerns after its use-life as they can be recycled. Regarding biodegradation, PLA is only biodegradable under industrial composting conditions [104]. Nevertheless, PLA and its natural fibre reinforced composites can be mechanically recycled by shredding and re-extrusion [105, 106]. Likewise, chemical recycling may be used to break down the PLA matrix into monomers or other chemicals using methods such as glycolysis, methanolysis and hydrolysis [107]. In addition, industrial filament extrusion may be used where large amounts of PLA materials is to be recycled. Ultimately, the selected materials will help to reduce overdependence on non-renewable resources, reduce waste generation, conserve resources and lower greenhouse emissions.

In another vein, the plant harakeke (*Phormium tenax*), used in this thesis is endemic to Aotearoa (New Zealand) and Norfolk Island. It is a monocotyledonous plant which is notable for its fibre aggregate commonly extracted from its leaves. Harakeke holds a significant cultural importance to New Zealand and this gave it the status of taonga (treasure) under the Article II of the Waitangi and Ngāi Tahu agreement Claims Settlement Act 1998 [45]. This status is based on the view that there is a direct relationship between humans and every known plant but some of the plant species are highly valued than others. Therefore, the use of these fibres as components of building materials would serve as a means for deriving economic benefits, while sustaining ancestral linkages.

1.5 Statement of thesis hypothesis

Natural fibre reinforced polymer composites often suffer from poor mechanical and thermal performance due to poor interface, associated with incompatibility between the hydrophilic fibres and the hydrophobic polymer matrices and presence of components such as lignin and hemicellulose in the fibre. The treatment of harakeke fibre will help to facilitate its compatibility with PLA, and improve its dispersion in the PLA matrix, thereby enhancing the mechanical strength and thermal stability of the PLA/harakeke fibre composite.

The conventional method of natural fibre treatment is the use of chemicals. However, to support sustainability, proper selection of processing conditions, and use of more environmentally friendly routes as alternative fibre treatment methods can help to produce more sustainable fibres suitable for composite development.

The matrix selected for this, PLA, is notable for its brittle behaviour. Incorporation of rubbery additive can help to lubricate the PLA chains and improve chain mobility. In addition, the rubbery additives might serve as energy absorber to accommodate the stress. It is envisaged that the reinforcement of PLA with harakeke fibre might not significantly improve the impact properties and toughness of the resulting composite in the same manner as it would do to the strength and modulus. So, the composition of the composite will be controlled while incorporating the toughening components to enhance the toughness of PLA without significant adverse effect to the strength and modulus of its reinforced composites.

1.6 Thesis objectives

The objective of this thesis was:

1. To extract natural fibre from harakeke through different methods such as chemical, mechanical, and enzymatic treatment, and to characterize the fibre for its suitability as reinforcement in PLA composites.

2. To produce harakeke fibre reinforced PLA at varying fibre content (wt.%) for development of high mechanical strength composites suitable for use as building material.

3. To improve the toughness of the reinforced PLA through the incorporation of rubbery components. To characterize the resulting composite to determine the optimum content of the rubbery component required for maximum mechanical, thermal and dynamic mechanical performance.

4. To compare the properties of reinforced PLA composite produced with differently (chemically, mechanically, and enzymatically) treated harakeke fibre.

1.7 Thesis outline

This thesis is divided into six chapters.

Chapter 1 is the introduction and overview of the thesis. It contains a short background of the thesis, literature review, significance of the thesis, the thesis objective the thesis outline.

Chapter 2 is a representation of the first article published from this thesis. The paper is focused on the effect of chemical treatment on the properties of harakeke fibre, and its composites with poly (lactic acid).

Chapter 3 contains the representation of the second article from this thesis. The paper focused on the effect of mechanical processing and enzymatic treatment on the properties of harakeke fibre. The article is currently under review, after revisions following peer review.

Chapter 4 contains another manuscript developed from the results of this thesis. It is based on attempts to improve the elongation at break of PLA-harakeke fibre composites through the incorporation of a rubbery component.

Chapter 5 contains a compilation of data from this thesis that are yet to be developed into publishable manuscripts. It is a comparison of the mechanical, and thermal properties of PLA-harakeke fibre composites produced from chemical treated, mechanically processed, and enzyme treated harakeke fibre.

Chapter 6 is the concluding chapter, and it presents the conclusions from the results obtained in this thesis including from published and yet to be published parts of the thesis. In addition, a section of the chapter is devoted to recommendations for subsequent studies.

CHAPTER 2

EFFECTS OF CHEMICAL TREATMENT ON HARAKEKE FIBRE AND ITS COMPOSITES WITH POLY (LACTIC ACID)

2.1 Chapter introduction

This chapter contains the actual reprint of one of the articles published from this thesis. The paper is focused on the effect of chemical treatment on the properties of harakeke fibre and its composites with poly(lactic acid) (PLA). The published article is titled “Combined digestion and bleaching of New Zealand flax /harakeke fibre and its effects on the mechanical, thermal, and dynamic mechanical properties of poly(lactic) acid matrix composites” [108]. The abstract is presented below:

Abstract: In this study, New Zealand flax (harakeke) fibre was initially modified through digestion in an alkali solution followed by bleaching with hydrogen peroxide and sodium silicate with the aim of improving thermal and mechanical performance of its composites, through increased interfacial bonding. X-ray diffraction analysis (XRD), Fourier transform infrared spectroscopy and lignin analysis showed that the combination of bleaching and alkali treatment resulted in a higher cellulose content than digestion alone. Fibre inclusion was found to increase the crystallinity of PLA, likely due to heterogeneous nucleation on the treated fibres, which in turn helped to improve the composite strength. The highest tensile strength, tensile modulus and thermal stability were achieved with the bleached fibre which is believed to be due to better fibre distribution and stronger interfacial interaction. This was supported by the adhesion factor and effectiveness coefficient calculated using the data obtained from dynamic mechanical analysis.

Keywords: A. Polymer matrix composites (PMCs); B. Mechanical properties, Adhesion; E. Injection moulding

2.2 Introduction

In recent years, there have been increasing efforts on developing environmentally friendly materials through a synergy between the principles of green chemistry, sustainability, and eco-efficiency [109, 110]. This is aimed at reducing the excessive dependence on fossil fuel and petroleum-based products [10, 111]. In this regard, biodegradable or renewable polymer-based composites are examples of materials that can be used. Interestingly, polymers are very versatile, can be used in different applications, and can be modified to meet specific purposes [112].

Poly (lactic) acid (PLA) is one polymer that has been widely investigated as a substitute for non-degradable high environmental impact polymers, as detailed in different research and review articles [113-116]. The strength and stiffness of PLA is sufficient for different packaging, medical, and other non-structural applications where high load bearing is not a priority. In addition, the inherent biodegradability and processability of PLA mean that its properties can be tuned to obtain whatever desired performance that is fit for purpose [112, 117]. Hence, PLA has been combined with natural fibres to produce environmentally benign composites with improved mechanical strength. This is partly associated with the salient properties of natural fibres such as low cost, renewability, biodegradability, recyclability, low density, high flexural strength, high modulus, and non-abrasiveness [91, 118].

Studies have shown that good interfacial shear strength (IFSS) in natural fibre reinforced PLA can significantly affect the composite strength. For example, the work by Setswalo et al. on mukwa/PLA composites demonstrated higher flexural properties with improved IFSS, obtained through fibre treatment [119]. Similarly, Tarrés et al. demonstrated that a weak interphase can result in reduced tensile strength [120]. In a different study, a hybrid natural fibre (coir/pineapple leaf fibres) system was used to reinforce PLA. It was found that the untreated hybrid biocomposite returned a higher damping factor and lower strength, attributed to weak interphase [121]. Generally, most studies on natural fibre reinforced PLA composites are focussed on improving interfacial interaction between PLA and the fibres through chemical bonding, or interfacial adhesion [113, 114, 116, 118]. However, too much fibre can lead to insufficient wetting by the matrix which in turn results in poor interface between the fibre and the matrix leading to reduced strength. In relation to that, there have been several articles on the effect of fibre content on the properties of PLA. For example, Abdallah et al. investigated the effect of varying fibre content (0-40 wt.%) on the mechanical and thermal insulation properties of date palm fibre reinforced PLA [122] and found that the tensile strength was remarkably high up to 20 wt.% fibre content. Serizawa et al. also reported 20 wt.% as the optimum fibre content in kenaf fibre reinforced PLA composites [123]. Similarly, Komal et al. reported 20 wt.% as the optimum fibre content after preparing 10-30 wt.% banana fibre reinforced PLA composites [124].

Generally, the conventional natural fibres used as reinforcement in PLA composites include oil palm empty fruit bunch, sisal, hemp, flax, coir, bagasse, banana, and jute [117, 125, 126]. In the past decade, there has been increasing interest in the use of fibres extracted from the leaves of *Phormium tenax* commonly called New Zealand flax (harakeke), as reinforcement in polymer composites [127, 128]. Harakeke is indigenous to New Zealand and the Norfolk Island, and it is a significant resource in Māori culture for making woven mats and containers. In terms of morphology and anatomy, harakeke leaves are clumped together in groups and tend to be folded at their stem. The leaves can grow to a length of about 3 m and extend to about 50-120 mm in width [47]. The structure of harakeke leaf is one that is typical of monocotyledons. There is a spiral overlap at the base of the fibre, which lies parallel to bundles of sclerenchyma fibres. These sclerenchyma fibres are bonded together by lignin and hemicellulose, but the bonds can be broken by dissolution in an alkali solution, or in boiling water [68].

Fibres obtained from harakeke leaves were historically used for producing cloaks, ropes, and for making baskets and fishing nets [66]. These uses suggest that harakeke leaves could offer good reinforcement properties. For example, ropes, cloaks and baskets require lightweight fibres that can be twisted or braided together to provide tensile strength. In addition, good extendibility (fibre extraction without breaking – high modulus) is very important for cloak, ropes and basket production and these properties are equally desirable for composite production. Therefore, some studies have explored the possibility of combining harakeke fibre with different polymers [65, 68, 129]. However, reports on harakeke fibre as reinforcement in injection moulded PLA for producing composites suitable for structural applications are few in the materials science literature. It is well known that the notable determinants of the suitability of composites for structural applications are the reinforcing ability of the fibre, compositional balance, and the extent of interfacial adhesion between the fibre and the matrix. Therefore, these are given prime consideration in this article.

Interfacial adhesion in natural fibre composites is commonly improved through chemical modification of the fibre, with most studies focussing on facilitating surface roughness through alkali treatment [130, 131]. This has produced significant improvement in tensile strength and tensile modulus due to removal of components that can lead to weak interface from the fibre. In addition, alkali treatment helps to expose the cellulose hydroxyl groups of the fibre for bonding with the matrix which in turn facilitates mechanical interlocking between the fibre and the matrix [132]. The use of coupling agents, or the combination of other chemical techniques with alkali treatment can also help to improve interfacial adhesion in natural fibre reinforced composites. Peroxide treatment is one of such chemical treatments that can be combined with alkali treatment to improve the chemical bonding between natural fibres and polymer matrices [117]. The mechanism of peroxide treatment suggests that it can generate good mechanical and thermal resilience in natural fibres, as well as facilitate strong chemical bonding and thermal resilience in fibre reinforced composites by acting as a fibre modifier and as a coupling agent [133]. In water and during heating, organic peroxides such as H_2O_2 decomposes to generate free radicals $HO\cdot$ which are highly unstable and very reactive. These radicals react with the hydroxyl groups on the fibre and produces a radical cellulosic fibre which is also very unstable and reactive thereby facilitating interfacial interactions between the fibre and the polymer matrix [134]. The complete decomposition of peroxide can be achieved by heating at higher temperatures [135, 136]. Peroxide treatment of natural fibres have been reported to reduce the water absorption tendency of the fibre and to also improve the thermal stability [135, 137].

Sapieha et al. [138] reported a significant improvement in the mechanical properties of low density polyethylene composites when the reinforcement was treated with peroxide. Likewise, peroxide treatment of sisal fibre was reported to considerably improve the tensile properties of sisal fibre reinforced low density polyethylene composites [139]. Despite the potential of peroxide treatment to produce significant improvements in composite properties, it is less commonly reported in the literature and so, it is worthy of deeper investigation. Therefore, the aim of this study is to investigate the effect of combined digestion and peroxide treatments on harakeke fibre, and its reinforcing properties in PLA composites as it relates to its suitability for structural applications.

2.3 Materials

The harakeke fibre used as reinforcing filler in this study was kindly supplied by Templeton Flax Milling Heritage Trust, New Zealand. The polymer matrix used is Ingeo™ Biopolymer 3052D poly (lactic acid) (PLA) from NatureWorks. This PLA is an injection molding grade with a specific gravity of 1.24 and melt flow rate (MFR) of 14 g/10 min (210 °C, 2.16 kg). Sodium hydroxide bulk grade solid pellets, sodium sulfite powder, and hydrogen peroxide (30%) were purchased from Sigma-Aldrich and used without further purification. In addition, extra pure sodium silicate (Na_2SiO_3) solution, and sulfuric acid (96%) were procured from Merck Millipore.

2.4 Methods

2.4.1 Preparation and treatment of harakeke fibre

The harakeke fibre, as received, had a length of about 1-1.5 m. After drying, the fibre was cut into 2-3 cm pieces using a guillotine. Weighed amounts of the chopped fibre were placed in stainless steel canisters and digested using a solution of 5 wt.% NaOH and 2 wt.% Na_2SO_3 in a lab-scale pulp digester. The ratio of fibre to solution was kept at 1:8, and a programmed controller was used to run the digester over a 4-step cycle which included a treatment temperature set at 160 ^oC and a holding time of 2 h. The 4-step cycle is made up of a first step which is the conditioning of the digester to reach a stable temperature of 30 ^oC, followed by a second step where the digester is heated to 160 ^oC. During the third step, the digester is held at 160 ^oC for 2 h and this is followed by the fourth step where the digester is cooled to below 60 ^oC before being opened and the fiber containing canisters are removed. After digestion, the treated fibre was thoroughly washed under a continuous water flow until the pH of the wash water was measured as neutral at pH 7. The washed and treated fibres were then dried in a laboratory oven set at 80 ^oC for 48 h after which the dried fibres were stored in a sealed plastic bag until used for further analysis and for composite fabrication.

Bleaching of harakeke was performed using a solution of H_2O_2 and Na_2SiO_3. For this process, 45 g of digested fibre was placed in 3 L of Milli-Q distilled water. The water was first heated to 70 ^oC, and the fibre was introduced under continuous stirring for about 15 min after which 75 mL of Na_2SiO_3 (2.5% by volume) was added. After 5 min, 150 mL of H_2O_2 (5% by volume) was added and the bleaching process was allowed to continue under rigorous stirring for an additional 10 min. After completion of the bleaching process, the bleached fibre was washed under a water flow until the waste wash water showed a neutral pH. Then the fibre was dried at 80 ^{o}C for 48 h and stored in a sealed plastic bag until used for further analysis and composite production.

2.4.2 Determination of lignin and carbohydrate content in harakeke fibre

The amount of lignin in the raw, digested, and bleached harakeke fibre was determined according to the Round Robin method for determination of Klason lignin as detailed in the Technical Association of the Pulp and Paper Industry (TAPPI) T 222 om-02 test methods. Briefly, weighed amounts of the dry fibre were digested in a 72% (w/w) H_2SO_4 solution inside a test tube, with the mixture being stirred with a glass rod until dissolution began. The mixture containing test tube was placed in a water bath for 1 h at 30 °C with occasional stirring. The mixture was further diluted to ~ 3% (w/w) H_2SO_4 in a beaker using distilled water, and placed in an autoclave set at 121 °C. After 1 h, the beaker was cooled to 80 °C and the mixture was filtered using a vacuum filter to separate the insoluble matter. The acid insoluble residue (AIR) was subsequently allowed to dry overnight at 105 °C and the dry weight of acid insoluble residue (viz., Klason lignin) was calculated using equation 2.1 as follows:

$$Acid\ insoluble\ residue\ (AIR) = \frac{m}{M}\ x\ 1000 \qquad 2.1$$

where, m is the dry weight of residue after acid hydrolysis, in g and M is the oven-dry weight of sample (100% dry matter) before acid hydrolysis, in g. The filtrate from the Klason lignin determination test was used to determine the acid soluble lignin, and the carbohydrate content of the samples. The amount of carbohydrates (cellulose and hemicellulose) was determined following a method described in literature for wood sugar analysis by anion chromatography [140]. Briefly, the carbohydrate analysis was performed by diluting the filtrate, adding an internal standard, 0.45 μm nylon filtering and running on a Dionex IC3000 instrument with eluent generation at 2mM KOH. Fucose was added to each hydrolysed filtrate sample as an internal standard. Fucose stock solution (10,000 ppm) is added to all samples/blank/QC/standards to give a final concentration of 10 ppm. Five (5) main sugars were determined such as Arabinose, Galactose, Glucose (Cellulose), Xylose and Mannose.

2.4.3 Production of PLA/harakeke composites

Composites were produced from PLA and harakeke fibre using digested and bleached fibres at different fibre content (0-30 wt.%). The composite components were mixed and compounded using a twin-screw extruder (Labtech LTE-20-44). Prior to extrusion, the dried treated fibres were sheared using a Sunbeam Multigrinder with blunt blades. Shearing was performed at a high rotational speed to defibrate the fibre. After this, the fibres were dried overnight in a conventional oven set at 105 °C. For the PLA granules, drying to moisture content < 0.1% was carried out using a vacuum oven set at 60 °C for 2 h. Then, extrusion was performed using a temperature profile in the range of 165-175 °C, with the feeding and die zones kept at 120 °C and 175 °C, respectively. After extrusion, the extruded materials were granulated using a Moretto GR knife mill plastic granulator with an inserted sieve to obtain granules of about 3 mm in length. After drying the granules to a moisture content < 0.1% by weight, test samples were prepared using an injection moulding machine (BOY 35A). The injection profile used for test sample preparation includes a feeding zone temperature of 150 °C, a compression zone temperature of 165-185 °C, a metering zone temperature of 190 °C, a nozzle temperature of 185 °C, a mould temperature of 35 °C, injection time of 0.5 s and cooling time of 30 s. For easy identification, the different composite batches produced were given code names, with values 10, 20 or 30 indicating the wt.% fibre content while DF or BF represents digested fibre or bleached fibre, respectively. For example, “PLA represents the neat PLA matrix while “PLA+20 BF” represents the composite containing 20 wt.% bleached fibre.

2.4.4 Fourier transform infrared (FTIR) spectroscopy

The functional groups on the raw harakeke fibre, and changes in the FTIR spectra of digested and bleached harakeke fibre were analysed with a Perkin Elmer® Spectrum 100 FTIR spectrometer. Spectral analysis of the PLA was performed and compared with similar IR analyses of the PLA/harakeke composites. The FTIR data were recorded over a wavelength range of 4000 - 400 cm^{-1} using the standard KBr pellet technique.

2.4.5 Scanning electron microscopy (SEM)

Surfaces of the raw, digested, and bleached harakeke fibre were observed on a Hitachi Regulus SU8230 field emission scanning electron microscope at 5 kV using a secondary electron detector. Likewise, the fractured surfaces of PLA and PLA/harakeke composites after tensile testing were examined. Prior to SEM observation, the samples were dried and mounted on aluminium stubs using double sided carbon tape. The mounted samples were subsequently sputter coated with a 5 nm layer of platinum in a Quorum Q150V sputtering equipment to make them conductive.

2.4.6 X-ray diffraction analysis

The XRD diffractograms of raw, digested, and bleached harakeke fibre were obtained using an EMPYREAN diffractometer system (PANalytical). The fibres were chopped and pressed into a disk, using a cylindrical steel mould. Then, analysis was performed over a range of 5−65^{o} at a scanning speed of 1° min^{-1} with a scan step of 0.02° using a CuKα radiation (λ=1.54 nm). The cellulose crystallinity index (*CrI %*) of the fibres was calculated following the Segal method, using equation 2.2.

$$CrI\% = \frac{I_{002}-I_{am}}{I_{002}} \text{ x } 100 \qquad 2.2$$

where, I_{002} is the maximum intensity of the (002) lattice diffraction peak of cellulose and I_{am} is the intensity of diffraction of the amorphous component. The Segal method has some limitations mainly because it cannot be used to estimate the amount of crystalline and amorphous material in cellulose [141]. Instead, it is useful for comparing the relative difference between samples for the following reasons. Also, there could be differences in peak location and peak height of the I_{am} peak from different materials (varying between 16^{o} - 20.7^{o}), while peak deconvolution method predicts that the peak is located around 21.5^{o} which indicates that the I_{am} value is often significantly underestimated [142]. In addition, there are usually around 4 crystalline peaks, but only the highest peak (002) is used in the calculation, thereby excluding the contribution from other crystalline peaks. As a result, too much emphasis is placed on the contribution from only one alignment of the cellulose crystal lattice. Furthermore, peaks in the cellulose diffraction spectrum are very broad and vary considerably in their width. So, a simple height comparison might not be sufficient to provide reasonable estimate of cellulose crystallinity [142].

Based on the limitations of the Segal method, it is mainly suitable for the relative comparison of samples from similar materials which might have been exposed to slightly different processing/treatment conditions [143]. So, it was adopted in this thesis.

2.4.7 Mechanical testing

The tensile test specimens for PLA and the composites were prepared according to EN ISO 527, while flexural test specimens were prepared according to EN ISO 178. These tests were conducted on an Instron® 5982 universal testing machine equipped with a 5 kN load cell, running at a crosshead speed of 5 mm min^{-1}, and 10 mm min^{-1} for tensile and flexural tests, respectively. During tensile testing, the strain was measured using a 25 mm extensometer fixed at the middle of the specimen. Prior to mechanical testing, the test specimens were preconditioned in a climate chamber at 23 ^{o}C and 50% relative humidity for 48 h. Five specimens were tested during tensile and flexural tests and average results were recorded for the tensile strength (TS), tensile modulus (TM), flexural strength (FS) and flexural modulus (FM). The mechanical testing results were analyzed in the statistical software Minitab® 18 using one-way analysis of variance (ANOVA) test. The significant differences among averages were calculated using Tukey's method with a 95 % of confidence. In addition, the toughness of the samples was calculated from the area under the stress-strain graph.

2.4.8 Thermogravimetric and differential scanning calorimetric analysis

Thermogravimetric analysis (TGA) was performed using a Perkin Elmer STA 8000 thermal analyzer. The sample, weighing about 10-20 mg was placed in a crucible and analysis was performed under argon atmosphere at a gas flow rate of 40 mL min^{-1} while being heated at 10 ^{o}C/min from 30 °C to 600 ^{o}C.

Differential scanning calorimetry analysis (DSC) of PLA and the composites was performed using a TA instrument (Netzsch DSC 3500 Sirius). Samples were heated from 20 to 200 ^{o}C at 10 ^{o}C/min under a nitrogen flow using a gas flow rate of 60 mL/min. From the DSC thermogram, the glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) were determined. In addition, the crystallinity (I_{DSC}) of PLA in the composite was calculated from the heat of fusion of the tested sample and a reference sample (PLA)with 100% crystallinity, using equation 2.3.

$$\%crystallinity\ (I_{DSC}) = \frac{\Delta H}{\Delta H_m W}\ x\ 100\% \qquad 2.3$$

where, ΔH and ΔH_m represents the heat of fusion of the samples, and a reference PLA with 100% crystallinity, respectively, while W is the mass fraction of the matrix. The crystallinity of PLA in the composites was calculated by using 93.6 J/g as the heat of fusion (ΔH_m) of reference PLA with 100% crystallinity [144].

2.4.9 Dynamic mechanical analysis

The dynamic mechanical analysis (DMA) was performed on a Perkin Elmer DMA800 Dynamic Mechanical Analyzer. A single cantilever mode was used to test the specimens (30 mm x 5 mm x 1.5 mm) by heating the specimens at a rate of 2 ºC/min from 23 °C to 140 ºC. The displacement amplitude was 20 µm and the test was performed at a frequency of 1 Hz.

2.5 Results and discussion on the raw and treated harakeke fibre

2.5.1 Compositional properties of raw, digested, and bleached harakeke fibre

The relative amount of cellulose, hemicellulose and lignin in harakeke fibre have been estimated and the composition of these components have been found to vary [32]. The variation in the components of natural fibres can be attributed to the presence of some other components such as pectin, waxes and water-soluble compounds, in addition, to cellulose, hemicellulose and lignin which are the three main components in natural fibres [30, 33]. The chemical compositions and structural parameters of some common natural fibres summarized in Table 1.2 confirms the variability of the chemical composition of most natural fibres. In the case of harakeke fibre, the factors responsible for variation in properties and chemical compositions include planting locations, climatic conditions, age of the plant and the type of extraction process [29, 31]. As presented in Table 1.2 it is evident that that the cellulose content in harakeke fibre is generally low, while its hemicellulose content is high compared to some other common natural fibres. So, while the strength of harakeke fibre is associated with its cellulose component, its toughness may be associated with its high hemicellulose content.

The lignin and carbohydrate content of the harakeke fibres analysed in this study are presented in Table 2.1. It is evident from the table that the raw fibre has higher lignin and hemicellulose content than the treated fibres. In contrast, the cellulose content is higher in the treated fibres than in the raw fibre. The cellulose content in the raw fibre was 46% and this increased to 77% in the digested, and 83% for the bleached fibre. The low cellulose content in the raw harakeke fibre is consistent with the date presented in Table 1.2. The higher cellulose content in the treated fibres can be attributed to the removal of non-cellulosic components from the fibre, which helped to increase the amount of cellulose per unit mass of the fibre. Removal of lignin and other non-cellulosic components from natural fibres can help to improve the crystalline nature of the fibre [65]. In turn the fibre strength, and the strength of its reinforced composites will be improved due to better reinforcing ability, and effective stress transfer within the composite as discussed in subsequent sections.

Table 2.1 Chemical composition, and XRD parameters of the crystalline phase of raw, digested, and bleached harakeke fibre

	Composition (wt.%)		
Fibre type	**Cellulose**	**Hemicellulose**	**Lignin**
Raw fibre	46.00	18.80	15.84
Digested fibre	77.30	13.30	3.37
Bleached fibre	82.55	12.80	2.73

XRD Properties

Parameters	**Raw fibre**	**Digested fibre**	**Bleached fibre**
Peak position (°)	22.24	22.45	22.66
FWHM	3.13	1.81	1.79
d (Å)	3.99	3.95	3.92
Crystallite size (nm)	21.71	37.20	36.83
Crystallinity Index (%)	72.79	79.75	81.50

* Raw fibre refers to the as-received harakeke fibre
* Digested fibre is the fibre harakeke fibre treated with 5% NaOH and 2% Na_2SO_3
* Bleached fibre refers to the harakeke fibre digested with 5% NaOH and 2% Na_2SO_3, and then bleached with 5% H_2O_2 and 2.5% Na_2SiO_3

2.5.2 X-ray diffraction (XRD) properties of harakeke fibre

The XRD traces of raw, digested, and bleached harakeke fibre are illustrated in Figure 2.1. The two conspicuous peaks in the XRD curves of the fibres around 2θ ≈ 22° and 2θ ≈ 16° represent the crystalline and amorphous components of cellulose, respectively [145]. The crystallinity index calculated from these peaks are included in Table 2.1. The crystallographic (002) plane of cellulose in the raw, digested, and bleached fibre appeared at 2θ positions of 22.24°, 22.45°, and 22.66°, respectively.

The shift in the 2θ position of the fibre after digestion, and further shift after bleaching suggests a decrease in the interplanar spacing of the (002) planes in the digested and bleached fibre, compared to the raw fibre. This is an indication of closer packing of cellulose crystals in the digested and bleached fibre, due to the removal of lignin, hemicellulose, and other non-cellulosic components from the fibre after treatment [146]. Hence, the lower FWHM values of the digested and bleached fibres could be due to formation of hydrogen bonds between the cellulose chains freed by the removal of binding structures like hemicellulose and lignin, which resulted in rearrangement and closer packing [147]. This is confirmed by the higher cellulose crystal size and crystallinity of the digested and bleached fibres, which is believed to be due to higher cellulose content as seen in Table 2.1. Lower FWHM values could also be due to the trans-crystallinity (crystal growth across or through individual crystals) induced in the cellulose structure, by the digestion and bleaching treatments. The crystallinity index values in Table 2.1 shows that the bleached fibre has a higher crystallinity index than the fibre subjected to digestion only. This indicates the presence of higher crystalline cellulose structure in the bleached fibre, and it aligns with the result obtained from the carbohydrate analysis (Table 2.1).

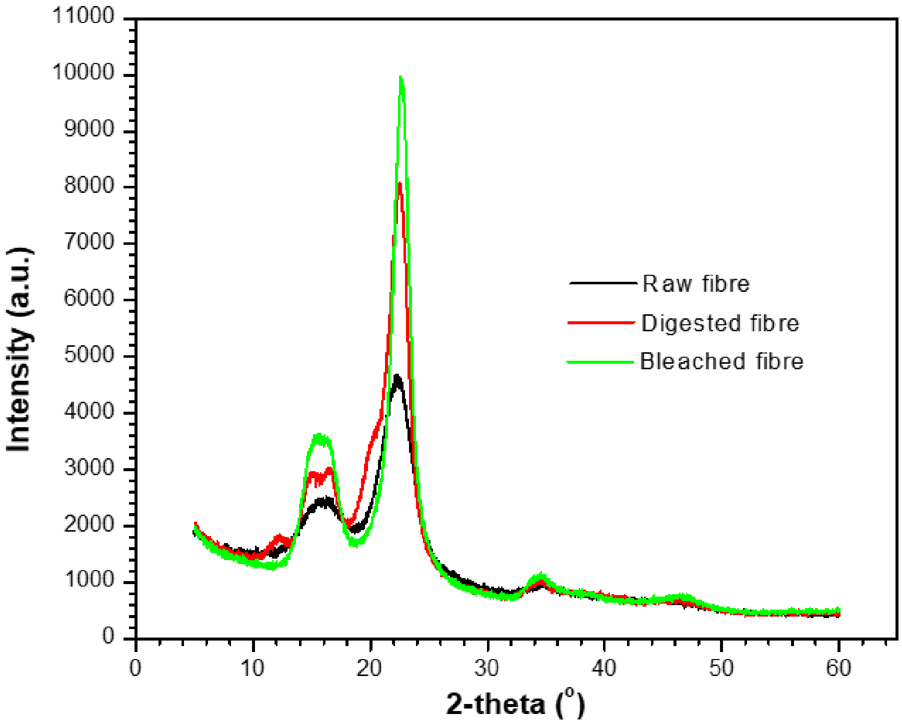


Figure 2.1 XRD traces of raw, digested, and bleached harakeke fibre

2.5.3 Morphological properties of raw, digested, and bleached harakeke fibre

The SEM images of raw, digested, and bleached harakeke fibre are shown in Figure 2.2. Surface of the raw fibre (Figure 2.2a) is smooth, likely due to the presence of cementing substances which tend to shield the fibre pores. These cementing substances can range from pectin, silica bodies, dirt particles and other soluble substances. In contrast, the surface of the digested fibre (Figure 2.2b) reveals rougher morphology which may be attributed to the removal of cementing substances from the fibre surface during digestion [148]. The alkali solution used for digestion helps to disrupt the bonding structure within the fibre, thereby removing the binding lignin and hemicellulose structures. This is responsible for the roughness observed on the fibre surface (Figure 2.2b) and has been reported to facilitate mechanical interlocking between matrices and fillers during composite production [147, 149]. Therefore, the effect of fibre treatment on the strength of the resulting composite is discussed in a subsequent section.

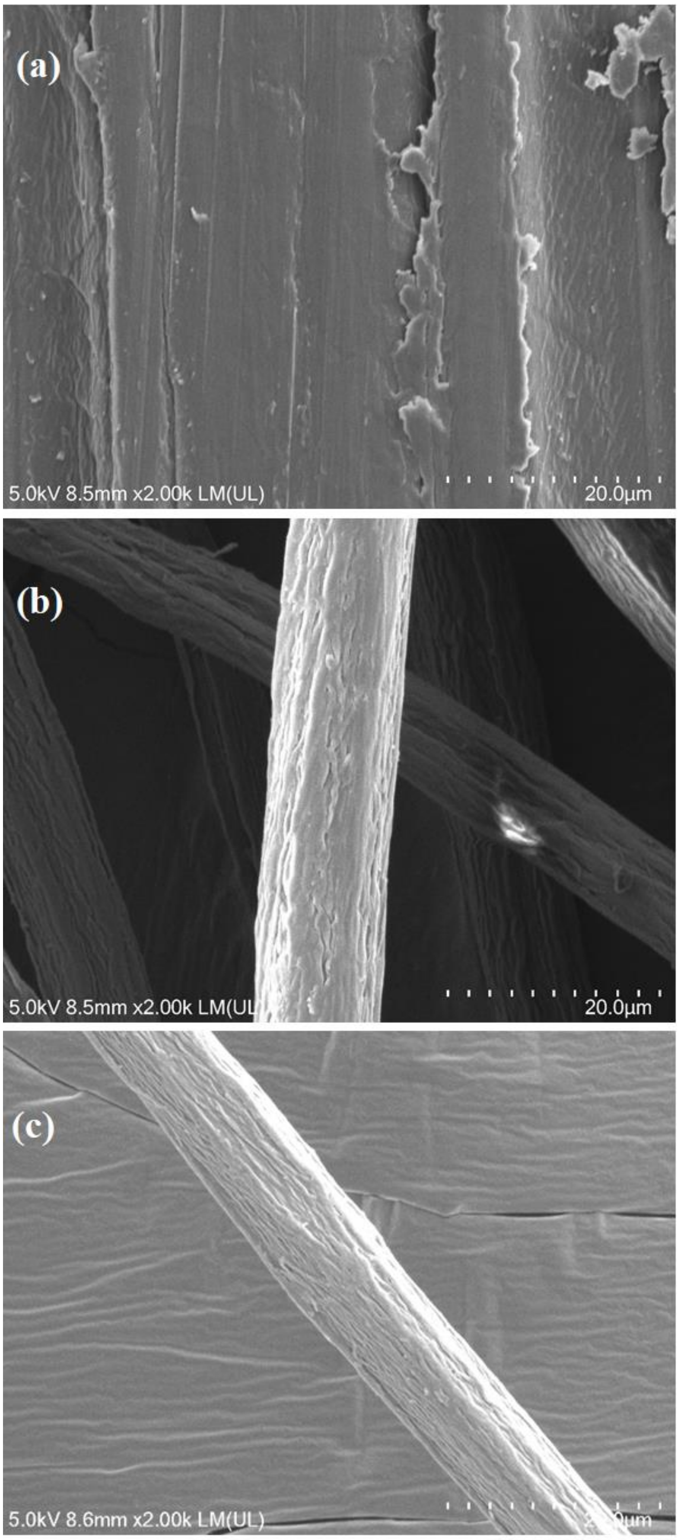


Figure 2.2 SEM images of (a) raw, (b) digested, and (c) bleached harakeke fibre

The SEM image of the bleached fibre (Figure 2.2c) reveals that the fibre is shrunken, with a rougher surface compared to Figure 2.2b. The bleaching treatment applied to the digested fibre helped to remove additional amounts of binding materials from the fibre, as presented in Table 2.1. This will invariably increase hydrogen bonding between the cellulose structures, due to removal of primary or secondary cell wall amorphous components [48, 150]. As the cellulose structure rearranges and packs more closely, the fibre shrinks, resulting in a reduced diameter, due to the increased fibrillation [147, 150]. The average diameters measured during SEM observation (result not shown) of the raw, digested, and bleached harakeke fibre were 495 µm, 11 µm, and 7 µm, respectively. The higher aspect ratio of the bleached fibre can help to facilitate fibre distribution during composite fabrication, thereby resulting in higher reinforcing ability and increased composite strength [145, 151]. Likewise, the opening of pores on the fibre surface can help to improve fibre-matrix adhesion [115, 152]. These aspects of the modified fibres will be discussed further under the section on mechanical properties of composites. The removal of cementing and binding structures from the fibre through treatment, and formation of hydrogen bonds were verified through FTIR analysis which is discussed in the next section.

2.5.4 Fourier transform infrared spectroscopy (FTIR) of harakeke fibre

The FTIR spectra of raw, digested, and bleached harakeke fibres are illustrated in Figure 2.3. The notable peaks in the spectra of the raw fibre includes the −OH stretching vibration around 3200-3600 cm^{-1} [145]. The C−H stretching vibration of cellulose and hemicellulose is evident around 2850-2950 cm^{-1} [153], while the peak at 1737 cm^{-1} represents the C=O stretching peak of ester and carboxylic components of hemicellulose and lignin [145, 153]. The peak at 1647 cm^{-1} represents the =CH vibration of the aromatic skeletal in lignin [145], while the peak at 1422 cm^{-1} is attributed to the $-CH_3$ asymmetric, and C−H symmetric deformation. The peak at 1060 cm^{-1} represents the in-plane deformation of the easily cleavable C−O−C linkage in lignin [145].

The −OH stretching vibration of bonded hydroxyl groups in the raw fibre shifted to a lower wavenumber in the digested and bleached fibre. This can be attributed to the structural changes caused by the removal of lignin and hemicellulose through fibre treatment and is believed to have influenced the reduced diameter of the treated fibre as discussed in section 2.5.3. It should be noted that the downward shift is further in the bleached fibre, compared to the digested fibre probably because more binding materials were removed with bleaching, than was removed with digestion alone as reported in Table 2.1

.

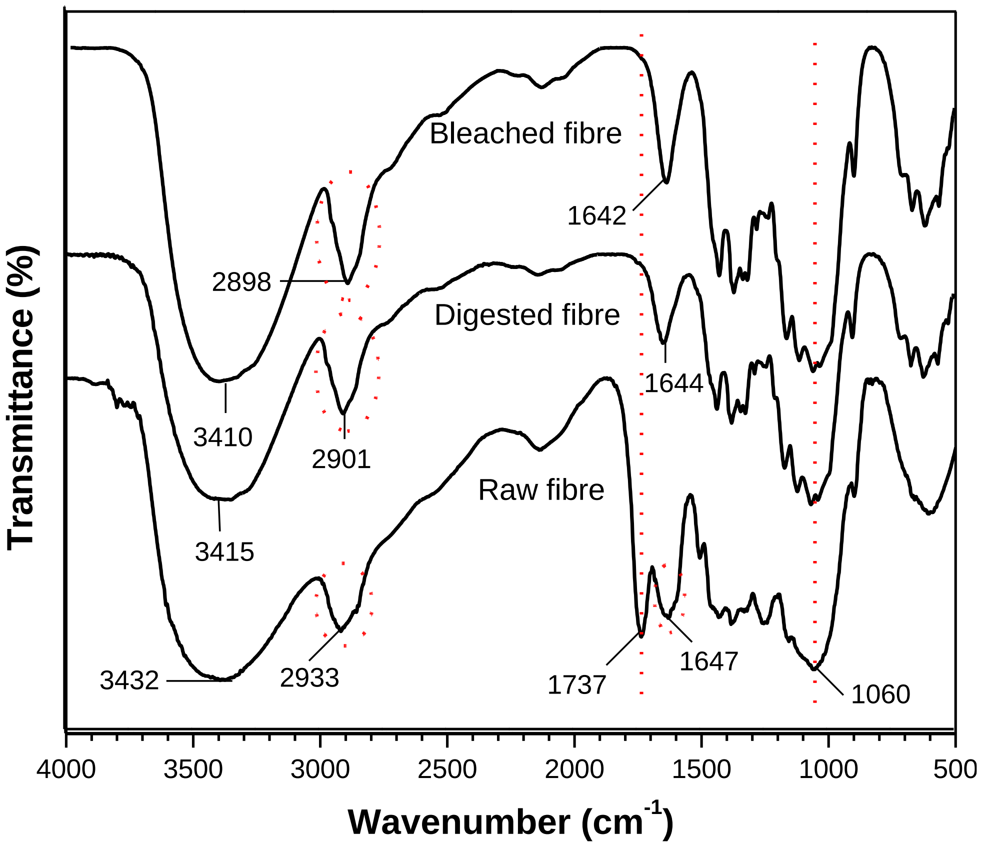


Figure 2.3 FTIR spectra of raw, digested, and bleached harakeke fibre

Another significant difference in the spectra of raw harakeke fibre and the treated fibres is the total disappearance of the C=O stretching peak at 1737 cm^{-1}. The absence of this peak in the spectra of the treated fibres confirm the dissolution of hemicellulose, and significant removal of lignin from the fibre during treatment [147, 153]. This explains the increased surface roughness of the digested and bleached fibres as shown in Figure 2.2b and Figure 2.2c. There is a downward shift in the stretching vibration of C−H in cellulose and hemicellulose from 2933 cm^{-1} in the raw fibre, to 2901 cm^{-1} in the digested fibre, and 2898 cm^{-1} in the bleached fibre. This is attributed to the removal of hemicellulose, and repacking of the cellulose structure. Furthermore, removal of binding structure, namely lignin from the treated fibres was confirmed by the downward shift of the vibrational frequency from the =CH groups in the aromatic skeletal (methyl, methylene and methoxy groups) of lignin around 1647 cm^{-1}. The downward shift of this peak is an indication of structural deformation of lignin [154], which was further confirmed by the split in the aromatic C−H in-plane deformation peak at 1060 cm^{-1}. The FTIR result supports the SEM observation, and the carbohydrate analysis.

2.5.5 Thermal properties of harakeke fibre

The TGA curves of raw and treated fibres are illustrated in Figure 2.4a. As seen in the figure, there is a general drop in weight of all the fibre in the temperature range from room temperature to around 130 °C due to the release of preabsorbed moisture [152]. Degradation in natural fibres generally starts at the amorphous regions, followed by the crystalline regions. The degradation of lignin starts around 160 °C, hemicellulose degradation starts around 220 °C, while cellulose degradation commences around 315 °C [152]. Although crystalline cellulose has higher degradation temperature, it has been revealed by literature that portions of the lignin component would normally degrade at higher temperature, in the range, and above the degradation temperature of crystalline cellulose [114, 155], due to the complex structure of lignin. Therefore, the early degradation observed in the raw fibre as seen in Figure 2.4a can be attributed to the degradation of amorphous non-cellulosic components such as lignin and hemicellulose. Due to the significant removal of non-cellulose components from the treated fibres, the thermal degradation in the treated fibres is mainly dependent on the crystalline cellulose, which accounts for the higher thermal stability of the treated fibres.

The thermal degradation temperature (T_d) of the fibres was derived from the DTG curve in Figure 2.4b. The thermal properties of the fibres, including onset temperature of thermal degradation (T_{onset}), and maximum thermal decomposition temperature (T_d) are presented in Table 2.2. In addition, the amounts of residue recorded at 600 °C are included in Table 2.2. The amount of residue recorded for the fibre as seen in Table 2.2 can be associated with the proportion of non-cellulosic components in the fibre which would appear in the form of char or ash residue [154, 156]. The relative lignin content of the fibres as discussed in section 2.5.1 and presented in Table 2.1 shows that the amount of lignin in the fibres is in the order of raw fibre > digested fibre > bleached fibre, and this is believed to have influenced the residue from the samples at 600 °C.

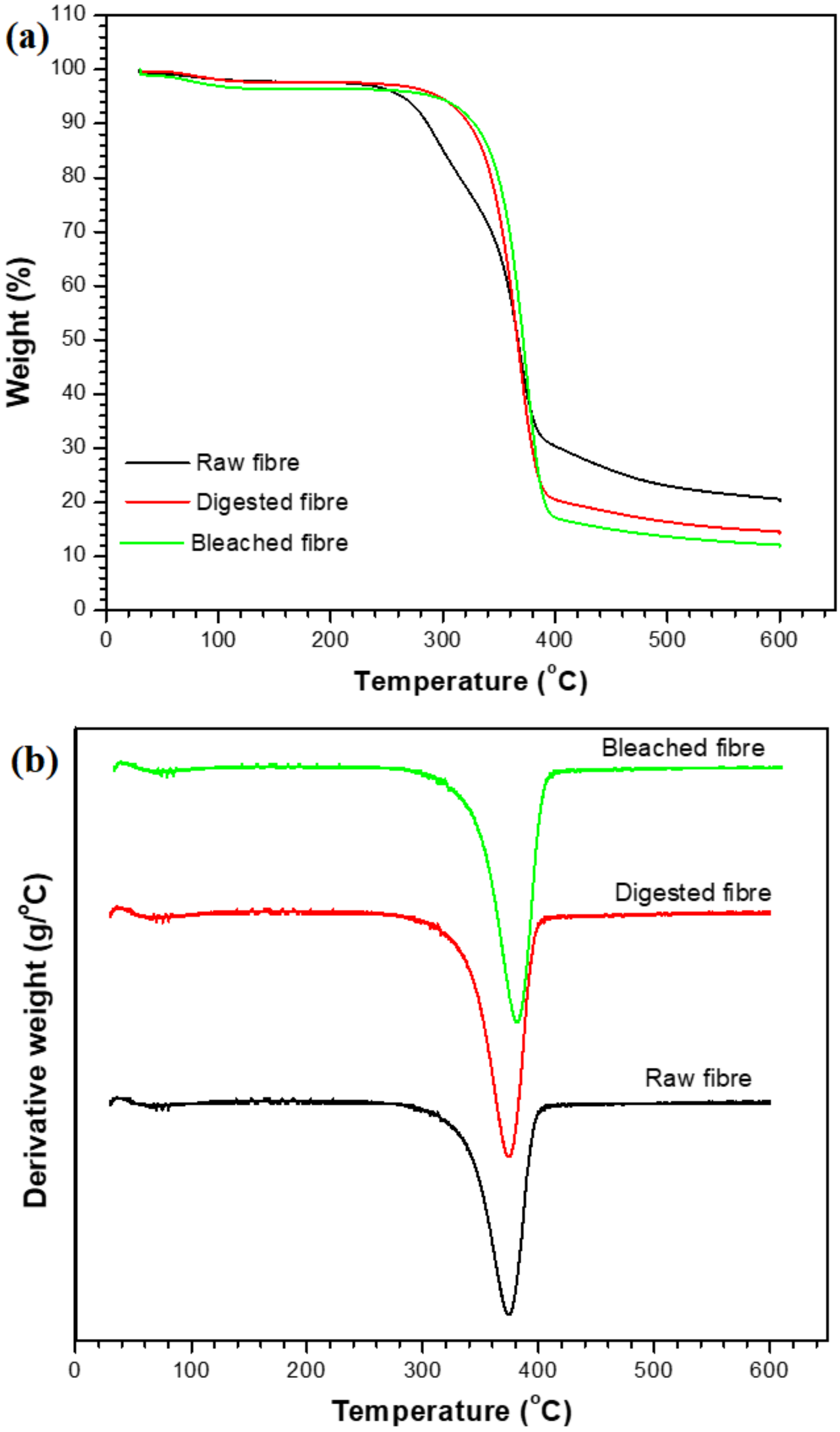


Figure 2.4 TGA curves of raw, digested, and bleached harakeke fibre

Table 2.2 shows that the onset of thermal degradation is faster in the raw fibre compared to the treated fibre which is not unexpected. In the case of the treated fibres, the T_{onset} of the bleached fibre is lower than that of the digested fibre. As discussed in sections 2.5.2 and 2.5.4, bleaching of harakeke fibre facilitated increased formation of intermolecular hydrogen bonds between the cellulose molecules. Therefore, the lower T_{onset} of the bleached fibre could be due to the large interface area created through bond formation, which might have permitted heat penetration at the unstable sites, particularly the amorphous regions of cellulose. Nevertheless, it is interesting that the T_d of the bleached fibre is higher than the digested fibre (see Figure 2.4 and Table 2.2), which indicates higher overall thermal stability of the bleached fibre, than the fibre digested alone. The higher thermal stability might be due to the higher number of hydrogen bonds in the bleached fibre which restricted the continued ingress of heat. As a result, there is a shift in the maximum decomposition temperature to the higher temperature range due to higher heat resistance of the more structured crystalline cellulose, as confirmed through XRD analysis and discussed in section 2.5.2.

Table 2.2 Thermal properties of raw, digested, and bleached harakeke fibre

Samples	**T_{onset} (ºC)**	**T_d (ºC)**	**Residual @ 600 (ºC)**	**E_a (kJ/mol)**
Raw Fibre	263.79	366.94	20.14	68.80
Digested Fibre	296.46	366.70	14.3	118.67
Bleached Fibre	291.29	371.50	11.80	125.61

In addition to its ability to help in determining the thermal degradation temperature (T_d), the DTG data can equally assist in calculating the activation energy associated with thermal degradation of natural fibres [147]. The activation energy (E_a) is a good indicator of the energy barrier that hinders molecular chain mobility in the fibre, which in turn retricts thermal degradation. Therefore, the thermal stability of the fibres was further investigated through kinetic study, using the TGA data according to the method described by Broido [157]. The kinetic parameter for thermal decomposition of the fibres was determined using equation 2.4 as follows:

$$ln\left(ln\frac{1}{y}\right) = -\frac{E_a}{RT} + ln\left(\frac{RZ}{E_a\beta}T_{max}^2\right) \qquad 2.4$$

where, y is the fraction of non-volatilized material as yet undecomposed, T_{max} is the temperature of the maximum reaction rate (ºC), β is the heating rate (ºC min^{-1}), Z is the frequency factor, E_a represents the activation energy (J mol^{-1}) and R is the gas constant (8.314 J mol^{-1} K^{-1}). The values of y can be obtained from the TGA data such that ln(ln(1/y)) can be calculated accordingly. By plotting a graph of 1/T (in Kelvin) on the x-axis and ln(ln (1/y)) on the y-axis, the activation energy (E_a) associated with thermal decomposition of the fibres can be determined from the slope of the graph [158]. The plot of 1/T vs ln(ln (1/y)) for the raw, digested and bleached harakeke fibre is presented in Figure S1 of the supplementary information section. The R^2 value of the plots for all the fibres are above 0.9 which indicates that the linearity of the graphs are in good agreement with the Broido equation, and the E_a values for thermal decomposition of the fibres are included in Table 2.2. As seen in Table 2.2, the E_a of the bleached fibre is higher than that of the raw and digested fibres, which confirms the higher thermal stability of the bleached fibre, and aligns with the TGA result.

