Treatment of Harakeke Fiber for Biocomposites

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Received 21 September 2008; accepted 6 December 2008
DOI 10.1002/app.29863
Published online 23 February 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The use of fiber from Harakeke (or New Zealand Flax plant) for the reinforcement of composites should be explored since Harakeke has similar properties to Sisal fiber. To maximize the cellulose content in the fiber, Harakeke fibers were prepared by thermal, combinative alkaline-thermal, and a novel combinative thermal-enzymatic-thermal treatments and characterized by scanning electron microscopy, Fourier transform infrared spectroscopy, and wide-angle X-ray spectroscopy. The characterization method provided an efficient and systematic method to evaluate the removal of amorphous components such as lignin and hemicelluloses. In particular, a sequential thermal-enzymatic-thermal fiber treatment produced fine discontinuous whiskers that could be useful for short fiber composites, whereas a combinative thermal-alkaline treatment resulted in thorough extraction of lignin and hemicelluloses. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2710–2715, 2009

Key words: fibers; electron microscopy; FTIR; WAXS

INTRODUCTION

A spectacular resurgence in the use of local natural fibers is currently underway due to their high specific strength and stiffness and the promise of delivering a low-cost and low carbon footprint alternative to petroleum-derived fiber reinforcements for polymer composites.[1–3] Natural fibers are biodegradable, renewable, nontoxic, and can favorably compete with glass fibers in terms of their specific mechanical properties.[2–4]

The high specific properties of wood and plant fibers can be attributed to their high cellulose content, making them some of the most mechanically efficient materials devised by nature.[4–7] The cellulose content of bast and leaf fibers varies from ~ 45 to 75% depending on the species; the remaining portion is a hierarchical assembly of various amorphous materials, such as proteins, wax, pectin, hemicelluloses, or lignin.[5,8,9] The amorphous components participate in the mechanical integrity of the plant fiber, although also facilitating physiological processes such as growth of the cell wall.[5,8,9] The variation in chemical composition of natural fibers according to plant species has been reviewed elsewhere.[3,8,10]

The main objective of fiber processing is to remove hemicelluloses, pectin, and wax from the middle lamella and primary cell wall surface, thereby separating fiber bundles into their individual cells (also variously referred to as primary or ultimate fibers). As a result, a larger surface area is available for bonding with the polymer matrix.[11–13]

Extraction of lignin or hemicelluloses may also increase the surface roughness of the fibers, resulting in improved mechanical interlocking with the polymer matrix.[14] Furthermore, both hemicelluloses and lignins contribute little to the fiber strength when compared with cellulose.[3,5,15] The degree of chemical and/or mechanical bonding between the cellulose fibers and polymer matrix controls the amount of stress transferred via the interface. Thus, interfacial bonding determines the overall strength of a composite.[1,16–19]

Strong water absorption,[20–22] low resistance to microbiological attack,[3,17] and poor chemical interaction with hydrophobic thermoplastics[1,17–19] are the main limiting issues of natural fiber composites, although these issues can be overcome to some extent through the use of fiber treatments.[21–23]

This work reports on the effect of different fiber treatments (thermal, combinative alkaline-thermal, and combinative thermal-enzymatic-thermal treatments) on fibers extracted from the leaf of the New Zealand native plant known traditionally as Harakeke (common name: "New Zealand flax"; scientific name: *Phormium tenax*). "Flax" is actually a misnomer in describing *P. tenax* since it is not biologically related to European flax (*Linum sp.*). The fibers derived from Harakeke for the production of rope, sacking, and other fibrous products constituted up to ~ 20% of New Zealand's total export income in the early 1920s until synthetic fibers were made

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Contract grant sponsor: Brian Mason Scientific and Technical Trust and University of Canterbury; contract grant number: U6513.

available.[24,25] Harakeke fiber is reported to have similar tensile properties to Sisal—a natural fiber offering considerable reinforcement in polymer matrix composites.[14,26–30] Two recent publications report the use of Harakeke fiber as a reinforcement in thermosetting epoxy matrices,[31,32] thereby proving the potential benefits of Harakeke fiber in biopolymer composites.

EXPERIMENTAL PROCEDURES

Experimental materials

Mechanically retted Harakeke fibers were obtained from the Foxton Flax Mill Museum, Foxton, New Zealand. The enzymes selected for this work were Pectinex® Ultra SP-L supplied by Novozymes. Pectinex® Ultra SP-L is prepared using a selected strain of *Aspergillus aculeatus*, containing pectolytic and hemicellulotic activities.

Fiber preparation

The defibrillation efficiency of subsequent fiber treatments was improved by breaking up fiber bundles prior to treatment using a laboratory scale carding machine. The subsequent preparation of Harakeke fiber was carried out by three different treatment routes, namely standard thermal, combinative thermal-alkaline, and combinative thermal-enzymatic-thermal treatments.

A standard thermal treatment involved placing $\sim$ 100 g of Harakeke in 750 mL of distilled water in an autoclave at 170°C and $\sim$ 10 bars for $\sim$ 1 h. In a combinative thermal-alkaline treatment, the standard thermal treatment was carried out as above except that the distilled water in the standard thermal treatment was replaced with a 2% NaOH solution. The treated fibers were then thoroughly rinsed in deionized water and dried at 130°C for 1.5–2 h. The rinsing and drying steps were carried out twice.

Initially, it was observed that enzymatic treatment of Harakeke did not result in effective defibrillation. Thus, a standard thermal treatment was used as a pretreatment to breakdown fiber bundles prior to enzymatic treatment. The thermally treated Harakeke ($\sim$ 100 g) was then immersed in 650 mL of a 58% Pectinex® solution, diluted with deionized water. The enzyme solution was stirred at 37°C and a pH of 3.5 to 4 to optimize enzymatic activity. The enzymatic treatment was performed for up to 30 h after which the fibers were thoroughly rinsed in deionized water. As a third and final step, another standard thermal treatment was used, resulting in a combinative thermal-enzymatic-thermal treatment.

Wide angle X-ray spectroscopy (WAXS)

X-ray patterns were obtained with a Philips PW1729 diffractometer using Cu Kα radiation (λ = 0.15418 nm), voltage of 50 kV, and current of 40 mA with 2θ increased in steps of 0.02°. Like other authors (Mwaikambo and Ansell, 2001), we chose to use Segal's crystallinity index (CrI) to calculate the crystallinity index of the fibers.[33,34] This index is defined as follows:

$$CrI = \frac{I_{(200)} - I_{amorphous}}{I_{(200)}} \quad (1)$$

where, $I_{(200)}$ is the intensity of the main diffraction peak of cellulose obtained from the crystallographic planes (200); this peak has 2θ values always comprised between 22.3° and 22.9°. $I_{amorphous}$ is the intensity of the amorphous peak of cellulose at 2θ = 18°. Peaks were assigned according to the monoclinic unit cell described by Sugiyama et al.[35] Trendlines averaged from 30 adjacent points were obtained from the raw data files and plotted as the resulting spectra. Spectra were obtained from Harakeke fibers after each of the different fiber treatments.

Fourier transform infrared spectroscopy (FTIR)

The KBr pellet method was used. Two milligrams of fibers $\sim$ 1–2 mm in length were mixed with 200 mg of KBr and mixed into a ball-mill for 5 min. Pellets about 1 mm thick were made by pressing the mixture for 2 min in a cylindrical mold with a 12 tons press; they were then dried for 48 h at 60°C. Fourier transform infrared spectra were acquired in transmission on an FTIR-8201 PC Shimadzu equipped with the software Hyper IR. They were averaged from a minimum of 16 scans from 4000 to 400 cm^{-1} and taken with a 2 cm^{-1} resolution. A linear baseline correction was performed on the absorbance curves.

Scanning electron microscopy (SEM)

A JEOL JSM6100 scanning electron microscope was used to observe carbon-coated fibers. Samples were mounted on carbon tabs, coated with a plasma sputtering apparatus, and then observed with a 20 kV accelerating voltage.