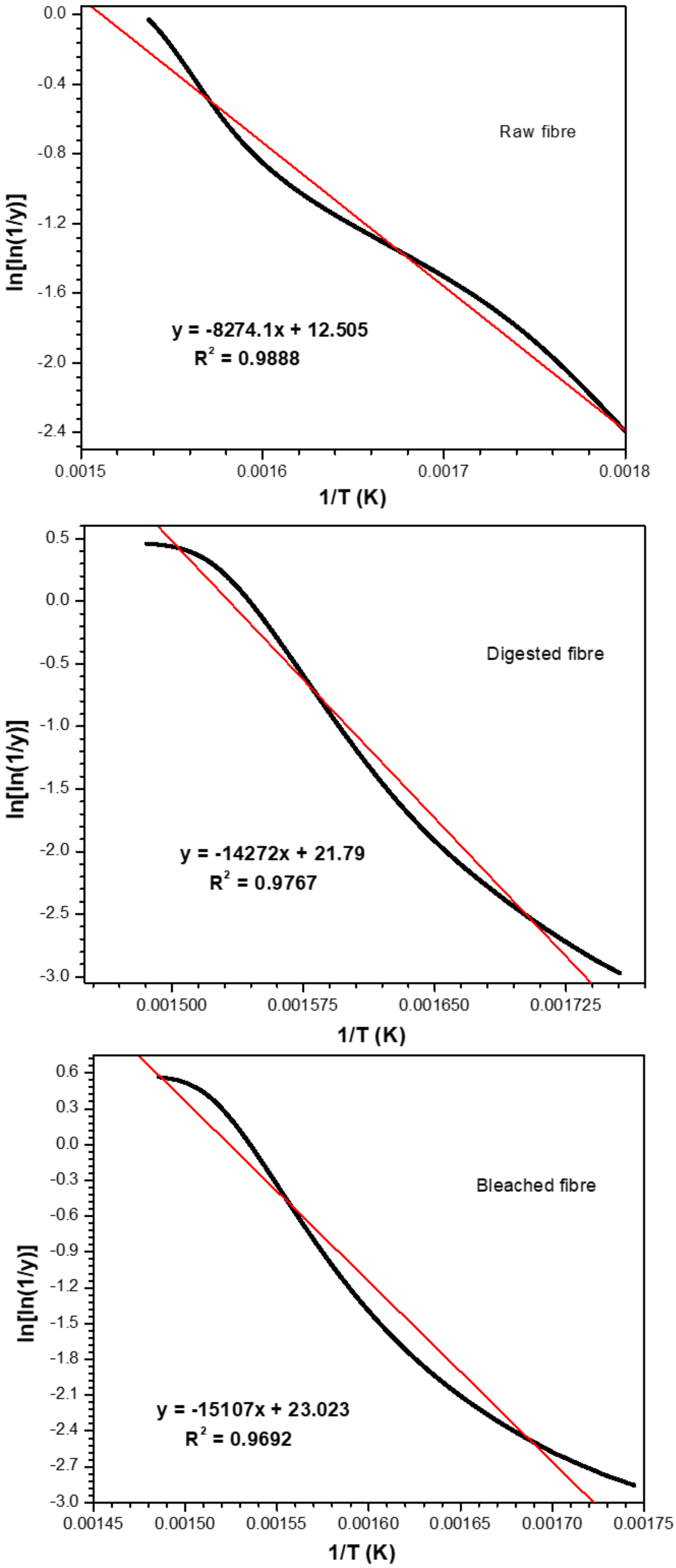


Figure S1 Plot of 1/T (K) vs ln[ln(1/y)] for raw, digested, and bleached harakeke fibre

2.6 Results and discussion on the properties of PLA/harakeke composites

2.6.1 Mechanical properties of PLA/harakeke composites

The mechanical properties of PLA and PLA/harakeke composites containing different wt.% (10-30 wt.%) of digested and bleached harakeke fibre are illustrated in Figure 2.5 with the error bars representing the standard deviation. It can be seen from Figure 2.5a that the tensile strength (TS) of the composites initially increased following the addition of fibre up to 20 wt.% fibre content. After the initial increase, the TS decreased when the fibre content was increased to 30 wt.%. On the other hand, the tensile modulus TM in Figure 2.5b reveals an increasing value with increasing fibre content. The initial increase in TS of the composites above the TS of neat PLA can be attributed to effective reinforcement and the transfer of stress from the PLA matrix to the reinforcing fibre. At 20 wt.% fibre, the TS is 73.06 MPa and 74.45 MPa for digested and bleached fibre composites, respectively compared to 62.85 MPa of neat PLA. Further increase in fibre content from 20 wt.% to 30 wt.% resulted in decline of TS. This observation agrees with what was reported in a similar study [122], which is believed to be due to less wetting of the fibre by the PLA matrix at 30 wt.% fibre content. Serizawa et al. investigated the effect of varying amounts of kenaf fibre on the properties of kenaf fibre reinforced PLA composite. They reported that the maximum flexural strength and modulus was attained at 20 wt.% fibre content [123]. Likewise, Komal et al., reported 20 wt.% banana fibre as the optimum fibre content when they varied the fibre content from 10-30 wt.% in banana fibre reinforced PLA composites [124]. A drop in mechanical performance of composites beyond what is defined as an optimum fibre content is often due to poor wetting of the fibre. Poor wetting will normally lead to agglomeration of fibre within the composite due to unfavourable distribution, thereby leading to the creation of large voids within the composite. As a result, the transfer of stress from the matrix to the reinforcing fibre will not be effective, which leads to the observed decrease in TS of the composites at 30 wt.% fibre content.

It is noteworthy that at the different fibre contents, the TS of bleached fibre composites is higher than the digested fibre. Literature revealed that the mechanical strength of natural fibre reinforced composites can be significantly influenced by the fibre diameter [112]. Specifically, large diameter fibres can trigger different local deformation processes within the composite including fibre pull-out, debonding of the fibre from the matrix, or fibre fracture [159]. As discussed in section 2.5.3, the diameter of bleached harakeke fibre is smaller than that in digested fibre. Therefore, the wider diameter of the digested fibre might have contributed to the lower strength of the digested fibre composites, compared to the bleached fibre composites as seen in Figure 2.5a. In another vein, treatment of fibre through bleaching with peroxide has been reported to facilitate interfacial bonding between the fibre and polymer matrices, by acting as a coupling agent [117, 153]. The coupling effect of the peroxide treatment is believed to have contributed to the higher strength of the bleached fibre composites. Fibre pull-out, debonding of fibre from matrix, fibre fracture, and the extent of interfacial adhesion in the composites was assessed through SEM observation of the fractured surfaces of the composites which forms the subject of the next section.

Similar trends can be seen in the FS in Figure 2.5c and the TS in Figure 2.5a and the reason for the trend is as stated in the previous paragraph. In contrast to the trend observed for TS and FS, the tensile modulus (TM) and flexural modulus (FM) of the samples illustrated in Figure 2.5b (TM) and Figure 2.5d (FM) shows an increasing trend as fibre content was increased. This can be attributed to the high modulus of harakeke fibre and suggests that the strength and modulus of PLA/harakeke composites depend on different factors. Specifically, the strength is believed to be influenced by factors such as wetting of fibre by the matrix, filler distribution, filler content, and fibre-matrix interfacial adhesion. In contrast, modulus of the composite seems to be more dependent on the filler content, fibre distribution in the matrix, and modulus of the fibre. Generally, in fibre reinforced polymer composites, there are always reports on the optimum fibre content for maximum strength. Generally, the optimum fibre content may be between 20-40 wt.% fibre content depending on the composite preparation method, type of filler, and matrix type. Some selected studies on natural fibre reinforced PLA composites are summarized in Table S1 in the supplementary information section. It is noteworthy that the TS and FS recorded at 20 wt.% fibre in this thesis is comparable and sometimes higher than most of the previously published reports on reinforced PLA composites, even at higher fibre contents [160, 161], which is an indication of the high reinforcing ability of harakeke fibre.

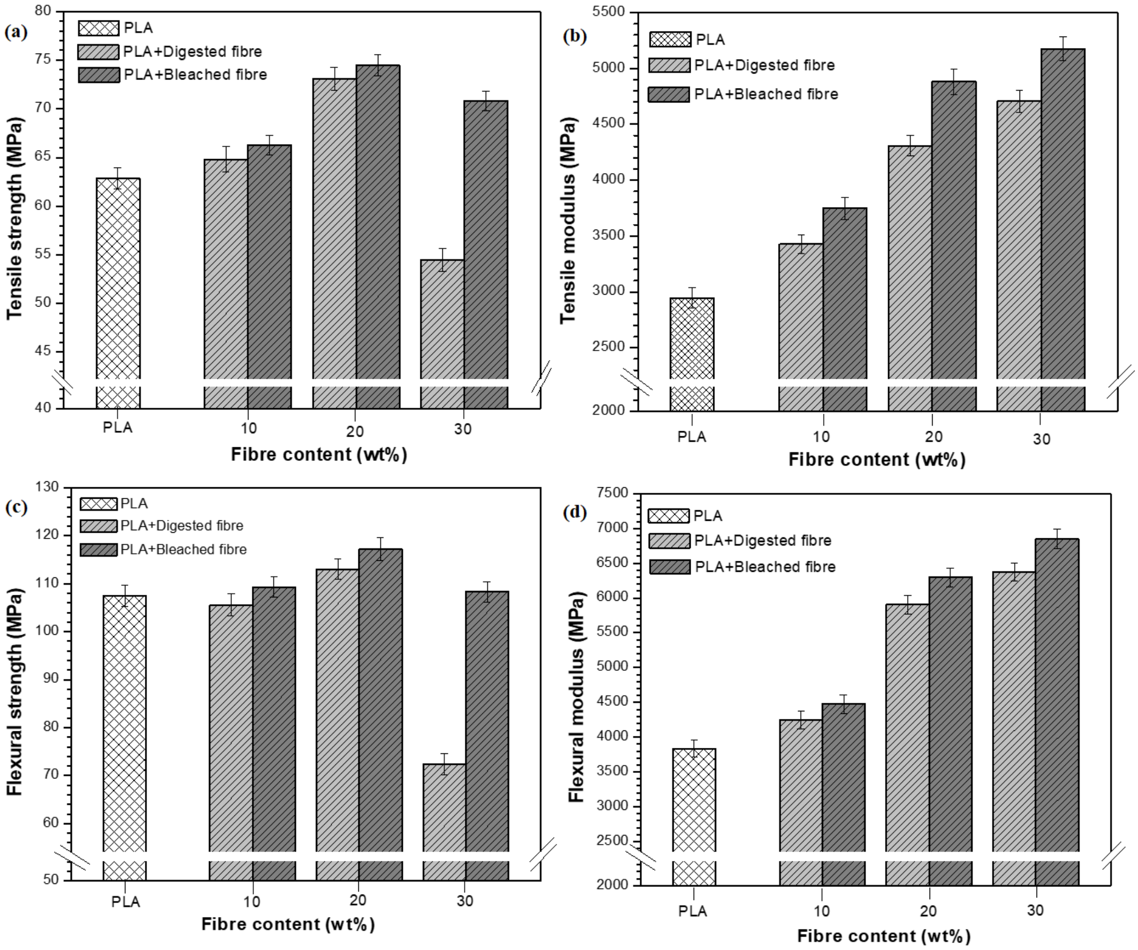


Figure 2.5 (a)Tensile strength, (b) tensile modulus, (c) flexural strength, and (d) flexural modulus of PLA and PLA/harakeke composites containing different wt.% of digested and bleached harakeke fibre. The error bars represent the standard deviation.

The boxplot from ANOVA of the tensile strength and flexural strength of PLA and PLA/harakeke composites containing different wt.% of digested and bleached harakeke fibre is illustrated in Figure 2.6 while the Tukey plot at 95% confidence for the samples is illustrated in Figure 2.7. Based on the Tukey method, the mean value of the samples are significantly different when the mean interval does not contain zero.

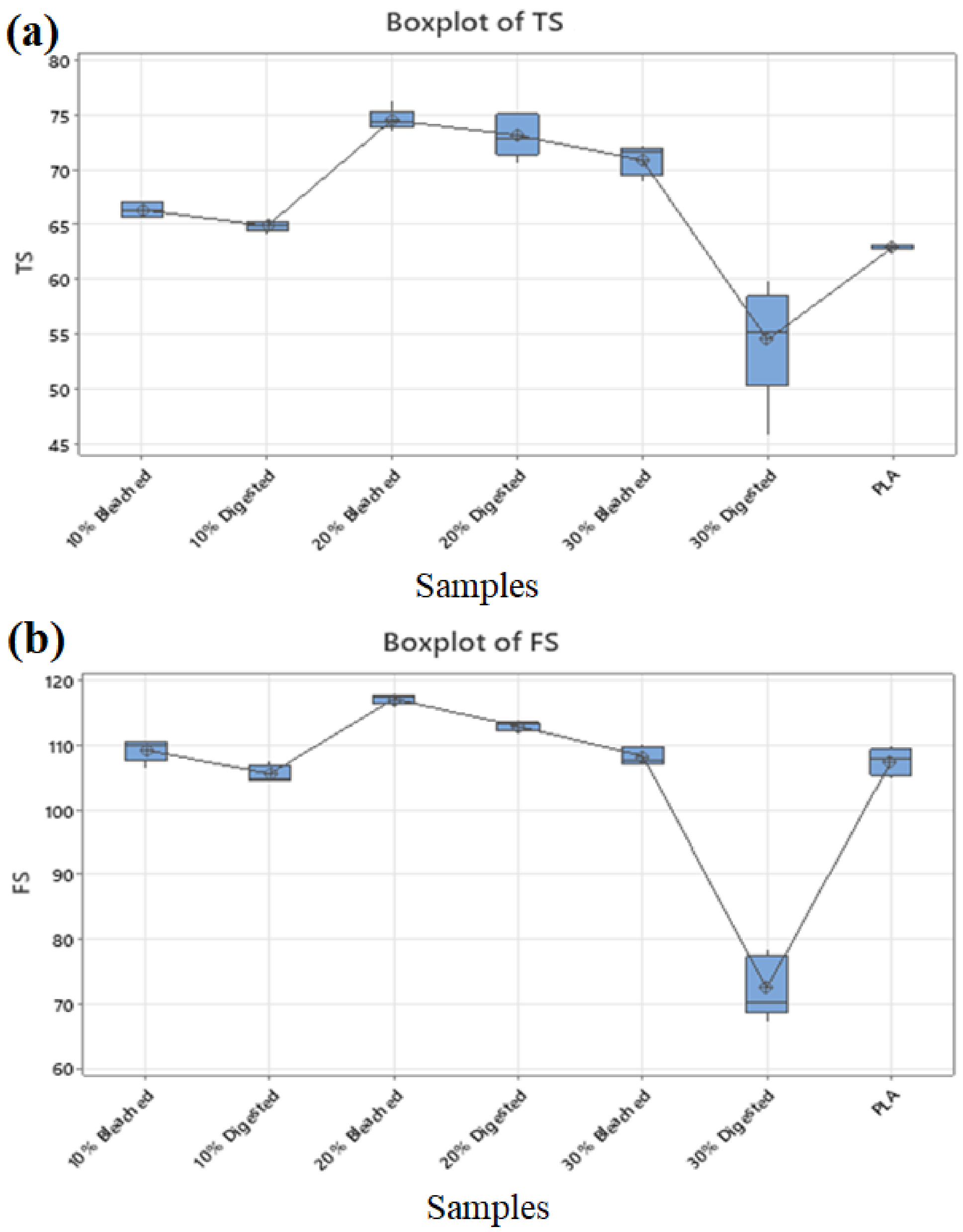


Figure 2.6 Boxplot of (a) tensile strength, and (b) flexural strength of PLA and PLA/harakeke composites containing different wt.% of digested and bleached harakeke fibre

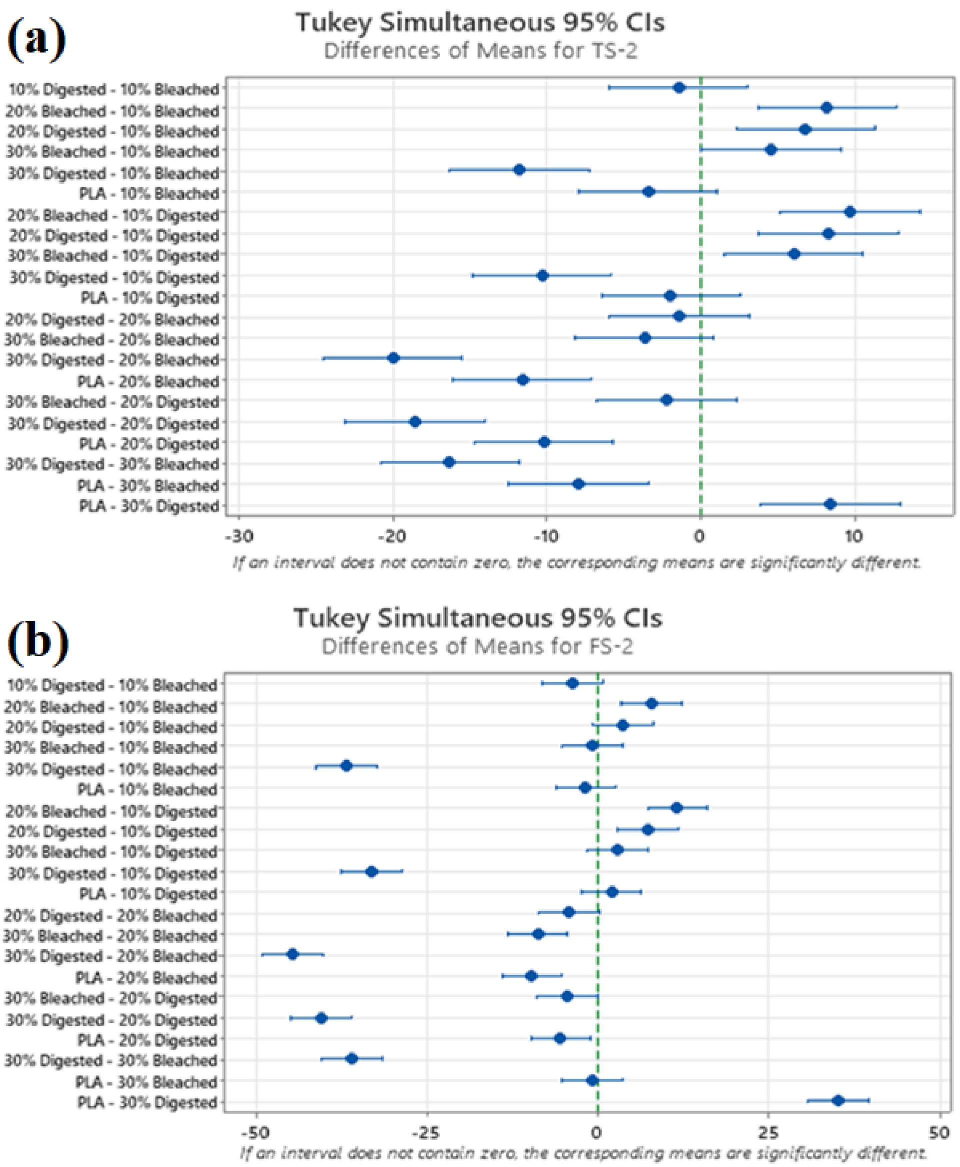


Figure 2.7 Tukey plot at 95% confidence for (a) tensile strength, and (b) flexural strength of PLA and PLA/harakeke composites containing different wt.% of digested and bleached harakeke fibre

The mean and mean grouping information using Tukey method and 95% confidence for the tensile strength and flexural strength of the samples are summarized in Table 2.3 and Table 2.4, respectively. Generally, from the Tukey table, means that do not share a letter are significantly different. Therefore, the significance of the mean differences in the samples are described by the mean intervals in Figure 2.7 and the different letters in Table 2.3 and Table 2.4. Based on the data in Table 2.4, the difference in 10 and 20 wt.% for the flexural strength are statistically significant for both the digested and bleached fibre composites. However, there is there an overlap in the statistical significance of 10 wt.% fibre content for the bleached fibre and 20 wt.% fibre content for the digested fibre composites. This is better illustrated by the Tukey plot of mean differences in Figure 2.7b. In the case of tensile strength, the data in Table 2.3 shows that there is a significant difference in the 10 and 20 wt.% fibre content which is supported by the Tukey plot of mean differences in Figure 2.7a.

Table 2.3 Mean and mean grouping information using Tukey method and 95% confidence for the tensile strength of PLA and PLA/harakeke composites containing different wt.% of digested and bleached harakeke fibre

Samples	**N**	**Mean**	**StDev**	**Grouping**	**95% CI**
PLA	7	62.85	0.20	B	(60.79, 64.91)
10% Digested	7	64.81	0.49	B	(62.75, 66.87)
10% Bleached	7	66.29	0.72	B	(64.23, 68.35)
20% Digested	7	73.06	1.95	A	(71.00, 75.12)
20% Bleached	7	74.47	1.07	A	(72.41, 76.53)
30% Digested	7	54.47	5.26	C	(52.41, 56.53)
30% Bleached	7	70.81	1.39	A	(68.75, 72.86)

Table 2.4 Mean and mean grouping information using Tukey method and 95% confidence for the flexural strength of PLA and PLA/harakeke composites containing different wt.% of digested and bleached harakeke fibre

Samples	**N**	**Mean**	**StDev**	**Grouping**	**95% CI**
PLA	7	107.54	2.04	C	(105.52, 109.56)
10% Digested	7	105.62	1.22	C	(103.60, 107.64)
10% Bleached	7	109.32	1.75	B C	(107.30, 111.34)
20% Digested	7	112.99	0.79	A B	(110.97, 115.01)
20% Bleached	7	117.22	0.75	A	(115.20, 119.24)
30% Digested	7	72.43	4.69	D	(70.41, 74.45)
30% Bleached	7	108.39	1.36	C	(106.37, 110.41)

2.6.2 Morphological properties

The SEM images of the fractured surface (after tensile testing) of neat PLA, and PLA/harakeke composites containing 20 wt.% and 30 wt.% fibre are shown in Figure 2.8. It can be seen from Figure 2.8a, that the fractured surface of neat PLA is smooth, which is expected of brittle materials like PLA. For the composites with 20 wt.% fibre, it is evident that the length of pulled out fibre in the digested fibre (DF) reinforced composite, PLA+20 DF (Figure 2.8b) is longer than for those observed in composite reinforced with fibres subjected to bleaching (BF) (PLA+20 BF) (Figure 2.8c). The shorter pull-out fibres in Figure 2.8c indicates stronger interfacial adhesion between PLA and the bleached fibre [112, 162]. Likewise, strands, believed to be PLA can be seen on the surface of PLA+20 BF (Figure 2.8c). It was reported in the literature that treatment of natural fibre with peroxide imparts ester functionality on the fibre surface [153, 163]. Hence, the peroxide bleaching of harakeke fibre in the present study has likely imparted ester functionality on the surface that will make the fibre more compatible with PLA. Therefore, the polymer strands seen in Figure 6c are believed to be due to stronger interfacial adhesion resulting from mechanical bonding between the PLA and the bleached fibre. The stronger interfacial adhesion is believed is believed to have contributed to the higher mechanical strength of the bleached fibre composites as discussed in section 2.6.1.

The SEM images of the composites containing 30 wt.% fibre reveal a higher number of pull-out holes on the composite fractured surface, which suggests a reduced fibre-matrix interaction between PLA and harakeke at 30 wt.% fibre content. When there is a higher percentage of fibre in the composite, it can result in poor wetting of the fibre by the matrix and would be responsible for the drop in mechanical strength of the composite at 30 wt.% fibre content, for both DF and BF as seen in Figure 2.5a and Figure 2.5c. Although a drop in mechanical strength was recorded for both fibre types at 30 wt.%, it is noteworthy that the alignment and orientation of fibre in the PLA+30 DF composite is lesser than in the PLA+30 BF. Comparing the SEM images, the better alignment in the bleached fibre composites can be confirmed by the number of fibres pointing forward from the fractured surface, rather than across it which suggests better alignment of the fibres. The lesser alignment of the fibres in the digested fibre composites, in addition to poor fibre wetting is believed to have contributed to the higher drop in mechanical strength of the DF reinforced composite at 30 wt.% fibre content, compared to that of the BF reinforced composite.

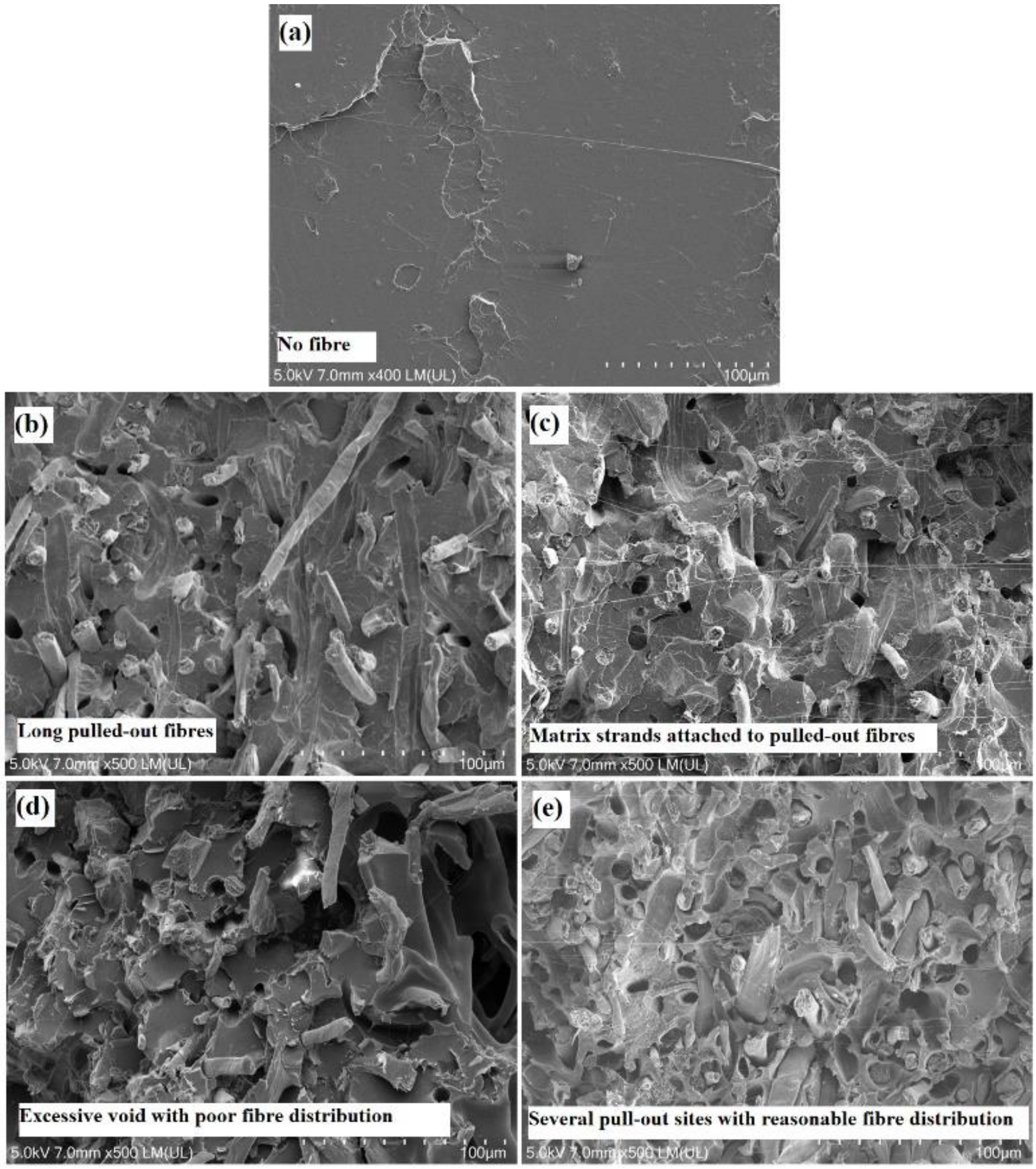


Figure 2.8 SEM images of (a) neat PLA, and PLA/harakeke composites containing (b) 20 wt.% DF, (c) 20 wt.% BF, (d) 30 wt.% DF, and (e) 30 wt.% BF

2.6.3 Fourier transform infrared spectroscopy of composites

The bonding structures and extent of interfacial interaction between PLA and the treated harakeke fibres was further investigated through FTIR analysis. It should be noted that for ease of comparison, only the composites containing 20 wt.% fibre is discussed in this section. The FTIR spectra of PLA, PLA+20 DF, and PLA+20 BF are illustrated in Figure 2.9. The band in the FTIR spectra of PLA and the composites around 3200-3650 cm^{-1} is due to the stretching vibration of the −OH groups in cellulose, and the terminal hydroxyl groups in PLA [145], while the band around 2850–3050 cm^{-1} is attributed to symmetric and asymmetric stretching of C−H from methyl and methylene groups in cellulose. The peak at 1750 cm^{-1} is assigned to the C=O stretching vibration of acetyl and carboxylic acids moieties [145], and the ester components from PLA. The peak at 1455 cm^{-1} is a characteristic $-CH_3$ bending mode, whereas the peak at 1379 cm^{-1} is attributed to C−H deformation [145]. In addition, stretching of the C–O group of carboxylic acid and the ester components of PLA is represented by the peak at 1091 cm^{-1}.

It can be seen in Figure 2.9 that the −OH stretching vibration around 3200-3650 cm^{-1} in the spectra of PLA was widened in the spectra of the composites which suggests an increased intermolecular number of hydrogen bond due to increased number of −OH groups available for bond formation in the fibre cellulose, brought about by surface modification [145] This is supported by the movement of the peak to a lower wavenumber in the spectra of the composites, which is attributed to the formation of hydrogen bonds between the −OH of the fibres, and the terminal hydroxyl groups of PLA. In addition, the interaction between PLA and the fibres can be through bond formation between the cellulose −OH group of the fibres and C=O of PLA [164]. The interaction is further confirmed by the peak shift from 1750 cm^{-1} in the spectra of neat PLA, to a lower wavenumber value in spectra of the PLA/harakeke composites which indicates esterification reaction between the terminal −COOH groups of PLA and the −OH groups of harakeke fibre [164].

It is noteworthy that the downward shift of the band around 3200-3650 cm^{-1} and the peak at 1750 cm^{-1} is more significant in the spectra of the bleached fibre composite (PLA+20 BF), compared to the digested fibre composite (PLA+20 DF). This is an indication of a higher interaction between the bleached fibre and PLA, and it aligns with the SEM observations discussed earlier. The higher interaction between PLA and the bleached fibre as confirmed through the FTIR analysis is believed to have contributed to the higher mechanical properties of the bleached fibre composites as discussed in section 2.6.1.

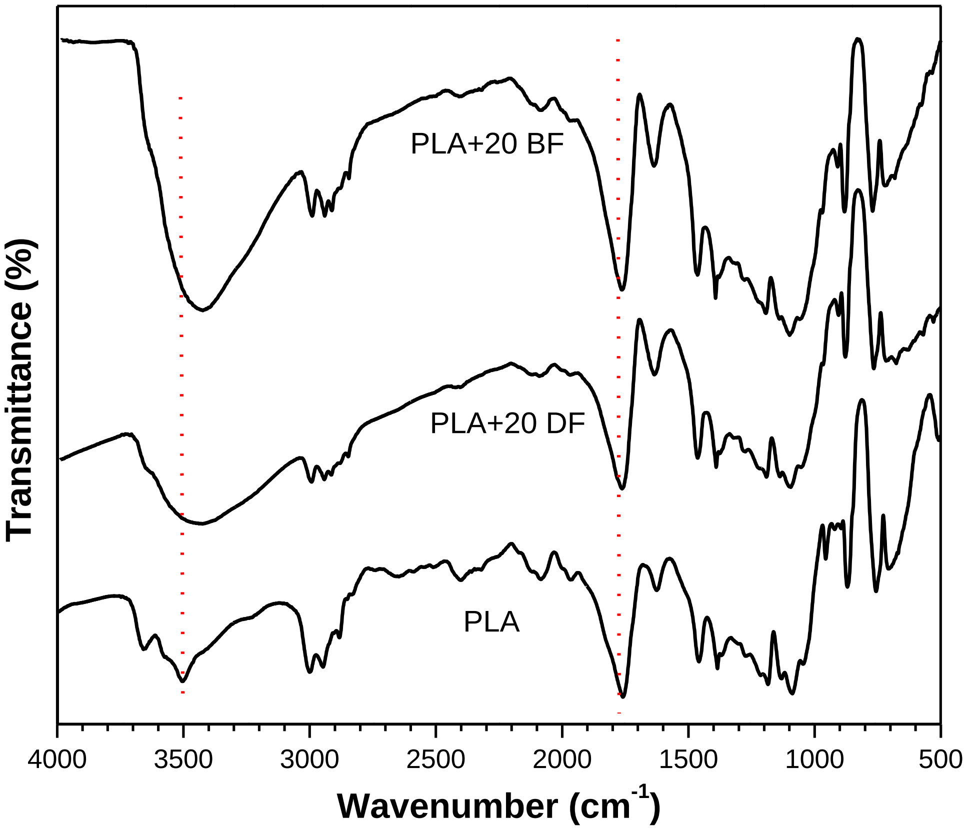


Figure 2.9 FTIR spectra of PLA, and PLA/harakeke composites containing different 20 wt.% of digested fibre (DF) and bleached harakeke fibre (BF)

2.6.4 Thermal properties of composites

The TGA curves of PLA and the composites are illustrated in Figure 2.10a. As seen in the figure, the TGA curves follow a similar trend. The onset of thermal degradation is above 300 °C and the drop in weight continued up to 400 °C. The onset of thermal degradation (T_{onset}) and the thermal degradation temperature T_d) of the samples are summarized in Table 2.5. In addition, the amount of residue remaining at $T \geq 500$ °C of the samples are included in Table 2.5. The T_{onset}, and T_d, of neat PLA is higher than that of the composites which is believed to be due to the intact structure of the PLA chains in neat PLA. The incorporation of fibres into PLA would distort the homogeneity of the PLA chain structure [122], which can in turn result in increased heat penetration sites as reported for micro crystalline cellulose (MCC) reinforced PLA composites [145]. It can also be due to the lower thermal stability of the fibre, compared to neat PLA [153]. From Figure 2.10a, and Table 2.5, it is evident that the bleached fibre composites are more thermally stable compared to the digested fibre composites, at all fibre contents.

The DSC thermograms of PLA and the composites are shown in Figure 2.10b. From the figure it is possible to discern three successively distinct transitions which represent the glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m). The DSC parameters of the samples were obtained from the thermograms, and the parameters are included in Table 2.5. It is evident in Figure 2.10b that the T_g of PLA was not significantly influenced by the inclusion of harakeke fibre. In contrast, the T_c of PLA in the composites can be seen to be notably influenced by the fibre. The addition of reinforcing fillers into semi crystalline polymers is known to result in an upward or downward shift in the T_c, and it often describes the ability of fillers to induce heterogeneous nucleation in the matrix [165]. The T_c of the samples presented in Figure 2.10b shows a downward shift in T_c of PLA in the composites which is an indication of faster crystallization in the composites [166], which confirms the heterogeneous nucleation on the harakeke fibre. When cold crystallization occurs, it often results in the formation of imperfect crystals which can be verified through the melting peak of the sample [110].

The split in the melting peak (T_m) of the composites compared to neat PLA (Figure 2.10b) can be attributed to the formation of imperfect crystals in the composite due to the crystallization effects of the fibre on PLA [65]. Usually, the imperfect crystals would melt at a lower temperature than the perfect crystals. Hence, the double peaks observed around the T_m of PLA in the composites is because of perfect and imperfect crystals within the composite, due to the heterogeneous nucleation effects of the fibre [65]. As seen in Figure 2.10b and presented in Table 2.5, the T_m of the composites is higher than that observed for neat PLA, most likely because the T_m of the composites was determined by the fusion of imperfect crystals formed during cold crystallization, and the fusion of spherulites formed during the process of recrystallization [110]. The effect of fibre treatment on the crystallization behaviour of PLA was further investigated through the calculation of the crystallinity index, using equation 2.3. The crystallinity index ($X_{DSC}\%$) of PLA and the composites are included in Table 2.5, which confirms the significant influence of fibre inclusion, on the crystallinity index of PLA. In addition, it was observed that at each fibre wt.% content, the bleached fibre composites exhibit a higher $X_{DSC}\%$ than the digested fibre composites. This indicates the formation of a larger number of crystallites within the bleached fibre composites and suggests that the bleached fibre did not only facilitate the formation of new crystals through heterogeneous nucleation but might also have led to the growth of existing spherulites. In another vein, the higher interfacial interaction between PLA and the bleached fibre as discussed in previous sections has favoured higher trans-crystallinity within the bleached fibre composite. Increased matrix crystallinity in known to support mechanical strength improvements in polymer composites. Therefore, the higher crystallinity of PLA in the bleached fibre composites than in the digested fibre composites might have contributed to the superior mechanical strength of the bleached fibre composites as discussed in section 2.6.1

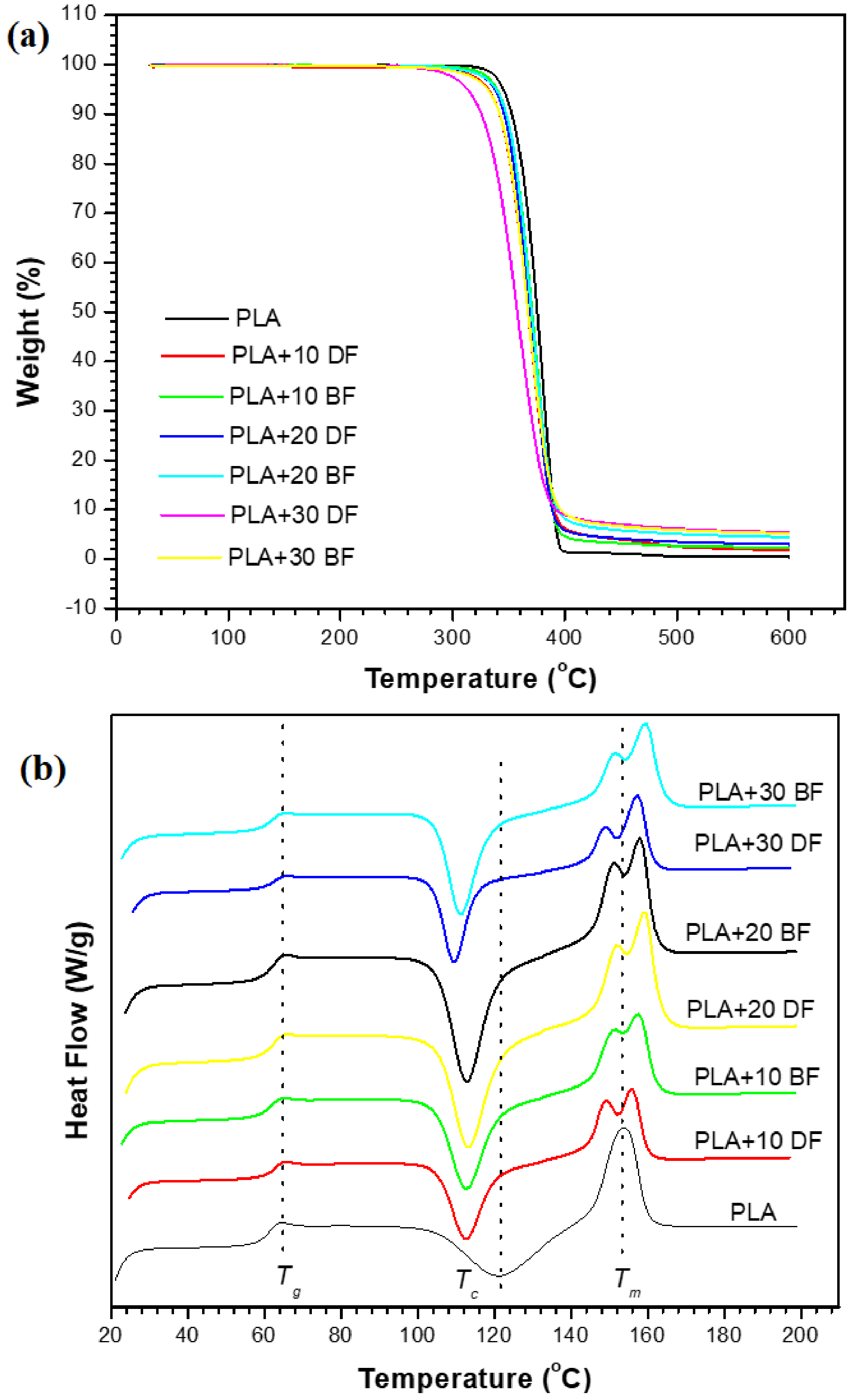


Figure 2.10 (a) TGA curves, and (b) DSC thermograms of PLA and PLA/harakeke composites containing different wt.% of digested fibre (DF) and bleached fibre (BF)

Table 2.5 Thermal properties of PLA and PLA/harakeke composites

TGA				**DSC**			
Sample Code	**T_{onset} (ºC)**	**T_d (ºC)**	**Residue (%) @T ≥ 500 (ºC)**	**T_g (ºC)**	**T_c (ºC)**	**T_m (ºC)**	**X_{DSC} (%)**
PLA	345.25	375.48	0.58	61.90	121.00	154.00	26.53
PLA +10 DF	333.13	367.94	2.18	62.08	115.70	156.70	32.27
PLA +10 BF	339.60	370.18	2.67	62.13	116.70	157.49	33.93
PLA +20 DF	337.56	368.79	3.49	62.65	116.70	157.70	34.52
PLA +20 BF	338.75	370.87	5.06	63.22	116.30	158.70	36.13
PLA +30 DF	313.21	357.60	6.14	63.07	115.98	157.95	41.41
PLA +30 BF	331.15	367.25	6.90	63.15	116.85	158.97	41.49

Literature revealed that one of the major factors influencing the thermal stability of composites, is the nature and strength of the fibre-matrix interfacial bonding [151]. Alkaline treatment of natural fibres increases the surface roughness of the fibres, thereby facilitating mechanical interlocking and interfacial adhesion between the fibre and matrix. In contrast, the dominant interfacial mechanism in peroxide treated fibres is chemical bonding [153]. The schematic illustration of the mechanism of reinforcement in digested and bleached harakeke fibre is shown in Figure 2.11. Results of the FTIR analysis and SEM observation discussed in previous sections suggests higher interaction between PLA and the bleached fibre, compared to the digested fibre. This can help to facilitate efficient distribution of thermal energy within the PLA/bleached fibre composite. The higher possibility for hydrogen bonding, and the increased distribution of fibre within the bleached fibre composites have both contributed to the higher thermal stability of the bleached fibre composites.

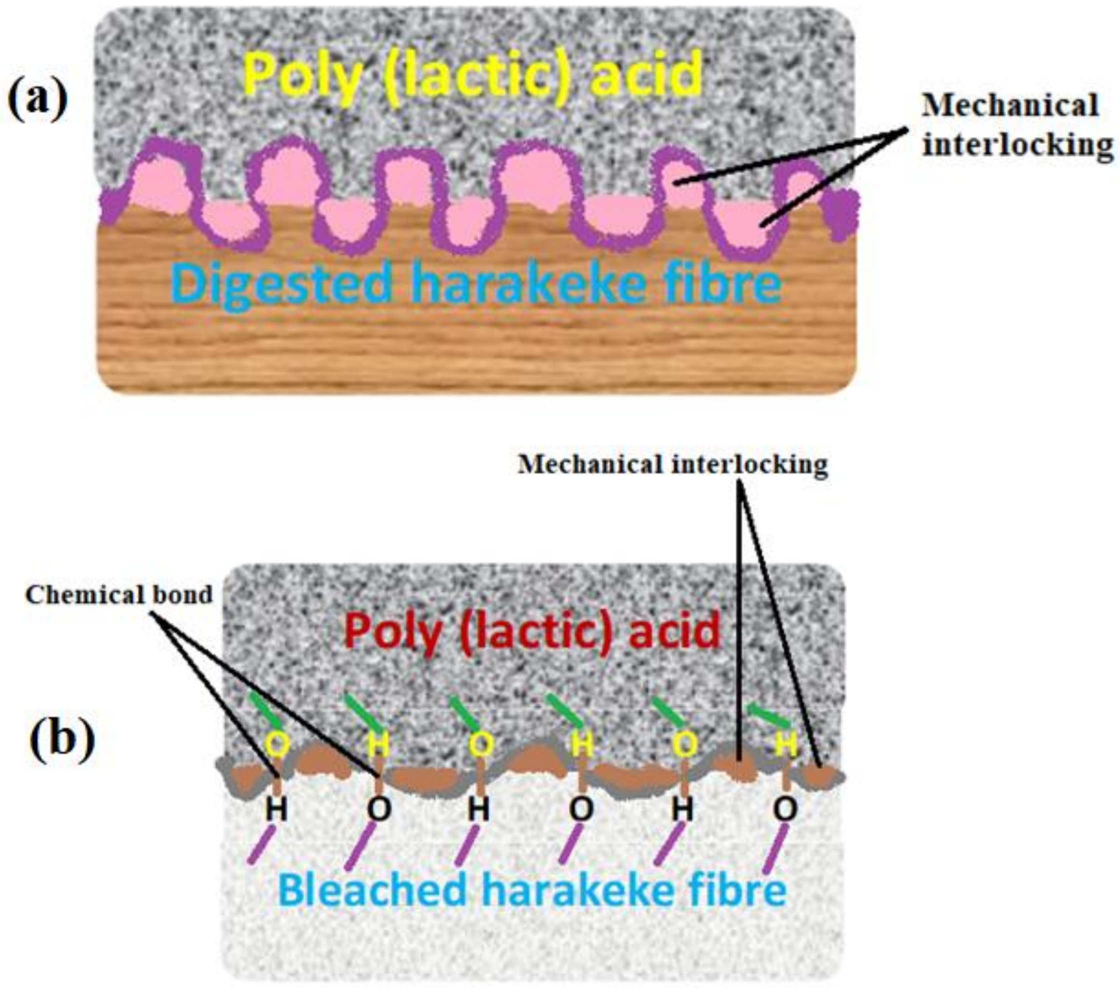


Figure 2.11 Illustration of the mechanism of PLA reinforcement by (a) digested, and (b) bleached harakeke fibre

2.6.5 Dynamic mechanical properties of PLA/harakeke composites

Dynamic mechanical analysis helps to determine the viscoelastic characteristics of polymer and polymer composites, and is generally investigated through the storage modulus, loss modulus and the damping factor [114, 167]. The storage modulus (E′) curves of PLA and the composites are illustrated in Figure 2.12a. It can be seen in Figure 2.12a that the E′ of PLA and the composites dropped steadily around the glass transition region of PLA, which is attributed to increased PLA chain mobility. Increased chain mobility would result in softening and segmental movement of PLA molecules, and would invariably produce a steep drop in E′ as seen in Figure 2.12a. It is significant that at elevated temperatures beyond the T_g of PLA, the E′ of the composites increased slightly around the crystallization temperature of PLA which is believed to be due to the stiffness imposed on the PLA chains, heterogeneous nucleation, and the crystallization of PLA on the fibre.

Figure 2.12a also shows that the E′ values of the composites are higher than in neat PLA which can be attributed to the stiffness imposed on PLA matrix by the reinforcing fibre. Increased stiffness would facilitate interfacial stress transfer within the composite [167]. Therefore, this accounts for the higher modulus of the composites, compared to neat PLA. It is clearly seen in Figure 2.12a that the increase in fibre content produced increasing modulus values such that the E′ of the composites reach a maximum at 30 wt.% fibre. It is significant that the improvement in E′ of the composites when fibre content was raised from 20 wt.% to 30 wt.% is not as large as the improvement seen when raising the fibre content from 10 wt.% to 20 wt.%. This suggests that the reinforcement produced through good fibre distribution, and interfacial interaction within the composite was more effective at 20 wt.% fibre content than at 30 wt.%. Generally, in reinforced composites, as the fibre content increases, it gets to a point (optimum fibre content) above which the fibre becomes excess and cannot be evenly wetted by the matrix [168, 169]. Poor wetting of the fibres will result in poor fibre distribution and agglomeration of fibres within the matrix thereby hindering effective stress transfer from the matrix to the fibre. As a result of agglomeration and poor stress transfer within the composite, there might be premature failure which would produce lower mechanical performance at fibre contents higher than the optimum.

Literature revealed that different factors can influence the E′ of composites, including matrix type, filler type, filler distribution, and filler-matrix interfacial adhesion [117, 151, 167]. Therefore, the higher E′ of the PLA-harakeke composites at 30 wt.% fibre content is not unexpected, considering the high modulus of harakeke fibre. It is interesting that at 20 wt.% fibre content, the bleached fibre composite (PLA+20 BF) exhibits a significantly higher E′ than in the digested fibre composite (PLA+20 DF). This can be associated with stronger interfacial bonding between PLA and the bleached fibre as discussed in sections 2.6.2 and 2.6.3, in addition to the stiffness imposed on PLA by the fibre. The decomposition of organic peroxides leads to the formation of free radicals ($RO^{\cdot}$) which are highly reactive. In the case of H_2O_2, OH radicals are produced, and these highly reactive radical can react with the hydroxyl groups of the fibre thereby forming strong chemical bonds [153]. This will reduce the hydrophilic tendency of the fibre, thereby increasing its compatibility with PLA which favours fibre distribution in the matrix. Improved fibre distribution will facilitate effective stress transfer from PLA to the bleached fibre, which will in turn enhance the ability of PLA to withstand mechanical strain through recoverable viscoelastic distortion. This is believed to be responsible for the higher E′ of the bleached fibre composites above the digested fibre composites. To further assess the strength of the interface in the composites, the damping parameter (tan delta (δ)) was analysed.