RESULTS AND DISCUSSION

WAXS

All of the fibers displayed a typical cellulose I diffraction spectrum with a (200) peak centered between 22.3 and 22.8°, a $(1\bar{1}0)$ peak at about 15.4°, a (110) peak at about 16.9°, and the (004) peak at

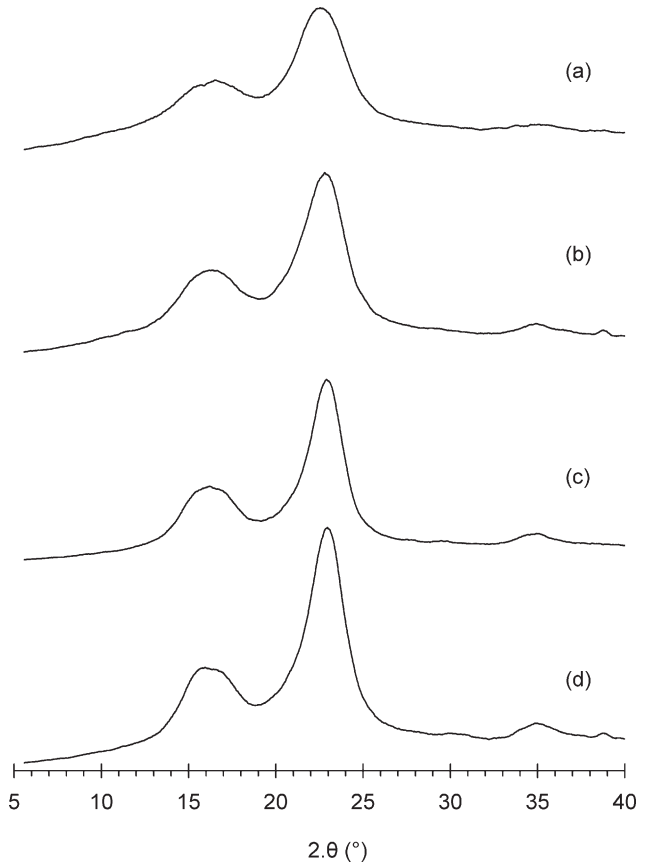

Figure 1 WAXS of Harakeke fibers (a) as-received and after a (b) thermal treatment, (c) thermal-alkaline treatment, and (d) thermal-enzymatic-thermal treatment.

about 34.8° (Fig. 1).[36,37] The transformation from cellulose I to cellulose II or amorphous cellulose is known to occur under thermal or alkaline treatments, although this was not observed due to the treatments being comparatively mild.[38,39] The crystallinity index (CrI) was found to depend on the chosen fiber treatment (Table I). CrI was determined to be 58.8% for the untreated Harakeke fiber, whereas the CrI increased with the fiber treatments and reached a maximum of 75.2% (found for the combinative thermal-alkaline treatment). The thermal treatment and combinative thermal-enzymatic treatment both increased the crystallinity of the untreated fiber by $\sim$ 6% and $\sim$ 9%, respectively, (Table I).

FTIR

The FTIR results show clear changes in the spectra at 2920, 2900, 2855, 1740, 1660, 1598, 1510, 1460, 900, and 890 cm^{-1}. The bands at 2920 and 2855 cm^{-1} are usually attributed to the C—H stretching mode in lignin, whereas the band at about 2900 cm^{-1} is associated to the C—H stretching in cellulose.[40–44] As expected, the bands associated with the C—H stretching of lignin are predominant in the untreated fiber while the band at 2900 cm^{-1} only appears as a weak shoulder [Fig. 2(a)]. For the thermal treatment and combinative thermal-alkaline treatment, the lignin bands decrease, whereas the cellulose band develops into a peak, suggesting the partial removal of the lignin [Fig. 2(b,c)]. In the case of the thermal-alkaline treatment, the bands at 2920 and 2850 cm^{-1} only appear as weak shoulders, whereas the spectrum in this region is dominated by the cellulose peak at about 2900 cm^{-1} [Fig. 2(c)], indicating that the alkaline treatment resulted in a thorough extraction of the lignin.

A similar trend in the treatment effect was observed on the intensity of the two characteristic lignin bands at 1510 and 1598 cm^{-1} and the band at 1460 cm^{-1} [Fig. 3(a–d)].[42,44,45] The two associated bands are assigned to the aromatic skeletal vibration of lignin, whereas the latter one is attributed to the C—H deformations in lignin—these three bands are not found in cellulose spectra.[42,44,45] Another band is also visible at 1660 cm^{-1} and is sufficiently close to 1670 cm^{-1} to be identified with the band assigned by Marchessault to lignin.[42] Once again, from the change in intensity of these lignin bands, it is plausible to assume that all of the treatments successfully reduce lignin content, with the alkaline treatment able to remove almost all of the lignin in Harakeke fiber [Fig. 3(c) and Table I].

The carbonyl band at 1740 cm^{-1} (Fig. 3) is of particular interest as it is a widely accepted signature for the presence of hemicelluloses in plant fiber.[33,42,44–46] An initially strong peak at 1740 cm^{-1} was progressively replaced by a weaker band after the initial thermal treatment [Fig. 3(a,b)]. The intensity of the 1740 cm^{-1} band decreased further when the thermal treatment was used in combination with the pectolitic solution [Fig. 3(d)] and disappeared completely when the fiber was

TABLE I
WAXS and FTIR Results

	Harakeke	Thermal treatment	Thermal-alkaline treatment	Thermal-enzymatic-thermal treatment
CrI (WAXS)	58.8%	64.7%	75.2%	67.8%
Hemicelluloses presence (FTIR)	yes	altered	no	altered
Lignin presence (FTIR)	yes	altered	weak	altered

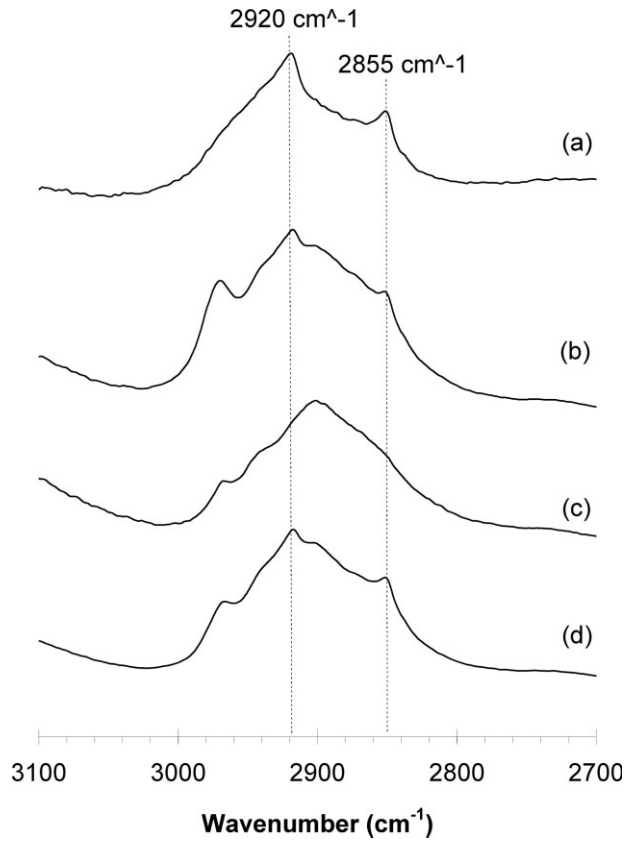

Figure 2 FTIR of the four fibers in the 3100–2700 cm^{-1} region for the (a) untreated fiber, (b) thermal treatment, (c) thermal-alkaline, and (d) thermal-enzymatic treatment.

treated by the hot alkaline process [Fig. 3(c)]. In summary, the hemicellulose content progressively decreased in the following order: untreated fiber-thermal treatment→combinative thermal-enzymatic→alkaline treatment.