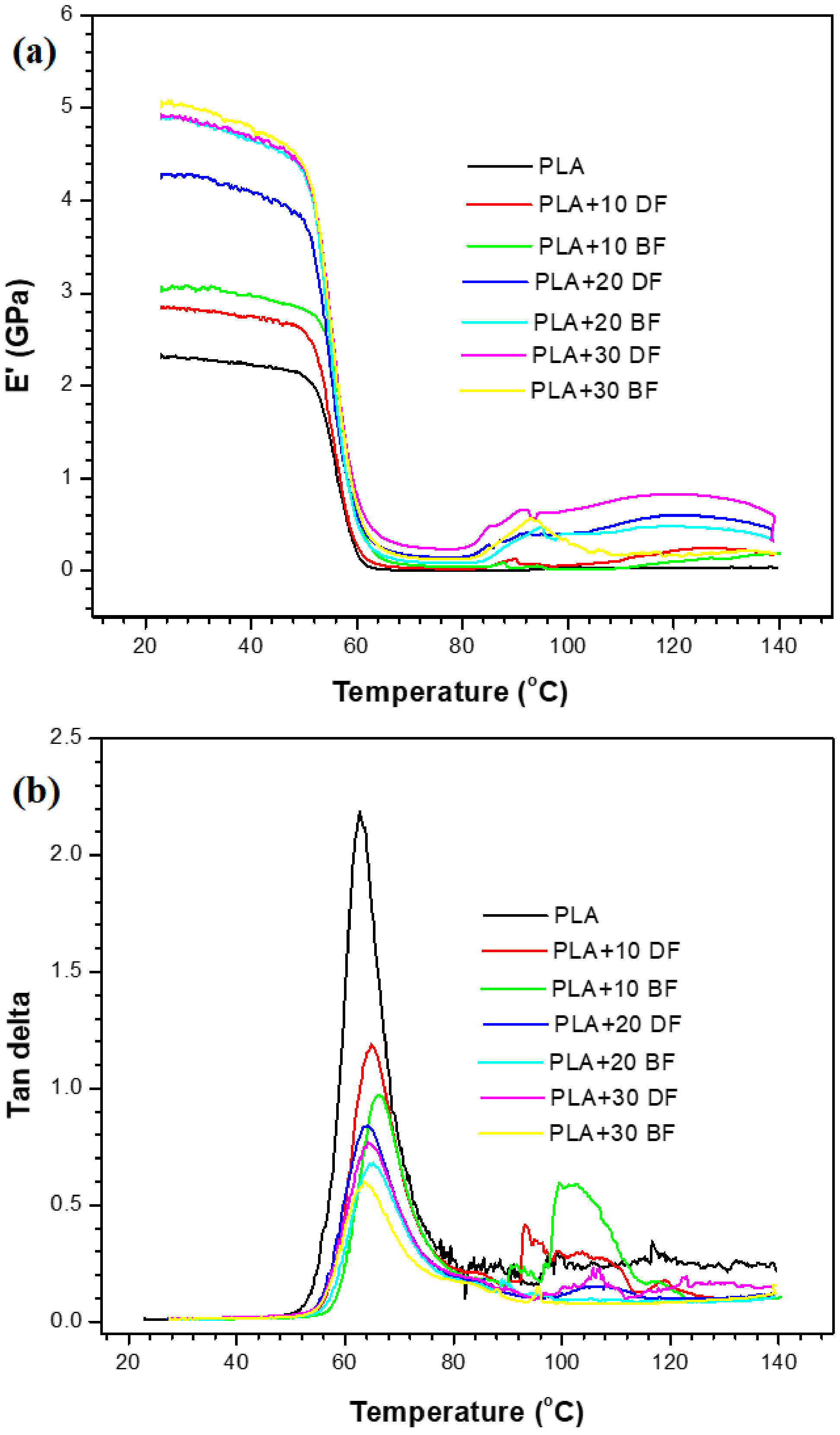


Figure 2.12 (a) Storage modulus, and (b) tan δ curves of PLA and PLA/harakeke composites containing different wt.% of digested and bleached harakeke fibres

The damping factor (tan *δ*) is the ratio of energy dissipated, to the energy stored when a material is subjected to dynamic constraints. The tan *δ* value is notable for its ability to accurately give an indication of the T_g of materials [167]. Usually, the T_g is obtained as the temperature at which the tan *δ* curve is at its maximum. The tan *δ* curves of PLA and the composites are illustrated in Figure 2.12b. The T_g obtained from the tan *δ* curves in Figure 2.12b and the maximum tan *δ* peak values are presented in Table 2.6. The T_g values obtained from the tan *δ* curves align with the DSC result which showed that the incorporation of harakeke only had little effect on the T_g of PLA. The data in Table 2.6 show that the maximum tan *δ* peak of the composites is lower than observed for neat PLA. It can be seen in Figure 2.12b that the reduction in tan *δ* of the composites compared to PLA is quite large which indicates that the incorporation of harakeke fibre was more influential on the tan *δ* peak than on the T_g of PLA. Therefore, the tan *δ* peak was further analysed for the best mechanical performance composite in this study (i.e. 20 wt.% fibre content), to investigate the extent of interfacial adhesion in the composite. The tan *δ* peak was used to determine the adhesion factor *A*, and effectiveness coefficient *C* of PLA+20 DF and PLA+20 BF, in comparison with neat PLA.

Table 2.6 Effectiveness coefficient, adhesion factor, and tan *δ* parameter of PLA and PLA/harakeke composites containing 20 wt.% fibre

Sample code	**Effectiveness coefficient (*C*)**	**Max tan δ peak value**	**Adhesion factor (*A*)**	**T_g (ºC)**
PLA	1.000	2.188	0.000	62.677
PLA +20 DF	0.071	0.841	-1.720	60.752
PLA +20 BF	0.053	0.681	-1.992	61.290

The adhesion factor describes the relationship between the molecular mobility of matrices around the fillers in reinforced composites, where good adhesion will reduce the molecular mobility thereby resulting in reduced adhesion factor. As reported in literature, the molecular mobility of polymer molecules around reinforcing fillers is often limited by strong interfacial adhesion between the matrix and the filler [167]. Hence, a strong interfacial adhesion would produce a low adhesion factor. The adhesion factor *A* of PLA and the composites was calculated using equation 2.5 as follows:

$$Adhesion\,factor\,(A) = \frac{1}{1-V_f}\frac{\tan\delta_c}{\tan\delta_p} - 1 \qquad 2.5$$

where, tan δ_c and tan δ_p are the relative damping factors for the composite and neat polymer, respectively, whereas V_f is the fraction (by mass) of the filler. The relative damping of the materials is obtained at the glass transition temperature as indicated by the maximum tan δ peak [154]. The calculated *A* values are included in Table 4. It is evident that the bleached fibre composite has the lowest *A* value which serves as confirmation of stronger interfacial adhesion between the bleached fibre and PLA. This agrees with the FTIR results discussed in section 2.6.3 and is believed to have significantly contributed to the higher dynamic mechanical performance of the bleached fibre composite. The effectiveness of reinforcement, using bleached and digested fibre was also investigated by calculating the effectiveness coefficient. The effectiveness coefficient is the ratio of the storage modulus E′ of the composite in the glassy and rubbery region in relation to the E′ of the pure resin in the glassy and rubbery region. The reason for taking the ratio in the glassy and rubbery region may be attributed to the fact that the polymer molecules are restricted from moving in the glassy region but are very mobile in the rubbery region. So, the influence of reinforcement on restrictions of the molecular chain mobility can be compared at these regions. Generally, high effectiveness coefficient indicates low effectiveness of the reinforcing filler. So, the effectiveness coefficient was obtained from the relationship between the ratio of the storage modulus E′ of the composite in the glassy and rubbery region, to that of the neat polymer. The effectiveness coefficient *C* was calculated using equation 2.6 as follows:

$$Effectiveness\,coefficient\,(C) = \frac{E'_g/E'_r\,(composite)}{E'_g/E'_r\,(resin)} \qquad 2.6$$

where, E'_g and E'_r represents the storage modulus in the glassy region and rubbery region, respectively. Generally, the reinforcing ability of the fibre is inversely proportional to the *C* value such that high reinforcing effectiveness will produce low *C* values. The calculated *C* value for PLA, and the composites are shown in Table 4 and the values confirms that the bleached fibre offers better reinforcing effectiveness to PLA than the digested fibre, thereby confirming the assumptions made based on the

SEM observation of composites fractured surface (see Figure 2.8 and section 2.6.2), and it aligns with the results discussed in section 2.6.1.

2.7 Conclusions

Composites were prepared from PLA with different contents of digested and bleached harakeke fibre compounded through extrusion and injection moulded. Compared to digestion alone, combined digestion and bleaching treatment removed larger amount of non-cellulosic components from the fibre, which resulted in higher cellulose content. As a result, the thermal stability of the fibre is increased as confirmed through thermal analysis and was attributed to the increased intermolecular cellulose hydrogen bonding in the digested and bleached fibre. Incorporation of the digested and bleached harakeke fibre into PLA produced higher mechanical and thermomechanical performance than the digested fibre alone. This was attributed to the effect of combined digestion and bleaching, which facilitated stronger interfacial interaction between PLA and the fibre, supported by the calculated adhesion factor and effectiveness coefficient.

The mechanical test results showed that 20 wt.% fibre was the optimum fibre content, and the composites strength recorded at this fibre content is comparable to what have been previously reported for higher fibre contents in some natural fibre reinforced composites. The result from this study shows that harakeke fibre is a promising reinforcement for PLA and may be used to produce composites that extends the applications of PLA beyond what may be achieved by using PLA alone. This includes decking, flooring, fencing, cladding, I-beams and columns. In addition, combination of digestion and bleaching treatment could present added benefits for improving the reinforcing ability of natural fibres in polymer composites, through increased fibre distribution and stronger interfacial bonding. Based on this study, further research is recommended for increasing the filler content by exploring different coupling additives to extend the use of harakeke fibre reinforced composites in more diverse structural applications.

CHAPTER 3

EFFECTS OF MECHANICAL PROCESSING AND ENZYMATIC TREATMENT ON THE PROPERTIES OF HARAKEKE FIBRE

3.1 Chapter introduction

This chapter contains the second manuscript published from this thesis. The article is titled “Mechanenzymatic production of natural fibre from harakeke (New Zealand flax) and its characterization for potential use in composites for building and construction applications” [170]. The abstract is presented below.

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.

Keywords: Enzymatic treatment, mechanical processing, reinforcement, natural fibres, fibrillation

3.2 Introduction

Polymer matrix based composite materials used in high performance applications are generally developed to combine the salient properties of different components in 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 [79, 171]. 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 [172-174]. In addition, natural fibres are less damaging to health, are renewable and biodegradable, and helps to reduce CO_2 emissions [84]. 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 [171, 173, 175].

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 [79-82]. 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 can also be used to process natural fibres intended for use as reinforcement in polymeric composites [83]. Mechanical extraction generally involves a series of procedures which help to clean and refine the fibre. However, mechanical extraction is a lengthy process which often leads to production costs higher, or on a par with synthetic fibres such as glass fibre [84]. 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.

To overcome the challenges associated with chemical, physical and mechanical approaches to natural fibre processing, the use of biological agents such as enzymes

[84] has become a rapidly expanding area of research. Enzymes are agents produced by biological organisms including fungi, bacteria, protozoans, termites, plants, and animals [85]. Generally, enzymatic modification of natural fibres requires lower water and energy input compared to chemical and physical methods. Enzymes are reaction-specific, and they catalyse chemical processes or decomposition under mild conditions even at low concentrations [85]. 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 [176]. 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 [177]. Likewise, it has been reported that the mechanical properties of thermoplastic composites were improved when enzyme treated hemp fibres were used as reinforcement [178]. 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 [179, 180]. 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 [85].

Based on these, it was 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 [181]. In addition, mechanical processing alone is often insufficient to achieve the surface functionalities required for good interfacial bonding of fibres with polymer matrices [181]. The use of enzymes can help to reduce the length of time, water and energy required for mechanical processing of fibre [179]. 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 produce 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 fibres from harakeke by using different method and chemicals [63, 66, 182]. 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.

3.3 Materials

The harakeke fibre processed in this study was kindly supplied by Templeton Flax Milling Heritage Trust, New Zealand. Pectinase enzymes (pectin degrading enzymes) from Aspergillus niger, laccase enzymes (lignin degrading 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.

3.4 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 ^{o}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 separation distances (400 µm, 300 µm, and 200 µm) as summarized in Table 3.1. After processing in the SMC, the fibre was subsequently sieved to drain off excess water and then stored in a 4 ^{o}C chiller until further analysis.

Table 3.1 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

The SMC processed fibre was subjected to enzymatic treatment using pectinase and laccase enzymes. The use of pectinase and laccase enzymes is aimed at removing the pectin and lignin components from the fibre so that the fibre cellulose can become available for interaction with the polymer matrix. The enzymatic treatment was performed by dispersing the fibre in a 5.0 pH 50 mM sodium acetate buffer (2.5% EDTA) at a ratio of 1:40 (fibre: buffer) to ensure complete wetting of fibres [183, 184]. The EDTA was added to the incubation medium to destabilize the pectin by complexing the cell wall bound calcium while the selected pH of 5.0 was selected because the chelating activities of EDTA is more efficient around this pH [185]. 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 ^{o}C in a New Brunswick Scientific innova 4300 incubator shaker. Then, 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). Laccase can only oxidize the phenolic fragments of lignin because of the random polymer nature of lignin and due to the low redox potential of laccase. So, small low molecular weight mediators with high redox potential than laccase (> 900 mV) are commonly added to oxidize the non-phenolic part of lignin [186]. Treatment with the laccase enzyme was performed through further incubation of the pectinase treated fibre for 3 h at 60 ^{o}C. The treated fibres were washed severally under water flow, sieved, and stored in a 4 ^{o}C chiller for further analysis.

3.5 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 and 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 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 ^oC/min from 30 °C to 600 ^oC 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 3.1:

$$Acid\ insoluble\ residue\ (AIR) = \frac{m}{M}\ x\ 1000 \qquad 3.1$$

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.

3.6 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. Figure 3.1 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 3.1. It is generally evident from Figure 3.1 that processing with the SMC helped to produce unitary (single) fibres. Figure 3.1b (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 Figure 3.1c (fibre processed 4 times each at 400 µm and 300 µm, and 2 times at 200 µm disc distance), and Figure 3.1d (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 3.1, 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, which 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 Figure 3.2, 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. Visual inspection showed that the number of fines produced during processing is in the order of Figure 3.1b < Figure 3.1c < Figure 3.1d and this can influence the reinforcing ability of the fibre.

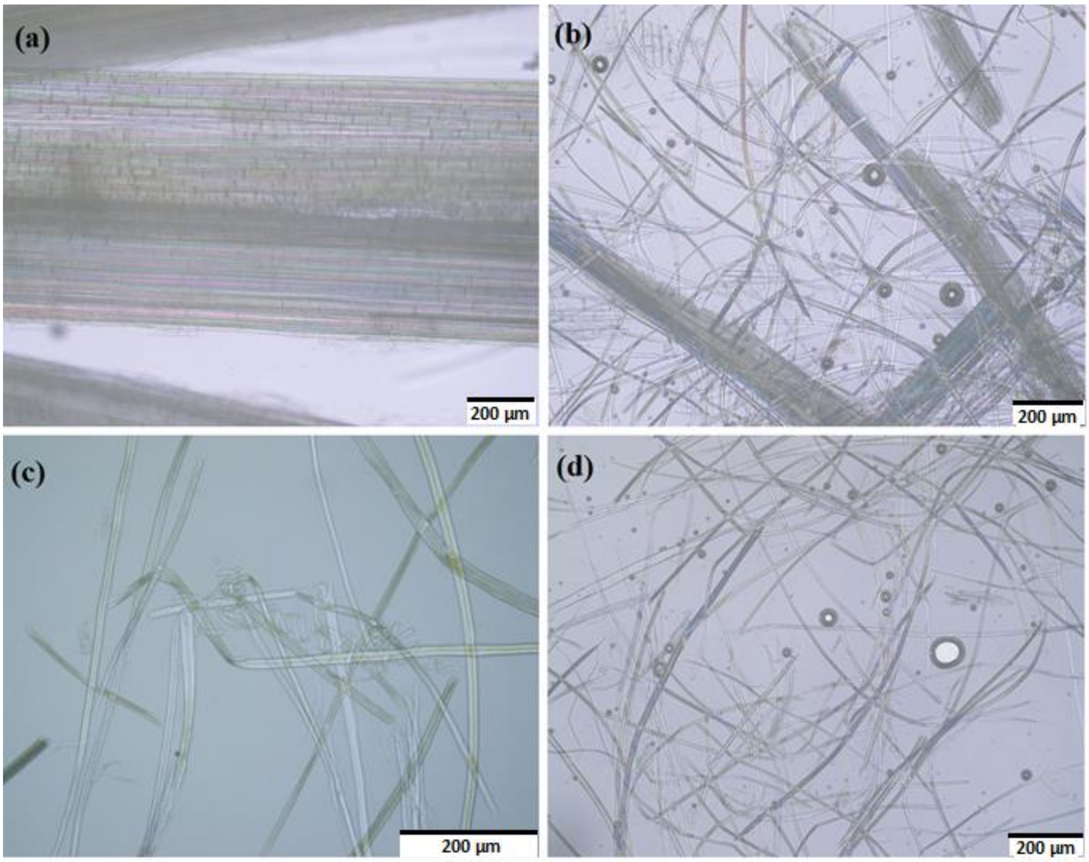


Figure 3.1 Optical microscope images of (a) unprocessed harakeke fibre, (b) fibres processed 4 times each at 400 µm and 300 µm disc distance, (c) fibres processed 4 times each at 400 µm and 300 µm, followed by 2 times at 200 µm disc distance, and (d) fibres processed 4 times each at 400 µm, 300 µm, and 200 µm disc distance

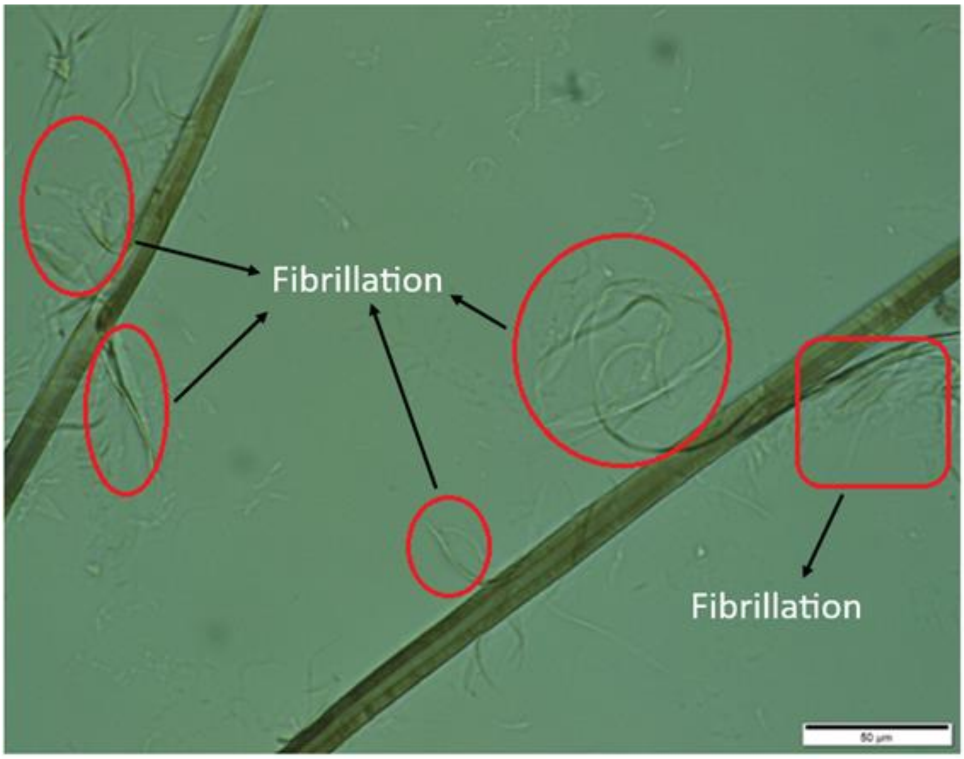


Figure 3.2 Optical microscope image showing fibrillated harakeke fibre after processing 4 times each at 400 µm and 300 µm, followed by 2 times at 200 µm disc distance in the SMC

Preliminary studies on the use of these processed fibres as reinforcement in poly (lactic acid) (PLA) composites suggested that the interfacial bonding between the fibre and matrix appears very low. Therefore, since unitary fibres and fibrillation 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 [84, 179]. Based on the specificity of enzymatic actions, the two enzymes selected in this thesis were selected to degrade some of the non-cellulosic components of the fibre. The laccase enzymes were aimed at lignin removal while the pectinase enzymes were selected to actualize the removal of pectin from the fibre.

The lignin content of the fibres is illustrated in Figure 3.3. 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 undoubtedly influence the compatibility of the fibre with polymer matrices as the cellulose hydroxyl groups of the fibre becomes more available to bond with the polymer matrices [87, 92, 187]. In addition, it will help to improve interfacial interactions that would normally enhance good stress transfer within the composite [87].

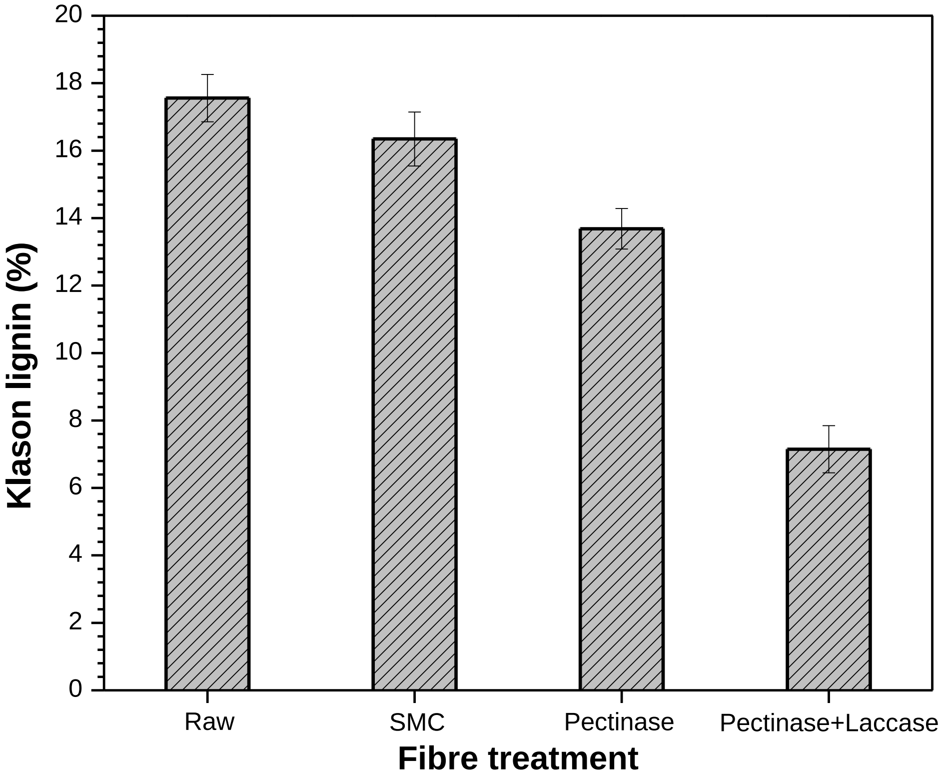


Figure 3.3 Lignin content of unprocessed (raw), SMC processed (SMC), SMC processed-pectinase treated (pectinase), and SMC processed-combined pectin and laccase treated (pectinase+laccase) harakeke fibres. The error bar represent the standard deviation of the values.

The FTIR spectra of unprocessed (raw), SMC processed (SMC) and SMC processed enzyme treated harakeke fibres are illustrated in Figure 3.5. 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 [108, 188]. 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 [188]. 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 [188].

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. Removal of lignin can be confirmed through FTIR analysis mainly be observing the C=O stretching peak at 1750 cm^{-1}. As seen in Figure 3.5, 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 Figure 3.3.

Generally, 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 [189]. 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. Lignin removal 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 Figure 3.3. 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. Specifically, the cellulose hydroxyl groups of the fibre would be exposed to interact with the functional groups of the polymers. The site for possible chemical interaction between PLA and the cellulose hydroxyl groups of the fibre are illustrated in Figure 3.4.

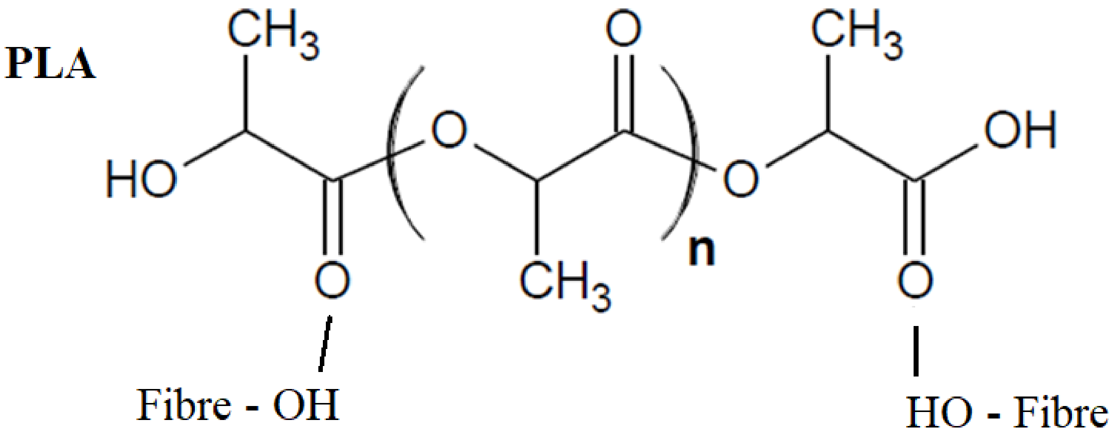


Figure 3.4 Sites for possible chemical interaction between PLA and the cellulose hydroxyl groups of harakeke fibre

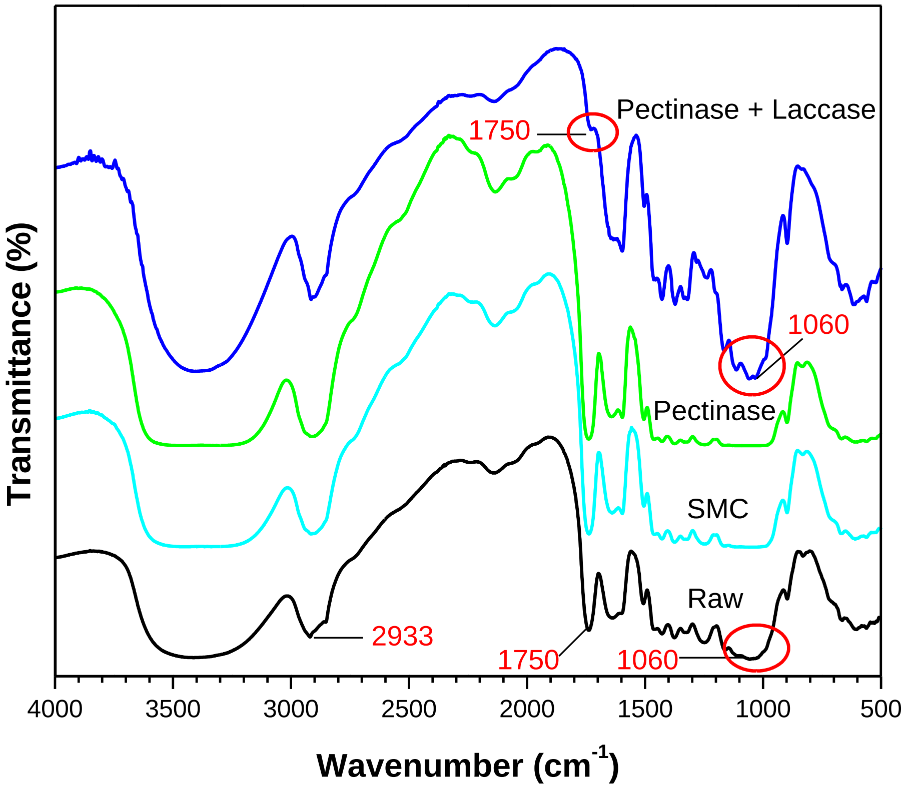


Figure 3.5 FTIR spectra of unprocessed (raw), SMC processed (SMC), SMC processed-pectinase treated (pectinase), and SMC processed-combined pectin and laccase treated (pectinase+laccase) harakeke fibres

The TGA and DTG curves of unprocessed harakeke fibre (Raw), SMC processed fibre (SMC), and SMC processed enzyme treated fibres are presented in Figure 3.6. 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 3.2. 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 which suggests that the amount of non-cellulose removed from the fibre is higher when combined enzyme was used and is supported by the lignin determination analysis, and it aligns with the FTIR analysis discussed in the previous paragraphs.

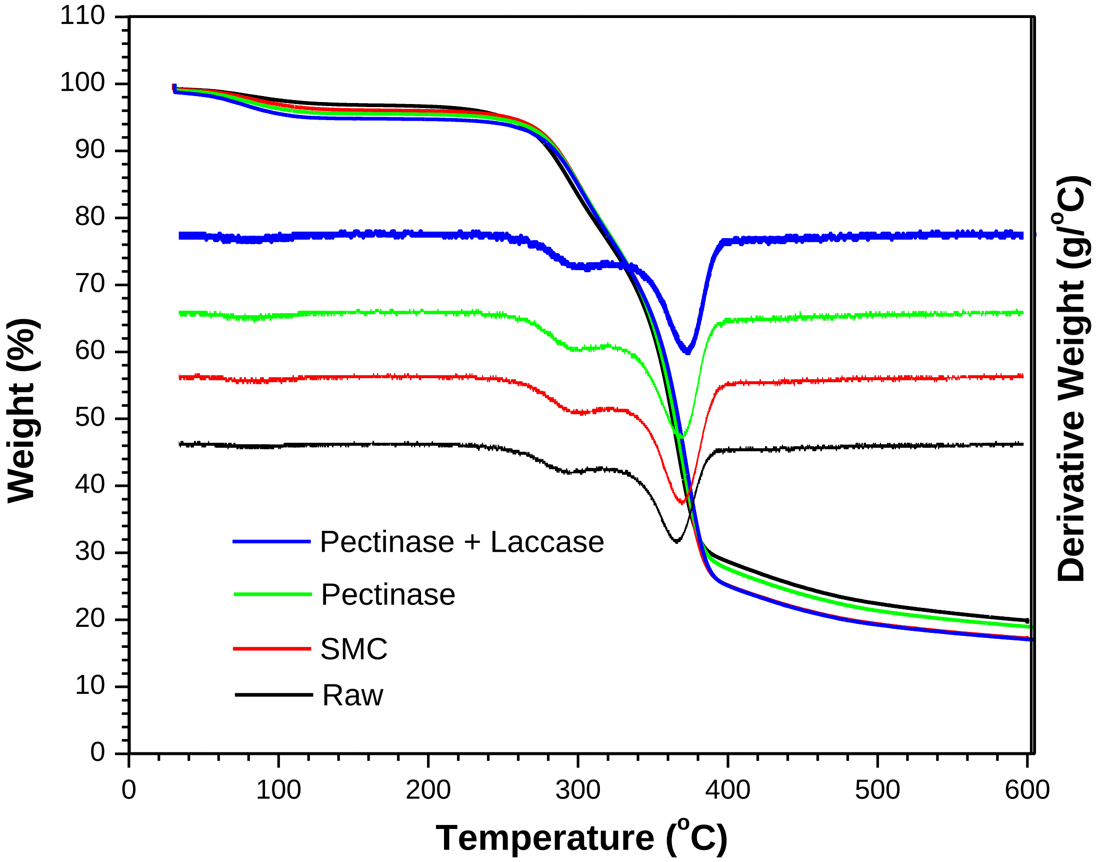


Figure 3.6 TGA and DTG curves of unprocessed harakeke fibre (Raw), harakeke fibre processed with the super masscolloider (SMC), harakeke fibre treated with pectinase enzyme (Pectinase), and harakeke fibre treated with combined pectinase and laccase enzymes (Pectinase + Laccase)

Table 3.2 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 DTG data is useful for determining the activation energy associated with thermal degradation of natural fibres [147], the activation energy (E_a) being a good indicator of the energy barrier that hinders molecular chain mobility in the fibre. The 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 [157]. The kinetic parameter for thermal decomposition of the fibres was calculated using equation 3.2:

$$ln\left(ln\frac{1}{y}\right) = -\frac{E_a}{RT} + ln\left(\frac{RZ}{E_a\beta}T_{max}^2\right) \qquad 3.2$$

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 the thermal decomposition of the fibres [158].

As presented in Figure 3.7, 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 3.2 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 will undoubtedly improve the thermal stability of their reinforced composites. One of the limitations to natural fibre reinforced composites is the limited processing temperature due to possible degradation of the fibre during processing at temperatures above 200 ^oC [77, 190]. So, removal of the low-temperature degrading components will help to improve the thermal stability of the fibre and its reinforced composites [190].

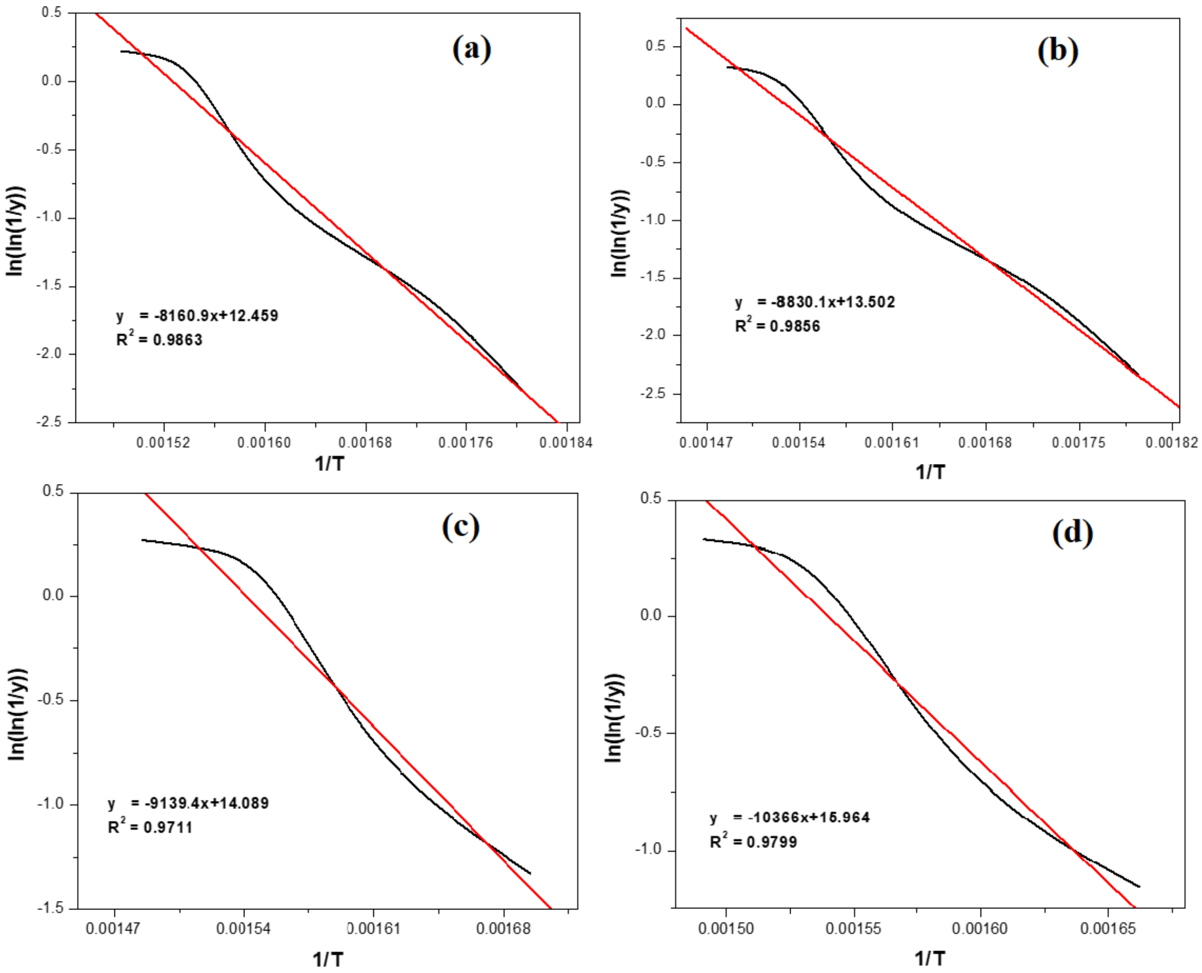


Figure 3.7 Broido curves of (a) unprocessed harakeke fibre (Raw), (b) harakeke fibre processed with the super masscolloider (SMC), (c) harakeke fibre treated with pectinase enzyme (pectinase), and (d) harakeke fibre treated with combined pectinase and laccase enzymes (pectinase + laccase)

3.7 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 combined mechanical and enzymatically 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 from 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.

CHAPTER 4

EFFECTS OF REACTIVE COMPATIBILIZATION ON THE PROPERTIES OF REINFORCED PLA COMPOSITES

4.1 Chapter introduction

This chapter contains the third manuscript published from this thesis, titled Reactive compatibilization of harakeke fibre-reinforced poly(lactic) acid/polybutylene succinate blend [191] and the abstract is presented below:

Abstract: Different blends of poly(lactic acid) (PLA) and polybutylene succinate (PBS), and their harakeke fibre reinforced composites were studied. Scanning electron microscopy showed that the PLA and PBS are incompatible and poorly miscible. Tensile strength and tensile modulus of the blends was found to reduce as the amount of PBS increased. Reinforcement alone was not able to significantly improve the mechanical performance of the blend, which is lower than that of neat PLA. Therefore, simultaneous reinforcement and reactive compatibilization were performed using harakeke fibre, and dicumyl peroxide as reinforcement and compatibilizer, respectively. This produced about 201% increase in the crystallinity of PLA. Compared to the PLA/PBS blend, the dual effect approach increased the tensile strength and tensile modulus by 31% and 148%, respectively. Likewise, dynamic mechanical analysis showed that the thermomechanical properties of the composite greatly improved.

Keywords: Reactive compatibilization; reinforcement; mechanical properties; poly (lactic acid) blend

4.2 Introduction

The rising environmental concerns associated with petroleum derived materials, and the growing awareness of the need to protect the environment have triggered an increased interest in environmentally friendly materials. As such, the past few decades have been graced with increasing efforts on the development of materials that can help to reduce global dependence on petroleum-based products [10, 192, 193]. At the forefront of this drive are materials developed from renewable, biobased, or biodegradable polymer-based composites [194-196]. This is partly due to the versatility of polymers, and their property tunability for desired applications [112]. In the last decade, there has been a continuous increase in the production of biopolymers, with a forecast estimating the global production of biopolymers to hit 2.43 million tons in 2024 [194, 197].

In particular, the market growth of poly (lactic acid) (PLA) is higher than its contemporaries because of its properties, such as high mechanical strength, sufficient biodegradability or compostability, excellent biocompatibility, good processability, and large-scale availability at a competitive price [198-200]. In addition, the production of PLA is reported to consume lesser energy (about 25-55%) and generate lower CO_2 emissions than conventional petroleum-based plastics [15, 201]. Therefore, the use of PLA has become increasingly acceptable in different sectors including building and construction, biomedicine, food packaging, industrial parts, and in the automobile industry [202, 203]. However, to extend the applications of PLA in structural and engineering products, there is need to address its inherent brittleness, and small elongation at break [192, 194, 204].

One effective approach to reduce the brittleness and increase the elongation at break of PLA is to blend it with other rubbery elastomers or plastics [205, 206]. Blends of PLA with different plastics like polyethylene [207], polycaprolactone [208], poly (butylene-adipate-co-terephthalate) (PBAT) [209], and poly (butylene succinate) (PBS) [210] have been investigated. Among these, PBS has the lowest environmental impact [211], and it also has good processability like PLA. Hence, efforts have been made to improve the elongation at break of PLA by adding different composition ratios of PBS [212]. However, PLA and PBS are only partially miscible [204], which often results in decreased tensile strength and modulus as PBS content increased in PLA/PBS blends

[213, 214]. In one study, a blend of PLA and PBS was reported to exhibit an elongation at break of 340% when the PBS content is 30 wt%. However, there is an undesirable decreases in the tensile strength and modulus of the blend [215].

As a result of the decreased tensile strength and modulus of the blend following the addition of PBS, reactive processing is seen as an effective method for improving the miscibility of PLA and its blends. As such, different coupling agents have been used to improve the miscibility of PLA blends. For example, glycidyl methacrylate (GMA) was used by Zhang et al. to process PLA/PBAT blends [216]. This helped to improve the interfacial adhesion between PLA and PBAT and resulted in increased mechanical performance. Likewise, another study reports the reactive processing of PLA, polycarbonate (PC), and PBAT ternary blends in the presence of dicumyl peroxide (DCP) as processing aid [217]. In the case of PLA/PBS blends, different processing aids have been used. Supthanyakul et al. used random poly (butylene succinate-co-lactic acid) (rPBSL) to facilitate compatibility and clarity in PLA/PBS blends [214], while Fortunati et al. prepared PLA/PBS films using Acetyl Tributyl Citrate (ATBC) and isosorbide diester (ISE) as processing aids [213]. In addition, other agents such as lysine tri-isocyanate [218], twice-functionalized organoclay (TFC) [219], and DCP [220] have been explored. Reports showed that the use of processing aids can help to improve miscibility and compatibility in the blends, thereby improving the elongation at break of PLA. However, there are still concerns about the decrease in strength and modulus of PLA as the amount of rubbery component increases.

Literature has also shown that the use of reinforcing fillers can help to improve the mechanical performance of PLA and its blends. In particular, the use of biobased fillers is seen as an effective way to improve performance and reduce cost, while maintaining the environmental friendliness of the composite. Hence, blends of PLA and PBS have been successfully prepared where biobased fillers such as kraft pulp, wood flour, bamboo powder, and microfibrillated cellulose (MFC) were used as reinforcement [221-223]. However, to the best of the authors' knowledge, there are no reports that combine the reinforcement strategy with reactive compatibilization to produce reinforced PLA blends with improved mechanical performance. Therefore, in this article, harakeke fibre was used as a reinforcing filler to improve the tensile strength and modulus of PLA/PBS blend. The choice of harakeke fibre is based on its confirmed capability to effectively reinforce PLA, as reported in previous studies [108, 224]. Then, DCP was used as a processing aid to improve the miscibility of PLA and PBS. The effect of PBS on the tensile strength and modulus of PLA, the effect of the reinforcing filler on reinforced PLA/PBS blends, and the influence of reactive compatibilization are discussed.

4.3 Materials

Poly (lactic acid) (PLA) was used as the polymer matrix in this study. The PLA used is an injection moulding grade PLA biopolymer (Ingeo™ 3052D) from NatureWorks and has a specific gravity of 1.24 and melt flow rate (MFR) of 14 g/10 min (210 °C, 2.16 kg). Poly butylene succinate (Bio-PBS FZ71) with a MFR of 22 g/10 min (190 °C, 2.16 kg) and a density of 1.26 g/cm^3 was supplied by PTT MCC Biochem Company Limited. Dicumyl peroxide (DCP) was purchased from Sigma Aldrich and used for reactive compatibilization of PLA and PBS. Harakeke (New Zealand flax) fibre was used as the reinforcing filler and it was supplied by Templeton Flax Milling Heritage Trust, New Zealand. Bulk sodium hydroxide solid pellets were procured from Sigma-Aldrich and used to treat the harakeke fibre.

4.4 Methods

4.4.1 Fibre preparation and treatment

The harakeke fibres obtained from the supplier were in bundles of about 1-1.5 m long. The fibre was first dried and chopped with a guillotine into pieces of about 2-3 cm. Weighed amounts of the chopped fibre was put in stainless steel canisters and a solution of 5 wt.% NaOH and 2 wt.% Na_2SO_3 was poured into the canister to obtain a fibre to solution ratio of 1:8. Then, fibre digestion was performed in a lab-scale pulp digester as described in literature [38]. The treated fibre was washed continuously with water until neutral pH was attained. Then, the fibre was dried in an oven at 80 °C for 48 h and kept in sealed plastic bags until it was used for composite preparation.

4.4.2 Production of blends and composites

Blends of PLA and PBS were prepared by varying the PBS content from 5-20 wt.%. The components were mixed and compounded using a TSE-16-TC twin-screw extruder at a screw speed of 100 rpm using a temperature profile in the range of 165-185 ^{o}C. Composite material was prepared by compounding 30 wt.% harakeke fibre with a selected PLA/PBS blend. The wt.% fibre used was based on the preliminary study. In addition, a composite material containing PLA, PBS, harakeke fibre, and dicumyl peroxide (DCP) was compounded in the extruder at the same conditions used for the blends and the composite without DCP. The amount (wt.%) of each component in the different category of composites prepared are presented in Table 4.1. Prior to extrusion of the fibre containing composites, the treated fibres were processed in a blunt Sunbeam Multigrinder to separate the fibres. Then the processed fibres were kept in a 105 ◦C conventional oven until it was used. The PLA and PBS granules were dried to moisture content < 0.1 % in a vacuum oven set at 60 ◦C for 2 h. The extrudates were granulated with a Moretto GR knife mill plastic granulator to obtain < 3 mm pellets. The granules were dried to a moisture content < 0.1 % by weight and was used to produce tensile test samples in a BOY 35A injection moulding machine. The extrusion and injection parameters are summarized in Table 4.2.

Table 4.1 Sample codes and the amount (wt.%) of individual component in the different samples

Sample code	**PLA (wt.%)**	**PBS (wt.%)**	**Fibre (wt.%)**	**DCP (wt.%)**
PLA	100	-	-	-
PBS	-	100	-	-
PLA+5% PBS	95	5	-	-
PLA+10% PBS	90	10	-	-
PLA+15% PBS	85	15	-	-
PLA+20% PBS	80	20	-	-
PLA+10% PBS+30% Fibre	60	10	30	-
PLA+10% PBS+30% Fibre+DCP	59.7	10	30	0.3

Table 4.2 Extrusion and injection moulding profiles for the preparation of PLA-PBS, PLA-PBS-fibre, and PLA-PBS-fibre-DCP composites

Extrusion Parameter		**PLA, blends, and composites**	**PBS**	**Injection moulding Parameter**		**PLA, blends, and composites**	**PBS**
	Unit	**Value**	**Value**		**Unit**	**Value**	**Value**
Feeding zone	(◦C)	165	60	Feeding zone	(◦C)	150	100
Zone 1,2	(◦C)	170	160	Compression zone	(◦C)	165-185	130
Zone 3, 4,	(◦C)	175	150	Metering zone	(◦C)	190	140
Zone 5,6,7,8	(◦C)	180	150	Nozzle	(◦C)	185	150
Zone 9	(◦C)	180	140	Mould	(◦C)	35	25
Die	(◦C)	185	140	Screw speed	(ccm/s)	43.1	43.1
Screw speed	(rpm)	100	60	Screw position	(mm)	30	30
				Injection pressure	(bar)	550-600	225
				Holding pressure	(bar)	600	600
				Injection time	(s)	0.5	0.72
				Cooling time	(s)	30	

4.4.3 Scanning electron microscopy (SEM)

Fractured surfaces of PLA, PBS, PLA/PBS blends and the reinforced composites were examined on a Hitachi Regulus SU8230 field emission scanning electron microscope. It should be noted that PBS did not fracture during tensile testing. So, the SEM image presented for PBS are from cryofracture samples. Double sided carbon tape was used to mount the dried samples on aluminium stubs, and the samples were then coated with a thin layer (5 nm) of platinum through sputtering in a Quorum Q150V sputtering equipment.

4.4.4 Mechanical testing

In preparation for testing, injection moulded tensile testing samples which were prepared according to EN ISO 527 specifications (span length = 65 mm, width = 10 mm, and thickness = 4 mm) were first kept in a 23 ◦C climate chamber for 48 h at 50% relative humidity. Tensile testing was then performed on a universal testing machine (Instron® 5982). The instrument is equipped with a 5 kN load cell and was operated at a crosshead speed of 5 mm/min. Tensile strain on the samples during testing, was measured with a 25 mm extensometer which was fixed at the middle of the specimen. Five specimens were tested per composite category and the average values of the tensile strength and tensile modulus were recorded.

4.4.5 Thermogravimetric and differential scanning calorimetric analysis

The thermal properties of the materials were performed in a Perkin Elmer STA 8000 thermal analyzer. About 10-20 mg of the samples were weighed and placed in a crucible. This was heated from 30 ◦C to 600 ◦C at a rate of 10 ◦C /min under an argon atmosphere, with a gas flow of 40 mL min^{-1}.

4.4.6 Differential scanning calorimetric analysis

Differential scanning calorimetry analysis (DSC) of the materials was performed in a TA instrument (Netzsch DSC 3500 Sirius). The samples, with weights of 10-15 mg were heated at a rate of 10 ◦C/min from 20 to 200 ◦C. Heating was performed under nitrogen gas flowing at 60 mL/min. The DSC thermogram obtained was used to determine the glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) of the samples. Furthermore, the crystallinity of PLA in the blend and composites was derived using the following equation:

$$\%crystallinity\ (I_{DSC}) = \frac{\Delta H}{\Delta H_m W}\ x\ 100\% \qquad 4.1$$

where, ΔH is the enthalpy of fusion of the samples, ΔH_m is the enthalpy of fusion of a reference PLA with 100 % crystallinity, and W is the mass fraction of the matrix. The crystallinity of PLA in the composites was calculated by using 93.6 J/g as the enthalpy of fusion (ΔH_m) of reference PLA with 100 % crystallinity [144].

4.4.7 Dynamic mechanical analysis

The viscoelastic properties of the materials were assessed through dynamic mechanical analysis (DMA) using a Perkin Elmer DMA800 instrument. Samples with dimensions 30 mm × 5 mm × 1.5 mm were fitted in a single cantilever configuration and heated from 23 ◦C to 140 ◦C at 2 ◦C/min from. The analysis was performed at a constant frequency of 1 Hz, while the displacement amplitude was 20 μm.

4.5 Results and Discussion

4.5.1 Morphological properties

The SEM images of of the fractured surface of PLA and PBS are shown in Figure 4.1. The image of PLA in Figure 1a reveals a smooth fracture which is typical of brittle materials like PLA. In contrast, the image of PBS in Figure 4.1b depicts an uneven fractured surface, associated with tough materials which supports that PBS is relatively tougher than PLA.

The SEM images of the fractured surface of PLA/PBS blends with different PBS content (5-20 wt.%) are presented in Figure 4.2. As seen in the image, the presence of dispersed voids created by the dispersed PBS in the continuous PLA matrix phase becomes increasingly noticeable as the PBS content increases. It is noteworthy that at the higher PBS contents, the domains of PBS were more conspicuous in the SEM images (as in Figure 4.2d). Similar observation has been reported by other researchers [204, 220] including spherical droplets of PBS conspicuously dispersed in the continuous PLA phase after blending. These domains indicate poor compatibility between PLA and PBS [204, 225], and can influence the tensile performance of the blends as discussed in a subsequent section.

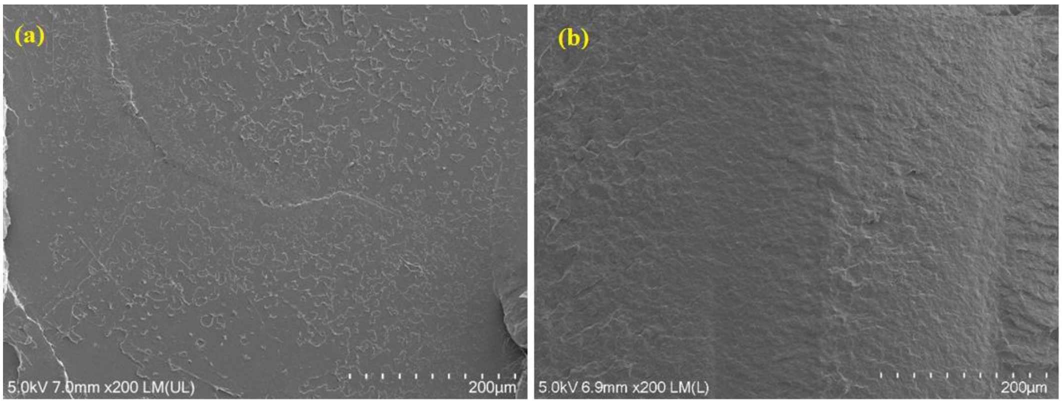


Figure 4.1 SEM images of the fractured surface of (a) PLA after tensile testing, and (b) cryofracture surface of PBS

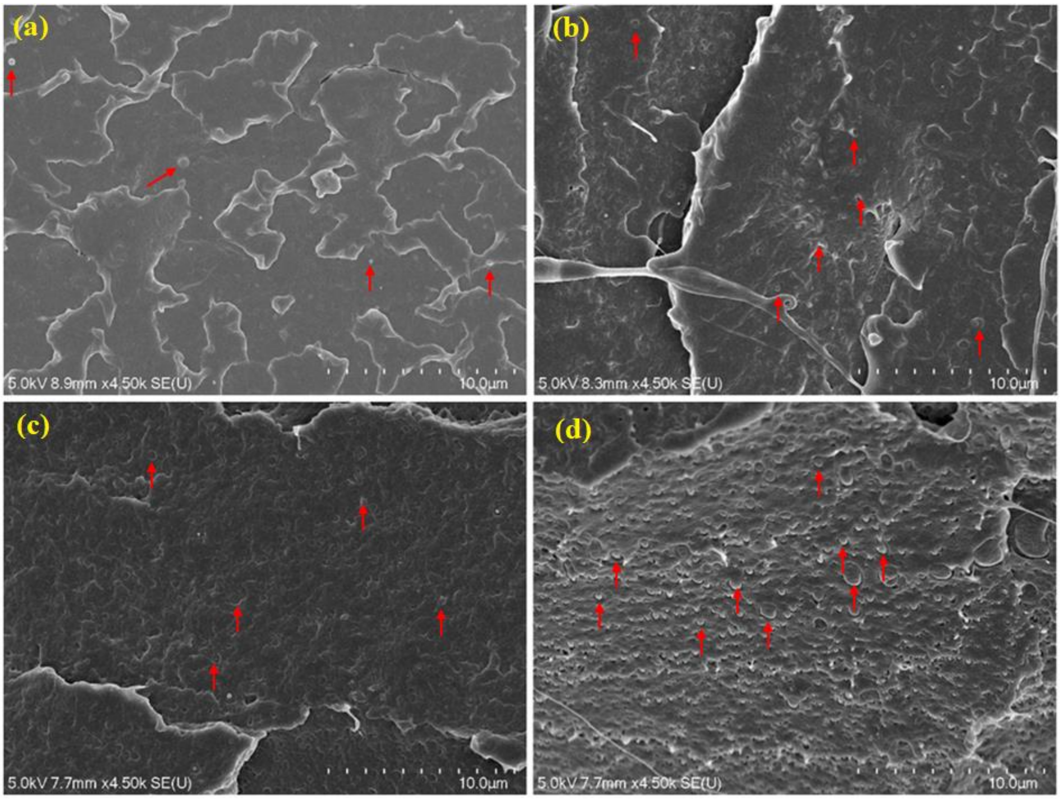


Figure 4.2 SEM images of the fractured surface of PLA/PBS blends containing (a) 5 wt.% (b) 10 wt.% (c) 15 wt.%, and (d) 20 wt.% PBS after tensile testing. The red arrows indicate the dispersion of PBS in the PLA matrix.

4.5.2 Mechanical properties

The tensile properties of PLA, PBS, and PLA-PBS blends containing different wt.% (5-20 wt.%) PBS are presented in Figure 4.3. It is evident in Figure 4.3 that the incorporation of PBS in the PLA matrix resulted in a decrease in the tensile strength (TS) and tensile modulus (TM). These decreases became larger as the PBS content increased from 5 wt.% to 20 wt.% such that compared to PLA, the largest reductions in TS an TM were observed for the PLA-PBS blend with the highest PBS content (20 wt.%). This is not unexpected, considering the lower TS and TM of PBS as illustrated in Figure 4.3. Asides the low mechanical properties of PBS, the SEM images in Figure 4.2 shows that PBS and PLA are only partially miscible, similar to reports in literature [204, 220]. Therefore, the low TS and TM of PBS, and the poor misciblility of PLA and PBS are believed to have contributed to the gradual drop in the tensile properties of the PLA-PBS blends with increasing PBS content.

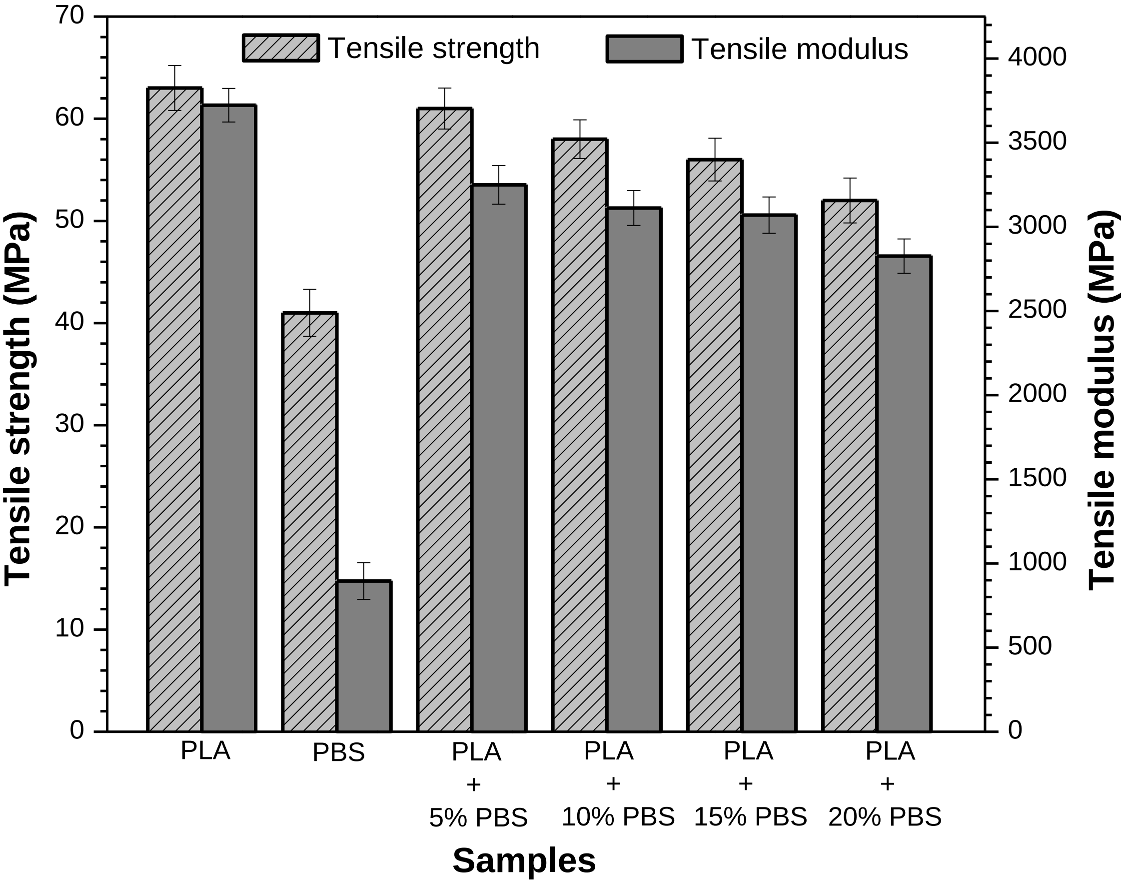


Figure 4.3 Tensile strength and tensile modulus of PLA, PBS, and PLA-PBS blends containing different wt.% PBS. The error bar represent the standard deviation of the values.

Based on the tensile properties of the blends and for easy comparison, a fixed amount (10 wt.%) of PBS content was selected and used in reinforced PLA/PBS blends. Preliminary studies and previous studies have shown that the addition of 20-30 wt./% harakeke fibre in PLA produced remarkable improvement in the tensile properties of the resulting composite [108, 224]. So, harakeke fibre (30 wt.%) was used as the reinforcement in the PLA/PBS blends. In addition, the compatibilization ability of DCP in PLA/PBS blends were reported previously [204, 220]. Therefore, DCP was incorporated in the reinforced PLA-PBS-fibre system, to facilitate reactive compatibilization of the components.

The tensile properties of PLA, PLA/PBS blend containing 10 wt.% PBS, reinforced PLA/PBS composite, and reinforced PLA/PBS composites with DCP are illustrated in Figure 4.4, while the values are presented in Table 4.3. As seen in Table 4.3, incorporation of 30 wt.% harakeke fibre in PLA produced little increase in the TS of the blend which is attributed to the reinforcing ability of the harakeke fibre and effective stress transfer within the composite. The effect of harakeke fibre inclusion is more pronounced in the TM than the TS which is attributed to the high modulus of harakeke fibre, as reported in literature [127, 128]. Although the addition of fibre helped to increase the TS of the blend, the data in Table 4.3 and Figure 4.4 shows that the TS of the PLA-PBS-fibre system (60 MPa) is still lower than the TS of neat PLA (63 MPa). This suggests a disruption in the reinforcing ability of harakeke fibre, probably due to the presence of PBS, in the PLA-PBS-fibre system. In addition, it can be due to the decrease in the volume of PLA (see Table 4.1) within the system [226], or the incompatibility of PLA and PBS.

Incorporation of dicumyl peroxide helped to improve the TS and TM of the PLA-PBS-fibre system. Compared to neat PLA, the TS and TM of the DCP compatibilized harakeke reinforced PLA/PBS blend increased by 21% and 107%, respectively. Likewise, compared to the PLA/PBS blend, incorporation of DCP increased the TS and TM of the composite with DCP by 31% and 148%, respectively. This can be attributed to the reactive compatibilization of the components through the coupling effects of DCP as described in literature [220]. Therefore, it is believed that the presence of DCP might have helped to facilitate good interfacial interactions that resulted in the improved TM and TS as illustrated in Figure 4.4 and presented in Table 4.3.

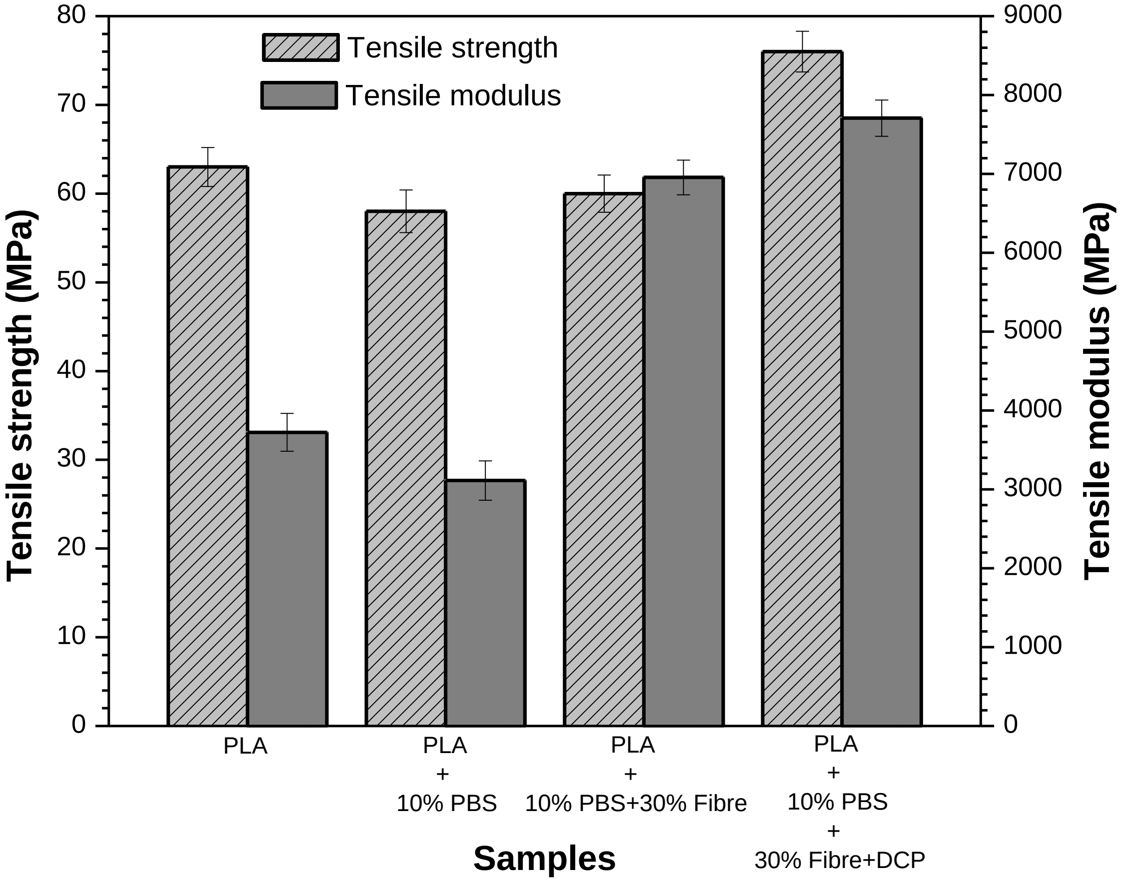


Figure 4.4 Tensile strength and tensile modulus of PLA, PLA/PBS blend, harakeke fibre reinforced PLA/PBS composite, and harakeke fibre reinforced PLA/PBS composite with DCP. The error bar represent the standard deviation of the values.

To assess the effect of chain lubrication and reactive compatibilization on the toughness of the different composite systems, the elongation at break was recorded during tensile testing. The elongation at break of PLA, PBS, PLA/PBS blend containing 10 wt.% PBS, reinforced PLA/PBS composite, and reinforced PLA/PBS composite with DCP are included in Table 4.3. As stated in section 4.4.2, the neat PBS did not fracture during tensile testing. So, the value of elongation at break recorded for neat PBS in Table 4.3 is the maximum value when the extensometer reached its limit. As seen in Table 4.3, the elongation at break of PBS would be more than 511% higher than PLA. As for the PLA/PBS blend, the elongation at break (3.62%) is about 64% higher than neat PLA. This is not unexpected considering the higher elongation at break of PBS. However, it is significant that the addition of harakeke fibre resulted in lower elongation at break, compared to PLA and the PLA/PBS blend, which is believed to be due to the presence of harakeke fibre which might have restricted the effective lubrication of the PLA chains by PBS. More surprising is the further reduction in the elongation at break of the composite with DCP (1.93%) compared to all the other samples. Whereas reactive compatibilization using DCP helped to improve the TS and TM of reinforced PLA/PBS blend, its elongation at break and toughness decreased.

Table 4.3 Mechanical properties of PLA, PBS, PLA/PBS blend, reinforced PLA/PBS composite, PLA/PBS composite with DCP

Sample code	**Tensile strength (MPa)**	**Tensile modulus (MPa)**	**Elongation @ break (%)**	**Fracture toughness**
PLA	63	3721	2.21	144.99
PBS*	41	896	>13.51*	471.52
PLA+10% PBS	58	3112	3.62	412.72
PLA+10% PBS+DCP	59	3550	2.81	423.24
PLA+10% PBS+30% Fibre	60	6955	2.19	103.65
PLA+10%PBS+30% Fibre+DCP	76	7707	1.93	95.18

* Neat PBS did not fracture during tensile bending. The elongation at break value recorded is the maximum value when the extensometer has reached its limit.

4.5.3 Thermogravimetric analysis

The TGA curves of PLA, PBS, PLA/PBS blend containing 10 wt.% PBS, reinforced PLA/PBS composite, and reinforced PLA/PBS composite with DCP are illustrated in Figure 4.5. The onset temperature for thermal degradation of the materials (T_{onset}), and their thermal degradation temperatures (T_d) are summarized in Table 4.4. It is evident in Figure 4.5 and Table 4.4 that PBS is more thermally stable than PLA, which indicates that it can be processed at higher temperatures compared to PLA. Figure 4.5 and Table 4.4 also shows that the thermal stability of PLA is higher than the PLA/PBS blend, and the composites. As discussed in section 4.5.1, section 4.5.2, and shown in Figure 4.2, PLA and PBS are incompatible and poorly miscible; so the voids created by the poor miscibility can serve as heat ingression sites which would permit excessive penetration of heat into the samples, thereby lowering its thermal stability. This might be responsible for the lower observed thermal stability of the PLA/PBS blend, compared to neat PLA. Similarly, it was stated in section 4.5.2 that the lower tensile strength of the reinforced PLA-PBS composites might have resulted from PBS molecules which are poorly miscible with PLA, thereby affecting effectivenenss of the reinforcing filler. This might have contributed to the reduced thermal stability of the reinforced PLA-PBS composite, compared to neat PLA. In addition, the lower thermal stability of the reinforced PLA-PBS composite can be attributed to the presence of harakeke fibre in the composites, due to the lower thermal stability of the fibre, compared to the PLA [108].

The incorporation of DCP helped to slightly raise the thermal degradation temperature of the PLA-PBS-fibre system. The reactive compatibilization facilitated by DCP might have helped to facilitate improved interfacial interactions within the system thereby slowing down heat penetration. Generally, there is the possibility for the creation of heat ingression sites in composites. Therefore, the high thermal stability of PBS, coupled with the improved interfacial adhesion believed to have been facilitated by the inclusion of DCP (section 4.5.2), might have helped to improve the thermal stability of the composites with DCP (Table 4.4).

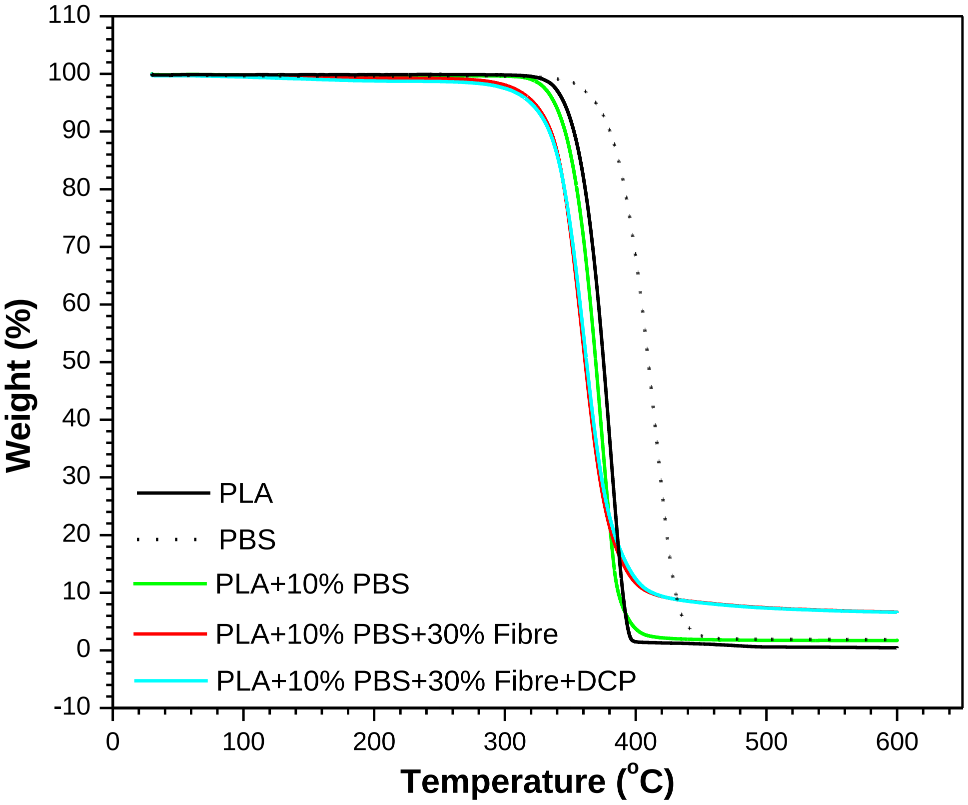


Figure 4.5 TGA curves of PLA, PBS, harakeke fibre reinforced PLA/PBS composite, and harakeke fibre reinforced PLA/PBS composite with DCP

Table 4.4 TGA parameters of PLA, PBS, harakeke fibre reinforced PLA/PBS composite, and harakeke fibre reinforced PLA/PBS composite with DCP. Standard deviation values are in parenthesis

	TGA		**DSC**			
Samples	**T_{onset} (◦C)**	**T_d (◦C)**	**T_g (◦C)**	**T_c (◦C)**	**T_m (◦C)**	**CrI_{DCS} (%)**
PLA	345	375	64.58(0.01)	129.52	153.68	11.05
PBS	369	409	-	-	117.23	-
PLA+10% PBS	338	370	63.62(0.33)	115.68	149.75	29.56
PLA+10% PBS+30% Fibre	322	361	65.84(0.30)	116.83	151.87	35.02
PLA+10% PBS+30% Fibre+DCP	319	362	64.93(0.08)	119.17	151.89	33.34

4.5.4 Differential scanning calorimetric analysis

The DSC curves of PLA, PBS, PLA/PBS blend containing 10 wt.% PBS, reinforced PLA/PBS composite, and reinforced PLA/PBS composite with DCP are illustrated in Figure 4.6, while the DSC data is included in Table 4.4. As seen in Figure 4.6, the glass transition (T_g) peak is not noticeable in the DSC curve of neat PBS, due to the low T_g of PBS (– 40 ◦C) which is outside the temperature range used for the samples. Likewise, PBS did not show any distinct crystallization (T_c) peak, the only noticeable peak being the melting point peak around 117 ◦C. Table 4.4 shows that the T_g of the PLA/PBS blend is lower than the T_g of neat PLA, which is attributed to the poor miscibility of PLA and PBS as discussed in section 4.5.1 and as stated in section 4.5.3, which might have disrupted the molecular bonds in PLA chains, thereby allowing the chains to move more easily. Generally, the T_g of polymer blends and reinforced polymers are influenced by factors such as chain ends, impurities and free volume [227]. The increase in these factors would reduce the T_g of the material. So, the poor miscibility of PLA and PBS, which creates free volume in the composite might have contributed to the lower T_g of the PLA/PBS blend, compared to neat PLA. Incorporation of harakeke fibre helped to improve the T_g of PLA, while also shifting the T_c to a lower temperature region. This suggests that the fibre helped to restrict the mobility of PLA chains, while also acting as nucleating agents for crystal formation and crystal growth. This is supported by the higher CrI% of the reinforced composites (Table 4.4), and it aligns with what had been previously reported in literature [73].

Generally, the inherent bulk crystallinity of semicrystalline materials like PLA often helps to enhance their mechanical properties [228]. Therefore, the improved crystallization activity of PLA in the reinforced composites are likely to have contributed to the increase in TS and TM of the reinforced composites as illustrated in Figure 4 and discussed in section 4.5.2.

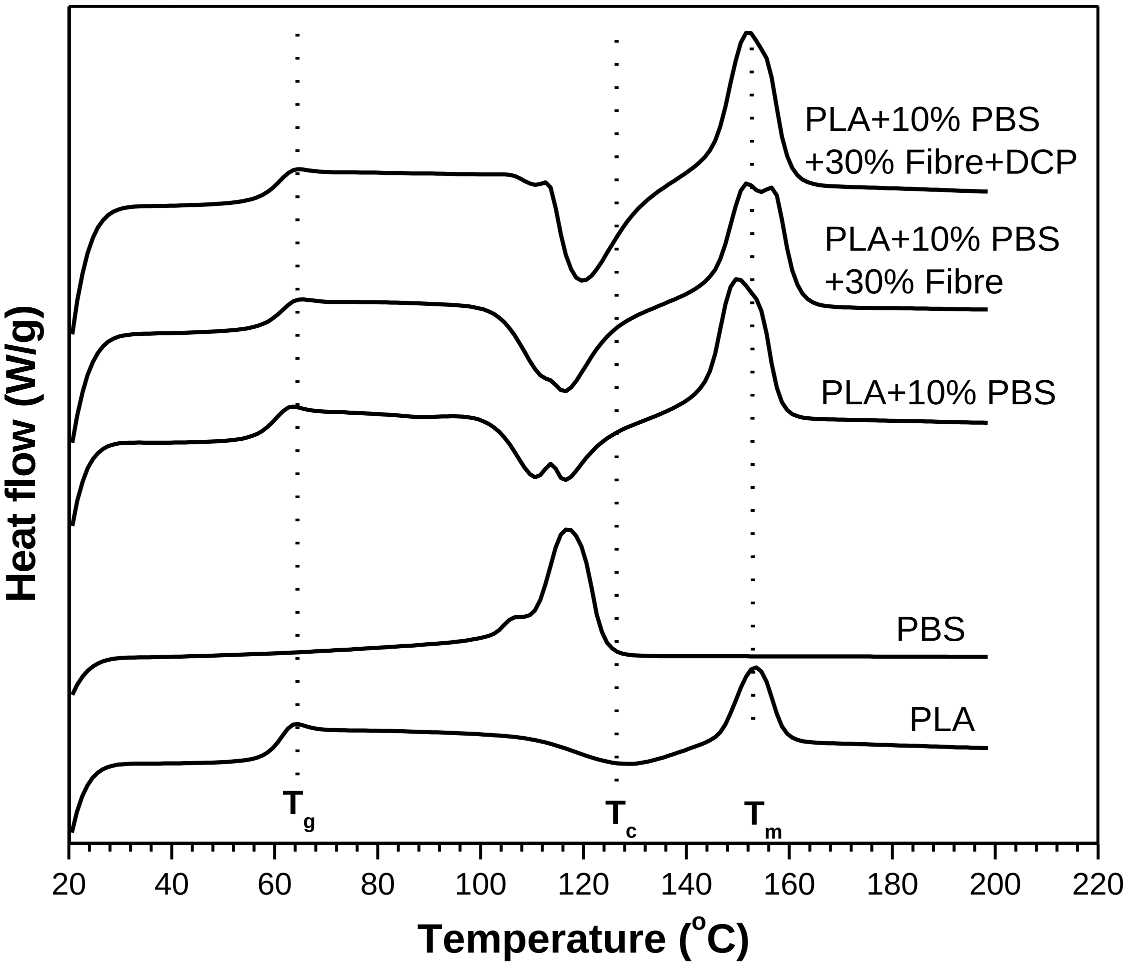


Figure 4.6 DSC curves of PLA, PBS, PLA/PBS blend, harakeke fibre reinforced PLA/PBS composite, and harakeke fibre reinforced PLA/PBS composite with DCP

4.5.5 Dynamic mechanical analysis

The thermomechanical properties of PLA, PLA/PBS blend, reinforced PLA/PBS composite, and reinforced PLA/PBS composite with DCP are illustrated through the dynamic mechanical analysis presented in Figure 4.7. It should be noted that the storage modulus (E′) and tan delta values of neat PBS is not included in the figure because of the temperature range selected for this analysis. The variation in storage modulus (E′) of the samples with temperature is presented in Figure 4.7a. There are no significant changes in the E′ of the samples below the glass transition region of PLA, but the E′ falls sharply around this region. In addition, it is evident from Figure 4.7a that the E′ of the neat PLA is higher than the PLA/PBS blend, but lower than the reinforced PLA-PBS system and reinforced PLA-PBS composite with DCP, which aligns with the mechanical test results discussed in section 4.5.2.

Different factors can contribute to the E′ of polymer blends and composites including matrix type, filler type, dispersion of filler, and interfacial adhesion [130, 144]. Therefore, the higher E′ of the composites is attributed to the presence of harakeke fibre in the composites, which due to its high stiffness, can impose some stiffness on PLA, thereby facilitating interfacial stress transfer within the composites. The higher E′ also supports the good reinforcing ability of harakeke fibre as reported in literature [108, 224]. In addition, it is noteworthy that whereas the incorporation of harakeke produced remarkable improvement in the E′ of the PLA/PBS blend, the addition of both harakeke fibre and DCP produced further increase in the E′ such that the E′ of the composite with DCP is higher than that of the composite without DCP. The higher E′ of the composite with DCP is believed to be due to the reactive compatibilization of PLA with PBS as reported in literature [204, 220], and possibly the coupling activity of DCP on components of the PLA-PBS-fibre-DCP system thereby aligning with the mechanical test result presented in Figure 3 and discussed in section 4.5.2. Coupling activities at the interface of the components would help to improve adhesion and might have enhanced the ability of PLA in the composites to withstand larger mechanical constraints through recoverable viscoelastic deformation.

The interfacial adhesion within the systems was further investigated from the loss factor or damping parameter (tan δ) of the samples. The tan δ of composites is largely influenced by the concentration of shear stress and viscoelastic energy dissipation [229], thereby causing the tan δ to depend largely on the interfacial adhesion between the filler and the matrix. Generally, lower tan δ values are obtained when the interfacial adhesion is high while a weak adhesion will result in higher tan δ values [229]. The tan δ plot of PLA, PLA/PBS blend containing 10 wt.% PBS, harakeke fibre reinforced PLA/PBS composite, and harakeke fibre reinforced PLA/PBS composite with DCP are illustrated in Figure 4.7b. As seen in Figure 4.7b, the tan δ value of PLA is significantly higher than the composites which is an indication of higher load bearing capacity of the composites, attributed to the presence of harakeke fibre as discussed in previous sections. Compared to the composites, the tan δ peak of the PLA/PBS blend is higher which suggests poor adhesion between PLA and PBS and is attributed to the poor miscibility of PLA and PBS (Figure 4.2) and as such confirms the incompatibility of PLA and PBS as discussed in previous sections. In addition, the improved compatibility of PLA and PBS after the addition of DCP is believed to have contributed to the decrease in tan δ of the composite with DCP, compared to the composite without DCP.

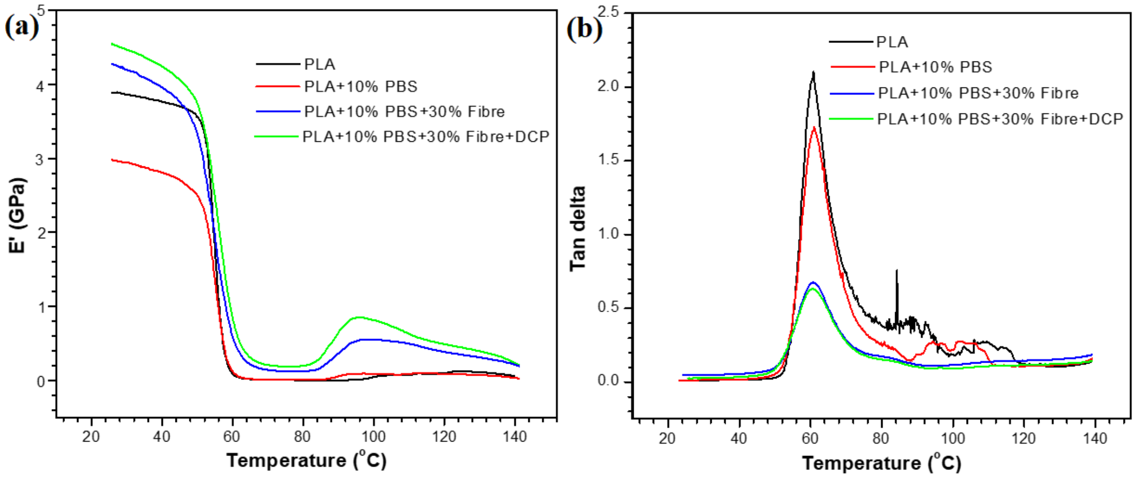


Figure 4.7 Thermomechanical properties of PLA, PLA/PBS blend, harakeke fibre reinforced PLA/PBS composite, and harakeke fibre reinforced PLA/PBS composite with DCP

4.6 Conclusions

Concurrent compatibilization and reinforcement of PLA/PBS blend were achieved. Incorporation of varying amounts of PBS in PLA to produce PLA/PBS blends resulted in reduced mechanical performance of the resulting blends due to incompatibility and poor miscibility of PLA and PBS as seen through scanning electron microscopy investigations. Addition of harakeke fibre as reinforcement in the PLA/PBS blends was not enough to raise the tensile strength of the resulting PLA-PBS composite to values above that of neat PLA. This is attributed to possible reduction in the effectiveness of harakeke fibre to reinforce the PLA-PBS blend, due to the poorly miscibility of PBS and PLA. Simultaneous reactive compatibilization and reinforcement of the PLA/PBS blends produced significant increases in the tensile strength, tensile modulus, storage modulus and crystallinity of the resulting composite. Regarding the elongation at break, the incorporation of harakeke seemed to have restricted the effective lubrication activities of PBS on the PLA chains. Whereas reactive compatibilization using DCP helped to improve the TS and TM of reinforced PLA/PBS blend, it does not seem to have had any positive impact on the toughness or elongation at break of the resulting composite. Overall, the main outcome of this study shows that PLA/PBS can be reactively compatibilized and reinforced at the same time thereby leading to the production of composites with significantly higher mechanical, thermal, and thermomechanical performance. Nevertheless, further research is recommended for exploring other compatibilizers that are more suitable for reinforced PLA/PBS blends to produce effectively reinforced, and toughened blends suitable for more diverse structural applications.

CHAPTER 5

PROPERTIES OF PLA COMPOSITES PREPARED WITH HARAKEKE FIBRE WITH DIFFERENT TREATMENTS

5.1 Chapter introduction

This chapter comprises the properties of PLA composites prepared using harakeke fibre with different treatments including chemically, mechanically, and enzymatically treated fibre. As discussed in Chapter 2, the chemical treatment of harakeke fibre produced significant improvement in the mechanical and thermal properties of PLA composites. However, in a bid to reduce the use of toxic chemicals, other routes such as mechanical processing, and enzymatic treatment of harakeke fibre were explored. Composites were prepared with these treated fibres, and their mechanical and thermal properties were evaluated and compared with neat PLA. To assess the level of significance in the difference in mechanical properties of PLA composites containing the differently treated fibres, the mechanical testing results were analyzed in the statistical software Minitab® 18. A one-way analysis of variance (ANOVA) test was performed and the significant differences among averages were calculated using Tukey's method with a 95 % of confidence.

5.2 Effect of chemically treated harakeke fibre on the mechanical properties of PLA-harakeke fibre composites

The mechanical properties of PLA, and PLA-harakeke fibre composites containing untreated (Raw), and chemically treated harakeke fibres are presented in Figure 5.1. The steps followed to produce the composites is described in Appendix A. As can be seen, the tensile strength (TS) and flexural strength (FS) of the composite prepared with the untreated fibre decreased compared to neat PLA. This is attributed to components such as lignin and hemicellulose in the untreated fibre, which are unfavourable to the mechanical properties of the fibre, and interfacial interactions in its reinforced composite [133]. Treatment of the fibre with a mixed solution of NaOH and Na_2SO_3 produced significant increase in the TS and FS of the composite. This can be attributed to the reduction of non-cellulosic components and increase in the cellulose content of the treated fibre. This helped to improve the mechanical properties of the fibre by increasing its cellulose content [133, 230], and to facilitate its processability and dispersion in the PLA matrix due to fibre separation into individual fibres, increased fibrillation, and improved stiffness. In addition, the removal of non-cellulosic components helped to increase the interfacial interactions within the composites due to the opening of cellulose hydroxyl groups to bond with the functional group of the matrix, thereby enhancing stress transfer within the composite, and improving the tensile and flexural strength of the composite [108].

In contrast to the TS and FS which decreased when the untreated fibre was compounded with PLA, the TM and FM of the PLA-harakeke fibre composites both increased regardless of whether the fibres were treated or not, which is attributed to the higher modulus of harakeke fibre, compared to PLA [224]. It is noteworthy that there is not much difference in the TM and FM of the composites regardless of whether the fibres were treated or not which suggests that the influence of the fibre on the modulus of the composite is more dependent on the modulus of the fibre, rather than fibre treatment.

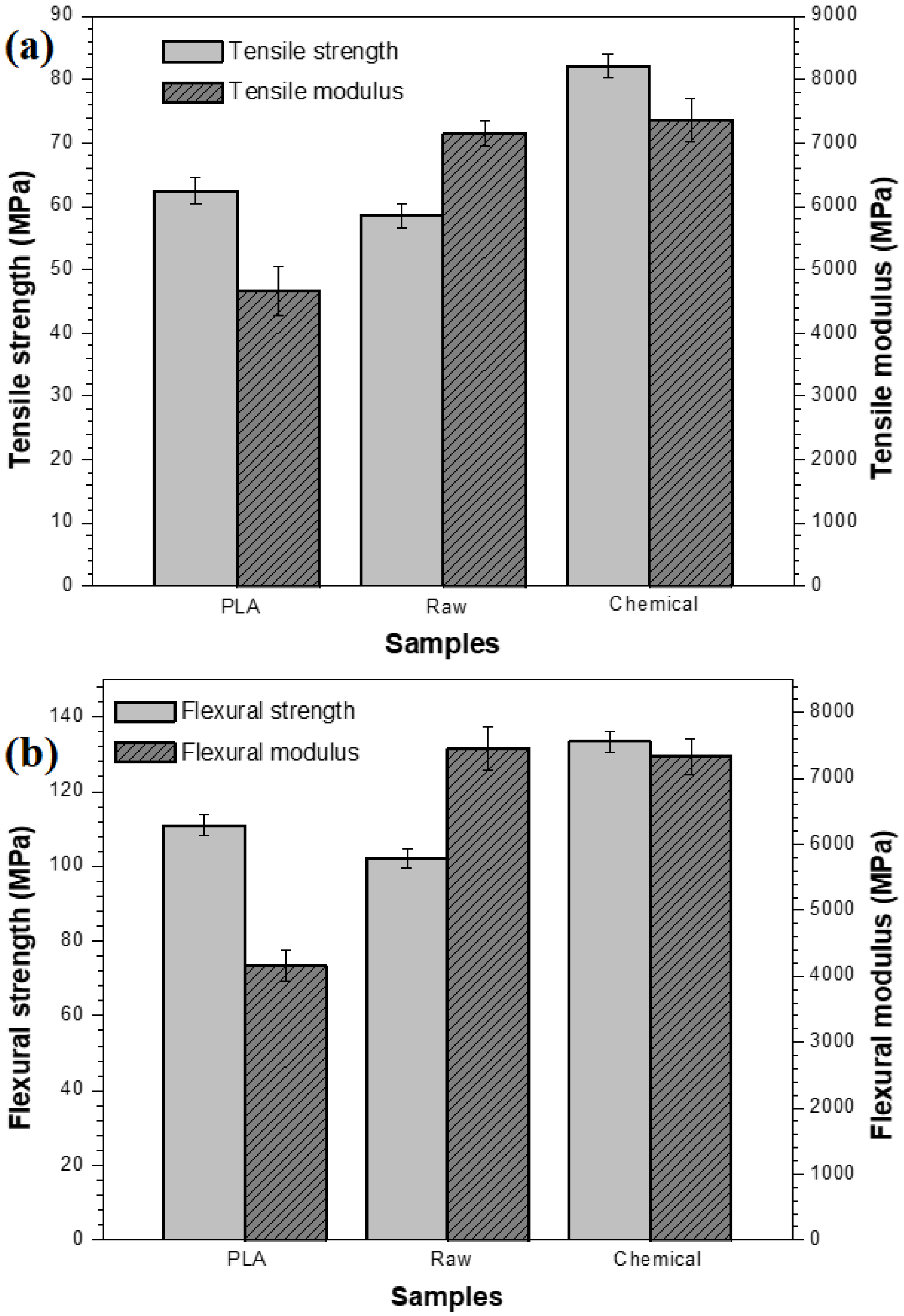


Figure 5.1 (a) Tensile, and (b) flexural properties of PLA, and PLA-harakeke fibre composites containing untreated and chemically treated harakeke fibres. The error bar represent the standard deviation of the values

5.3 Effect of mechanically processed harakeke fibre on the mechanical properties of PLA-harakeke fibre composites

The mechanical properties of PLA, and PLA-harakeke fibre composites containing untreated (Raw), and mechanically processed harakeke fibre are presented in Figure 5.2. The mechanically processed fibres were processed with the super masscolloider at different disc distance such as 200 µm, 300 µm, and 400 µm. As can be seen, the composite with fibres processed at a disc distance of 200 µm has the highest TS and FS as illustrated in Figure 5.2a and Figure 5.2b, respectively. The impoved TS and FS is attributed to the better distribution of fibres in the matrix brought about by the reduction in the number of fibre bundles [231], which helped to overcome agglomeration and stress concentration within the composite, thereby preventing premature fracture. This is supported by the optical microscopy images in Figure 3.1 and the discussion in section 3.6 about the reduction in the number of fibre bundles in the SMC processed fibres as the disc distance became smaller. In addition, the higher TS and FS of the composite prepared with the 200-µm disc distance fibres can be attributed to the fibrillation of the fibres (see Figure 3.2), which would help to improve its stiffness [224], and is believed to have supported its reinforcing ability.

The TM and FM of PLA, and PLA-harakeke fibre composites containing untreated (Raw), and mechanically processed harakeke fibre are included in Figure 5.2a and Figure 5.2b, respectively. In contrast to the TS and FS, the TM and FM of the samples decreased as the disc distance decreased from 400 to 200 µm, which suggests a gradual decrease in the modulus of the fibre as the processing cycles increases, and as the disc distance decreased.

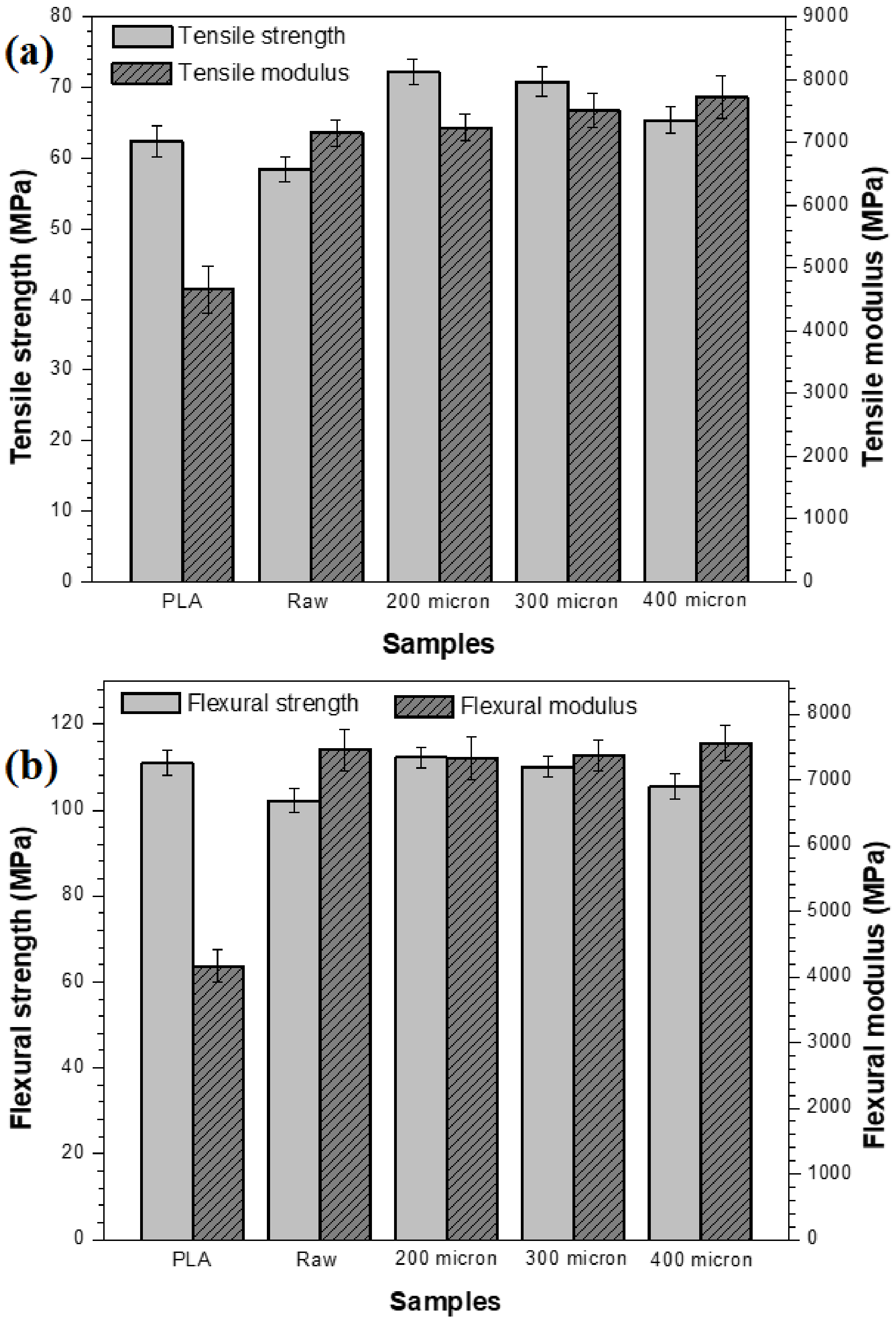


Figure 5.2 (a)Tensile, and (b) flexural properties of PLA and PLA-harakeke fibre composites containing untreated and mechanically processed harakeke fibres. The error bar represent the standard deviation of the values.

5.4 Effect of enzymatically treated harakeke fibre on the mechanical properties of PLA-harakeke fibre composites

The mechanical properties of PLA, and PLA-harakeke fibre composites containing untreated (Raw), and enzymatically treated harakeke fibre are presented in Figure 5.3. The difference between this enzymatic treatment and the combined mechanical and enzymatic treatment described in section 3.4 is that the fibres discussed here were not subjected to initial mechanical processing with the super masscolloider. In addition, instead of incubation in an incubator shaker, the treatment was performed in a controlled temperature environment and only pectinase enzyme was used instead of the combined pectinase and laccase enzyme used for the treatment described in section 3.4. As seen in Figure 5.3a and Figure 5.3b, the TS and FS of the composites increased when the enzymatically treated fibres were compounded with PLA. The fibres subjected to 2 weeks exposure to the enzymes produced composites with higher TS and FS compared to the ones subjected to 1 week exposure.

Figure 5.4 shows the SEM images of the untreated, 1-week enzymatically treated, and 2-weeks enzymatically treated harakeke fibres. As seen in the figure, the surface of the untreated fibre (Figure 5.4a) is rough, coarse, and covered with materials believed to be pectin and other waxes. In addition, the fibre appears to be in a bundle rather than as fibrils. In contrast, the surface of the 1-week treated fibre (Figure 5.4b) is smoother, and pores can be seen on the fibre surface, which is believed to be due to the degradation of pectin, which binds the fibre cellulose to the other components such as lignin and hemicellulose. As a result, the fibrils within the fibre are separated as highlighted on the image.

Compared to the fibre treated for 1 week, the surface of the 2-weeks treated fibre (Figure 5.4c) reveals several pores, and more fibrillation, which suggests that the pectinase enzymes continued their pectin degradation beyond one week of fibre treatment. This is believed to have contributed to the slight increase in TS and FS of the composite with 2 weeks treated fibre, compared to the untreated fibre composite and the composite with 1 week treated fibre.

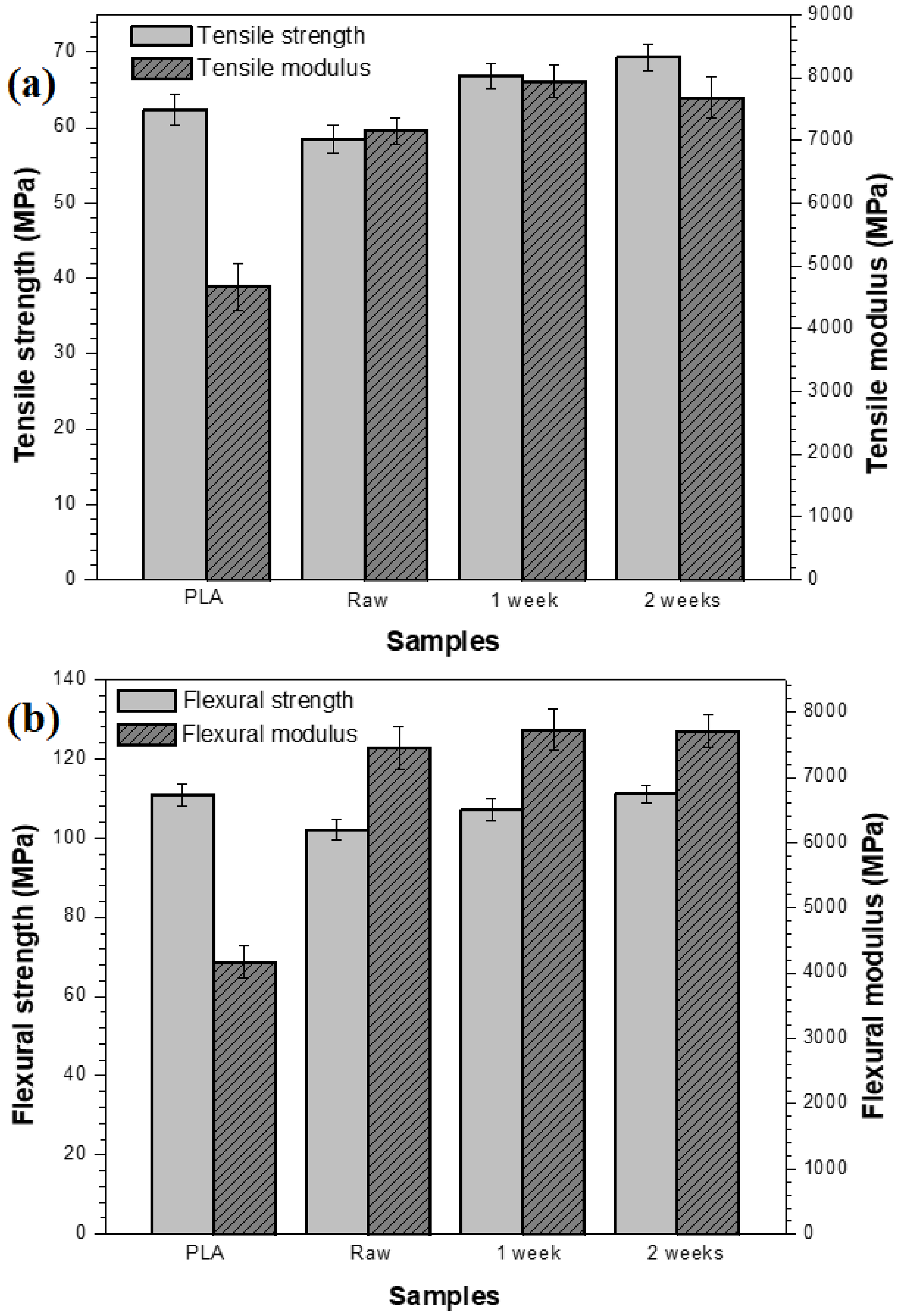


Figure 5.3 (a) Tensile, and (b) flexural properties of PLA and PLA-harakeke fibre composites containing untreated and enzymatically treated (1 week and 2 weeks) harakeke fibres. The error bar represent the standard deviation of the values.