SEM

The untreated Harakeke fibers were commonly observed in the form of a bundle [Fig. 4(a)]. The fibers exhibited a very smooth surface after being defibrillated via a mechanical process which is attributed to the waxes and pectins usually found on the surface of higher plant fibers in the natural state [Fig. 4(b)].[8,33] All of the treatments removed the "sleeve" of pectins and waxes from the surface of the primary fiber (Fig. 5), which was also observed in connection with fiber bundles being broken into primary fibers of $\sim$ 10 μm in diameter. The extent of fibrillation of the bundles was found to depend on the treatment applied. For example, the standard thermal treatment would leave some bundles intact, whereas the alkaline treatment usually resulted in thorough splitting of fiber bundles. Interestingly, the combinative thermal-enzymatic-thermal treatment yielded the most extensive defibrillation, although shortening of Harakeke fibers also occurred, resulting in whisker-like fibers down to 100 μm in length.

The fiber surface obtained after the three treatments revealed 200–500 nm diameter cellulose fibrils orientated in the fiber direction. The cellulose fibrils were embedded in a polysaccharide matrix of smooth appearance that represents the primary cell wall, that consists of hemicelluloses, lignin, and pectin.[1,8] However, none of the treatments in this work resulted in isolation of cellulose nanofibrils. All of

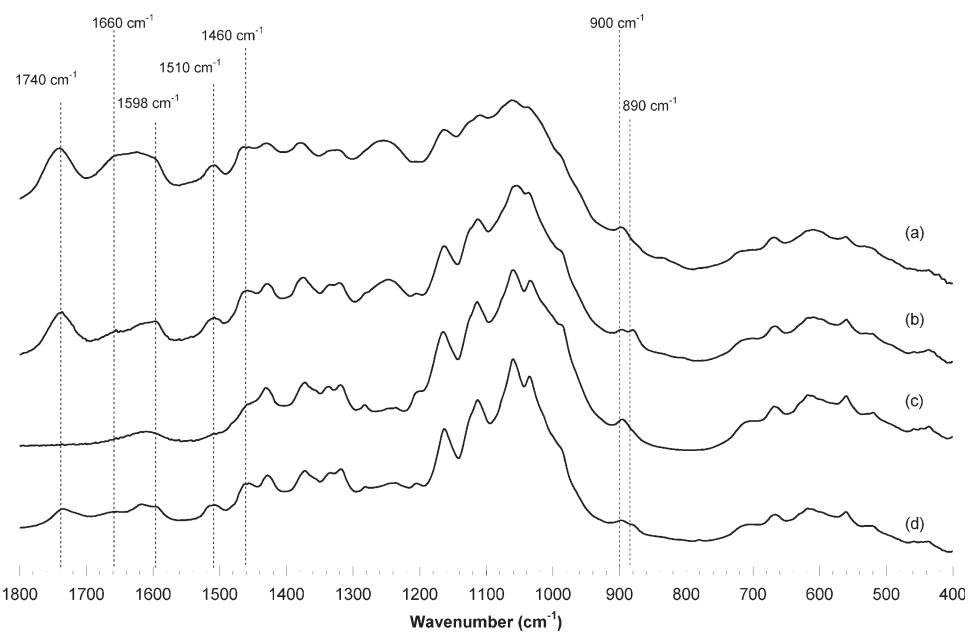

Figure 3 FTIR of the four fibers in the 1800–400 cm^{-1} region for the (a) untreated fiber, (b) thermal treatment, (c) thermal-alkaline, and (d) thermal-enzymatic treatment.