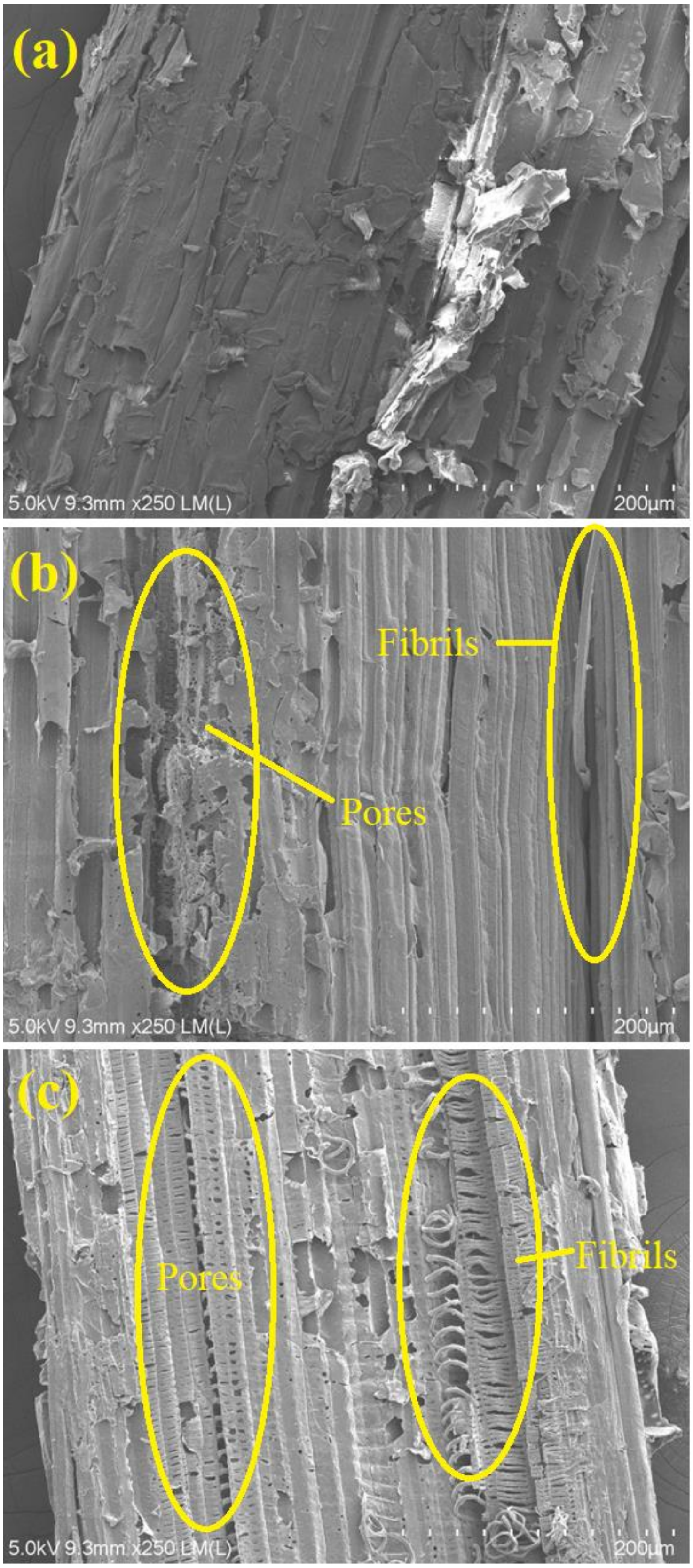


Figure 5.4 SEM images of (a) untreated harakeke fibre, and harakeke fibre treated with pectinase enzymes for (b) 1 week, and (c) 2 weeks

The TM and FM of the PLA, and PLA-harakeke fibre composites containing untreated (Raw), and enzyme treated harakeke fibre are included in Figure 5.3a, and Figure 5.3b, respectively. As seen in the images, the modulus of the composites decreased when the 2-weeks treated fibre was compounded with PLA. It is well known that excessive enzymatic action can affect the mechanical properties of fibres. Therefore, the lower TM And FM of the 2-weeks enzymatically fibre composite, compared to the 1-week treated fibre composite is attributed to possible decrease in the fibre modulus, perhaps due to the excessive fibrillation and creation of excessive number pores on the fibre surface when subjected to 2 weeks of enzymatic treatment.

Based on the results discussed in section 5.3, and section 5.4, the composite with fibres processed at 200 µm disc distance and the composite with fibres treated enzymatically for 2 weeks were selected, respectively. These were compared with the composite with chemically treated fibres, and their comparative mechanical and thermal properties are discussed in the subsequent subsections.

5.5 Mechanical properties of PLA and PLA composites containing harakeke fibre with different treatments

The mechanical properties of PLA, and PLA-harakeke fibre composites containing different treated harakeke fibres are presented in Figure 5.5. As can be seen among the composites, the chemically treated fibre composite has the highest TS and FS compared while the enzyme treated fibre composite has the highest TM and FM. The higher TS and FS of the chemically treated fibre composite is attributed to better reinforcing ability, due to the removal of non-cellulosic components from the fibre as discussed in section 2.5.1, and section 2.6.1. The removal of non-cellulosic components helped to increase the cellulose content of the fibre, improved the fibre strength, enhanced the reinforcing ability of the fibre, and improved interfacial adhesion between the fibre and PLA. These contributed to the higher TS and FS of the chemically treated fibre composite.

In contrast, the higher TM and FM of the enzymatically treated fibre composite is attributed to the higher modulus of the fibre due to the milder condition of the enzymatic treatment. The milder condition of the enzymatic treatment is believed to have helped to ensure less reduction in the fibre modulus, thereby contributing more to the TM and FM of the PLA composite compared to the chemically and mechanically treated fibres.

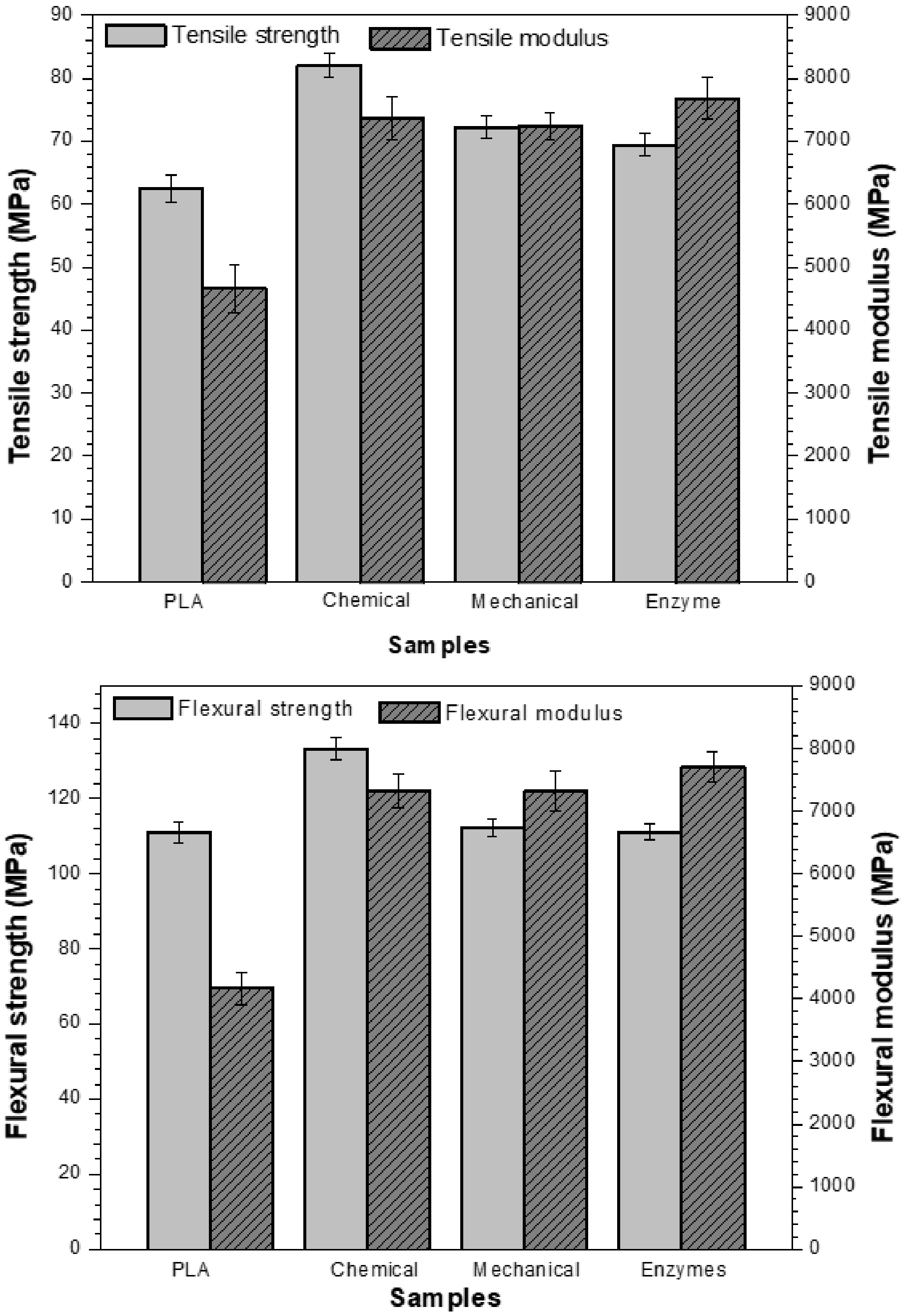


Figure 5.5 Comparison of the (a) tensile, and (b) flexural properties of PLA and PLA-harakeke fibre composites containing untreated and treated (chemical, mechanical and enzyme) harakeke fibres. The error bar represent the standard deviation of the values.

The boxplot from ANOVA of the tensile strength and flexural strength of PLA and PLA-harakeke fibre composites containing untreated and treated (chemical, mechanical and enzyme) harakeke fibres is illustrated in Figure 5.6 while the Tukey plot at 95% confidence for the samples is illustrated in Figure 5.7. In addition, the mean and mean grouping information using Tukey method and 95% confidence for the tensile strength and flexural strength of the samples are summarized in Table 5.1 and Table 5.2, respectively. Based on the Tukey method, the mean value of the samples are significantly different when the mean interval does not contain zero. The mean and mean grouping information using Tukey method and 95% confidence for the tensile strength and flexural strength of the samples are summarized in Table 5.1 and Table 5.2, respectively.

Generally, from the Tukey table, means that do not share a letter are significantly different. Therefore, the significance of the mean differences in the samples are described by the mean intervals in Figure 5.7 and the different letters in Table 5.1 and Table 5.2. Based on the data in Table 5.1, the difference in the tensile strength of the PLA composites with differently treated fibre is statistically significant which is supported by the Tukey plot in Figure 5.7a. In contrast, the data in Table 5.2 and Figure 57b indicates that there is no significant statistical difference in the Young's modulus of the composites.

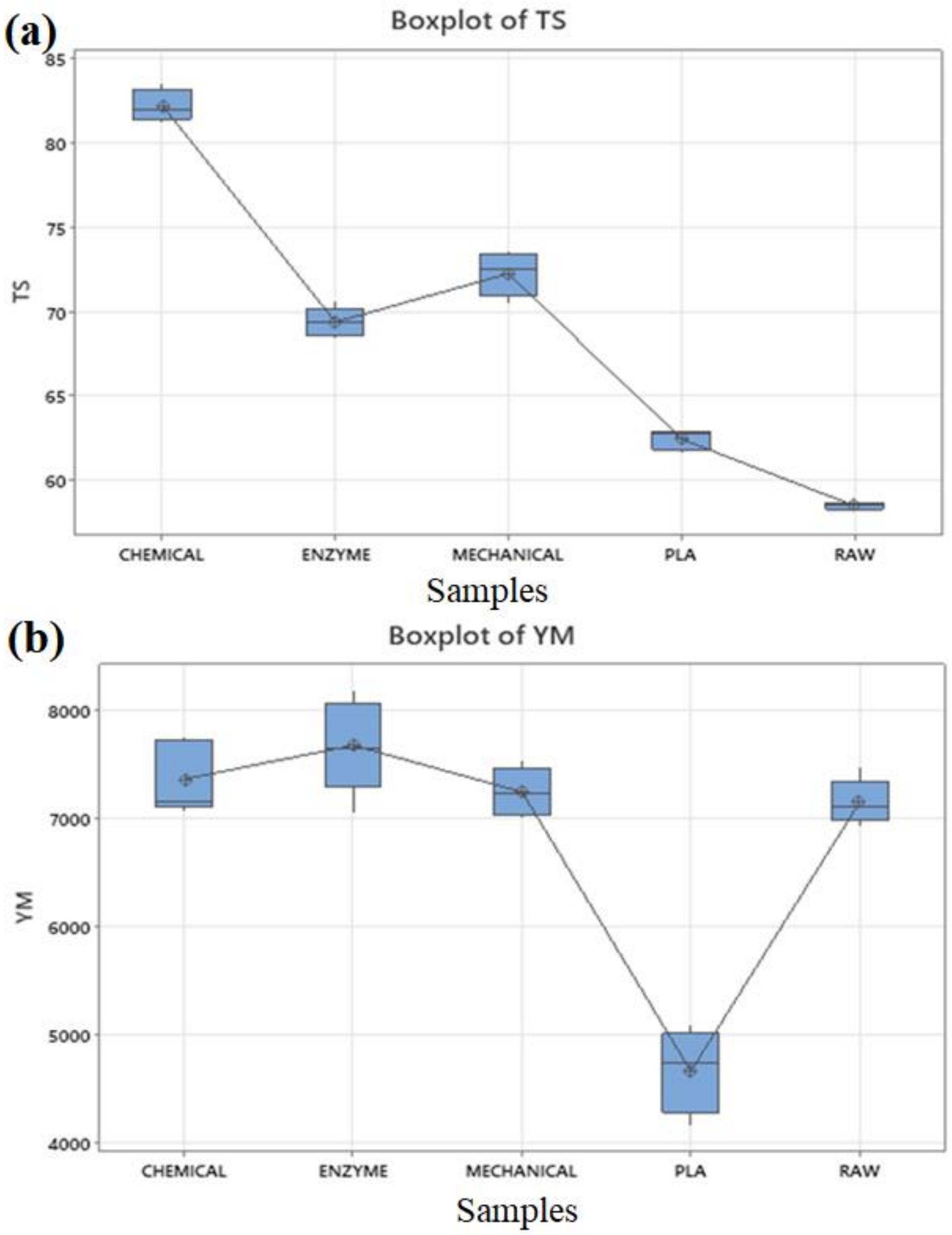


Figure 5.6 Boxplot of (a) tensile strength, and (b) Young’s modulus of PLA and PLA-harakeke fibre composites containing untreated and treated (chemical, mechanical and enzyme) harakeke fibres

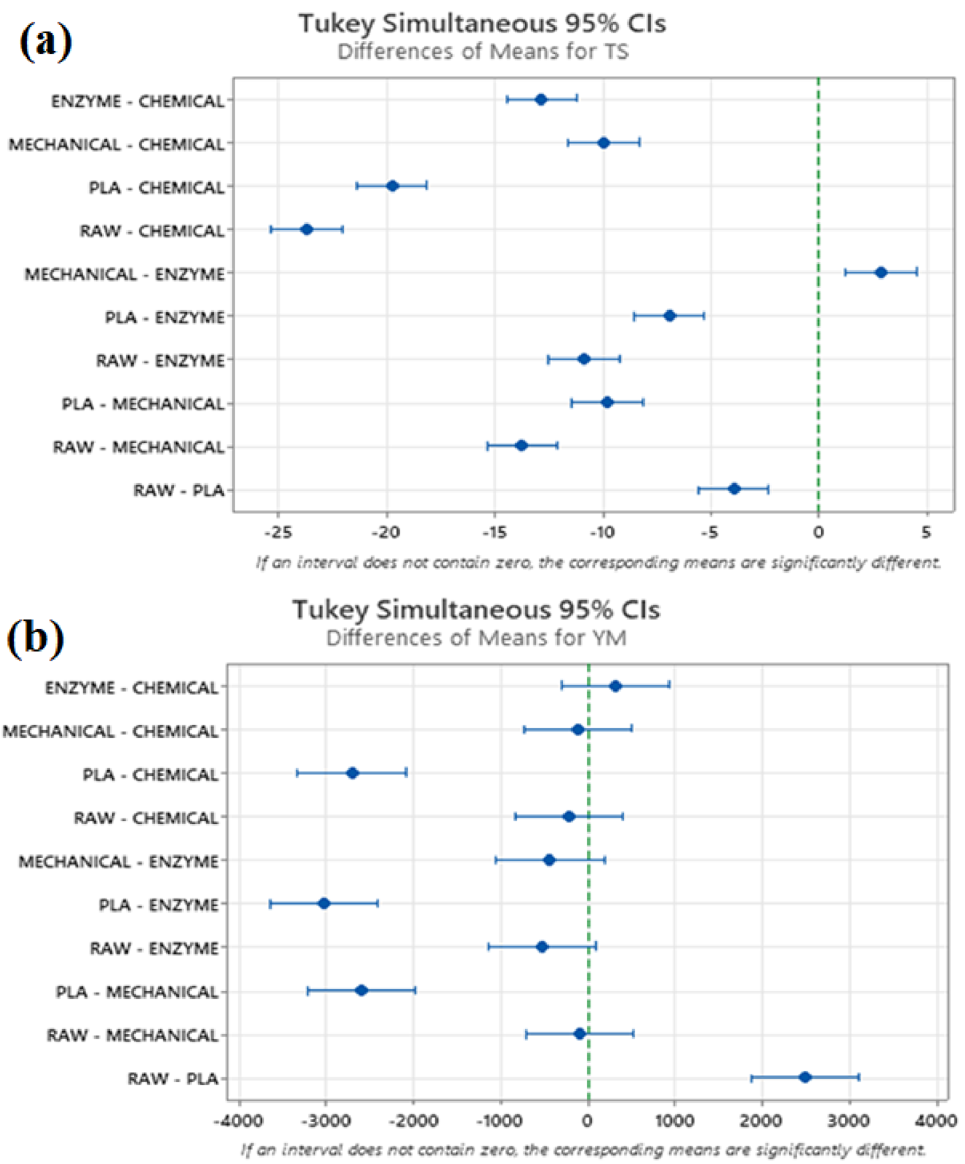


Figure 5.7 Tukey plot with 95% confidence for (a) tensile strength, and (b) Young's modulus of PLA and PLA-harakeke fibre composites containing untreated and treated (chemical, mechanical and enzyme) harakeke fibres

Table 5.1 Mean and mean grouping information using Tukey method and 95% confidence for the tensile strength PLA and PLA-harakeke fibre composites containing untreated and treated (chemical, mechanical and enzyme) harakeke fibres

Samples	**N**	**Mean**	**StDev**	**Grouping**	**95% CI**
PLA	5	62.444	0.595	D	(61.640, 63.248)
Raw	5	58.494	0.1857	E	(57.690, 59.298)
Chemical	5	82.174	0.924	A	(81.370, 82.978)
Mechanical	5	72.224	1.318	B	(71.420, 73.028)
Enzyme	5	69.362	0.855	C	(68.558, 70.166)

Table 5.2 Mean and mean grouping information using Tukey method and 95% confidence for the Young’s modulus of PLA and PLA-harakeke fibre composites containing untreated and treated (chemical, mechanical and enzyme) harakeke fibres

Samples	**N**	**Mean**	**StDev**	**Grouping**	**95% CI**
PLA	5	4662	381	B	(4357, 4967)
Raw	5	7152	211	A	(6847, 7456)
Chemical	5	7364	336	A	(7059, 7669)
Mechanical	5	7249	220	A	(6941, 7551)
Enzyme	5	7677	428	A	(7372, 7982)

5.6 Thermogravimetry properties of PLA and PLA composites containing harakeke fibre with different treatments

The TGA curves of PLA, and PLA composites containing different treated harakeke fibres are illustrated in Figure 5.8. As can be seen the TGA curves follow a similar trend. The onset of thermal degradation is above 280 °C and the drop in weight continued up to around 390 °C. The onset of thermal degradation (T_{onset}) and the thermal degradation temperature (T_d) of the samples are summarized in Table 5.3. In addition, the amount of residue remaining at $T \geq 500$ °C of the samples are included in Table 5.3. As seen in Table 5.3, the T_{onset} of the composites decreased compared to neat PLA which is believed to be due to the intact structure of the PLA molecular chains which helped to restrict initial heat penetration. The lower T_{onset} of the composites is attributed to the presence of fibres in the PLA matrix which can distort the homogeneity of the PLA chains [122], due to the creation of interfacial regions that can act as heat penetration sites [145]. In addition, the lower T_{onset} of the composites can be attributed to the lower thermal stability of the fibre, compared to neat PLA and reduction in the molecular mass of PLA [153]. As can be seen in Figure 5.8 and Table 5.3, the T_d of the composites with the chemically treated, and mechanically processed fibres increased compared to neat PLA. This is attributed to the treatment and processing of the fibre, which facilitated fibre distribution and improved interfacial interaction within the composite thereby restricting thermal degradation. In contrast to the chemically and mechanically treated fibre composites, the T_d of the enzymatically treated fibre composite decreased. As stated earlier, only pectinase enzyme was used to treat the fibre discussed in this section and pectinase mainly facilitates the removal of pectin, but it is non-active towards removal of lignin and hemicellulose. So, the lower T_d of the composite with enzymatically treated fibre is attributed to the less thermally stable components such as lignin and hemicellulose in the fibre, which accelerated thermal degradation in the composite.

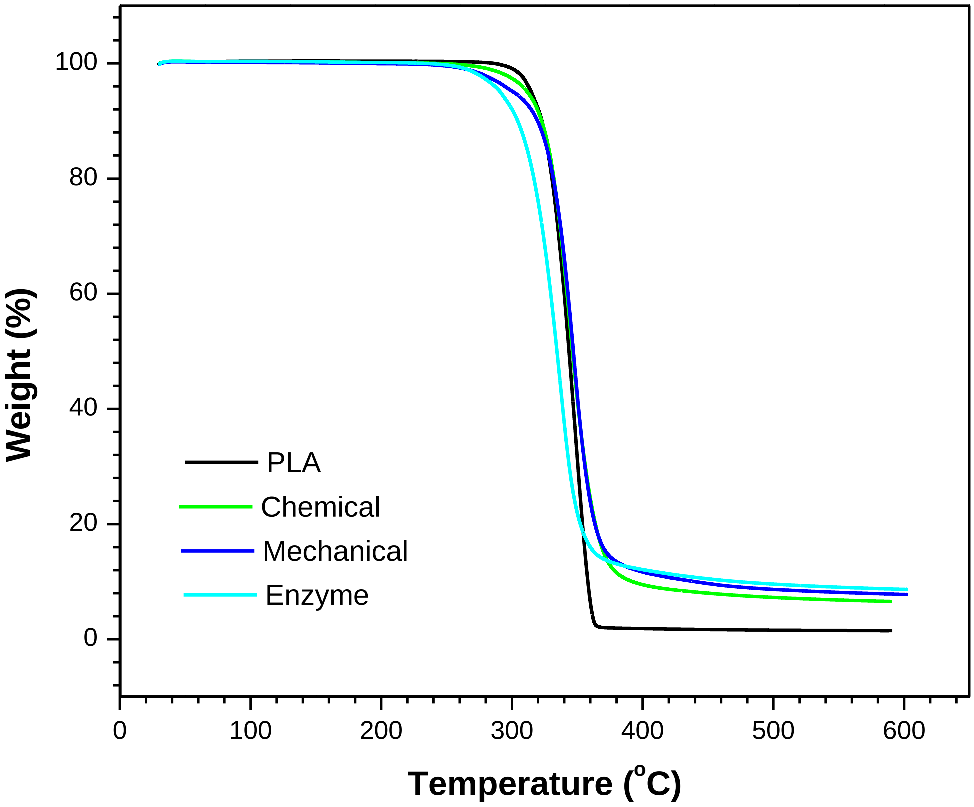


Figure 5.8 TGA curves of PLA and PLA-harakeke fibre composites with different treated harakeke fibres

Table 5.3 TGA paramemters of PLA and PLA-harakeke fibre composites with different treated harakeke fibres

Sample code	**T_{onset} (°C)**	**T_d (°C)**	**Residue (%) at T ≥ 500 °C**
PLA	314.83	350.14	1.58
Chemical	311.74	355.52	7.23
Mechanical	301.04	355.23	8.62
Enzyme	291.02	343.23	9.54

5.7 Differential scanning calorimetric properties of PLA and PLA composites containing harakeke fibre with different treatments

The DSC thermograms of PLA and PLA composites containing different treated harakeke fibres are shown in Figure 5.9. Three successively distinct transitions can be seen in the figure, which represents the glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m). The DSC parameters of the samples were obtained from the thermograms, and the parameters are summarized in Table 5. It is evident in Figure 5.9 that the T_g of PLA was not significantly influenced by the inclusion of harakeke fibre. In contrast, the T_c of PLA in the composites can be seen to be notably influenced by the fibre.

The addition of reinforcing fillers into semi crystalline polymers is known to result in an upward or downward shift in the T_c, and the extent of shift often describes the ability of fillers to induce heterogeneous nucleation in the matrix [165]. The T_c of the samples presented in Figure 5.9 shows a downward shift in T_c of PLA in the composite with the chemically treated fibre. This is an indication of faster crystallization in the composite [166], due to heterogeneous nucleation on the chemically treated harakeke fibre which created more crystallization sites for the PLA molecules. As for the other composites, the upward shift in the T_c compared to neat PLA is an indication of slower crystallization within the composite possibly due to the suppressed occurrence of heterogeneous nucleation emanating from low interfacial interactions within these composites.

The split in the melting peak (T_m) of the samples is attributed to the formation of both perfect and imperfect crystals in the samples due to the heterogeneous nucleation activities within the samples. The effect of fibre treatment on the crystallization behaviour of PLA was further investigated through the calculation of the crystallinity index described by Equation 4.1. The crystallinity index ($X_{DSC}\%$) of PLA and the composites are included in Table 5.4, which confirms the significant influence of fibre inclusion, on the crystallinity index of PLA. Compared to neat PLA, the crystallinity index of all the composites increased regardless of the type of fibre treatment which indicates that harakeke fibre can act as a nucleating agent to accelerate the crystallization of PLA. As seen in Table 5.4, the crystallinity index was higher in the chemically treated fibre composite than the other composites. This indicates that the increased interfacial interaction between PLA and treated harakeke fibres could further help the fibre surface to act as nucleation sites for PLA crystallization.

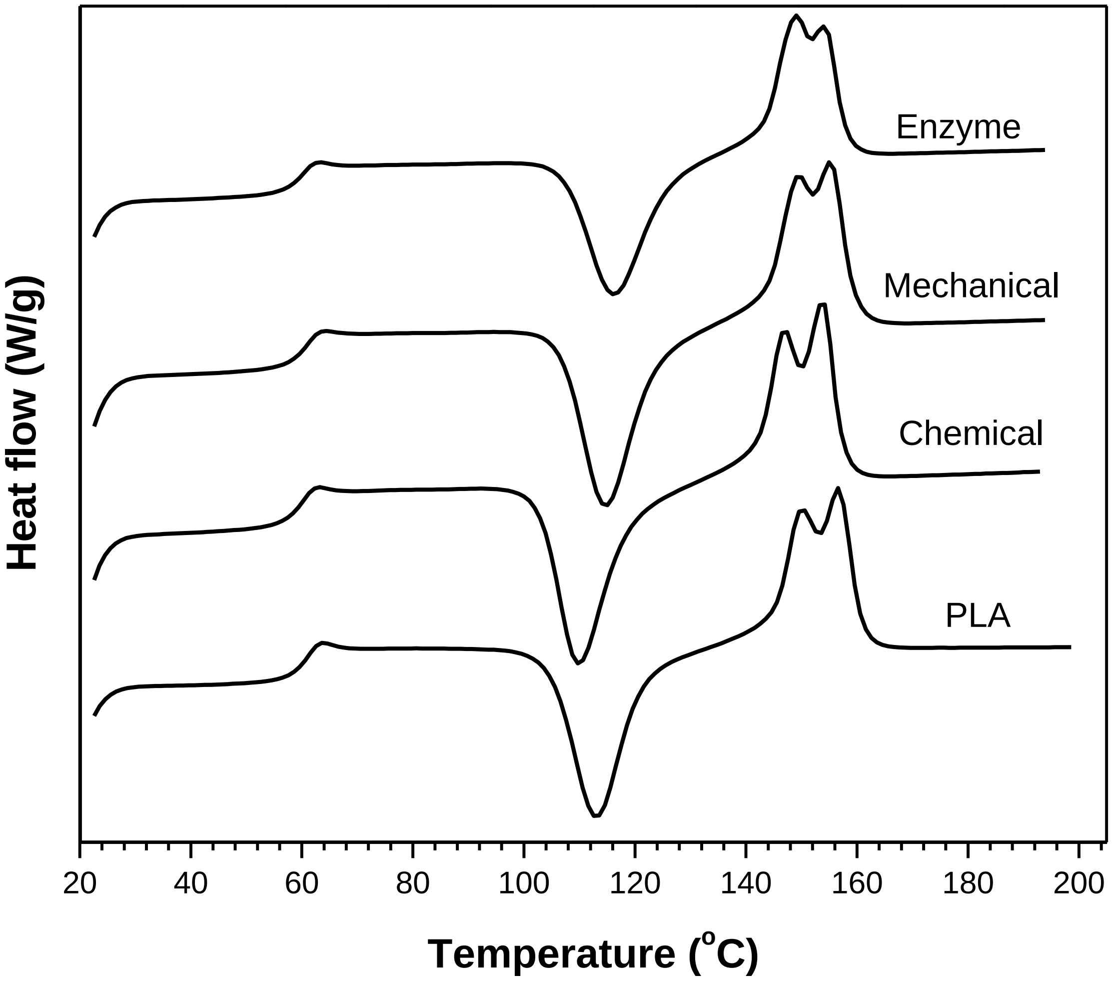


Figure 5.9 DSC diffractograms of PLA and PLA-harakeke fibre composites containing different treated harakeke fibres

Table 5.4 DSC parameters of PLA and PLA-harakeke composites containing different treated harakeke fibres

Sample code	**T_g (°C)**	**T_c (°C)**	**T_m (°C)**	**X_{DSC} (%)**
PLA	63.80	113.12	156.65	29.41
Chemical	64.63	111.14	158.19	35.40
Mechanical	65.45	117.32	158.97	36.07
Enzyme	64.32	118.63	158.48	36.26

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Chapter introduction

This chapter presents the conclusions from the findings in this thesis.

6.2 Conclusions

Composites were prepared through extrusion of PLA and harakeke fibre and test samples were prepared through injection moulding. To modify the fibre properties and to improve the composite properties, three different approaches were used to modify the fibre such as chemical, mechanical, and enzymatic treatments.

Chemical treatment of harakeke fibre was performed through combined digestion and bleaching, and these helped to reduce the amount of non-cellulosic components such as lignin and hemicellulose in the fibre. Compared to digestion alone, combined digestion and bleaching treatment removed larger amount of non-cellulosic components from the fibre, and therefore higher cellulose content. The thermal stability of the chemically treated fibre was notably increased, as confirmed through thermal analysis, and was attributed to the removal of non-cellulosic components which are responsible for poor thermal stability of the fibre, as well as increased stability of the intermolecular cellulose hydrogen bonding. Chemical treatment of the fibre increased the composite's tensile strength from 62±1.02 MPa to 82±0.98 MPa at 30 wt.% fibre content. This was believed to be due to the reduction of non-cellulosic components like lignin and hemicellulose which facilitated intermolecular cellulose bonding in the fibre. So, cellulose, being the main determinant of the fibre strength helped to improve the mechanical properties and reinforcing ability of the fibre. In addition, removal on the non-cellulosic components helped to increase interfacial interactions and stress transfer within the composite because the cellulose hydroxy groups became more available to bond with the functional groups of the PLA matrix. The tensile and flexural performance suggests that harakeke fibre is a promising reinforcement for PLA to produce high performance composites suitable for structural applications.

In addition, mechanical processing of harakeke fibre was performed using a super masscolloider with different disc separation distances such as 200 µm, 300 µm, and 400 µm. It was found that the super masscolloider was able to refine the fibre and produce unitary fibres from harakeke. Composites were prepared by incorporating these fibres in PLA and it was found that the composite with fibres processed at a disc distance of 200 µm had the highest TS and FS due to the reduction in fibre bundles, and fibrillation of the fibres which is believed to have helped to improve its stiffness and facilitated its reinforcing ability as a result of the reduced tendency to fracture, and reduced agglomeration of fibre.

Enzymatic treatment of harakeke fibre was also performed, using pectinase for 1 and 2 weeks. It was found that 2 weeks of enzymatic treatment resulted in fibres that produced reinforced PLA composites with higher TS and FS compared to the ones treated for 1 week. This is attributed to the degradation of larger amount of pectin which opened more pores on the fibre for mechanical interlocking with the PLA matrix which was supported by SEM observation.

Combined mechanical processing using a super masscolloider, followed by enzymatic treatment was also explored to extract fibres from harakeke. Optical microscopy revealed that mechanical processing with the super masscolloider was able to refine the fibre and produce unitary fibres from harakeke. In addition, the removal of non-cellulosic components was achieved to different extents when enzymes were used to modify the mechanically processed fibre. Thermal analysis showed that the thermal stability of the fibres treated with both mechanical and enzymatic treatments is higher than the ones that were only mechanically processed which is assumed to be due to reduced amount of non-cellulosic components. The pectinase enzyme helped to remove pectin from the fibre, thereby facilitating fibre separation from bundles into individual fibres. In contrast, combination of laccase and pectinase enzymes removed more non-cellulosic components from harakeke fibre compared to when the pectinase enzyme was used alone. This was attributed to the further removal of lignin by the laccase enzyme, compared to the disruption of pectin structure, which was mainly achieved when the pectinase enzyme was used alone. The combination of mechanical processing and enzymatic treatment of harakeke fibre demonstrates that large scale environmentally friendly and good quality fibres, suitable for composites can be produced. Notably, large volume of fibre can be processed using the super masscolloider, with the total avoidance of organic chemical since only water is required for processing, and the fibre quality can be improved through removal of non-cellulosic components by enzymes.

Generally, it was found that treatment of harakeke fibre helped to improve the strength and Young's modulus of its reinforced PLA composites. In a bid to improve the elongation at break of PLA-harakeke fibre composites, polybutylene succinate (PBS) was first blended with PLA, and reactive compatibilization of the reinforced of PLA/PBS blend was performed using dicumyl peroxide (DCP). Initially, the incorporation of up to 10 wt.% PBS in PLA increased the elongation at break but decreased the tensile strength and Young's modulus of the resulting blends. The reduction in strength and Young's modulus of the blends were believed to be due to incompatibility and poor miscibility of PLA and PBS as seen through scanning electron microscopy investigations. Through reactive compatibilization, TS and TM of the DCP compatibilized harakeke reinforced PLA/PBS blend increased by 21% and 107%, respectively but did not have positive impacts on the elongation at break of the composite. This was attributed to restricted lubrication of PLA molecular chains by PBS in the PLA-harakeke fibre composite. Overall, the main results from the study showed that PLA/PBS can be reactively compatibilized and reinforced at the same time thereby leading to the production of composites with significantly higher mechanical, thermal, and thermomechanical performance than composites that were not compatibilized.

Overall, comparing the effects of the different treatments covered, composites with chemically treated fibre were found to have the highest tensile and flexural strength while the composites with the enzymatically treated fibre had the highest tensile and flexural modulus. The higher TS and FS of the chemically treated fibre composites was attributed to the better reinforcing ability of the chemically treated fibre, due to the removal of non-cellulosic components from the fibre which resulted in improved interfacial interactions within the composite. On the other hand, the higher TM and FM of the enzymatically treated fibre composites was attributed to the milder condition of the enzymatic treatment which was believed to have helped to ensure less reduction in the fibre's Young's modulus, thereby contributing more to the TM and FM of the PLA composite compared to the chemically and mechanically treated fibres. Thermal analysis showed that the less thermally stable components such as lignin and hemicellulose in the fibres lowered the degradation temperature of the composites.

6.3 Recommendations for future studies

Based on the results presented in this thesis, it is recommended that treatment of harakeke fibre using a combination of different enzymes should be further explored for the removal of lignin, pectin, and hemicellulose from the fibre. This could help to increase the cellulose content of the fibre, improve the fibre distribution in matrices through increased compatibility, and enhance the reinforcing ability of the fibre when used in composites. To facilitate large scale extraction of fibres from harakeke, a combination of mechanical processing and enzymatic treatment should be further explored.

It is also recommended that subsequent studies should focus on increasing the fibre content in PLA-harakeke fibre composites and exploring different coupling additives to extend the use of harakeke fibre reinforced composites in more diverse structural applications.

In this thesis, the study on reactive compatibilization of reinforced PLA-PBS blends showed that composites with significantly improved mechanical, thermal, and thermomechanical performance can be developed. However, the use of PBS did not improve the elongation at break of reinforced PLA composites. So, further research is recommended for exploring other rubbery additives that can help to improve the toughness and elongation at break of reinforced PLA without causing significant decreases in the tensile strength and Young's modulus of its composites. In addition, it is recommended that DSC analysis of PLA/PBS blends in future studies should extend to sub ambient temperature to reach the glass transition temperature of PBS. Furthermore, an in-depth study of the Fox equation to better explain the miscibility of PLA and PBS and how the T_g of neat PLA was altered by the presence of PBS.

REFERENCES

[1] Thomas S, Paul S, Pothan L, Deepa B. Natural fibres: structure, properties and applications. Cellulose Fibers: Bio-and Nano-Polymer Composites: Green Chemistry and Technology. 2011:3-42.

[2] Rowell R. Natural fibres: types and properties. Properties and performance of natural-fibre composites: Elsevier; 2008. p. 3-66.

[3] Asyraf MRM, Syamsir A, Zahari NM, Supian ABM, Ishak MR, Sapuan SM, et al. Product development of natural fibre-composites for various applications: Design for sustainability. Polymers. 2022;14(5):920.

[4] Prakash SO, Sahu P, Madhan M, Johnson Santhosh A. A Review on Natural Fibre-Reinforced Biopolymer Composites: Properties and Applications. International Journal of Polymer Science. 2022;2022(1):7820731.

[5] Ali M. Natural fibres as construction materials. Materials and Technologies (NOCMAT 2009). 2009;6:9.

[6] Oladele IO, Omotosho TF, Adediran AA. Polymer-based composites: an indispensable material for present and future applications. International Journal of Polymer Science. 2020;2020(1):8834518.

[7] Tamošaitienė J, Parham S, Sarvari H, Chan DW, Edwards DJ. A Review of the Application of Synthetic and Natural Polymers as Construction and Building Materials for Achieving Sustainable Construction. Buildings. 2024;14(8):2569.

[8] Jose J, Al-Harthi MA, AlMa'adeed MA-A, Bhadra Dakua J, De SK. Effect of graphene loading on thermomechanical properties of poly(vinyl alcohol)/starch blend. Journal of Applied Polymer Science. 2015;132(16).

[9] Pappu A, Patil V, Jain S, Mahindrakar A, Haque R, Thakur VKJIjobm. Advances in industrial prospective of cellulosic macromolecules enriched banana biofibre resources: A review. 2015;79:449-58.

[10] Rangappa SM, Siengchin S, Dhakal HN. Green-composites: Ecofriendly and sustainability. Applied Science and Engineering Progress. 2020;13(3):183-4.

[11] Beg MDH, Islam MR, Mamun AA, Heim H-P, Feldmann M, Akindoyo JO. Characterization of polyamide 6.10 composites incorporated with microcrystalline cellulose fiber: Effects of fiber loading and impact modifier. Advances in Polymer Technology. 2018;37(8):3412-20.

[12] Mallick PK. Fiber-reinforced composites: materials, manufacturing, and design: CRC press; 2007.

[13] George A, Sanjay M, Srisuk R, Parameswaranpillai J, Siengchin S. A comprehensive review on chemical properties and applications of biopolymers and their composites. International journal of biological macromolecules. 2020;154:329-38.

[14] Jamshidian M, Tehrany EA, Imran M, Jacquot M, Desobry S. Poly-Lactic Acid: production, applications, nanocomposites, and release studies. Comprehensive reviews in food science and food safety. 2010;9(5):552-71.

[15] Rasal RM, Janorkar AV, Hirt DE. Poly (lactic acid) modifications. Progress in polymer science. 2010;35(3):338-56.

[16] Lim L-T, Auras R, Rubino M. Processing technologies for poly (lactic acid). Progress in polymer science. 2008;33(8):820-52.

[17] Nagarajan V, Mohanty AK, Misra M. Perspective on polylactic acid (PLA) based sustainable materials for durable applications: Focus on toughness and heat resistance. ACS Sustainable Chemistry & Engineering. 2016;4(6):2899-916.

[18] Chen Y, Geever LM, Killion JA, Lyons JG, Higginbotham CL, Devine DM. Review of multifarious applications of poly (lactic acid). Polymer-Plastics Technology and Engineering. 2016;55(10):1057-75.

[19] Ferreira F, Dufresne A, Pinheiro I, Souza D, Gouveia R, Mei L, et al. How do cellulose nanocrystals affect the overall properties of biodegradable polymer nanocomposites: A comprehensive review. European polymer journal. 2018;108:274-85.

[20] Jaszkiewicz A, Meljon A, Bledzki A. Mechanical and thermomechanical properties of PLA/Man-made cellulose green composites modified with functional chain extenders—A comprehensive study. Polymer Composites. 2018;39(5):1716-23.

[21] Wang G, Zhang D, Li B, Wan G, Zhao G, Zhang A. Strong and thermal-resistance glass fiber-reinforced polylactic acid (PLA) composites enabled by heat treatment. International journal of biological macromolecules. 2019;129:448-59.

[22] Wang G, Zhang D, Wan G, Li B, Zhao G. Glass fiber reinforced PLA composite with enhanced mechanical properties, thermal behavior, and foaming ability. Polymer. 2019;181:121803.

[23] Hamad K, Kaseem M, Ayyoob M, Joo J, Deri F. Polylactic acid blends: The future of green, light and tough. Progress in Polymer Science. 2018;85:83-127.

[24] Akindoyo JO, Beg MDH, Ghazali S, Heim HP, Feldmann M. Impact modified PLA-hydroxyapatite composites – Thermo-mechanical properties. Composites Part A: Applied Science and Manufacturing. 2018;107:326-33.

[25] Scaffaro R, Maio A, Gulino EF, Megna B. Structure-property relationship of PLA-Opuntia Ficus Indica biocomposites. Composites Part B: Engineering. 2019;167:199-206.

[26] Farah S, Anderson DG, Langer R. Physical and mechanical properties of PLA, and their functions in widespread applications—A comprehensive review. Advanced drug delivery reviews. 2016;107:367-92.

[27] Natureworksllc. Building and Construction. https://www.natureworksllc.com/Ingeo-in-Use/Building-and-Construction: NatureWorks.

[28] Natureworksllc. Ingeo In Use. https://www.natureworksllc.com/Ingeo-in-Use/Electronics-and-Appliances NatureWorks.

[29] Gantri. Plant Polymers. https://www.gantri.com/materials Gantri.

[30] Eco-friendly Decorative Materials: Turning Nature into Living Space. https://www.lxhausys.com/business/index.jsp?cid=22

[31] Sumrith N, Techawinyutham L, Sanjay MR, Dangtungee R, Siengchin S. Characterization of Alkaline and Silane Treated Fibers of 'Water Hyacinth Plants' and Reinforcement of 'Water Hyacinth Fibers' with Bioepoxy to Develop Fully Biobased Sustainable Ecofriendly Composites. Journal of Polymers and the Environment. 2020;28(10):2749-60.

[32] Vinod A, Sanjay M, Suchart S, Jyotishkumar P. Renewable and sustainable biobased materials: An assessment on biofibers, biofilms, biopolymers and biocomposites. Journal of Cleaner Production. 2020;258:120978.

[33] Pervaiz M, Sain MM. Carbon storage potential in natural fiber composites. Resources, conservation and Recycling. 2003;39(4):325-40.

[34] Madhu P, Sanjay M, Senthamaraikannan P, Pradeep S, Saravanakumar S, Yogesha B. A review on synthesis and characterization of commercially available natural fibers: Part-I. Journal of Natural Fibers. 2018.

[35] Madhu P, Sanjay M, Senthamaraikannan P, Pradeep S, Saravanakumar S, Yogesha B. A review on synthesis and characterization of commercially available natural fibers: Part II. Journal of Natural Fibers. 2019;16(1):25-36.

[36] Hammajam AA, El-Jummah AM, Ismarrubie ZN. The green composites: Millet Husk Fiber (MHF) filled Poly Lactic Acid (PLA) and degradability effects on environment. Open Journal of Composite Materials. 2019;9(03):300.

[37] Indran S, Raj RE. Characterization of new natural cellulosic fiber from Cissus quadrangularis stem. Carbohydrate polymers. 2015;117:392-9.

[38] Akindoyo JO, Beg MDH, Ghazali SB, Islam MR, Mamun AA. Preparation and Characterization of Poly(lactic acid)-Based Composites Reinforced with Poly Dimethyl Siloxane/Ultrasound-Treated Oil Palm Empty Fruit Bunch. Polymer-Plastics Technology and Engineering. 2015;54(13):1321-33.

[39] Jorfi M, Foster EJ. Recent advances in nanocellulose for biomedical applications. Journal of Applied Polymer Science. 2015;132(14).

[40] Xu S, Yu W, Yao X, Zhang Q, Fu Q. Nanocellulose-assisted dispersion of graphene to fabricate poly(vinyl alcohol)/graphene nanocomposite for humidity sensing. Composites Science and Technology. 2016;131:67-76.

[41] Akindoyo JO, Ismail NH, Mariatti M. Performance of poly (vinyl alcohol) nanocomposite reinforced with hybrid TEMPO mediated cellulose-graphene filler. Polymer Testing. 2019;80:106140.

[42] Roohani M, Habibi Y, Belgacem NM, Ebrahim G, Karimi AN, Dufresne A. Cellulose whiskers reinforced polyvinyl alcohol copolymers nanocomposites. European Polymer Journal. 2008;44(8):2489-98.

[43] Kargarzadeh H, Mariano M, Gopakumar D, Ahmad I, Thomas S, Dufresne A, et al. Advances in cellulose nanomaterials. Cellulose. 2018;25(4):2151-89.

[44] Scheeles S. Safeguarding indigenous knowledge and access to plant resources through partnership: A New Zealand perspective. International Journal of Rural Law and Policy. 2015(2):1-9.

[45] Lowe B, Carr D, McCallum R, Myers T, Niven B, Cameron R, et al. Identifying harakeke (Phormium tenax) cultivars using whītau and fibre aggregate properties. Natural fibres in Australasia: proceedings of the combined (NZ and AUS) conference of the Textile Institute, Dunedin2009. p. 15-7.

[46] Hector J. Phormium tenax as a fibrous plant: Government Printer, South Africa; 1889.

[47] Wehi PM, Clarkson BD. Biological flora of New Zealand 10. Phormium tenax, harakeke, New Zealand flax. New Zealand Journal of Botany. 2007;45(4):521-44.

[48] Duchemin B, Staiger MP. Treatment of Harakeke fiber for biocomposites. Journal of applied polymer science. 2009;112(5):2710-5.

[49] De Rosa IM, Kenny JM, Puglia D, Santulli C, Sarasini F. Tensile behavior of New Zealand flax (Phormium tenax) fibers. Journal of Reinforced Plastics and Composites. 2010;29(23):3450-4.

[50] Jayaraman K, Halliwell R. Harakeke (phormium tenax) fibre–waste plastics blend composites processed by screwless extrusion. Composites Part B: Engineering. 2009;40(7):645-9.

[51] Best E. The Whare Kohonga (the" nest House") and Its Lore, Comprising Data Pertaining to Procreation, Baptism, and Infant Betrothal, &c., Contributed by Members of the Ngali-Kahungunu Tribe of the North Island of New Zealand: Government Printer, South Africa; 1975.

[52] Colenso W. On the geographic and economic botany of the North Island of New Zealand. Transactions of the New Zealand Institute1868. p. 233-83.

[53] Best E. Forest lore of the Maori. Dominion Museum Bulletin, no. 14. Government Printer Wellington, New Zealand; 1942.

[54] Brooker SG, Cambie RC, Cooper RC. New Zealand medicinal plants: Heinemann; 1987.

[55] Newman RH, Clauss EC, Carpenter JEP, Thumm A. Epoxy composites reinforced with deacetylated Phormium tenax leaf fibres. Composites Part A: Applied Science and Manufacturing. 2007;38(10):2164-70.

[56] Riley M. Harakeke: New Zealand Flax: an historical perspective and overview of current research into future use. 2004.

[57] Brethauer S, Shahab RL, Studer MH. Impacts of biofilms on the conversion of cellulose. Applied microbiology and biotechnology. 2020;104:5201-12.

[58] Daniels V. Factors affecting the deterioration of the cellulosic fibres in black-dyed New Zealand flax (Phormium tenax). Studies in conservation. 1999;44(2):73-85.

[59] Mwaikambo L. Review of the history, properties and application of plant fibres. African Journal of Science and Technology. 2006;7(2):121.

[60] John MJ, Thomas S. Biofibres and biocomposites. Carbohydrate polymers. 2008;71(3):343-64.

[61] Mishra S, Mohanty AK, Drzal LT, Misra M, Hinrichsen G. A review on pineapple leaf fibers, sisal fibers and their biocomposites. Macromolecular Materials and Engineering. 2004;289(11):955-74.

[62] Furtado F, Flores-Sahagun T, Franco TS. Analysis of Polymeric Composites of Phormium Tenax. Biointerface Research in Applied Chemistry. 2022;13(2):1-16.

[63] Fortunati E, Puglia D, Monti M, Peponi L, Santulli C, Kenny J, et al. Extraction of cellulose nanocrystals from Phormium tenax fibres. Journal of Polymers and the Environment. 2013;21:319-28.

[64] Mwaikambo LY, Ansell MP. Mechanical properties of alkali treated plant fibres and their potential as reinforcement materials II. Sisal fibres. Journal of materials science. 2006;41:2497-508.

[65] De Rosa IM, Iannoni A, Kenny JM, Puglia D, Santulli C, Sarasini F, et al. Poly (lactic acid)/Phormium tenax composites: Morphology and thermo-mechanical behavior. Polymer Composites. 2011;32(9):1362-8.

[66] Cruthers NM, Carr DJ, Laing RM, Niven BE. Structural differences among fibers from six cultivars of harakeke (Phormium tenax, New Zealand flax). Textile research journal. 2006;76(8):601-6.

[67] Newman RH, Clauss EC, Carpenter JE, Thumm A. Epoxy composites reinforced with deacetylated Phormium tenax leaf fibres. Composites Part A: Applied Science and Manufacturing. 2007;38(10):2164-70.

[68] Le Guen MJ, Newman RH. Pulped Phormium tenax leaf fibres as reinforcement for epoxy composites. Composites Part A: Applied Science and Manufacturing. 2007;38(10):2109-15.

[69] Krause Sammartino L, Aranguren MI, Reboredo MM. Chemical and mechanical characterization of two South-American plant fibers for polymer reinforcement: Caranday Palm and Phormium. Journal of applied polymer science. 2010;115(4):2236-45.

[70] De Rosa IM, Santulli C, Sarasini F. Mechanical and thermal characterization of epoxy composites reinforced with random and quasi-unidirectional untreated Phormium tenax leaf fibers. Materials & Design (1980-2015). 2010;31(5):2397-405.

[71] Ba L, El Abbassi I, Ngo T-T, Pliya P, Kane CSE, Darcherif A-M, et al. Experimental Investigation of Thermal and Mechanical Properties of Clay Reinforced with Typha australis: Influence of Length and Percentage of Fibers. Waste and Biomass Valorization. 2021;12(5):2723-37.

[72] Panyakaew S, Fotios S. New thermal insulation boards made from coconut husk and bagasse. Energy and buildings. 2011;43(7):1732-9.

[73] Akindoyo JO, Beg MDH, Ghazali S, Heim HP, Feldmann M. Effects of surface modification on dispersion, mechanical, thermal and dynamic mechanical properties of injection molded PLA-hydroxyapatite composites. Composites Part A: Applied Science and Manufacturing. 2017;103:96-105.

[74] McKay I, Vargas J, Yang L, Felfel RM. A review of natural fibres and biopolymer composites: progress, limitations, and enhancement strategies. Materials. 2024;17(19):4878.

[75] Joseph P, Rabello MS, Mattoso L, Joseph K, Thomas S. Environmental effects on the degradation behaviour of sisal fibre reinforced polypropylene composites. composites science and technology. 2002;62(10-11):1357-72.

[76] Mahzan S, Fitri M, Zaleha M. UV radiation effect towards mechanical properties of Natural Fibre Reinforced Composite material: A Review. IOP conference series: materials science and engineering: IOP Publishing; 2017. p. 012021.

[77] Azwa Z, Yousif B, Manalo A, Karunasena W. A review on the degradability of polymeric composites based on natural fibres. Materials & Design. 2013;47:424-42.

[78] Volkmer T, Noël M, Arnold M, Strautmann J. Analysis of lignin degradation on wood surfaces to create a UV-protecting cellulose rich layer. International Wood Products Journal. 2016;7(3):156-64.

[79] Sanjay M, Siengchin S, Parameswaranpillai J, Jawaid M, Pruncu CI, Khan A. A comprehensive review of techniques for natural fibers as reinforcement in composites: Preparation, processing and characterization. Carbohydrate polymers. 2019;207:108-21.

[80] Senthamaraikannan P, Kathiresan M. Characterization of raw and alkali treated new natural cellulosic fiber from Coccinia grandis. L. Carbohydrate Polymers. 2018;186:332-43.

[81] Saravanakumar S, Kumaravel A, Nagarajan T, Moorthy IG. Effect of chemical treatments on physicochemical properties of Prosopis juliflora fibers. International Journal of Polymer Analysis and Characterization. 2014;19(5):383-90.

[82] Akindoyo JO, Beg MDH, Ghazali S, Islam MR. Effects of poly (dimethyl siloxane) on the water absorption and natural degradation of poly (lactic acid)/oil-palm empty-fruit-bunch fiber biocomposites. Journal of Applied Polymer Science. 2015;132(45).

[83] Bourmaud A, Beaugrand J, Shah DU, Placet V, Baley C. Towards the design of high-performance plant fibre composites. Progress in Materials Science. 2018;97:347-408.

[84] De Prez J, Van Vuure AW, Ivens J, Aerts G, Van de Voorde I. Enzymatic treatment of flax for use in composites. Biotechnology Reports. 2018;20:e00294.

[85] Summerscales J. A review of bast fibres and their composites: Part 4~ organisms and enzyme processes. Composites Part A: Applied Science and Manufacturing. 2021;140:106149.

[86] Bendourou FE, Suresh G, Laadila MA, Kumar P, Rouissi T, Dhillon GS, et al. Feasibility of the use of different types of enzymatically treated cellulosic fibres for polylactic acid (PLA) recycling. Waste Management. 2021;121:237-47.

[87] Brodowsky HM, Hennig A, Müller MT, Werner A, Zhandarov S, Gohs U. Laccase-enzyme treated flax fibre for use in natural fibre epoxy composites. Materials. 2020;13(20):4529.

[88] Gulati D, Sain M. Fungal-modification of natural fibers: a novel method of treating natural fibers for composite reinforcement. Journal of Polymers and the Environment. 2006;14:347-52.

[89] Janardhnan S, Sain M. Bio-treatment of natural fibers in isolation of cellulose nanofibres: impact of pre-refining of fibers on bio-treatment efficiency and nanofiber yield. Journal of Polymers and the Environment. 2011;19:615-21.

[90] Ferreira DP, Cruz J, Fangueiro R. Surface modification of natural fibers in polymer composites. Green composites for automotive applications: Elsevier; 2019. p. 3-41.

[91] Pickering KL, Efendy MA, Le TM. A review of recent developments in natural fibre composites and their mechanical performance. Composites Part A: Applied Science and Manufacturing. 2016;83:98-112.

[92] George M, Mussone PG, Bressler DC. Surface and thermal characterization of natural fibres treated with enzymes. Industrial Crops and Products. 2014;53:365-73.

[93] Geremew A, De Winne P, Demissie TA, De Backer H. Treatment of natural fiber for application in concrete pavement. Advances in Civil Engineering. 2021;2021:1-13.

[94] Vishnu Vardhini K, Murugan R, Surjit R. Effect of alkali and enzymatic treatments of banana fibre on properties of banana/polypropylene composites. Journal of Industrial Textiles. 2018;47(7):1849-64.

[95] Karaduman Y, Gokcan D, Onal L. Effect of enzymatic pretreatment on the mechanical properties of jute fiber-reinforced polyester composites. Journal of Composite Materials. 2013;47(10):1293-302.

[96] Vigneswaran C, Jayapriya J. Effect on physical characteristics of jute fibres with cellulase and specific mixed enzyme systems. The Journal of the Textile Institute. 2010;101(6):506-13.

[97] Saha P, Chowdhury S, Roy D, Adhikari B, Kim JK, Thomas S. A brief review on the chemical modifications of lignocellulosic fibers for durable engineering composites. Polymer Bulletin. 2016;73:587-620.

[98] Kenned JJ, Sankaranarayanasamy K, Kumar CS. Chemical, biological, and nanoclay treatments for natural plant fiber-reinforced polymer composites: A review. Polymers and Polymer Composites. 2021;29(7):1011-38.

[99] Werchefani M, Lacoste C, Belguith H, Gargouri A, Bradai C. Effect of chemical and enzymatic treatments of alfa fibers on polylactic acid bio-composites properties. Journal of Composite Materials. 2020;54(30):4959-67.

[100] Gibeop N, Lee D, Prasad CV, Toru F, Kim BS, Song JI. Effect of plasma treatment on mechanical properties of jute fiber/poly (lactic acid) biodegradable composites. Advanced Composite Materials. 2013;22(6):389-99.

[101] Ahmad R, Hamid R, Osman S. Physical and chemical modifications of plant fibres for reinforcement in cementitious composites. Advances in Civil Engineering. 2019;2019.

[102] Latif R, Wakeel S, Zaman Khan N, Noor Siddiquee A, Lal Verma S, Akhtar Khan Z. Surface treatments of plant fibers and their effects on mechanical properties of fiber-reinforced composites: A review. Journal of Reinforced Plastics and Composites. 2019;38(1):15-30.

[103] Stapulionienė R, Vaitkus S, Vėjelis S, Sankauskaitė A. Investigation of thermal conductivity of natural fibres processed by different mechanical methods. International Journal of Precision Engineering and Manufacturing. 2016;17:1371-81.

[104] Way C, Wu DY, Cram D, Dean K, Palombo E. Processing Stability and Biodegradation of Polylactic Acid (PLA) Composites Reinforced with Cotton Linters or Maple Hardwood Fibres. Journal of Polymers and the Environment. 2013;21(1):54-70.

[105] Finnerty J, Rowe S, Howard T, Connolly S, Doran C, Devine DM, et al. Effect of Mechanical Recycling on the Mechanical Properties of PLA-Based Natural Fiber-Reinforced Composites. Journal of Composites Science. 2023;7(4):141.

[106] Badia JD, Ribes-Greus A. Mechanical recycling of polylactide, upgrading trends and combination of valorization techniques. European Polymer Journal. 2016;84:22-39.

[107] McKeown P, Jones MD. The chemical recycling of PLA: A review. Sustainable Chemistry. 2020;1(1):1-22.

[108] Akindoyo JO, Pickering K, Beg MD, Mucalo M. Combined digestion and bleaching of New Zealand flax/harakeke fibre and its effects on the mechanical, thermal, and dynamic mechanical properties of poly (lactic) acid matrix composites. Composites Part A: Applied Science and Manufacturing. 2023;164:107326.

[109] Scaffaro R, Lopresti F, Botta L. PLA based biocomposites reinforced with Posidonia oceanica leaves. Composites Part B: Engineering. 2018;139:1-11.

[110] Serra-Parareda F, Delgado-Aguilar M, Espinach FX, Mutjé P, Boufi S, Tarrés Q. Sustainable plastic composites by polylactic acid-starch blends and bleached kraft hardwood fibers. Composites Part B: Engineering. 2022;238:109901.

[111] Girijappa YT, Rangappa SM, Parameswaranpillai J, Siengchin S. Natural fibers as sustainable and renewable resource for development of eco-friendly composites: A comprehensive review. Frontiers in Materials, 6, 226 (2019). 2019.

[112] Bartos A, Nagy K, Anggono J, Purwaningsih H, Móczó J, Pukánszky B. Biobased PLA/sugarcane bagasse fiber composites: Effect of fiber characteristics and interfacial adhesion on properties. Composites Part A: Applied Science and Manufacturing. 2021;143:106273.

[113] Samouh Z, Molnar K, Boussu F, Cherkaoui O, El Moznine R. Mechanical and thermal characterization of sisal fiber reinforced polylactic acid composites. Polymers for Advanced Technologies. 2019;30(3):529-37.

[114] Rajeshkumar G, Seshadri SA, Devnani G, Sanjay M, Siengchin S, Maran JP, et al. Environment friendly, renewable and sustainable poly lactic acid (PLA) based natural fiber reinforced composites–A comprehensive review. Journal of Cleaner Production. 2021;310:127483.

[115] Mazzanti V, Pariante R, Bonanno A, de Ballesteros OR, Mollica F, Filippone G. Reinforcing mechanisms of natural fibers in green composites: Role of fibers morphology in a PLA/hemp model system. Composites science and technology. 2019;180:51-9.

[116] Yang X, Fan W, Ge S, Gao X, Wang S, Zhang Y, et al. Advanced textile technology for fabrication of ramie fiber PLA composites with enhanced mechanical properties. Industrial Crops and Products. 2021;162:113312.

[117] Getme AS, Patel B. A review: Bio-fiber's as reinforcement in composites of polylactic acid (PLA). Materials Today: Proceedings. 2020;26:2116-22.

[118] Ighalo JO, Adeyanju CA, Ogunniyi S, Adeniyi AG, Abdulkareem SA. An empirical review of the recent advances in treatment of natural fibers for reinforced plastic composites. Composite Interfaces. 2021;28(9):925-60.

[119] Setswalo K, Oladijo O, Namoshe M, Akinlabi E, Sanjay M. The mechanical properties of alkali and laccase treated pterocarpus angolensis (mukwa)-polylactic acid (PLA) composites. International Journal of Biological Macromolecules. 2022;217:398-406.

[120] Tarrés Q, Melbø JK, Delgado-Aguilar M, Espinach F, Mutjé P, Chinga-Carrasco G. Micromechanics of tensile strength of thermo-mechanical pulp reinforced poly (lactic) acid biodegradable composites. Journal of Natural Fibers. 2022;19(15):9931-44.

[121] Siakeng R, Jawaid M, Asim M, Fouad H, Awad S, Saba N, et al. Flexural and dynamic mechanical properties of alkali-treated coir/pineapple leaf fibres reinforced polylactic acid hybrid biocomposites. Journal of Bionic Engineering. 2021;18:1430-8.

[122] Al Abdallah H, Abu-Jdayil B, Iqbal MZ. Improvement of mechanical properties and water resistance of bio-based thermal insulation material via silane treatment. Journal of Cleaner Production. 2022;346:131242.

[123] Serizawa S, Inoue K, Iji M. Kenaf-fiber-reinforced poly (lactic acid) used for electronic products. Journal of Applied Polymer Science. 2006;100(1):618-24.

[124] Komal UK, Lila MK, Singh I. PLA/banana fiber based sustainable biocomposites: A manufacturing perspective. Composites Part B: Engineering. 2020;180:107535.

[125] Akindoyo JO, Hossen Beg MD, Ghazali S, Islam MR. The effects of wettability, shear strength, and Weibull characteristics of fiber-reinforced poly (lactic acid) composites. Journal of Polymer Engineering. 2016;36(5):489-97.

[126] Sanjay M, Madhu P, Jawaid M, Senthamaraikannan P, Senthil S, Pradeep S. Characterization and properties of natural fiber polymer composites: A comprehensive review. Journal of Cleaner production. 2018;172:566-81.

[127] Aruan Efendy MG, Pickering KL. Comparison of harakeke with hemp fibre as a potential reinforcement in composites. Composites Part A: Applied Science and Manufacturing. 2014;67:259-67.

[128] Le TM, Pickering KL. The potential of harakeke fibre as reinforcement in polymer matrix composites including modelling of long harakeke fibre composite strength. Composites Part A: Applied Science and Manufacturing. 2015;76:44-53.

[129] Newman RH, Le Guen MJ, Battley MA, Carpenter JE. Failure mechanisms in composites reinforced with unidirectional Phormium leaf fibre. Composites Part A: Applied Science and Manufacturing. 2010;41(3):353-9.

[130] Akindoyo JO, Beg MDH, Ghazali SB, Islam MR, Mamun AA. Preparation and characterization of poly (lactic acid)-based composites reinforced with poly dimethyl siloxane/ultrasound-treated oil palm empty fruit bunch. Polymer-Plastics Technology and Engineering. 2015;54(13):1321-33.

[131] Oksman K, Skrifvars M, Selin J-F. Natural fibres as reinforcement in polylactic acid (PLA) composites. Composites science and technology. 2003;63(9):1317-24.

[132] Verma D, Goh KL. Effect of mercerization/alkali surface treatment of natural fibres and their utilization in polymer composites: Mechanical and morphological studies. Journal of Composites Science. 2021;5(7):175.

[133] Kabir MM, Wang H, Lau KT, Cardona F. Chemical treatments on plant-based natural fibre reinforced polymer composites: An overview. Composites Part B: Engineering. 2012;43(7):2883-92.

[134] Sreekala M, Kumaran M, Joseph S, Jacob M, Thomas S. Oil palm fibre reinforced phenol formaldehyde composites: influence of fibre surface modifications on the mechanical performance. Applied Composite Materials. 2000;7:295-329.

[135] Kalaprasad G, Francis B, Thomas S, Kumar CR, Pavithran C, Groeninckx G, et al. Effect of fibre length and chemical modifications on the tensile properties of intimately mixed short sisal/glass hybrid fibre reinforced low density polyethylene composites. Polymer international. 2004;53(11):1624-38.

[136] Li X, Tabil LG, Panigrahi S. Chemical treatments of natural fiber for use in natural fiber-reinforced composites: a review. Journal of Polymers and the Environment. 2007;15:25-33.

[137] Wang B, Panigrahi S, Tabil L, Crerar W. Pre-treatment of flax fibers for use in rotationally molded biocomposites. Journal of reinforced plastics and composites. 2007;26(5):447-63.

[138] Sapieha S, Allard P, Zang Y. Dicumyl peroxide-modified cellulose/LLDPE composites. Journal of Applied Polymer Science. 1990;41(9-10):2039-48.

[139] Joseph K, Thomas S, Pavithran C. Effect of chemical treatment on the tensile properties of short sisal fibre-reinforced polyethylene composites. Polymer. 1996;37(23):5139-49.

[140] Pettersen RC. Wood Sugar Analysis by Anion Chromatography. Journal of Wood Chemistry and Technology. 1991;11(4):495-501.

[141] Chukhchin DG, Malkov AV, Tyshkunova IV, Mayer LV, Novozhilov EV. Diffractometric method for determining the degree of crystallinity of materials. Crystallography Reports. 2016;61(3):371-5.

[142] Thygesen A, Oddershede J, Lilholt H, Thomsen AB, Ståhl K. On the determination of crystallinity and cellulose content in plant fibres. Cellulose. 2005;12(6):563-76.

[143] Park S, Baker JO, Himmel ME, Parilla PA, Johnson DK. Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulase performance. Biotechnology for Biofuels. 2010;3(1):10.

[144] Akindoyo JO, Beg MDH, Ghazali S, Heim HP, Feldmann M, Mariatti M. Simultaneous impact modified and chain extended glass fiber reinforced poly(lactic acid) composites: Mechanical, thermal, crystallization, and dynamic mechanical performance. Journal of Applied Polymer Science. 2021;138(5):49752.

[145] Bhiogade A, Kannan M, Devanathan S. Degradation kinetics study of Poly lactic acid(PLA) based biodegradable green composites. Materials Today: Proceedings. 2020;24:806-14.

[146] Sawpan MA, Pickering KL, Fernyhough A. Effect of various chemical treatments on the fibre structure and tensile properties of industrial hemp fibres. Composites Part A: Applied Science and Manufacturing. 2011;42(8):888-95.

[147] Kathirselvam M, Kumaravel A, Arthanarieswaran V, Saravanakumar S. Characterization of cellulose fibers in Thespesia populnea barks: Influence of alkali treatment. Carbohydrate polymers. 2019;217:178-89.

[148] Jaiswal D, Devnani G, Rajeshkumar G, Sanjay M, Siengchin S. Review on extraction, characterization, surface treatment and thermal degradation analysis of new cellulosic fibers as sustainable reinforcement in polymer composites. Current Research in Green and Sustainable Chemistry. 2022;5:100271.

[149] Tiwari YM, Sarangi SK. Characterization of raw and alkali treated cellulosic Grewia Flavescens natural fiber. International Journal of Biological Macromolecules. 2022;209:1933-42.

[150] Ramlee NA, Jawaid M, Zainudin ES, Yamani SAK. Modification of oil palm empty fruit bunch and sugarcane bagasse biomass as potential reinforcement for composites panel and thermal insulation materials. Journal of Bionic Engineering. 2019;16:175-88.

[151] Rahman MZ. Mechanical and damping performances of flax fibre composites–A review. Composites Part C: Open Access. 2021;4:100081.

[152] Chougan M, Ghaffar SH, Al-Kheetan MJ, Gecevicius M. Wheat straw pre-treatments using eco-friendly strategies for enhancing the tensile properties of bio-based polylactic acid composites. Industrial Crops and Products. 2020;155:112836.

[153] Goriparthi BK, Suman KNS, Mohan Rao N. Effect of fiber surface treatments on mechanical and abrasive wear performance of polylactide/jute composites. Composites Part A: Applied Science and Manufacturing. 2012;43(10):1800-8.

[154] Puglia D, Monti M, Santulli C, Sarasini F, De Rosa IM, Kenny JM. Effect of alkali and silane treatments on mechanical and thermal behavior of Phormium tenax fibers. Fibers and Polymers. 2013;14:423-7.

[155] Hong H, Xiao R, Guo Q, Liu H, Zhang H. Quantitively characterizing the chemical composition of tailored bagasse fiber and its effect on the thermal and mechanical properties of polylactic acid-based composites. Polymers. 2019;11(10):1567.

[156] Qin L, Qiu J, Liu M, Ding S, Shao L, Lü S, et al. Mechanical and thermal properties of poly(lactic acid) composites with rice straw fiber modified by poly(butyl acrylate). Chemical Engineering Journal. 2011;166(2):772-8.

[157] Broido A. A simple, sensitive graphical method of treating thermogravimetric analysis data. Journal of Polymer Science Part A-2: Polymer Physics. 1969;7(10):1761-73.

[158] Oza S, Ning H, Ferguson I, Lu N. Effect of surface treatment on thermal stability of the hemp-PLA composites: Correlation of activation energy with thermal degradation. Composites Part B: Engineering. 2014;67:227-32.

[159] Sato N, Kurauchi T, Sato S, Kamigaito O. Reinforcing mechanism by small diameter fiber in short fiber composite. Journal of composite materials. 1988;22(9):850-73.

[160] Gunti R, Ratna Prasad AV, Gupta AVSSKS. Mechanical and degradation properties of natural fiber-reinforced PLA composites: Jute, sisal, and elephant grass. Polymer Composites. 2018;39(4):1125-36.

[161] Hu R, Lim J-K. Fabrication and mechanical properties of completely biodegradable hemp fiber reinforced polylactic acid composites. Journal of Composite Materials. 2007;41(13):1655-69.

[162] Georgiopoulos P, Kontou E, Georgousis G. Effect of silane treatment loading on the flexural properties of PLA/flax unidirectional composites. Composites Communications. 2018;10:6-10.

[163] Liu XY, Dai GC. Surface modification and micromechanical properties of jute fiber mat reinforced polypropylene composites. Express Polym Lett. 2007;1:299-307.

[164] Sawpan MA, Pickering KL, Fernyhough A. Effect of fibre treatments on interfacial shear strength of hemp fibre reinforced polylactide and unsaturated polyester composites. Composites Part A: Applied Science and Manufacturing. 2011;42(9):1189-96.

[165] Akindoyo JO, Beg MDH, Ghazali S, Heim H-P, Feldmann M, Mariatti M. Synergized high-load bearing bone replacement composite from poly(lactic acid) reinforced with hydroxyapatite/glass fiber hybrid filler—Mechanical and dynamic mechanical properties. Polymer Composites. 2021;42(1):57-69.

[166] Ruz-Cruz MA, Herrera-Franco PJ, Flores-Johnson EA, Moreno-Chulim MV, Galera-Manzano LM, Valadez-González A. Thermal and mechanical properties of PLA-based

multiscale cellulosic biocomposites. Journal of Materials Research and Technology. 2022;18:485-95.

[167] Saba N, Jawaid M, Alothman OY, Paridah MT. A review on dynamic mechanical properties of natural fibre reinforced polymer composites. Construction and Building Materials. 2016;106:149-59.

[168] Amuthakkannan P, Manikandan V, Jappes JW, Uthayakumar M. Effect of fibre length and fibre content on mechanical properties of short basalt fibre reinforced polymer matrix composites. Materials Physics and Mechanics. 2013;16(2):107-17.

[169] Shah DU, Schubel PJ, Licence P, Clifford MJ. Determining the minimum, critical and maximum fibre content for twisted yarn reinforced plant fibre composites. Composites Science and Technology. 2012;72(15):1909-17.

[170] Akindoyo JO, Pickering K, Mucalo M, Beg MD, Hicks J. Mechanenzymatic production of natural fibre from harakeke (New Zealand flax) and its characterization for potential use in composites for building and construction applications. Industrial Crops and Products. 2024;214:118507.

[171] Awais H, Nawab Y, Amjad A, Anjang A, Akil HM, Abidin MSZ. Environmental benign natural fibre reinforced thermoplastic composites: A review. Composites Part C: Open Access. 2021;4:100082.

[172] Dixit S, Goel R, Dubey A, Shivhare PR, Bhalavi T. Natural fibre reinforced polymer composite materials-a review. Polymers from renewable resources. 2017;8(2):71-8.

[173] Syduzzaman M, Al Faruque MA, Bilisik K, Naebe M. Plant-based natural fibre reinforced composites: a review on fabrication, properties and applications. Coatings. 2020;10(10):973.

[174] Huda MS, Drzal LT, Mohanty AK, Misra M. Chopped glass and recycled newspaper as reinforcement fibers in injection molded poly (lactic acid)(PLA) composites: A comparative study. Composites science and technology. 2006;66(11-12):1813-24.

[175] Akindoyo JO, Husney NAAb, Ismail NH, Mariatti M. Structure and performance of poly (lactic acid)/poly (butylene succinate-co-L-lactate) blend reinforced with rice husk and coconut shell filler. Polymers and Polymer Composites. 2021;29(7):992-1002.

[176] Li Y, Pickering KL. Hemp fibre reinforced composites using chelator and enzyme treatments. Composites science and technology. 2008;68(15-16):3293-8.

[177] Yao Y, Dou H, Liu T, Wang S, Gao Y, Kang J, et al. Micro-and nano-scale mechanisms of enzymatic treatment on the interfacial behaviors of sisal fiber reinforced bio-based epoxy resin. Industrial Crops and Products. 2023;194:116319.

[178] Saleem Z, Rennebaum H, Pudel F, Grimm E. Treating bast fibres with pectinase improves mechanical characteristics of reinforced thermoplastic composites. Composites Science and Technology. 2008;68(2):471-6.

[179] Boey JY, Yusoff SB, Tay GS. A review on the enhancement of composite's interface properties through biological treatment of natural fibre/lignocellulosic material. Polymers and Polymer Composites. 2022;30:09673911221103600.

[180] Sindhu R, Binod P, Pandey A. Biological pretreatment of lignocellulosic biomass–an overview. Bioresour Technol. 2016;199(2016):76-82.

[181] Norrrahim MNF, Huzaifah MRM, Farid MAA, Shazleen SS, Misenan MSM, Yasim-Anuar TAT, et al. Greener Pretreatment Approaches for the Valorisation of Natural Fibre Biomass into Bioproducts. Polymers. 2021;13(17):2971.

[182] Carr D, Cruthers N, Laing R, Niven B. Fibers from three cultivars of New Zealand flax (Phormium tenax). Textile research journal. 2005;75(2):93-8.

[183] Chaari R, Khlif M, Mallek H, Bradai C, Lacoste C, Belguith H, et al. Enzymatic treatments effect on the poly (butylene succinate)/date palm fibers properties for bio-composite applications. Industrial crops and products. 2020;148:112270.

[184] Akin DE, Foulk JA, Dodd RB, McAlister III DD. Enzyme-retting of flax and characterization of processed fibers. Journal of biotechnology. 2001;89(2-3):193-203.

[185] Adamsen APS, Akin DE, Rigsby LL. Chelating Agents and Enzyme Retting of Flax. Textile Research Journal. 2002;72(4):296-302.

[186] Kunamneni A, Ballesteros A, Plou FJ, Alcalde M. Fungal laccase—a versatile enzyme for biotechnological applications. Communicating current research and educational topics and trends in applied microbiology. 2007;1:233-45.

[187] Brodowsky HM, Hennig A. Micromechanical Tests on Natural Fibre Composites with Enzymatically Enhanced Fibre–Matrix Adhesion. Materials Circular Economy. 2022;4(1):5.

[188] Sisti L, Totaro G, Vannini M, Fabbri P, Kalia S, Zatta A, et al. Evaluation of the retting process as a pre-treatment of vegetable fibers for the preparation of high-performance polymer biocomposites. Industrial Crops and Products. 2016;81:56-65.

[189] Ponnusamy DA, Gajendiran H, Mansingh BB, Binoj JS. Diffractional, spectroscopical, morphological, and thermal analysis of pretreated/enzyme modified cellulosic Cocos nucifera L. peduncle fiber. Biomass Conversion and Biorefinery. 2023:1-12.

[190] Araújo J, Waldman W, De Paoli M. Thermal properties of high density polyethylene composites with natural fibres: Coupling agent effect. Polymer degradation and stability. 2008;93(10):1770-5.

[191] Akindoyo JO, Pickering K, Beg MD, Mucalo M. Reactive compatibilization of harakeke fiber-reinforced poly(lactic) acid/polybutylene succinate blend. Journal of Applied Polymer Science. 2024;141(40):e56030.

[192] Gu Z, Zhang J, Cao W, Liu X, Wang J, Zhang X, et al. Extraordinary toughness and heat resistance enhancement of biodegradable PLA/PBS blends through the formation of a small amount of interface-localized stereocomplex crystallites during melt blending. Polymer. 2022;262:125454.

[193] Thyavihalli Girijappa YG, Mavinkere Rangappa S, Parameswaranpillai J, Siengchin S. Natural Fibers as Sustainable and Renewable Resource for Development of Eco-Friendly Composites: A Comprehensive Review. Frontiers in Materials. 2019;6.

[194] Arrigo R, D'Anna A, Frache A. Fully bio-based ternary polymer blends: structural characterization and mechanical behavior. Materials Today Sustainability. 2023;21:100314.

[195] Wojnowska-Baryła I, Kulikowska D, Bernat K. Effect of Bio-Based Products on Waste Management. Sustainability. 2020;12(5):2088.

[196] Chen X, Yan N. A brief overview of renewable plastics. Materials Today Sustainability. 2020;7-8:100031.

[197] Mtibe A, Motloung MP, Bandyopadhyay J, Ray SS. Synthetic Biopolymers and Their Composites: Advantages and Limitations—An Overview. Macromolecular Rapid Communications. 2021;42(15):2100130.

[198] Hu K, Huang D, Jiang H, Sun S, Ma Z, Zhang K, et al. Toughening Biosourced Poly(lactic acid) and Poly(3-hydroxybutyrate-co-4-hydroxybutyrate) Blends by a Renewable Poly(epichlorohydrin-co-ethylene oxide) Elastomer. ACS Omega. 2019;4(22):19777-86.

[199] Hamad K, Kaseem M, Yang H, Deri F, Ko Y. Properties and medical applications of polylactic acid: A review. Express Polym Lett. 2015;9(5).

[200] D’Anna A, Arrigo R, Frache A. Rheology, morphology and thermal properties of a PLA/PHB/clay blend nanocomposite: the influence of process parameters. Journal of Polymers and the Environment. 2022;30(1):102-13.

[201] Tripathi N, Misra M, Mohanty AK. Durable polylactic acid (PLA)-based sustainable engineered blends and biocomposites: Recent developments, challenges, and opportunities. ACS Engineering Au. 2021;1(1):7-38.

[202] Banerjee R, Ray SS. An overview of the recent advances in polylactide-based sustainable nanocomposites. Polymer Engineering & Science. 2021;61(3):617-49.

[203] Ahmad A, Banat F, Alsafar H, Hasan SW. An overview of biodegradable poly (lactic acid) production from fermentative lactic acid for biomedical and bioplastic applications. Biomass Conversion and Biorefinery. 2024;14(3):3057-76.

[204] Cai H, Cao C, Zheng Y, Liu D, Xia X, Sun X, et al. A facile strategy for compatibilization of PLA/PBS blends by incorporating camellia seed powder. Macromolecular Materials and Engineering. 2023;308(5):2200581.

[205] Chen Y, Wang W, Yuan D, Xu C, Cao L, Liang X. Bio-based PLA/NR-PMMA/NR ternary thermoplastic vulcanizates with balanced stiffness and toughness:“soft–hard” core–shell continuous rubber phase, in situ compatibilization, and properties. ACS Sustainable Chemistry & Engineering. 2018;6(5):6488-96.

[206] Ma P, Hristova-Bogaerds D, Goossens J, Spoelstra A, Zhang Y, Lemstra P. Toughening of poly (lactic acid) by ethylene-co-vinyl acetate copolymer with different vinyl acetate contents. European Polymer Journal. 2012;48(1):146-54.

[207] Anderson KS, Hillmyer MA. The influence of block copolymer microstructure on the toughness of compatibilized polylactide/polyethylene blends. Polymer. 2004;45(26):8809-23.

[208] Fortelny I, Ujcic A, Fambri L, Slouf M. Phase Structure, Compatibility, and Toughness of PLA/PCL Blends: A Review. Frontiers in Materials. 2019;6.

[209] Mohammadi M, Heuzey M-C, Carreau PJ, Taguet A. Morphological and Rheological Properties of PLA, PBAT, and PLA/PBAT Blend Nanocomposites Containing CNCs. Nanomaterials. 2021;11(4):857.

[210] Messin T, Marais S, Follain N, Guinault A, Gaucher V, Delpouve N, et al. Biodegradable PLA/PBS multinanolayer membrane with enhanced barrier performances. Journal of Membrane Science. 2020;598:117777.

[211] Changwichan K, Silalertruksa T, Gheewala SH. Eco-Efficiency Assessment of Bioplastics Production Systems and End-of-Life Options. Sustainability. 2018;10(4):952.

[212] Deng Y, Thomas NL. Blending poly(butylene succinate) with poly(lactic acid): Ductility and phase inversion effects. European Polymer Journal. 2015;71:534-46.

[213] Fortunati E, Puglia D, Iannoni A, Terenzi A, Kenny JM, Torre L. Processing Conditions, Thermal and Mechanical Responses of Stretchable Poly (Lactic Acid)/Poly (Butylene Succinate) Films. Materials. 2017;10(7):809.

[214] Supthanyakul R, Kaabbuathong N, Chirachanchai S. Random poly(butylene succinate-co-lactic acid) as a multi-functional additive for miscibility, toughness, and clarity of PLA/PBS blends. Polymer. 2016;105:1-9.

[215] Aliotta L, Vannozzi A, Panariello L, Gigante V, Coltelli M-B, Lazzeri A. Sustainable Micro and Nano Additives for Controlling the Migration of a Biobased Plasticizer from PLA-Based Flexible Films. Polymers. 2020;12(6):1366.

[216] Zhang N, Wang Q, Ren J, Wang L. Preparation and properties of biodegradable poly(lactic acid)/poly(butylene adipate-co-terephthalate) blend with glycidyl methacrylate as reactive processing agent. Journal of Materials Science. 2009;44(1):250-6.

[217] Kanzawa T, Tokumitsu K. Mechanical properties and morphological changes of poly(lactic acid)/polycarbonate/poly(butylene adipate-co-terephthalate) blend through reactive processing. Journal of Applied Polymer Science. 2011;121(5):2908-18.

[218] Harada M, Ohya T, Iida K, Hayashi H, Hirano K, Fukuda H. Increased impact strength of biodegradable poly(lactic acid)/poly(butylene succinate) blend composites by using isocyanate as a reactive processing agent. Journal of Applied Polymer Science. 2007;106(3):1813-20.

[219] Chen G-X, Kim H-S, Kim E-S, Yoon J-S. Compatibilization-like effect of reactive organoclay on the poly(l-lactide)/poly(butylene succinate) blends. Polymer. 2005;46(25):11829-36.

[220] Ji D, Liu Z, Lan X, Wu F, Xie B, Yang M. Morphology, rheology, crystallization behavior, and mechanical properties of poly(lactic acid)/poly(butylene succinate)/dicumyl peroxide reactive blends. Journal of Applied Polymer Science. 2014;131(3).

[221] Chuayjuljit S, Wongwaiwattanakul C, Chaiwutthinan P, Prasassarakich P. Biodegradable poly(lactic acid)/poly(butylene succinate)/wood flour composites: Physical and morphological properties. Polymer Composites. 2017;38(12):2841-51.

[222] Vorawongsagul S, Pratumpong P, Pechyen C. Preparation and foaming behavior of poly (lactic acid)/poly (butylene succinate)/cellulose fiber composite for hot cups packaging application. Food Packaging and Shelf Life. 2021;27:100608.

[223] He L, Song F, Li D-F, Zhao X, Wang X-L, Wang Y-Z. Strong and tough polylactic acid based composites enabled by simultaneous reinforcement and interfacial compatibilization of microfibrillated cellulose. ACS Sustainable Chemistry & Engineering. 2020;8(3):1573-82.

[224] Beg MDH, Pickering KL, Gauss C. The effects of alkaline digestion, bleaching and ultrasonication treatment of fibre on 3D printed harakeke fibre reinforced polylactic acid composites. Composites Part A: Applied Science and Manufacturing. 2023;166:107384.

[225] Chen R-y, Zou W, Wu C-r, Jia S-k, Huang Z, Zhang G-z, et al. Poly(lactic acid)/poly(butylene succinate)/calcium sulfate whiskers biodegradable blends prepared by vane extruder: Analysis of mechanical properties, morphology, and crystallization behavior. Polymer Testing. 2014;34:1-9.

[226] Taib RM, Ghaleb ZA, Mohd Ishak ZA. Thermal, mechanical, and morphological properties of polylactic acid toughened with an impact modifier. Journal of Applied Polymer Science. 2012;123(5):2715-25.

[227] Nurazzi NM, Asyraf MRM, Rayung M, Norrrahim MNF, Shazleen SS, Rani MSA, et al. Thermogravimetric Analysis Properties of Cellulosic Natural Fiber Polymer Composites: A Review on Influence of Chemical Treatments. Polymers. 2021;13(16):2710.

[228] Pongtanayut K, Thongpin C, Santawitee O. The Effect of Rubber on Morphology, Thermal Properties and Mechanical Properties of PLA/NR and PLA/ENR Blends. Energy Procedia. 2013;34:888-97.

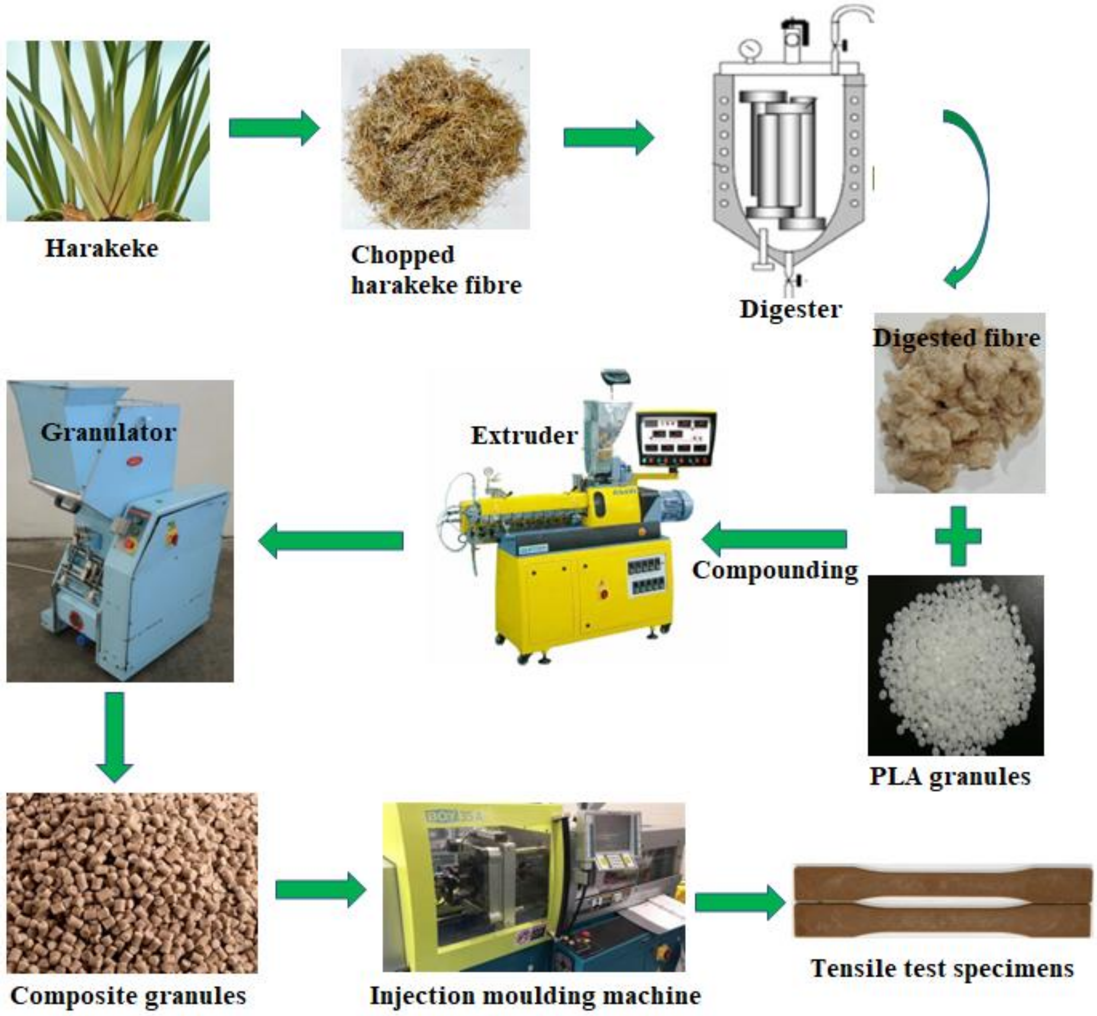
[229] Krishna KV, Kanny K. The effect of treatment on kenaf fiber using green approach and their reinforced epoxy composites. Composites Part B: Engineering. 2016;104:111-7.

[230] Abdelmouleh M, Boufi S, Belgacem M, Duarte A, Salah AB, Gandini A. Modification of cellulosic fibres with functionalised silanes: development of surface properties. International Journal of Adhesion and Adhesives. 2004;24(1):43-54.

[231] Sathishkumar TP, Navaneethakrishnan P, Shankar S, Rajasekar R. Characterization of new cellulose sansevieria ehrenbergii fibers for polymer composites. Composite Interfaces. 2013;20(8):575-93.

APPENDIX A

PRODUCTION OF PLA-HARAKEKE FIBRE COMPOSITES USING CHEMICALLY TREATED HARAKEKE FIBRE



APPENDIX B
ACTUAL PRINT OF PAPERS PUBLISHED FROM THIS THESIS

Composites: Part A 164 (2023) 107326

Contents lists available at ScienceDirect

Composites Part A

journal homepage: www.elsevier.com/locate/compositesa

Combined digestion and bleaching of New Zealand flax /harakeke fibre and its effects on the mechanical, thermal, and dynamic mechanical properties of poly(lactic) acid matrix composites

John O. Akindoyo *, Kim Pickering, Mohammad Dalour Beg, Michael Mucalo

School of Science and Engineering, The University of Waikato, Private Bag 3105, Hamilton, New Zealand

A R T I C L E I N F O

Keywords:
A. Polymer matrix composites (PMCs)
B. Mechanical properties, Adhesion
E. Injection moulding

A B S T R A C T

In this study, New Zealand flax (harakeke) fibre was initially modified through digestion in an alkali solution followed by bleaching with hydrogen peroxide and sodium silicate with the aim of improving thermal and mechanical performance of its composites, through increased interfacial bonding. X-ray diffraction analysis (XRD), Fourier transform infrared spectroscopy and lignin analysis showed that the combination of bleaching and alkali treatment resulted in a higher cellulose content than digestion alone. Fibre inclusion was found to increase the crystallinity of PLA, likely due to heterogeneous nucleation on the treated fibres, which in turn helped to improve the composite strength. The highest tensile strength, tensile modulus and thermal stability were achieved with the bleached fibre which is believed to be due to better fibre distribution and stronger interfacial interaction. This was supported by the adhesion factor and effectiveness coefficient calculated using the data obtained from dynamic mechanical analysis.

1. Introduction

In recent years, there have been increasing efforts on developing environmentally friendly materials through a synergy between the principles of green chemistry, sustainability, and eco-efficiency [1,2]. This is aimed at reducing the excessive dependence on fossil fuel and petroleum-based products [3,4]. In this regard, biodegradable or renewable polymer-based composites are examples of materials that can be used. This is because polymers are very versatile, can be used in different applications, and can be modified to meet specific purposes [5].

Poly (lactic) acid (PLA) is one polymer that has been widely investigated as a substitute for non-degradable high environmental impact polymers, as detailed in different research and review articles [6–9]. The strength and stiffness of PLA is sufficient for different packaging, medical, and other non-structural applications where high load bearing is not a priority. In addition, the inherent biodegradability and processability of PLA mean that its properties can be tuned to obtain whatever desired performance that is fit for purpose [5,10]. Hence, PLA has been combined with natural fibres to produce environmentally benign composites with improved mechanical strength. This is partly associated with the salient properties of natural fibres such as low cost, renewability, biodegradability, recyclability, low density, high flexural strength, high modulus, and non-abrasiveness [11,12]. Studies have shown that good interfacial shear strength (IFSS) in natural fibre reinforced PLA can significantly affect the composite strength. For example, the work by Setswalo et al. on mukwa/PLA composites demonstrated higher flexural properties with improved IFSS, obtained through fibre treatment [13]. Similarly, Tarrés et al. demonstrated that a weak interphase can result in reduced tensile strength [14]. In a different study, a hybrid natural fibre (coir/pineapple leaf fibres) system was used to reinforce PLA. It was found that the untreated hybrid biocomposite returned a higher damping factor and lower strength, attributed to weak interphase [15]. Generally, most studies on natural fibre reinforced PLA composites are focussed on improving interfacial interaction between PLA and the fibres through chemical bonding, or interfacial adhesion [6,7,9,11]. However, too much fibre can lead to insufficient wetting by the matrix which in turn results in poor interface between the fibre and the matrix leading to reduced strength. In relation to that, there have been several articles on the effect of fibre content on the properties of PLA. For example, Abdallah et al. investigated the effect of varying fibre content (0–40 wt%) on the mechanical and thermal insulation properties of date palm fibre reinforced PLA [16], and found that the tensile strength was remarkably high up to 20 wt% fibre content. Serizawa et al.

---

* Corresponding author.
E-mail address: blessedbode@ymail.com (J.O. Akindoyo).

https://doi.org/10.1016/j.compositesa.2022.107326
Received 7 August 2022; Received in revised form 13 November 2022; Accepted 15 November 2022
Available online 19 November 2022
1359-835X/© 2022 Elsevier Ltd. All rights reserved.

also reported 20 wt% as the optimum fibre content in kenaf fibre reinforced PLA composites [17]. Similarly, Komal et al. reported 20 wt% as the optimum fibre content after preparing 10–30 wt% banana fibre reinforced PLA composites [18].

Generally, the conventional natural fibres used as reinforcement in PLA composites include oil palm empty fruit bunch, sisal, hemp, flax, coir, bagasse, banana, and jute [10,19,20]. In the past decade, there has been increasing interest in the use of fibres extracted from the leaves of *Phormium tenax* commonly called New Zealand flax (harakeke), as reinforcement in polymer composites. Harakeke is indigenous to New Zealand and the Norfolk Island, and it is a significant resource in Māori culture for making woven mats and containers. In terms of morphology and anatomy, harakeke leaves are clumped together in groups and tend to be folded at their stem. The leaves can grow to a length of about 3 m, and extend to about 50–120 mm in width [21]. The structure of harakeke leaf is one that is typical of monocotyledons. There is a spiral overlap at the base of the fibre, which lies parallel to bundles of sclerenchyma fibres. These sclerenchyma fibres are bonded together by lignin and hemicellulose, but the bonds can be broken by dissolution in an alkali solution, or in boiling water [22]. Fibres obtained from harakeke leaves were historically used for producing cloaks, ropes, and for making baskets and fishing nets [23]. These uses suggest that harakeke leaves could offer good reinforcement properties. Therefore, some studies have explored the possibility of combining harakeke fibre with different polymers [22,24,25]. However, reports on harakeke fibre as reinforcement in injection moulded PLA for producing composites suitable for structural applications are few in the materials science literature. It is well known that the notable determinants of the suitability of composites for structural applications are the reinforcing ability of the fibre, compositional balance, and the extent of interfacial adhesion between the fibre and the matrix. Therefore, these are given prime consideration in this article.

Interfacial adhesion in natural fibre composites is commonly improved through chemical modification of the fibre, with most studies focussing on facilitating surface roughness through alkali treatment [26,27]. This has reportedly produced significant improvement in tensile strength and tensile modulus due to removal of components that can lead to weak interface from the fibre. In addition, alkali treatment helps to expose the cellulose hydroxyl groups of the fibre for bonding with the matrix which in turn facilitates mechanical interlocking between the fibre and the matrix [28]. The use of coupling agents, or the combination of other chemical techniques with alkali treatment can also help to improve interfacial adhesion in natural fibre reinforced composites. Peroxide treatment is one of such chemical treatments that can be combined with alkali treatment to improve the chemical bonding between natural fibres and polymer matrices [10]. The mechanism of peroxide treatment suggests that it can generate good mechanical and thermal resilience in natural fibres, as well as facilitate strong chemical bonding and thermal resilience in fibre reinforced composites by acting as a fibre modifier and as a coupling agent. Despite the potential of peroxide treatment to produce significant improvements in composite properties, it is less commonly reported in the literature and so, it is worthy of deeper investigation. Therefore, the aim of this study is to investigate the effect of combined digestion and peroxide treatments on harakeke fibre, and its reinforcing properties in PLA composites as it relates to its suitability for structural applications.

2. Materials and methods

2.1. *Materials*

The harakeke fibre used as reinforcing filler in this study was kindly supplied by Templeton Flax Milling Heritage Trust, New Zealand. The polymer matrix used is Ingeo™ Biopolymer 3052D poly (lactic acid) (PLA) from NatureWorks. This PLA is an injection molding grade with a specific gravity of 1.24 and melt flow rate (MFR) of 14 g/10 min (210 °C, 2.16 kg). Sodium hydroxide bulk grade solid pellets, sodium sulfite powder, and hydrogen peroxide (30 %) were purchased from Sigma-Aldrich and used without further purification. In addition, extra pure sodium silicate (Na_2SiO_3) solution, and sulfuric acid (96 %) were procured from Merck Millipore.

2.2. *Methods*

2.2.1. *Preparation and treatment of harakeke fibre*

The harakeke fibre, as received, had a length of about 1–1.5 m. After drying, the fibre was cut into 2–3 cm pieces using a guillotine. Weighed amounts of the chopped fibre were placed in stainless steel canisters and digested using a solution of 5 wt% NaOH and 2 wt% Na_2SO_3 in a lab-scale pulp digester. The ratio of fibre to solution was kept at 1:8, and a programmed controller was used to run the digester over a 4-step cycle which included a treatment temperature set at 160 °C and a holding time of 2 h. After digestion, the treated fibre was thoroughly washed under a continuous water flow until the pH of the wash water was measured as neutral at pH 7. The washed and treated fibres were then dried in a laboratory oven set at 80 °C for 48 h after which the dried fibres were stored in a sealed plastic bag until used for further analysis and for composite fabrication.

Bleaching of harakeke was performed using a solution of H_2O_2 and Na_2SiO_3. For this process, 45 g of digested fibre was placed in 3 L of Milli-Q distilled water. The water was first heated to 70 °C, and the fibre was introduced under continuous stirring for about 15 min after which 75 mL of Na_2SiO_3 (2.5 % by volume) was added. After 5 min, 150 mL of H_2O_2 (5 % by volume) was added and the bleaching process was allowed to continue under rigorous stirring for an additional 10 min. After completion of the bleaching process, the bleached fibre was washed under a water flow until the waste wash water showed a neutral pH. Then the fibre was dried at 80 °C for 48 h and stored in a sealed plastic bag until used for further analysis and composite production.

2.2.2. *Determination of lignin and carbohydrate content in harakeke fibre*

The amount of lignin in the raw, digested, and bleached harakeke fibre was determined according to the Round Robin method for determination of Klason lignin as detailed in the Technical Association of the Pulp and Paper Industry (TAPPI) T 222 om-02 test methods. Briefly, weighed amounts of the dry fibre were digested in a 72 % (w/w) H_2SO_4 solution inside a test tube, with the mixture being stirred with a glass rod until dissolution began. The mixture containing test tube was placed in a water bath for 1 h at 30 °C with occasional stirring. The mixture was further diluted to − 3 % (w/w) H_2SO_4 in a beaker using distilled water, and placed in an autoclave set at 121 °C. After 1 h, the beaker was cooled to 80 °C and the mixture was filtered using a vacuum filter to separate the insoluble matter. The acid insoluble residue (AIR) was subsequently allowed to dry overnight at 105 °C and the dry weight of acid insoluble residue (viz., Klason lignin) was calculated using equation (1) as follows:

$$Acidinsolubleresidue(AIR) = \frac{m}{M}x1000 \tag{1}$$

where, m is the dry weight of residue after acid hydrolysis, in g and M is the oven-dry weight of sample (100 % dry matter) before acid hydrolysis, in g. The filtrate from the Klason lignin determination test was used to determine the acid soluble lignin, and the carbohydrate content of the samples. The carbohydrate (cellulose and hemicellulose) content was determined following a method described in literature for wood sugar analysis by anion chromatography [29].

2.2.3. *Production of PLA/harakeke composites*

Composites were produced from PLA and harakeke fibre using digested and bleached fibres at different fibre content (0–30 wt%). The composite components were mixed and compounded using a twin screw extruder (Labtech LTE-20–44). Prior to extrusion, the dried treated fibres were sheared using a Sunbeam Multigrinder with blunt blades.

Shearing was performed at a high rotational speed to defibrate the fibre. After this, the fibres were dried overnight in a conventional oven set at 105 °C. For the PLA granules, drying to moisture content < 0.1 % was carried out using a vacuum oven set at 60 °C for 2 h. Then, extrusion was performed using a temperature profile in the range of 165–175 °C, with the feeding and die zones kept at 120 °C and 175 °C, respectively. After extrusion, the extruded materials were granulated using a Moretto GR knife mill plastic granulator with an inserted sieve to obtain granules of about 3 mm in length. After drying the granules to a moisture content < 0.1 % by weight, test samples were prepared using an injection moulding machine (BOY 35A). The injection profile used for test sample preparation includes a feeding zone temperature of 150 °C, a compression zone temperature of 165–185 °C, a metering zone temperature of 190 °C, a nozzle temperature of 185 °C, a mould temperature of 35 °C, injection time of 0.5 s and cooling time of 30 s. For easy identification, the different composite batches produced were given code names, with values 10, 20 or 30 indicating the wt.% fibre content while DF or BF represents digested fibre or bleached fibre, respectively. For example, "PLA represents the neat PLA matrix while "PLA + 20 BF" represents the composite containing 20 wt% bleached fibre.

2.2.4. *Fourier transform infrared (FTIR) spectroscopy*

The functional groups on the raw harakeke fibre, and changes in the FTIR spectra of digested and bleached harakeke fibre were analysed with a Perkin Elmer® Spectrum 100 FTIR spectrometer. Spectral analysis of the PLA was performed and compared with similar IR analyses of the PLA/harakeke composites. The FTIR data were recorded over a wavelength range of 4000–400 cm^{-1} using the standard KBr pellet technique.

2.2.5. *Scanning electron microscopy (SEM)*

Surfaces of the raw, digested, and bleached harakeke fibre were observed on a Hitachi Regulus SU8230 field emission scanning electron microscope. Likewise, the fractured surfaces of PLA and PLA/harakeke composites after tensile testing were examined. Prior to SEM observation, the samples were dried and mounted on aluminium stubs using double sided carbon tape. The mounted samples were subsequently sputter coated with a 5 nm layer of platinum in a Quorum Q150V sputtering equipment to make them conductive.

2.2.6. *X- ray diffraction analysis*

The XRD diffractograms of raw, digested, and bleached harakeke fibre were obtained using an EMPYREAN diffractometer system (PANalytical). The fibres were chopped and pressed into a disk, using a cylindrical steel mould. Then, analysis was performed over a range of 5 – 65° at a scanning speed of 1° min^{-1} with a scan step of 0.02° using a CuKα radiation (λ = 1.54 nm) The cellulose crystallinity index (*CrI* %) of the fibres was calculated following the Segal method, using equation (2).

$$CrI\% = \frac{I_{002} - I_{am}}{I_{002}} \text{ x } 100 \tag{2}$$

where, I_{002} is the maximum intensity of the (0 0 2) lattice diffraction peak of cellulose and I_{am} is the intensity of diffraction of the amorphous component.

2.2.7. *Mechanical testing*

The tensile test specimens for PLA and the composites were prepared according to EN ISO 527, while flexural test specimens were prepared according to EN ISO 178. These tests were conducted on an Instron® 5982 universal testing machine equipped with a 5 kN load cell, running at a crosshead speed of 5 mm min^{-1}, and 10 mm min^{-1} for tensile and flexural tests, respectively. During tensile testing, the strain was measured using a 25 mm extensometer fixed at the middle of the specimen. Prior to mechanical testing, the test specimens were preconditioned in a climate chamber at 23 °C and 50 % relative humidity for 48 h. Five specimens were tested during tensile and flexural tests and average results were recorded for the tensile strength (TS), tensile modulus (TM), flexural strength (FS) and flexural modulus (FM).

2.2.8. *Thermogravimetric and differential scanning calorimetric analysis*

Thermogravimetric analysis (TGA) was performed using a Perkin Elmer STA 8000 thermal analyzer. The sample, weighing about 10–20 mg was placed in a crucible and analysis was performed under argon atmosphere at a gas flow rate of 40 mL min^{-1} while being heated at 10 °C/min from 30 °C to 600 °C.

Differential scanning calorimetry analysis (DSC) of PLA and the composites was performed using a TA instrument (Netzsch DSC 3500 Sirius). Samples were heated from 20 to 200 °C at 10 °C/min under a nitrogen flow using a gas flow rate of 60 mL/min. From the DSC thermogram, the glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) were determined. In addition, the crystallinity (I_{DSC}) of PLA in the composite was calculated from the heat of fusion of the tested sample and a reference sample (PLA)with 100 % crystallinity, using equation (3).

$$\%crystallinity(I_{DSC}) = \frac{\Delta H}{\Delta H_{m} W} x100\% \tag{3}$$

where, ΔH and ΔH_m represents the heat of fusion of the samples, and a reference PLA with 100 % crystallinity, respectively, while W is the mass fraction of the matrix. The crystallinity of PLA in the composites was calculated by using 93.6 J/g as the heat of fusion (ΔH_m) of reference PLA with 100 % crystallinity [30].

2.2.9. *Dynamic mechanical analysis*

The dynamic mechanical analysis (DMA) was performed on a Perkin Elmer DMA800 Dynamic Mechanical Analyzer. A single cantilever mode was used to test the specimens (30 mm × 5 mm × 1.5 mm) by heating the specimens at a rate of 2 °C/min from 23 °C to 140 °C. The displacement amplitude was 20 μm and the test was performed at a frequency of 1 Hz.

3. Results and discussion

3.1. *Composition and properties of harakeke fibre*

3.1.1. *Composition of raw, digested, and bleached harakeke fibre*

The lignin and carbohydrate content of the fibres are presented in Table 1. It is evident from the table that the raw fibre has higher lignin

Table 1
Chemical composition, and XRD parameters of the crystalline phase of raw, digested, and bleached harakeke fibre.

	Composition (wt.%)		
Fibre type	Cellulose	Hemicellulose	Lignin
Raw fibre	46.00	18.80	15.84
Digested fibre	77.30	13.30	3.37
Bleached fibre	82.55	12.80	2.73

XRD Properties

Parameters	Raw fibre	Digested fibre	Bleached fibre
Peak position (°)	22.24	22.45	22.66
FWHM	3.13	1.81	1.79
d (Å)	3.99	3.95	3.92
Crystallite size (nm)	21.71	37.20	36.83
Crystallinity Index (%)	72.79	79.75	81.50

* Raw fibre refers to the as-received harakeke fibre.

* Digested fibre is the fibre harakeke fibre treated with 5% NaOH and 2% Na_2SO_3.

* Bleached fibre refers to the harakeke fibre digested with 5% NaOH and 2% Na_2SO_3, and then bleached with 5% H_2O_2 and 2.5% Na_2SiO_3.

and hemicellulose content than the treated fibres. In contrast, the cellulose content is higher in the treated fibres than in the raw fibre. The cellulose content in the raw fibre was 46 % and this increased to 77 % in the digested, and 83 % for the bleached fibre. The higher cellulose content in the treated fibres can be attributed to the removal of non-cellulosic components from the fibre, which served to increase the amount of cellulose per unit mass of the fibre. Removal of lignin and other non-cellulosic components from natural fibres can help to improve the crystalline nature of the fibre. This will in turn improve the fibre strength, and the strength of its reinforced composites due to increased reinforcing ability, and effective stress transfer within the composite. This is further discussed in subsequent sections.

3.1.2. X-ray diffraction (XRD) properties of harakeke fibre

The XRD traces of raw, digested, and bleached harakeke fibre are illustrated in Fig. 1. The two conspicuous peaks in the XRD curves of the fibres around $2\theta \approx 22^\circ$ and $2\theta \approx 16^\circ$ represent the crystalline and amorphous components of cellulose, respectively [31]. The crystallinity index calculated from these peaks are included in Table 1. The crystallographic (0 0 2) plane of cellulose in the raw, digested, and bleached fibre appeared at 2θ positions of 22.24°, 22.45°, and 22.66°, respectively.

The slight shift in the 2θ position of the fibre after digestion, and further shift after bleaching suggests a decrease in the interplanar spacing of the (0 0 2) planes in the digested and bleached fibre, compared to the raw fibre. This is an indication of closer packing of cellulose crystals in the digested and bleached fibre, due to the removal of lignin, hemicellulose, and other non-cellulosic components from the fibre after treatment [32]. Hence, the lower FWHM values of the digested and bleached fibres could be due to formation of hydrogen bonds between the cellulose chains freed by the removal of binding structures like hemicellulose and lignin, which resulted in rearrangement and closer packing [33]. This is confirmed by the higher cellulose crystal size and crystallinity of the digested and bleached fibres, which is believed to be due to higher cellulose content as seen in Table 1. Lower FWHM values could also be due to the *trans*-crystallinity (crystal growth across or through individual crystals) induced in the cellulose structure, by the digestion and bleaching treatments. The crystallinity index values in Table 1 shows that the bleached fibre has a higher crystallinity index than the fibre subjected to digestion only. This indicates the presence of higher crystalline cellulose structure in the bleached fibre, and this aligns with the result obtained from the carbohydrate analysis (Table 1).

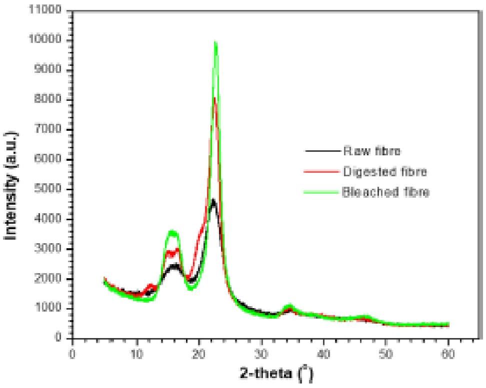


Fig. 1. XRD traces of raw, digested, and bleached harakeke fibre.

3.1.3. Morphological properties of raw, digested, and bleached harakeke fibre

The SEM images of raw, digested, and bleached harakeke fibre are shown in Fig. 2. Surface of the raw fibre (Fig. 2a) is smooth, likely due to the presence of cementing substances which tend to shield the fibre pores. These cementing substances can range from pectin, silica bodies, dirt particles and other soluble substances. In contrast, the surface of the digested fibre (Fig. 2b) reveals rougher morphology which may be attributed to the removal of cementing substances from the fibre surface during digestion [34]. The alkali solution used for digestion helps to disrupt the bonding structure within the fibre, thereby removing the

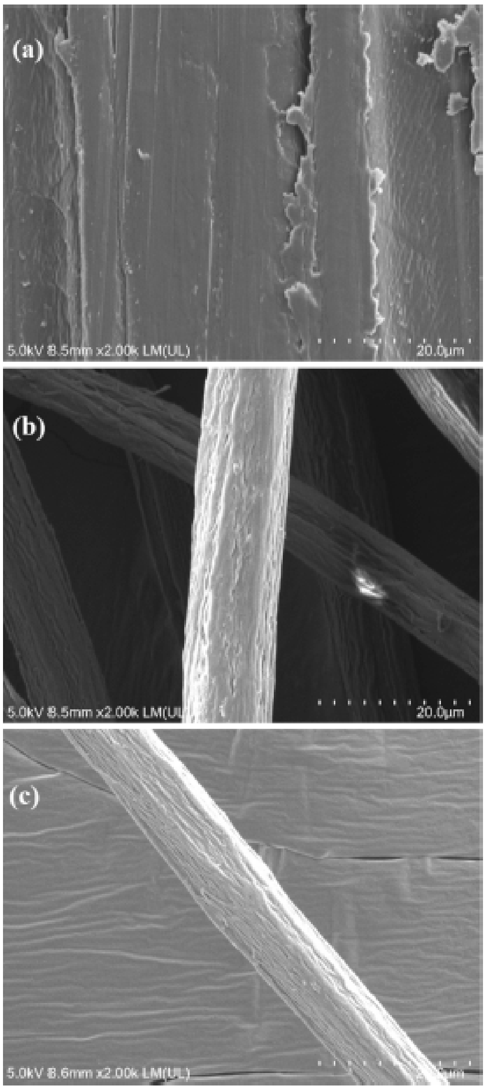


Fig. 2. SEM images of (a) raw, (b) digested, and (c) bleached harakeke fibre.

binding lignin and hemicellulose structures. This is responsible for the roughness observed on the fibre surface (Fig. 2b) and has been reported to facilitate mechanical interlocking between matrices and fillers during composite production [33,35]. Therefore, this effect of fibre treatment on the strength of the resulting composite will be discussed in a later section.

The SEM image of the bleached fibre (Fig. 2c) reveals that the fibre is shrunken, with a rougher surface compared to Fig. 2b. The bleaching treatment applied to the digested fibre helped to remove additional amounts of binding structure from the fibre, as presented in Table 1. This will invariably increase hydrogen bonding between the cellulose structures, due to removal of primary or secondary cell wall amorphous components [36,37]. As the cellulose structure rearranges and packs more closely, the fibre shrinks, resulting in a reduced diameter, due to the increased fibrillation [33,36]. The average diameters measured during SEM observation (result not shown) of the raw, digested, and bleached harakeke fibre were 495 µm, 11 µm, and 7 µm, respectively. The higher aspect ratio of the bleached fibre can help to facilitate fibre distribution during composite fabrication, thereby resulting in higher reinforcing ability and increased composite strength [31,38]. Likewise, the opening of pores on the fibre surface can help to improve fibre–matrix adhesion [8,39]. These aspects of the modified fibres will be discussed further under the section on mechanical properties of composites. The removal of cementing and binding structures from the fibre through treatment, and formation of hydrogen bonds were verified through FTIR analysis which is discussed in the next section.

3.1.4. Fourier transform infrared spectroscopy (FTIR) of harakeke fibre

The FTIR spectra of raw, digested, and bleached harakeke fibres are illustrated in Fig. 3. The notable peaks in the spectra of the raw fibre includes the − OH stretching vibration around 3200–3600 cm^{-1} [31]. The C—H stretching vibration of cellulose and hemicellulose is evident around 2850–2950 cm^{-1} [40], while the peak at 1737 cm^{-1} represents the C=O stretching peak of ester and carboxylic components of hemicellulose and lignin [31,40]. The peak at 1647 cm^{-1} represents the = CH vibration of the aromatic skeletal in lignin [31], while the peak at 1422 cm^{-1} is attributed to the —CH_3 asymmetric, and C—H symmetric deformation. The peak at 1060 cm^{-1} represents the in-plane deformation of the easily cleavable C—O—C linkage in lignin [31].

The —OH stretching vibration of bonded hydroxyl groups in the raw fibre shifted to a lower wavenumber in the digested and bleached fibre. This can be attributed to the structural changes caused the removal of lignin and hemicellulose through fibre treatment. This is believed to have influenced the reduced diameter of the treated fibre as discussed in section 3.1.3. It should be noted that the downward shift is further in the bleached fibre, compared to the digested fibre probably because more binding structures were removed with bleaching, than was removed with digestion alone as reported in Table 1.

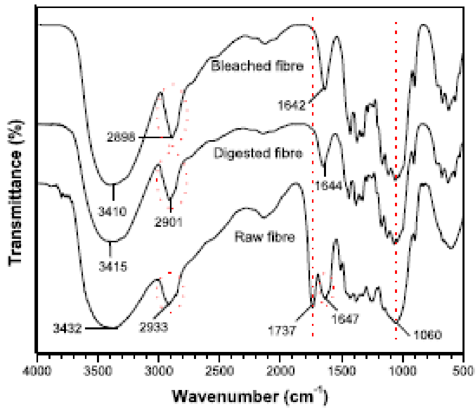


Fig. 3. FTIR spectra of raw, digested, and bleached harakeke fibre.

Another significant difference in the spectra of raw harakeke fibre and the treated fibres is the total disappearance of the C=O stretching peak at 1737 cm^{-1}. The absence of this peak in the spectra of the treated fibres confirm the dissolution of hemicellulose, and significant removal of lignin from the fibre during treatment [33,40]. This explains the increased surface roughness of the digested and bleached fibres as shown in Fig. 2b and 2c. There is a downward shift in the stretching vibration of C—H in cellulose and hemicellulose from 2933 cm^{-1} in the raw fibre, to 2901 cm^{-1} in the digested fibre, and 2898 cm^{-1} in the bleached fibre. This is attributed to the removal of hemicellulose, and repacking of the cellulose structure. Furthermore, removal of binding structure, namely lignin from the treated fibres was confirmed by the downward shift of the vibrational frequency from the = CH groups in the aromatic skeletal (methyl, methylene and methoxy groups) of lignin around 1647 cm^{-1}. The downward shift of this peak is an indication of structural deformation of lignin [41], which was further confirmed by the split in the aromatic C—H in-plane deformation peak at 1060 cm^{-1}. This FTIR result supports the SEM observation, and the carbohydrate analysis.

3.1.5. Thermal properties of harakeke fibre

The TGA curves of raw and treated fibres are illustrated in Fig. 4a. As seen in the figure, there is a general drop in weight of all the fibre types in the temperature range from room temperature to around 130 °C due to the release of preabsorbed moisture [39]. Degradation in natural fibres generally starts at the amorphous regions, followed by the crystalline regions. The degradation of lignin starts around 160 °C, hemicellulose degradation starts around 220 °C, while cellulose degradation commences around 315 °C [39]. Although crystalline cellulose has higher degradation temperature, it has been revealed by literature that portions of the lignin component would normally degrade at higher temperature, in the range, and above the degradation temperature of crystalline cellulose [7,42], due to the complex structure of lignin. Therefore, the early degradation observed in the raw fibre as seen in Fig. 4a can be attributed to the degradation of amorphous non-cellulosic components such as lignin and hemicellulose. Due to the significant removal of non-cellulose components from the treated fibres, the thermal degradation in the treated fibres is mainly dependent on the crystalline cellulose. This is responsible for the higher thermal stability of the treated fibres.

The thermal degradation temperature (T_d) of the fibres was derived from the DTG curve in Fig. 4b. The thermal properties of the fibres, including onset temperature of thermal degradation (T_{onset}), and maximum thermal decomposition temperature (T_d) are presented in Table 2. In addition, the amounts of residue recorded at 600 °C are included in Table 2. The amount of residue recorded for the fibre as seen in Table 2 can be associated with the proportion of non-cellulosic components in the fibre which would appear in the form of char or ash residue [41,43]. The relative lignin content of the fibres as discussed in section 3.1.1 and presented in Table 1 shows that the amount of lignin in the fibres is in the order of raw fibre > digested fibre > bleached fibre. Therefore, this is believed to have influenced the residue from the samples at 600 °C.

Table 2 shows that the onset of thermal degradation is faster in the raw fibre compared to the treated fibre which is not unexpected. In the case of the treated fibres, the T_{onset} of the bleached fibre is lower than that of the digested fibre. As discussed in sections 3.1.2 and 3.1.4, bleaching of harakeke fibre facilitated increased formation of intermolecular hydrogen bonds between the cellulose molecules Therefore, the lower T_{onset} of the bleached fibre could be due to the large interface area created through bond formation. This might have permitted heat

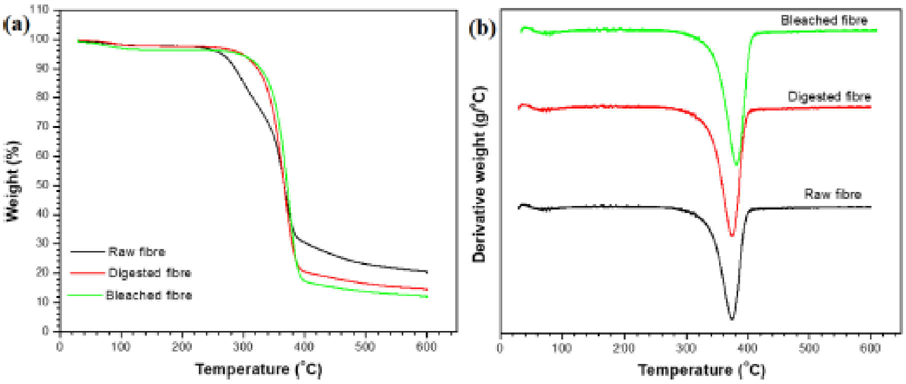


Fig. 4. TGA curves of raw, digested, and bleached harakeke fibre.

Table 2
Thermal properties of raw, digested, and bleached harakeke fibre.

Samples	T_{onset} (°C)	T_d (°C)	Residual @ 600 (°C)	E_a (kJ/mol)
Raw Fibre	263.79	366.94	20.14	68.80
Digested Fibre	296.46	366.70	14.3	118.67
Bleached Fibre	291.29	371.50	11.80	125.61

penetration at the unstable sites, particularly the amorphous regions of cellulose. Nevertheless, it is interesting that the T_d of the bleached fibre is higher than the digested fibre (see Fig. 4 and Table 2). This indicates higher overall thermal stability of the bleached fibre, than the fibre digested alone. The reason for this might be due to the higher number of hydrogen bonds in the bleached fibre which restricted the continued ingress of heat. This will invariably shift the maximum decomposition temperature to the higher temperature range due to higher heat resistance of the more structured crystalline cellulose, as confirmed through XRD analysis and discussed in section 3.1.2.

In addition to its ability to help in determining the thermal degradation temperature (T_d), the DTG data can equally assist in calculating the activation energy associated with thermal degradation of natural fibres [33]. The activation energy (E_a) is a good indicator of the energy barrier that hinders molecular chain mobility in the fibre, which in turn retricts thermal degradation. Therefore, the thermal stability of the fibres was further investigated through kinetic study, using the TGA data according to the method described by Broido [44]. The kinetic parameter for thermal decomposition of the fibres was determined using equation (4) as follows:

$$ln(ln\frac{1}{y}) = -\frac{E_a}{RT} + ln(\frac{RZ}{E_a\beta}T^2_{max}) \tag{4}$$

where, y is the fraction of non-volatilised material as yet undecomposed, T_{max} is the temperature of the maximum reaction rate (°C), β is the heating rate (°C min^{-1}), Z is the frequency factor, E_a represents the activation energy (J mol^{-1}) and R is the gas constant (8.314 J mol^{-1} K^{-1}). The values of y can be obtained from the TGA data such that ln(ln (1/y)) can be calculated accordingly. By plotting a graph of 1/T (in Kelvin) on the x-axis and ln(ln (1/y)) on the y-axis, the activation energy (E_a) associated with thermal decomposition of the fibres can be determined from the slope of the graph [45]. The plot of 1/T vs ln(ln (1/y)) for the raw, digested and bleached harakeke fibre is presented in Fig. S1 of the supplementary information section. The R^2 value of the plots for all the fibres are above 0.9 which indicates that the linearity of the graphs are in good agreement with the Broido equation, and the E_a values for thermal decomposition of the fibres are included in Table 2. As seen in Table 2, the E_a of the bleached fibre is higher than that of the raw and digested fibres. This confirms the higher thermal stability of the bleached fibre, and this aligns with the TGA result.

3.2. Properties of PLA/harakeke composites

3.2.1. Mechanical properties of PLA/harakeke composites

The mechanical properties of PLA and PLA/harakeke composites containing different wt.% (10–30 wt%) of digested and bleached harakeke fibre are illustrated in Fig. 5. It can be seen from Fig. 5a that the tensile strength (TS) of the composites initially increased following the addition of fibre up to 20 wt% fibre content. After this, the TS decreased when the fibre content was increased to 30 wt%. On the other hand, the tensile modulus TM in Fig. 5b reveals an increasing value with increasing fibre content. The initial increase in TS of the composites above the TS of neat PLA can be attributed to effective reinforcement and the transfer of stress from the PLA matrix to the reinforcing fibre. At 20 wt% fibre, the TS is 73.06 MPa and 74.45 MPa for digested and bleached fibre composites, respectively compared to 62.85 MPa of neat PLA. Further increase in fibre content from 20 wt% to 30 wt% resulted in decline of TS. This observation agrees with what was reported in a similar study [16], which is believed to be due to less wetting of the fibre by the PLA matrix at this fibre content. Serizawa et al., investigated the effect of varying amounts of kenaf fibre on the properties of kenaf fibre reinforced PLA composite. They reported that the maximum flexural strength and modulus was attained at 20 wt% fibre content [17]. Likewise, Komal et al., reported 20 wt% banana fibre as the optimum fibre content when they varied the fibre content from 10 to 30 wt% in banana fibre reinforced PLA composites [18]. A drop in mechanical performance of composites beyond what is defined as an optimum fibre content is often due to poor wetting of the fibre. Poor wetting will normally lead to agglomeration of fibre within the composite due to unfavourable distribution, thereby leading to the creation of large voids within the composite. As a result of this, the transfer of stress from the matrix to the reinforcing fibre will not be effective, which leads to the observed decrease in TS of the composites at 30 wt% fibre content.

It is noteworthy that at the different fibre contents, the TS of bleached fibre composites is higher than the digested fibre. Literature revealed that the mechanical strength of natural fibre reinforced composites can be significantly influenced by the fibre diameter [5]. Specifically, large diameter fibres can trigger different local deformation processes within the composite including fibre pull-out, debonding of the fibre from the matrix, or fibre fracture. As discussed in section 3.1.3,

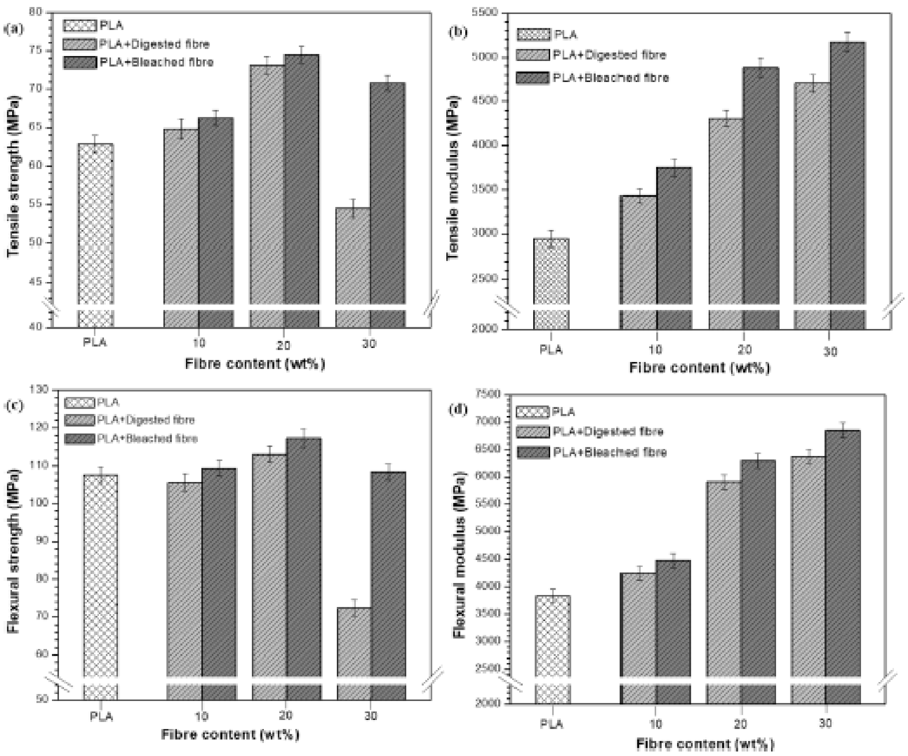


Fig. 5. (a) Tensile strength, (b) tensile modulus, (c) flexural strength, and (d) flexural modulus of PLA and PLA/harakeke composites containing different wt.% values of digested and bleached harakeke fibre.

the diameter of bleached harakeke fibre is smaller than that in digested fibre. Therefore, the wider diameter of the digested fibre might have contributed to the lower strength of the digested fibre composites, compared to the bleached fibre composites as seen in Fig. 5a. In another vein, treatment of fibre through bleaching with peroxide has been reported to facilitate interfacial bonding between the fibre and polymer matrices, by acting as a coupling agent [10,40]. This is believed to have contributed to the higher strength of the bleached fibre composites. Fibre pull-out, debonding of fibre from matrix, fibre fracture, and the extent of interfacial adhesion in the composites was assessed through SEM observation of the fractured surfaces of the composites which forms the subject of the next section.

Similar trends can be seen in the FS in Fig. 5c and the TS in Fig. 5a and the reason for this trend is as stated in the previous paragraph. In contrast to the trend observed for TS and FS, the tensile modulus (TM) and flexural modulus (FM) of the samples illustrated in Fig. 5b (TM) and Fig. 5d (FM) shows an increasing trend as fibre content was increased. This can be attributed to the high modulus of harakeke fibre, and this suggest that the strength and modulus of PLA/harakeke composites depend on different factors. Specifically, the strength is believed to be influenced by such factors such as wetting of fibre by the matrix, filler distribution, filler content, and fibre–matrix interfacial adhesion. In contrast, modulus of the composite seems to be more dependent on the filler content, and modulus of the fibre. Generally, in fibre reinforced polymer composites, there are always reports on the optimum fibre content for maximum strength. This is usually between 20 and 40 wt% fibre content depending on the composite preparation method, type of filler, and matrix type. Some selected studies on natural fibre reinforced PLA composites are summarized in Table S1 in the supplementary information section. It is noteworthy that the TS and FS recorded at 20 wt % fibre in this study is comparable to most of the previously published reports on reinforced PLA composites, even at higher fibre content values. This is a testament to the high reinforcing ability of harakeke fibre.

3.2.2. *Morphological properties*

The SEM images of the fractured surface (after tensile testing) of neat PLA, and PLA/harakeke composites containing 20 wt% and 30 wt% fibre are shown in Fig. 6. It can be seen from Fig. 6a, that the fractured surface of neat PLA is smooth, which is expected of brittle materials like PLA. For the composites with 20 wt% fibre, it is evident that the length of pulled out fibre in the digested fibre (DF) reinforced composite, PLA + 20 DF (Fig. 6b) is longer than for those observed in composite reinforced with fibres subjected to bleaching (BF) (PLA + 20 BF) (Fig. 6c). The shorter pull-out fibres in Fig. 6c indicates stronger interfacial adhesion between PLA and the bleached fibre [5,46]. Likewise, strands, believed to be PLA can be seen on the surface of PLA + 20 BF (Fig. 6c). In relation to this, it was reported in the literature that treatment of natural fibre with peroxide imparts ester functionality on the fibre surface [40,47]. Hence, the peroxide bleaching of harakeke fibre in the present study has likely imparted ester functionality on the surface that will make the fibre more compatible with PLA. Therefore, the polymer

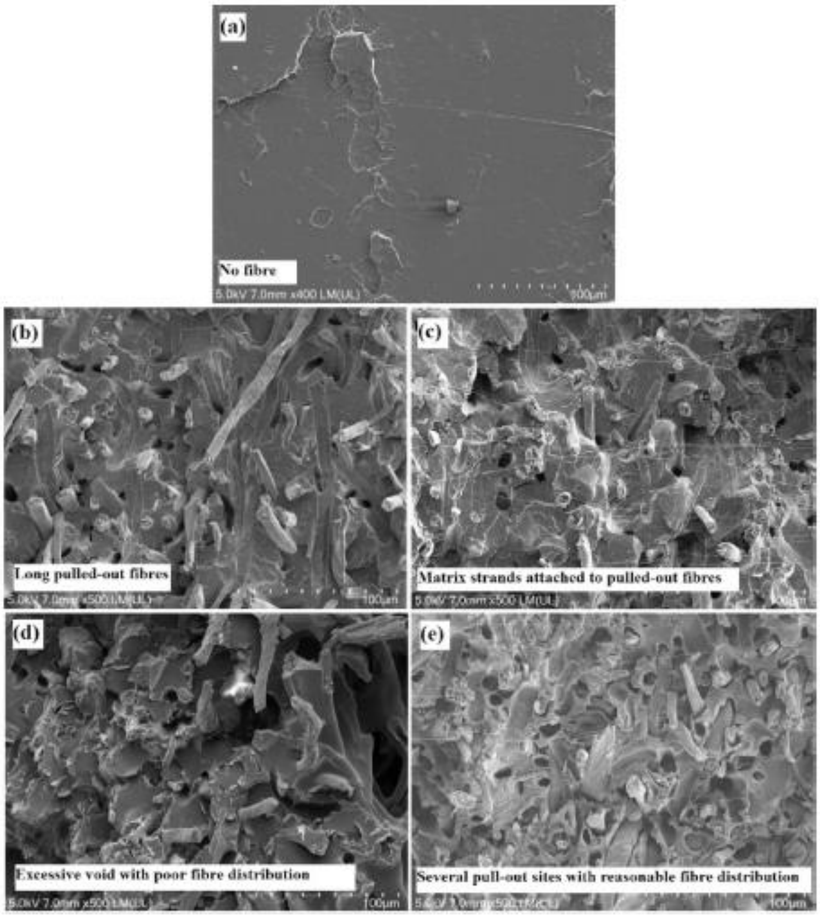


Fig. 6. SEM images of (a) neat PLA, and PLA/harakeke composites containing (b) 20 wt% DF, (c) 20 wt% BF, (d) 30 wt% DF, and (e) 30 wt% BF.

strands seen in Fig. 6c are believed to be due to stronger interfacial adhesion resulting from mechanical bonding between the PLA and the bleached fibre. This, it is believed, has contributed to the higher mechanical strength of the bleached fibre composites as discussed in section 3.2.1.

The SEM images of the composites containing 30 wt% fibre reveal a higher number of pull-out holes on the composite fractured surface. This suggests a reduced fibre–matrix interaction between PLA and harakeke at 30 wt% fibre content. When there is a higher percentage of fibre in the composite, this can result in poor wetting of the fibre by the matrix and would be responsible for the drop in mechanical strength of the composite at 30 wt% fibre content, for both DF and BF as seen in Fig. 5a and 5c. Although a drop in mechanical strength was recorded for both fibre types at 30 wt%, it is noteworthy that the alignment and orientation of fibre in the PLA + 30 DF composite is lesser than in the PLA + 30 BF composites. This, in addition to poor fibre wetting is believed to have contributed to the higher drop in mechanical strength of the DF reinforced composite at 30 wt% fibre content, compared to that of the BF reinforced composite.

3.2.3. Fourier transform infrared spectroscopy of composites

The bonding structures and extent of interfacial interaction between PLA and the treated harakeke fibres was further investigated through FTIR analysis. It should be noted that for ease of comparison, only the composites containing 20 wt% fibre is discussed in this section. The FTIR spectra of PLA, PLA + 20 DF, and PLA + 20 BF are illustrated in Fig. 7. The band in the FTIR spectra of PLA and the composites around 3200–3650 cm^{-1} is due to the stretching vibration of the —OH groups in cellulose, and the terminal hydroxyl groups in PLA [31], while the band around 2850–3050 cm^{-1} is attributed to symmetric and asymmetric stretching of C—H from methyl and methylene groups in cellulose. The peak at 1750 cm^{-1} is assigned to the C=O stretching vibration of acetyl and carboxylic acids moieties [31], and the ester components from PLA. The peak at 1455 cm^{-1} is a characteristic —CH_3 bending mode, whereas the peak at 1379 cm^{-1} is attributed to C—H deformation [31]. In addition, stretching of the C—O group of carboxylic acid and the ester components of PLA is represented by the peak at 1091 cm^{-1}.

It can be seen in Fig. 7 that the —OH stretching vibration around 3200–3650 cm^{-1} in the spectra of PLA was widened in the spectra of the composites which suggests an increased intermolecular number of

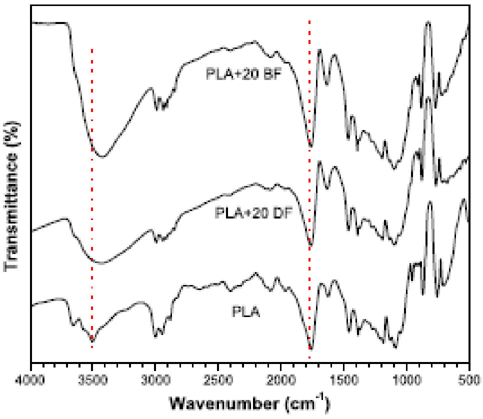


Fig. 7. FTIR spectra of PLA, and PLA/harakeke composites containing different 20 wt% of digested fibre (DF) and bleached harakeke fibre (BF).

hydrogen bond due to increased number of —OH groups available for bond formation in the fibre cellulose, brought about by surface modification [31] This is supported by the slight movement of this peak to a lower wavenumber in the spectra of the composites, which is attributed to the formation of hydrogen bonds between the —OH of the fibres, and the terminal hydroxyl groups of PLA. In addition, the interaction between PLA and the fibres can be through bond formation between the cellulose —OH group of the fibres and C=O of PLA [48]. This is confirmed by the slight peak shift from 1750 cm^{-1} in the spectra of neat PLA, to a lower wavenumber value in spectra of the PLA/harakeke composites which indicates esterification reaction between the terminal —COOH groups of PLA and the —OH groups of harakeke fibre [48].

It is noteworthy that the downward shift of the band around 3200–3650 cm^{-1} and the peak at 1750 cm^{-1} is more significant than the shift observed in the spectra of the bleached fibre composite (PLA + 20 BF), compared to the digested fibre composite (PLA + 20 DF). This is an indication of a higher interaction between the bleached fibre and PLA, and this aligns with the SEM observations discussed earlier. The higher interaction between PLA and the bleached fibre as confirmed through this FTIR analysis is believed to have contributed to the higher mechanical properties of the bleached fibre composites as discussed in section 3.2.1.

3.2.4. *Thermal properties of composites*

The TGA curves of PLA and the composites are illustrated in Fig. 8a. As seen in the figure, the TGA curves follow a similar trend. The onset of thermal degradation is above 300 °C and the drop in weight continued up to 400 °C. The onset of thermal degradation (T_{onset}) and the thermal degradation temperature T_d) of the samples are summarized in Table 3. In addition, the amount of residue remaining at T ≥ 500 °C of the samples are included in Table 3. The T_{onset}, and T_d, of neat PLA is higher than that of the composites which is believed to be due to the intact structure of the PLA chains in neat PLA. The incorporation of fibres into PLA would distort the homogeneity of the PLA chain structure [16], which can in turn result in increased heat penetration sites as reported for micro crystalline cellulose (MCC) reinforced PLA composites [31]. It can also be due to the lower thermal stability of the fibre, compared to neat PLA [40]. From Fig. 8a, and Table 3, it is evident that the bleached fibre composites are more thermally stable compared to the digested fibre composites, at all fibre contents.

The DSC thermograms of PLA and the composites are shown in Fig. 8b. From this figure it is possible to discern three successively distinct transitions which represent the glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m). The DSC parameters of the samples were obtained from the thermograms, and the parameters are included in Table 3. It is evident in Fig. 8b that the T_g of PLA was not significantly influenced by the inclusion of harakeke fibre. In contrast, the T_c of PLA in the composites can be seen to be notably influenced by the fibre. The addition of reinforcing fillers into semi crystalline polymers is known to result in an upward or downward shift in the T_c, and this often describes the ability of fillers to induce heterogeneous nucleation in the matrix [49]. The T_c of the samples presented in Fig. 8b shows a downward shift in T_c of PLA in the composites. This is an indication of faster crystallisation in the composites [50], which confirms the aforementioned heterogeneous nucleation activities on the harakeke fibre. When cold crystallisation occurs, it often results in the formation of imperfect crystals which can be verified through the melting peak of the sample [2].

The split in the melting peak (T_m) of the composites compared to neat PLA (Fig. 8b) can be attributed to the formation of imperfect crystals in the composite due to the crystallisation effects of the fibre on PLA. Usually, the imperfect crystals would melt at a lower temperature than the perfect crystals themselves. Hence, the double peaks observed around the T_m of PLA in the composites is because of perfect and imperfect crystals within the composite, due to the heterogeneous

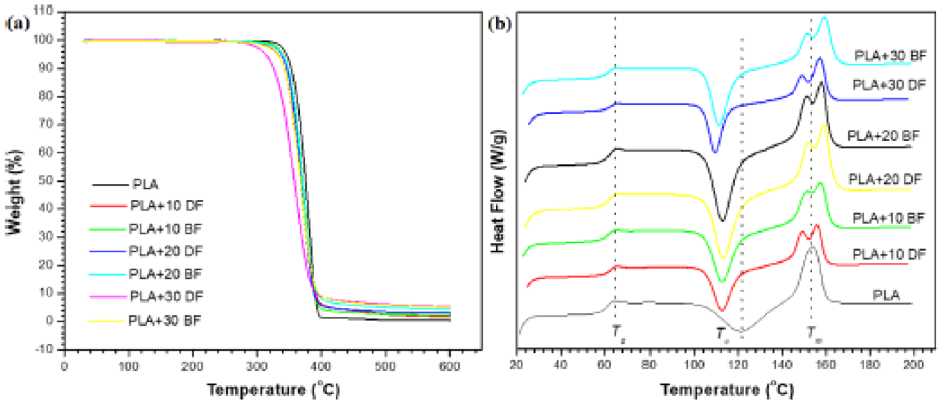


Fig. 8. (a) TGA curves, and (b) DSC thermograms of PLA and PLA/harakeke composites containing different wt.% of digested fibre (DF) and bleached fibre (BF).

Table 3
Thermal properties of PLA and PLA/harakeke composites.

TGA				DSC			
Sample code	T_{onset} (°C)	T_d (°C)	Residue (%) at T ≥ 500 °C	T_g (°C)	T_c (°C)	T_m (°C)	X_{DSC} (%)
PLA	345.25	375.48	0.58	61.90	121.00	154.00	26.53
PLA + 10 DF	333.13	367.94	2.18	62.08	115.70	156.70	32.27
PLA + 10 BF	339.60	370.18	2.67	62.13	116.70	157.49	33.93
PLA + 20 DF	337.56	368.79	3.49	62.65	116.70	157.70	34.52
PLA + 20 BF	338.75	370.87	5.06	63.22	116.30	158.70	36.13
PLA + 30 DF	313.21	357.60	6.14	63.07	115.98	157.95	41.41
PLA + 30 BF	331.15	367.25	6.90	63.15	116.85	158.97	41.49

nucleation effects of the fibre. As seen in Fig. 8b and presented in Table 3, the T_m of the composites is higher than that observed for neat PLA, most likely because the T_m of the composites was determined by the fusion of imperfect crystals formed during cold crystallisation, and the fusion of spherulites formed during the process of recrystallisation [2]. The effect of fibre treatment on the crystallisation behaviour of PLA was further investigated through the calculation of the crystallinity index, using equation (3). The crystallinity index (X_{DSC}%) of PLA and the composites are included in Table 3, which confirms the significant influence of fibre inclusion, on the crystallinity index of PLA. In addition, it was observed that at each fibre wt.% content, the bleached fibre composites exhibit a higher X_{DSC}% than the digested fibre composites. This indicates the formation of a larger number of crystallites within the bleached fibre composites and indicates that the bleached fibre did not only facilitate the formation of new crystals through heterogeneous nucleation but would also have led to the growth of existing spherulites. In another vein, the higher interfacial interaction between PLA and the bleached fibre as discussed in previous sections has favoured higher *trans*-crystallinity within the bleached fibre composite. Increased matrix crystallinity in known to support mechanical strength improvements in polymer composites. Therefore, the higher crystallinity of PLA in the bleached fibre composites than in the digested fibre composites has contributed to the superior mechanical strength of the bleached fibre composites as discussed in section 3.2.1.

Literature on this subject has revealed that one of the major factors influencing the thermal stability of composites, is the nature and strength of the fibre–matrix interfacial bonding [38]. Alkaline treatment of natural fibres increases the surface roughness of the fibres, thereby facilitating mechanical interlocking and interfacial adhesion between the fibre and matrix. In contrast, the dominant interfacial mechanism in peroxide treated fibres is chemical bonding [40]. The schematic illustration of the mechanism of reinforcement in digested and bleached harakeke fibre is shown in Fig. 9. Results of the FTIR analysis and SEM observation discussed in previous sections suggests higher interaction between PLA and the bleached fibre, compared to the digested fibre. This can help to facilitate efficient distribution of thermal energy within the PLA/bleached fibre composite. The higher possibility for hydrogen bonding, and the increased distribution of fibre within the bleached fibre composites have both contributed to the higher thermal stability of the bleached fibre composites.

3.2.5. *Dynamic mechanical properties of PLA/harakeke composites*

Dynamic mechanical analysis helps to determine the viscoelastic characteristics of polymer and polymer composites, and this is generally investigated through the storage modulus, loss modulus and the damping factor [7,51]. The storage modulus (E′) curves of PLA and the composites are illustrated in Fig. 10a. It can be seen in Fig. 10a that the E′ of PLA and the composites dropped steadily around the glass transition region of PLA, which is attributed to increased PLA chain mobility. Increased chain mobility would result in softening and segmental movement of PLA molecules, and this would invariably produce a steep drop in E′ as seen in Fig. 10a. The figure also shows that the E′ values of the composites are higher than in neat PLA which can be attributed to the stiffness imposed on PLA matrix by the reinforcing fibre. Increased stiffness would facilitate interfacial stress transfer within the composite [51].Therefore, this accounts for the higher modulus of the composites, compared to neat PLA. It is clearly seen in Fig. 10a that the increase in fibre content produced increasing modulus values such that the E′ of the composites reach a maximum at 30 wt% fibre. It is significant that the improvement in E′ of the composites when fibre content was raised from 20 wt% to 30 wt% is not as large as the improvement seen when raising the fibre content from 10 wt% to 20 wt%. This suggests that the reinforcement produced through good fibre distribution, and interfacial interaction within the composite was more effective at 20 wt% fibre content than at 30 wt%.

Literature has revealed that different factors can influence the E′ of composites, including matrix type, filler type, filler distribution, and filler-matrix interfacial adhesion [10,38,51]. Therefore, the higher E′ of the PLA-harakeke composites at 30 wt% fibre content is not unexpected, considering the high modulus of harakeke fibre. It is interesting that at 20 wt% fibre content, the bleached fibre composite (PLA + 20 BF) exhibits a significantly higher E′ than in the digested fibre composite (PLA + 20 DF). This can be associated with stronger interfacial bonding between PLA and the bleached fibre as discussed in sections 3.2.2 and 3.2.3, in addition to the stiffness imposed on PLA by the fibre. The decomposition of organic peroxides leads to the formation of free

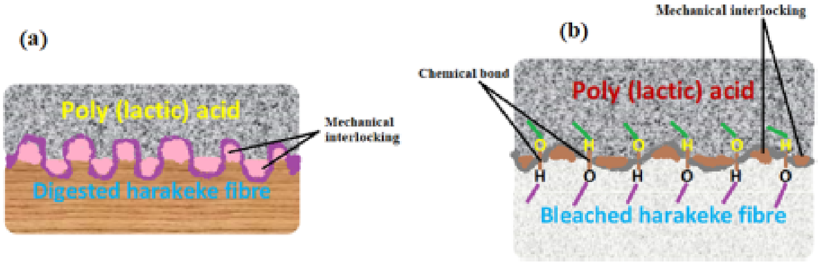


Fig. 9. Illustration of the mechanism of PLA reinforcement by (a) digested, and (b) bleached harakeke fibre.

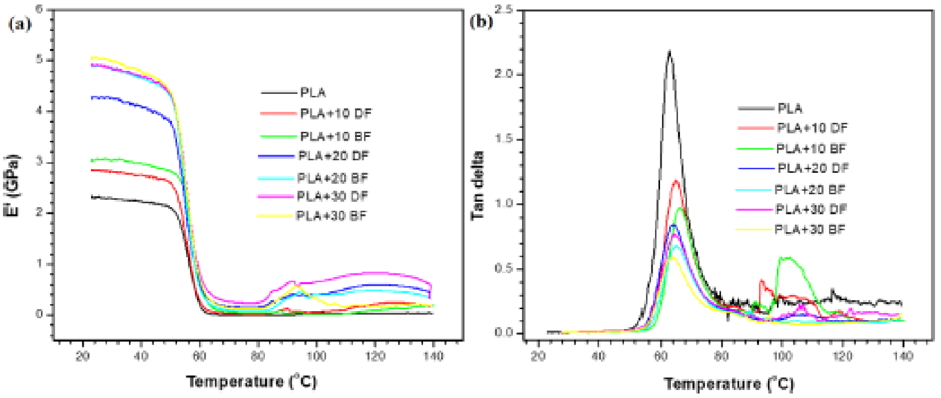


Fig. 10. (a) Storage modulus, and (b) tan δ curves of PLA and PLA/harakeke composites containing different wt.% of digested and bleached harakeke fibre.

radicals (RO) which are highly reactive. In the case of H_2O_2, OH radicals are produced and this highly reactive radical can react with the hydroxyl groups of the fibre thereby forming strong chemical bonds [40]. This will reduce the hydrophilic tendency of the fibre, thereby increasing its compatibility with PLA which favours fibre distribution in the matrix. Improved fibre distribution will facilitate effective stress transfer from PLA to the bleached fibre, which will in turn enhance the ability of PLA to withstand mechanical strain through recoverable viscoelastic distortion. This is believed to be responsible for the higher E' of the bleached fibre composites above the digested fibre composites. To further assess the strength of the interface in the composites, the damping parameter (tan delta (δ)) was analysed.

The damping factor (tan δ) is the ratio of energy dissipated, to the energy stored when a material is subjected to dynamic constraints. The tan δ value is notable for its ability to accurately give an indication of the T_g of materials [51]. Usually, the T_g is obtained as the temperature at which the tan δ curve is at its maximum. The tan δ curves of PLA and the composites are illustrated in Fig. 10b. The T_g obtained from the tan δ curves in Fig. 10b and the maximum tan δ peak values are presented in Table 4. The T_g values obtained from the tan δ curves align with the DSC result which showed that the incorporation of harakeke only slightly affected the of T_g of PLA. The data in Table 4 show that the maximum tan δ peak of the composites is lower than observed for neat PLA. It can be seen in Fig. 10b that the reduction in tan δ of the composites compared to PLA is quite large which indicates that the incorporation of harakeke fibre was more influential on the tan δ peak than on the T_g of PLA. Therefore, the tan δ peak was further analysed for the best mechanical performance composite in this study (i.e. 20 wt% fibre content), to investigate the extent of interfacial adhesion in the composite. The tan δ peak was used to determine the adhesion factor A, and effectiveness coefficient C of PLA + 20 DF and PLA + 20 BF, in comparison with neat PLA.

As reported in literature, the molecular mobility of polymer molecules around reinforcing fillers is often limited by strong interfacial adhesion between the matrix and the filler [51]. Hence, a strong interfacial adhesion would produce a low adhesion factor. The adhesion factor A of PLA and the composites was calculated using equation (5) as follows:

$$Adhesionfactor(A) = \frac{1}{1 - V_f}\frac{\tan\delta_c}{\tan\delta_p} - 1 \quad (5)$$

where, tan δ_c and tan δ_p are the relative damping factors for the composite and neat polymer, respectively, whereas V_f is the fraction (by mass) of the filler. The relative damping of the materials is obtained at the glass transition temperature as indicated by the maximum in the tan δ peak [41]. The calculated A values are included in Table 4. It is evident that the bleached fibre composite has the lowest A value which serves as confirmation of stronger interfacial adhesion between the bleached fibre and PLA. This agrees with the FTIR results discussed in section 3.2.3 and this is believed to have significantly contributed to the higher dynamic mechanical performance of the bleached fibre composite. The effectiveness of reinforcement, using bleached and digested fibre was also investigated by calculating the effectiveness coefficient. The effectiveness coefficient was obtained from the relationship between the ratio of the storage modulus E' of the composite in the glassy and rubbery region, to that of the neat polymer. The effectiveness coefficient C was calculated using equation (6) as follows:

$$Effectivenesscoefficient(C) = \frac{E'_g/E'_r(composite)}{E'_g/E'_r(resin)} \quad (6)$$

where, E'_g and E'_r represents the storage modulus in the glassy region and rubbery region, respectively. Generally, the reinforcing ability of the fibre is inversely proportional to the C value such that high reinforcing effectiveness will produce low C values. The calculated C value for PLA, and the composites are shown in Table 4 and the values confirms that the bleached fibre offers better reinforcing effectiveness to PLA than the digested fibre. This confirms the assumptions made based on the SEM observation of composites fractured surface (see Fig. 6 and section 3.2.2), and it aligns with the results discussed in section 3.2.1.

Table 4
Effectiveness coefficient, adhesion factor, and tan δ parameter of PLA and PLA/harakeke composites containing 20 wt% fibre.

Sample code	Effectiveness coefficient (C)	Max tan δ peak value	Adhesion factor (A)	T_g (°C)
PLA	1.000	2.188	0.000	62.677
PLA + 20 DF	0.071	0.841	−1.720	60.752
PLA + 20 BF	0.053	0.681	−1.992	61.290

4. Conclusion

Composites were prepared from PLA with different contents of digested and bleached harakeke fibre compounded through extrusion and injection moulded. Compared to digestion alone, combined digestion and bleaching treatment removed larger amount of non-cellulosic components from the fibre, which resulted in higher cellulose content. This increased the thermal stability of the fibre as confirmed through thermal analysis, which was attributed to the increased intermolecular cellulose hydrogen bonding in the digested and bleached fibre. Incorporation of the digested and bleached harakeke fibre into PLA produced higher mechanical and thermomechanical performance than the digested fibre alone. This was attributed to the effect of combined digestion and bleaching, which facilitated stronger interfacial interaction between PLA and the fibre, supported by the calculated adhesion factor and effectiveness coefficient. The mechanical test results showed that 20 wt % fibre was the optimum fibre content and the composites strength recorded at this fibre content is comparable to what have been previously reported for higher fibre contents in some natural fibre reinforced composites. The result from this study shows that harakeke fibre is a promising reinforcement for PLA to produce high performance composites suitable for structural applications. In addition, combination of digestion and bleaching treatment could present added benefits for improving the reinforcing ability of natural fibres in polymer composites, through increased fibre distribution and stronger interfacial bonding. Based on this study, further research is recommended for increasing the filler content by exploring different coupling additives to extend the use of harakeke fibre reinforced composites in more diverse structural applications.

CRediT authorship contribution statement

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

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.

Acknowledgement

The authors acknowledge the funding from the New Zealand Ministry of Business, Innovation and Employment, under the Āmiomio Aotearoa project hosted by The University of Waikato (UOWX2004). The first author also appreciates the financial support through a Research & Enterprise Award (108023) provided by the University of Waikato.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.compositesa.2022.107326.

References

[1] Scaffaro R, Lopresti F, Botta L. PLA based biocomposites reinforced with Posidonia oceanica leaves. Compos B Eng 2018;139:1–11.

[2] Serra-Parareda F, Delgado-Aguilar M, Espinach FX, Mutjé P, Boufi S, Tarrés Q. Sustainable plastic composites by polylactic acid-starch blends and bleached kraft hardwood fibers. Compos Part B: Eng 2022:109901.

[3] Rangappa SM, Siengchin S, Dhakal HN. Green-composites: Ecofriendly and sustainability. Appl Sci Eng Prog 2020;13(3):183–4.

[4] Thyavihalli Girijappa YG, Mavinkere Rangappa S, Parameswaranpillai J, Siengchin S. Natural fibers as sustainable and renewable resource for development of eco-friendly composites: a comprehensive review. Front Mater 2019;6.

[5] Bartos A, Nagy K, Anggono J, Antoni, Purwaningsih H, Móczó J, et al. Biobased PLA/sugarcane bagasse fiber composites: Effect of fiber characteristics and interfacial adhesion on properties. Compos A Appl Sci Manuf 2021;143:106273.

[6] Samouh Z, Molnar K, Boussu F, Cherkaoui O, El Moznine R. Mechanical and thermal characterization of sisal fiber reinforced polylactic acid composites. Polym Adv Technol 2019;30(3):529–37.

[7] Rajeshkumar G, Arvindh Seshadri S, Devnani GL, Sanjay MR, Siengchin S, Prakash Maran J, et al. Environment friendly, renewable and sustainable poly lactic acid (PLA) based natural fiber reinforced composites–A comprehensive review. J Clean Prod 2021;310:127483.

[8] Mazzanti V, Pariante R, Bonanno A, de Ballesteros OR, Mollica F, Filippone G. Reinforcing mechanisms of natural fibers in green composites: Role of fibers morphology in a PLA/hemp model system. Compos Sci Technol 2019;180:51–9.

[9] Yang X, Fan W, Ge S, Gao X, Wang S, Zhang Y, et al. Advanced textile technology for fabrication of ramie fiber PLA composites with enhanced mechanical properties. Ind Crop Prod 2021;162:113312.

[10] Getme AS, Patel B. A review: Bio-fiber's as reinforcement in composites of polylactic acid (PLA). Mater Today: Proc 2020;26:2116–22.

[11] Ighalo JO, Adeyanju CA, Ogunniyi S, Adeniyi AG, Abdulkareem SA. An empirical review of the recent advances in treatment of natural fibers for reinforced plastic composites. Compos Interfaces 2021;28(9):925–60.

[12] Pickering KL, Efendy MA, Le TM. A review of recent developments in natural fibre composites and their mechanical performance. Compos A Appl Sci Manuf 2016;83:98–112.

[13] Setswalo K, Oladijo O, Namoshe M, Akinlabi E, Sanjay M. The mechanical properties of alkali and laccase treated pterocarpus angolensis (mukwa)-polylactic acid (PLA) composites. Int J Biol Macromol 2022;217:398–406.

[14] Tarrés Q, Melbø JK, Delgado-Aguilar M, Espinach F, Mutjé P, Chinga-Carrasco G. Micromechanics of tensile strength of thermo-mechanical pulp reinforced poly (lactic) acid biodegradable composites. J Nat Fibers 2022;1–14.

[15] Siakeng R, Jawaid M, Asim M, Fouad H, Awad S, Saba N, et al. Flexural and dynamic mechanical properties of alkali-treated coir/pineapple leaf fibres reinforced polylactic acid hybrid biocomposites. J Bionic Eng 2021;18(6):1430–8.

[16] Al Abdallah H, Abu-Jdayil B, Iqbal MZ. Improvement of mechanical properties and water resistance of bio-based thermal insulation material via silane treatment. J Clean Prod 2022;346:131242.

[17] Serizawa S, Inoue K, Iji M. Kenaf-fiber-reinforced poly (lactic acid) used for electronic products. J Appl Polym Sci 2006;100(1):618–24.

[18] Komal UK, Lila MK, Singh I. PLA/banana fiber based sustainable biocomposites: a manufacturing perspective. Compos B Eng 2020;180:107535.

[19] Sanjay MR, Madhu P, Jawaid M, Senthamaraikannan P, Senthil S, Pradeep S. Characterization and properties of natural fiber polymer composites: A comprehensive review. J Clean Prod 2018;172:566–81.

[20] Akindoyo JO, Beg MDH, Ghazali S, Islam MR. The effects of wettability, shear strength, and Weibull characteristics of fiber-reinforced poly (lactic acid) composites. J Polym Eng 2016;36(5):489–97.

[21] Wehi PM, Clarkson BD. Biological flora of New Zealand 10. Phormium tenax, harakeke, New Zealand flax. N Z J Bot 2007;45(4):521–44.

[22] Le Guen MJ, Newman RH. Pulped Phormium tenax leaf fibres as reinforcement for epoxy composites. Compos A Appl Sci Manuf 2007;38(10):2109–15.

[23] Cruthers NM, Carr DJ, Laing RM, Niven BE. Structural differences among fibers from six cultivars of harakeke (Phormium tenax, New Zealand flax). Text Res J 2006;76(8):601–6.

[24] De Rosa IM, Iannoni A, Kenny JM, Puglia D, Santulli C, Sarasini F, et al. Poly (lactic acid)/Phormium tenax composites: Morphology and thermo-mechanical behavior. Polym Compos 2011;32(9):1362–8.

[25] Newman RH, Le Guen MJ, Battley MA, Carpenter JE. Failure mechanisms in composites reinforced with unidirectional Phormium leaf fibre. Compos A Appl Sci Manuf 2010;41(3):353–9.

[26] Oksman K, Skrifvars M, Selin JF. Natural fibres as reinforcement in polylactic acid (PLA) composites. Compos Sci Technol 2003;63(9):1317–24.

[27] Akindoyo JO, Beg MDH, Ghazali SB, Islam MR, Mamun AA. Preparation and characterization of poly (lactic acid)-based composites reinforced with poly dimethyl siloxane/ultrasound-treated oil palm empty fruit bunch. Polym-Plast Technol Eng 2015;54(13):1321–33.

[28] Verma D, Goh KL. Effect of mercerization/alkali surface treatment of natural fibres and their utilization in polymer composites: mechanical and morphological studies. J Compos Sci 2021;5(7):175.

[29] Pettersen RC. Wood sugar analysis by anion chromatography. J Wood Chem Technol 1991;11(4):495–501.

[30] Akindoyo JO, Beg MDH, Ghazali S, Heim HP, Feldmann M, Mariatti M. Simultaneous impact modified and chain extended glass fiber reinforced poly (lactic acid) composites: Mechanical, thermal, crystallization, and dynamic mechanical performance. J Appl Polym Sci 2021;138(5):49752.

[31] Bhiogade A, Kannan M, Devanathan S. Degradation kinetics study of Poly lactic acid (PLA) based biodegradable green composites. Mater Today: Proc 2020;24:806–14.

[32] Sawpan MA, Pickering KL, Fernyhough A. Effect of various chemical treatments on the fibre structure and tensile properties of industrial hemp fibres. Compos A Appl Sci Manuf 2011;42(8):888–95.

[33] Kathirselvam M, Kumaravel A, Arthanarieswaran V, Saravanakumar S. Characterization of cellulose fibers in Thespesia populnea barks: Influence of alkali treatment. Carbohydr Polym 2019;217:178–89.

[34] Jaiswal D, Devnani GL, Rajeshkumar G, Sanjay MR, Siengchin S. Review on extraction, characterization, surface treatment and thermal degradation analysis of

new cellulosic fibers as sustainable reinforcement in polymer composites. Curr Res Green Sustain Chem 2022;5:100271.

[35] Tiwari YM, Sarangi SK. Characterization of raw and alkali treated cellulosic Grewia Flavescens natural fiber. Int J Biol Macromol 2022;209:1933–42.

[36] Duchemin B, Staiger MP. Treatment of Harakeke fiber for biocomposites. J Appl Polym Sci 2009;112(5):2710–5.

[37] Ramlee NA, Jawaid M, Zainudin ES, Yamani SAK. Modification of oil palm empty fruit bunch and sugarcane bagasse biomass as potential reinforcement for composites panel and thermal insulation materials. J Bionic Eng 2019;16(1): 175–88.

[38] Rahman MZ. Mechanical and damping performances of flax fibre composites–A review. Composites Part C: Open Access 2021;4:100081.

[39] Chougan M, Ghaffar SH, Al-Kheetan MJ, Gecevicius M. Wheat straw pre-treatments using eco-friendly strategies for enhancing the tensile properties of bio-based polylactic acid composites. Ind Crop Prod 2020;155:112836.

[40] Goriparthi BK, Suman K, Rao NM. Effect of fiber surface treatments on mechanical and abrasive wear performance of polylactide/jute composites. Compos A Appl Sci Manuf 2012;43(10):1800–8.

[41] Puglia D, Monti M, Santulli C, Sarasini F, De Rosa IM, Kenny JM. Effect of alkali and silane treatments on mechanical and thermal behavior of Phormium tenax fibers. Fibers Polym 2013;14(3):423–7.

[42] Hong H, Xiao R, Guo Q, Liu H, Zhang H. Quantitively characterizing the chemical composition of tailored bagasse fiber and its effect on the thermal and mechanical properties of polylactic acid-based composites. Polymers 2019;11(10):1567.

[43] Qin L, Qiu J, Liu M, Ding S, Shao L, Lü S, et al. Mechanical and thermal properties of poly(lactic acid) composites with rice straw fiber modified by poly(butyl acrylate). Chem Eng J 2011;166(2):772–8.

[44] Broido A. A simple, sensitive graphical method of treating thermogravimetric analysis data. J Polym Sci Part A-2: Polym Phys 1969;7(10):1761–73.

[45] Oza S, Ning H, Ferguson I, Lu N. Effect of surface treatment on thermal stability of the hemp-PLA composites: Correlation of activation energy with thermal degradation. Compos B Eng 2014;67:227–32.

[46] Georgiopoulos P, Kontou E, Georgousis G. Effect of silane treatment loading on the flexural properties of PLA/flax unidirectional composites. Compos Commun 2018; 10:6–10.

[47] Liu X, Dai G. Surface modification and micromechanical properties of jute fiber mat reinforced polypropylene composites. Express Polym Lett 2007;1(5):299–307.

[48] Sawpan MA, Pickering KL, Fernyhough A. Effect of fibre treatments on interfacial shear strength of hemp fibre reinforced polylactide and unsaturated polyester composites. Compos A Appl Sci Manuf 2011;42(9):1189–96.

[49] Akindoyo JO, Beg M, Ghazali S, Heim HP, Feldmann M, Mariatti M. Synergized high-load bearing bone replacement composite from poly (lactic acid) reinforced with hydroxyapatite/glass fiber hybrid filler—Mechanical and dynamic mechanical properties. Polym Compos 2021;42(1):57–69.

[50] Ruz-Cruz M, Herrera-Franco P, Flores-Johnson E, Moreno-Chulim M, Galera-Manzano L, Valadez-González A. Thermal and mechanical properties of PLA-based multiscale cellulosic biocomposites. J Mater Res Technol 2022;18:485–95.

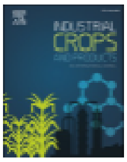
[51] Saba N, Jawaid M, Alothman OY, Paridah MT. A review on dynamic mechanical properties of natural fibre reinforced polymer composites. Constr Build Mater 2016;106:149–59.

Industrial Crops & Products 214 (2024) 118507

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop



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

John O. Akindoyo [a,*], Kim Pickering [a], Michael Mucalo [b], Mohammad Dalour Beg [a], Joanna Hicks [c]

[a] *School of Engineering, University of Waikato, Hamilton, New Zealand*
[b] *School of Science, University of Waikato, Hamilton, New Zealand*
[c] *School of Health, University of Waikato, Hamilton, New Zealand*

ARTICLE INFO

Keywords:
Enzymatic treatment
Mechanical processing
Reinforcement
Natural fibres
Fibrillation

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.

---

[*] Corresponding author.
E-mail address: blessedbode@ymail.com (J.O. Akindoyo).

https://doi.org/10.1016/j.indcrop.2024.118507
Received 30 November 2023; Received in revised form 10 March 2024; Accepted 3 April 2024
Available online 6 April 2024
0926-6690/© 2024 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

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. *Characterisations*

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

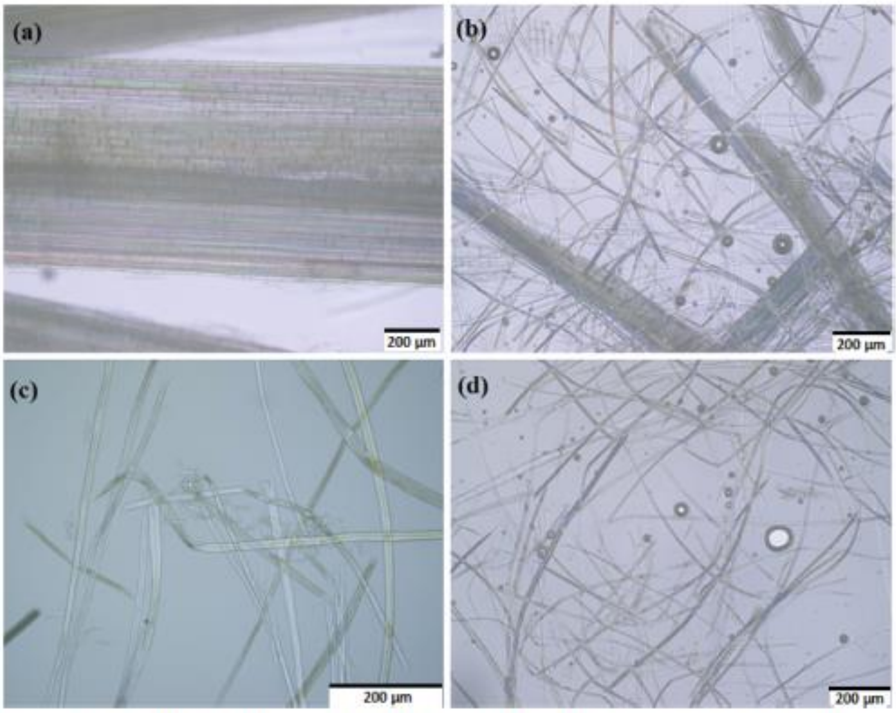


Fig. 1. Optical microscope images of (a) unprocessed harakeke fibre, (b) fibre processed 4 times each at 400 µm and 300 µm disc distance, (c) fibre processed 4 times each at 400 µm and 300 µm, followed by 2 times at 200 µm disc distance, and (d) fibre processed 4 times each at 400 µm, 300 µm, and 200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

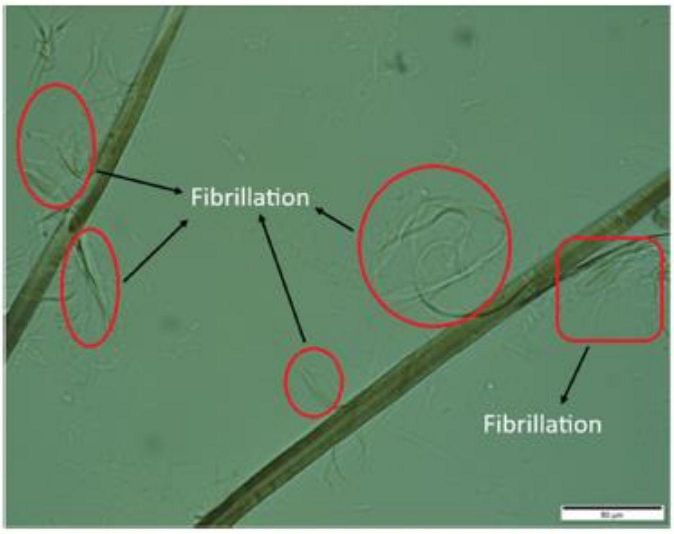


Fig. 2. Optical microscope image showing fibrillated harakeke fibre after processing 4 times each at 400 µm and 300 µm, followed by 2 times at 200 µm disc distance in the SMC.

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.

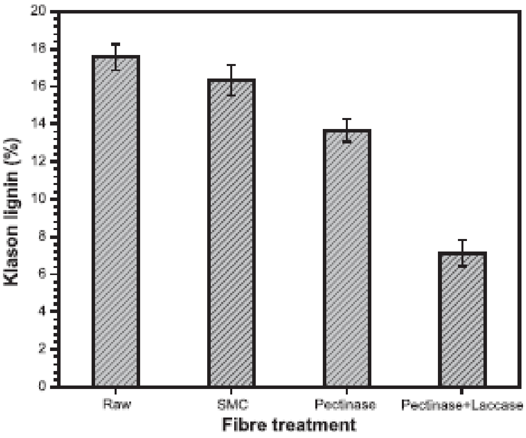


Fig. 3. Lignin content of unprocessed (raw), SMC processed (SMC), SMC processed-pectinase treated (pectinase), and SMC processed-combined pectin and laccase treated (pectinase+laccase) harakeke fibres.

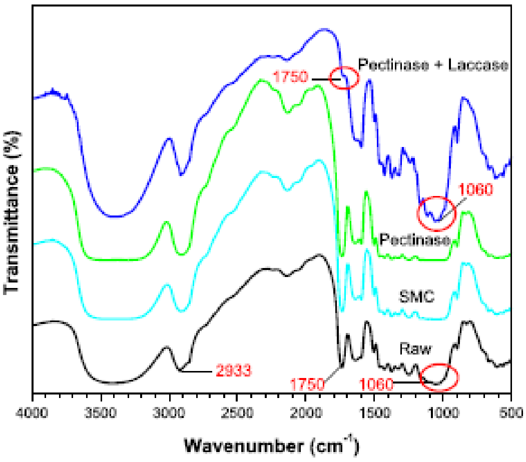


Fig. 4. FTIR spectra of unprocessed (raw), SMC processed (SMC), SMC processed-pectinase treated (pectinase), and SMC processed-combined pectin and laccase treated (pectinase+laccase) harakeke fibres.

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 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

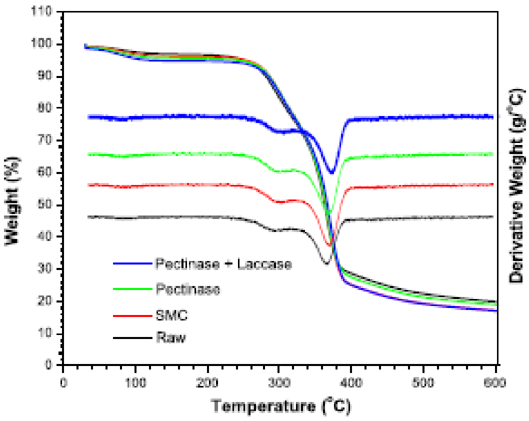


Fig. 5. TGA and DTG curves of unprocessed harakeke fibre (Raw), harakeke fibre processed with the super masscolloider (SMC), harakeke fibre treated with pectinase enzyme (Pectinase), and harakeke fibre treated with combined pectinase and laccase enzymes (Pectinase + Laccase).

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-volatilised 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

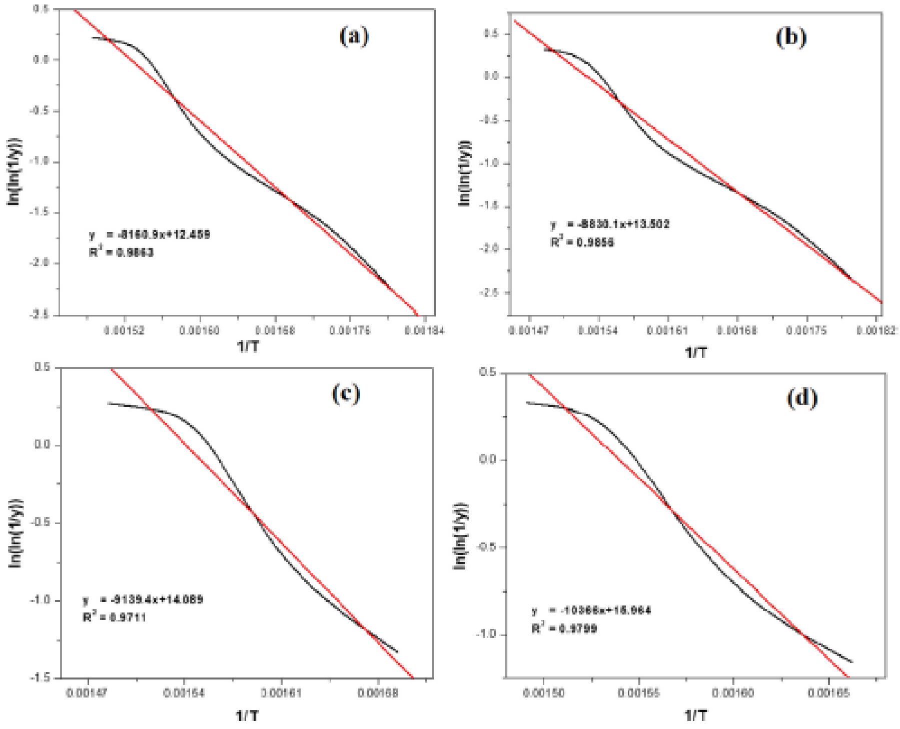


Fig. 6. Broido curves of (a) unprocessed harakeke fibre (Raw), (b) harakeke fibre processed with the super masscolloider (SMC), (c) harakeke fibre treated with pectinase enzyme (pectinase), and (d) harakeke fibre treated with combined pectinase and laccase enzymes (pectinase + laccase).

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.

Acknowledgements

The authors acknowledge the funding from the New Zealand

Ministry of Business, Innovation and Employment, under the Āmiomio Aotearoa project hosted by The University of Waikato (UOWX2004). The first author also appreciates the financial support through a Research & Enterprise Award (108023) provided by the University of Waikato.

References

Akindoyo, J.O., Beg, M.D.H., Ghazali, S., Islam, M.R., 2015. Effects of poly (dimethyl siloxane) on the water absorption and natural degradation of poly (lactic acid)/oil-palm empty-fruit-bunch fiber biocomposites. J. Appl. Polym. Sci. 132 (45).

Akindoyo, J.O., Husney NAAb, Ismail, N.H., Mariatti, M., 2020. Structure and performance of poly(lactic acid)/poly(butylene succinate-co-L-lactate) blend reinforced with rice husk and coconut shell filler. Polym. Polym. Compos. 29 (7), 992–1002.

Akindoyo, J.O., Pickering, K., Beg, M.D., Mucalo, M., 2023. Combined digestion and bleaching of New Zealand flax/harakeke fibre and its effects on the mechanical, thermal, and dynamic mechanical properties of poly (lactic) acid matrix composites. Compos. Part A: Appl. Sci. Manuf. 164, 107326.

Awais, H., Nawab, Y., Amjad, A., Anjang, A., Md Akil, H., Zainol Abidin, M.S., 2021. Environmental benign natural fibre reinforced thermoplastic composites: a review. Compos. Part C: Open Access 4, 100082.

Boey, J.Y., Yusoff, S.B., Tay, G.S., 2022. A review on the enhancement of composite's interface properties through biological treatment of natural fibre/lignocellulosic material. Polym. Polym. Compos. 30, 09673911221103600.

Bourmaud, A., Beaugrand, J., Shah, D.U., Placet, V., Baley, C., 2018. Towards the design of high-performance plant fibre composites. Prog. Mater. Sci. 97, 347–408.

Broido, A., 1969. A simple, sensitive graphical method of treating thermogravimetric analysis data. J. Polym. Sci. Part A-2: Polym. Phys. 7 (10), 1761–1773.

De Prez, J., Van Vuure, A.W., Ivens, J., Aerts, G., Van de Voorde, I., 2018. Enzymatic treatment of flax for use in composites. Biotechnol. Rep. 20, e00294.

Dixit, S., Goel, R., Dubey, A., Shivhare, P.R., Bhalavi, T., 2017. Natural fibre reinforced polymer composite materials-a review. Polym. Renew. Resour. 8 (2), 71–78.

Huda, M.S., Drzal, L.T., Mohanty, A.K., Misra, M., 2006. Chopped glass and recycled newspaper as reinforcement fibers in injection molded poly (lactic acid)(PLA) composites: a comparative study. Compos. Sci. Technol. 66 (11-12), 1813–1824.

Kathirselvam, M., Kumaravel, A., Arthanarieswaran, V., Saravanakumar, S., 2019. Characterization of cellulose fibers in thespesia populnea barks: influence of alkali treatment. Carbohydr. Polym. 217, 178–189.

Li, Y., Pickering, K.L., 2008. Hemp fibre reinforced composites using chelator and enzyme treatments. Compos. Sci. Technol. 68 (15), 3293–3298.

Oza, S., Ning, H., Ferguson, I., Lu, N., 2014. Effect of surface treatment on thermal stability of the hemp-PLA composites: correlation of activation energy with thermal degradation. Compos. Part B: Eng. 67, 227–232.

Ponnusamy, D.A., Gajendiran, H., Mansingh, B.B., Binoj, J.S., 2023. Diffractional, spectroscopical, morphological, and thermal analysis of pretreated/enzyme modified cellulosic Cocos nucifera L. peduncle fiber. Biomass. Convers. Biorefinery.

Saleem, Z., Rennebaum, H., Pudel, F., Grimm, E., 2008. Treating bast fibres with pectinase improves mechanical characteristics of reinforced thermoplastic composites. Compos. Sci. Technol. 68 (2), 471–476.

Sanjay, M., Siengchin, S., Parameswaranpillai, J., Jawaid, M., Pruncu, C.I., Khan, A., 2019. A comprehensive review of techniques for natural fibers as reinforcement in composites: preparation, processing and characterization. Carbohydr. Polym. 207, 108–121.

Saravanakumar, S.S., Kumaravel, A., Nagarajan, T., Moorthy, I.G., 2014. Effect of chemical treatments on physicochemical properties of prosopis juliflora fibers. Int. J. Polym. Anal. Charact. 19 (5), 383–390.

Senthamaraikannan, P., Kathiresan, M., 2018. Characterization of raw and alkali treated new natural cellulosic fiber from Coccinia grandis. L. Carbohydr. Polym. 186, 332–343.

Sindhu, R., Binod, P., Pandey, A., 2016. Biological pretreatment of lignocellulosic biomass–an overview. Bioresour. Technol. 199, 76–82.

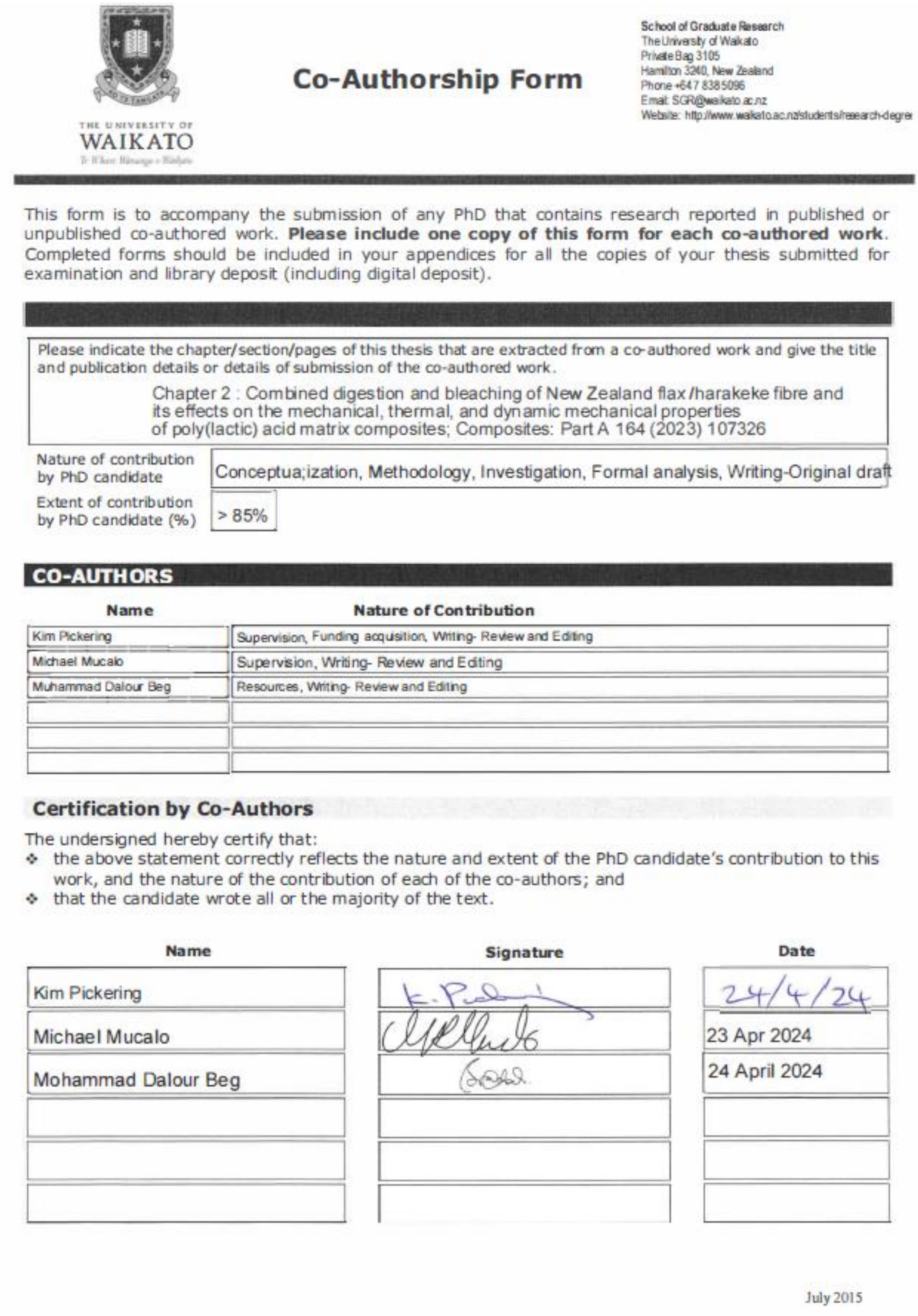
Sisti, L., Totaro, G., Vannini, M., Fabbri, P., Kalia, S., Zatta, A., et al., 2016. Evaluation of the retting process as a pre-treatment of vegetable fibers for the preparation of high-performance polymer biocomposites. Ind. Crops Prod. 81, 56–65.

Summerscales, J., 2021. A review of bast fibres and their composites: part 4~ organisms and enzyme processes. Compos. Part A: Appl. Sci. Manuf. 140, 106149.

Syduzzaman, M., Al Faruque, M.A., Bilisik, K., Naebe, M., 2020. Plant-based natural fibre reinforced composites: a review on fabrication, properties and applications. Coatings 10 (10), 973.

Yao, Y., Dou, H., Liu, T., Wang, S., Gao, Y., Kang, J., et al., 2023. Micro- and nano-scale mechanisms of enzymatic treatment on the interfacial behaviors of sisal fiber reinforced bio-based epoxy resin. Ind. Crops Prod. 194, 116319.

APPENDIX C
CO-AUTHORS FORMS



THE UNIVERSITY OF WAIKATO
Te Whare Wānanga o Waikato

Co-Authorship Form

School of Graduate Research
The University of Waikato
Private Bag 3105
Hamilton 3240, New Zealand
Phone +647 838 5096
Email: SGR@waikato.ac.nz
Website: http://www.waikato.ac.nz/students/research-degre

This form is to accompany the submission of any PhD that contains research reported in published or unpublished co-authored work. **Please include one copy of this form for each co-authored work.** Completed forms should be included in your appendices for all the copies of your thesis submitted for examination and library deposit (including digital deposit).

Please indicate the chapter/section/pages of this thesis that are extracted from a co-authored work and give the title and publication details or details of submission of the co-authored work.

Chapter 2 : Combined digestion and bleaching of New Zealand flax /harakeke fibre and its effects on the mechanical, thermal, and dynamic mechanical properties of poly(lactic) acid matrix composites; Composites: Part A 164 (2023) 107326

Nature of contribution by PhD candidate	Conceptua;ization, Methodology, Investigation, Formal analysis, Writing-Original draft
Extent of contribution by PhD candidate (%)	> 85%

CO-AUTHORS

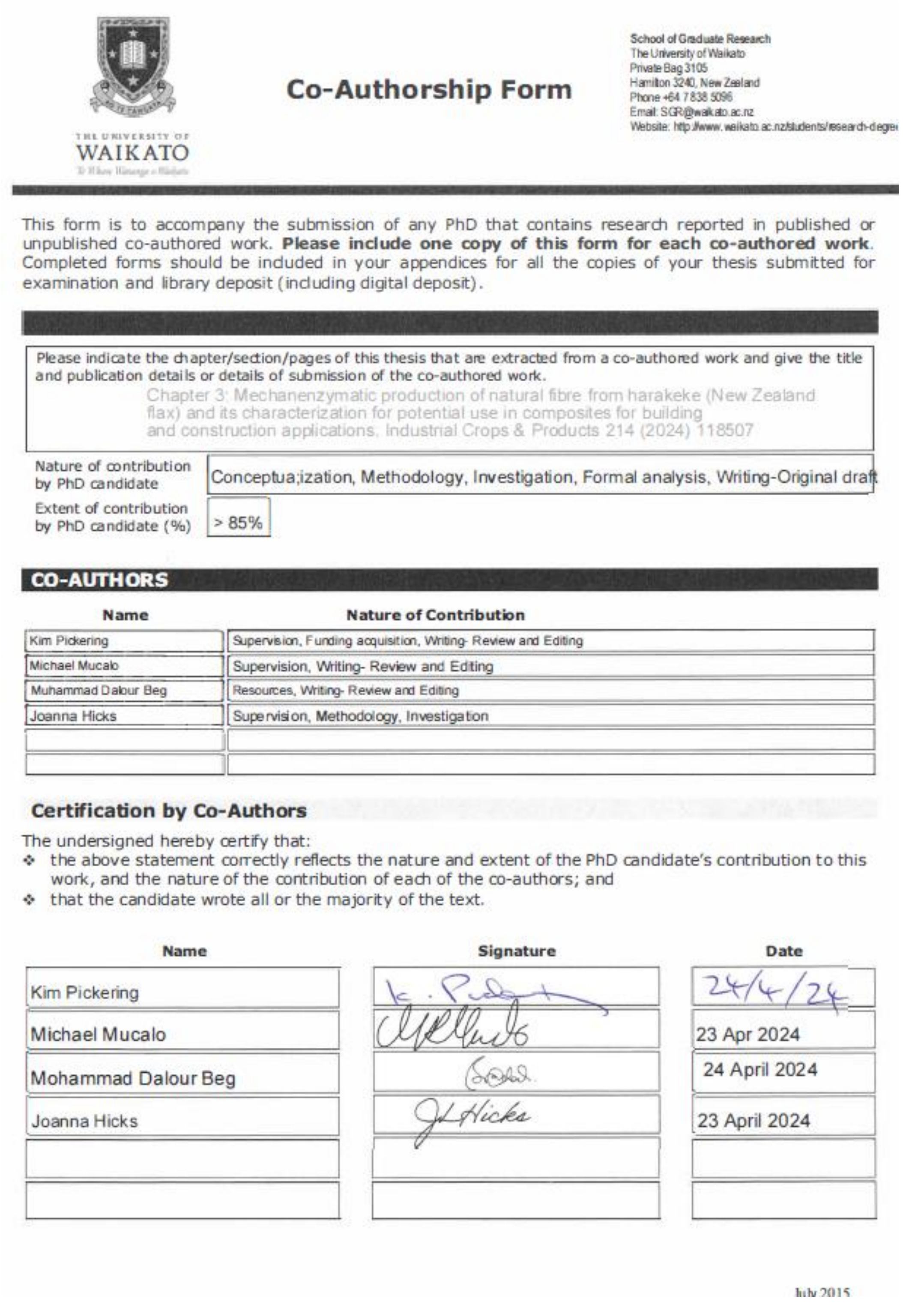
Name	Nature of Contribution
Kim Pickering	Supervision, Funding acquisition, Writing- Review and Editing
Michael Mucalo	Supervision, Writing- Review and Editing
Muhammad Dalour Beg	Resources, Writing- Review and Editing

Certification by Co-Authors

The undersigned hereby certify that:
- the above statement correctly reflects the nature and extent of the PhD candidate's contribution to this work, and the nature of the contribution of each of the co-authors; and
- that the candidate wrote all or the majority of the text.

Name	Signature	Date
Kim Pickering		24/4/24
Michael Mucalo		23 Apr 2024
Mohammad Dalour Beg		24 April 2024

July 2015



THE UNIVERSITY OF
WAIKATO

Co-Authorship Form

School of Graduate Research
The University of Waikato
Private Bag 3105
Hamilton 3240, New Zealand
Phone +64 7 838 5096
Email: SGR@waikato.ac.nz
Website: http://www.waikato.ac.nz/students/research-degre

This form is to accompany the submission of any PhD that contains research reported in published or unpublished co-authored work. **Please include one copy of this form for each co-authored work**. Completed forms should be included in your appendices for all the copies of your thesis submitted for examination and library deposit (including digital deposit).

Please indicate the chapter/section/pages of this thesis that are extracted from a co-authored work and give the title and publication details or details of submission of the co-authored work.

Chapter 3: Mechanenzymatic production of natural fibre from harakeke (New Zealand flax) and its characterization for potential use in composites for building and construction applications. Industrial Crops & Products 214 (2024) 118507

Nature of contribution by PhD candidate	Conceptua;ization, Methodology, Investigation, Formal analysis, Writing-Original draft
Extent of contribution by PhD candidate (%)	> 85%

CO-AUTHORS

Name	Nature of Contribution
Kim Pickering	Supervision, Funding acquisition, Writing- Review and Editing
Michael Mucalo	Supervision, Writing- Review and Editing
Muhammad Dalour Beg	Resources, Writing- Review and Editing
Joanna Hicks	Supervision, Methodology, Investigation

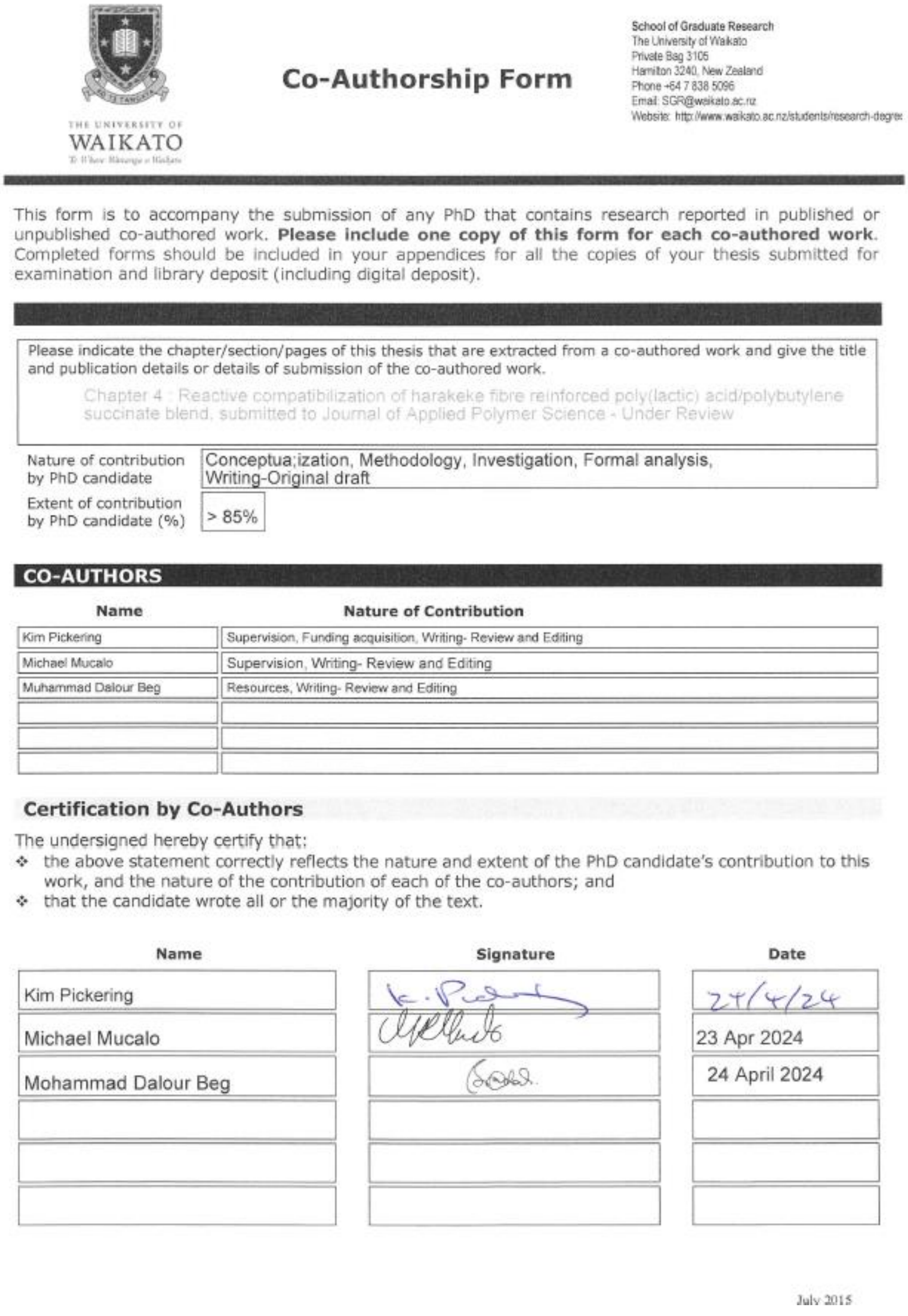
Certification by Co-Authors

The undersigned hereby certify that:

- the above statement correctly reflects the nature and extent of the PhD candidate's contribution to this work, and the nature of the contribution of each of the co-authors; and
- that the candidate wrote all or the majority of the text.

Name	Signature	Date
Kim Pickering		24/4/24
Michael Mucalo		23 Apr 2024
Mohammad Dalour Beg		24 April 2024
Joanna Hicks	J Hicks	23 April 2024

July 2015



THE UNIVERSITY OF
WAIKATO
Te Whare Wānanga o Waikato

School of Graduate Research
The University of Waikato
Private Bag 3105
Hamilton 3240, New Zealand
Phone +64 7 838 5096
Email: SGR@waikato.ac.nz
Website: http://www.waikato.ac.nz/students/research-degre

Co-Authorship Form

This form is to accompany the submission of any PhD that contains research reported in published or unpublished co-authored work. **Please include one copy of this form for each co-authored work.** Completed forms should be included in your appendices for all the copies of your thesis submitted for examination and library deposit (including digital deposit).

Please indicate the chapter/section/pages of this thesis that are extracted from a co-authored work and give the title and publication details or details of submission of the co-authored work.

Chapter 4 : Reactive compatibilization of harakeke fibre reinforced poly(lactic) acid/polybutylene succinate blend, submitted to Journal of Applied Polymer Science - Under Review

Nature of contribution by PhD candidate	Conceptua;ization, Methodology, Investigation, Formal analysis, Writing-Original draft
Extent of contribution by PhD candidate (%)	> 85%

CO-AUTHORS

Name	Nature of Contribution
Kim Pickering	Supervision, Funding acquisition, Writing- Review and Editing
Michael Mucalo	Supervision, Writing- Review and Editing
Muhammad Dalour Beg	Resources, Writing- Review and Editing

Certification by Co-Authors

The undersigned hereby certify that:

- the above statement correctly reflects the nature and extent of the PhD candidate's contribution to this work, and the nature of the contribution of each of the co-authors; and
- that the candidate wrote all or the majority of the text.

Name	Signature	Date
Kim Pickering		24/4/24
Michael Mucalo		23 Apr 2024
Mohammad Dalour Beg		24 April 2024

July 2015