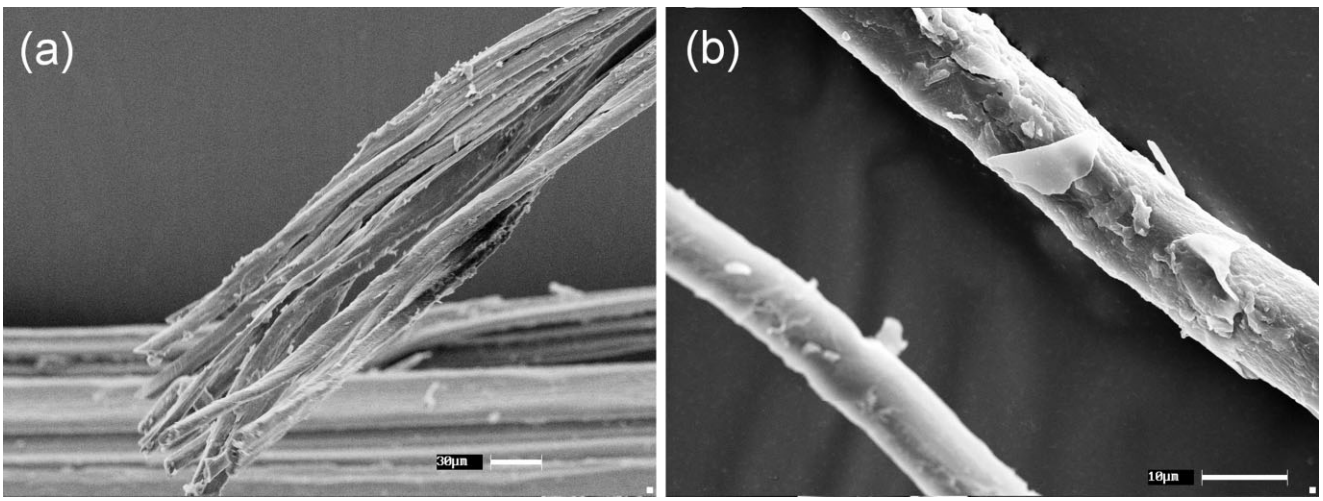

Figure 4 Scanning electron micrograph of Harakeke fiber before treatment in (a) bundle form and (b) fiber form.

the treatments seemed to produce a rougher fiber surface. The fiber surface roughness was higher after the combinative thermal-alkaline treatment compared with the standard thermal or thermal-enzymatic treatment, as shown by atomic force microscopy (unpublished results). The increase in fiber roughness can be attributed to the thorough extraction of hemicellulose and lignin from the cell wall, as shown by FTIR.

Synthesis of the WAXS, FTIR, and SEM results

It is known that *P. tenax* contains a high proportion of lignin (~ 8.1–16 wt %) and hemicelluloses (~ 30 wt %).[15,24] A large portion of alkali extractable compounds is thought to be hemicelluloses, mainly xylan. The by-products from the above process are likely to be water-soluble oligosaccharides.[47] As witnessed by FTIR, all the treatments at least resulted in the partial removal of lignins and hemicelluloses (Figs. 2, 3, and Table I). It is well-known from the literature that the appropriate thermal, enzymatic, and alkaline treatments all have the capacity to remove some of the pectins, lignins, and hemicelluloses.[8,24,33,40,48] The removal of those amorphous components translated into an increase of the apparent crystallinity of the fiber (Fig. 1 and Table I), as observed somewhere else.[33] In general, the amount of transformation from the initial fiber to the harshest modification followed this order: thermal treatment $\leq$ combinative thermal enzymatic $<$ combinative thermal alkaline. This is well-reflected in the surface appearance of the fibers, as observed by SEM (Fig. 5). Overall, the more efficient the treatment, the rougher the fiber surface was. This surface roughness can be attributed to the wrinkling of the fiber surface due to the radial shrinkage of the fiber when the primary or secondary cell wall amorphous components (pectins, hemicellulose, or lignin) are extracted. In general, the combinative thermal-alkaline treatment resulted in apparently total hemicellulose extraction and thorough lignin removal; in turn, the aforementioned rougher surface was produced.

Of particular interest, the enzymatic treatment produced a whisker-like material that had lost the initial long characteristic aspect ratio of the Harakeke fiber. The lateral and longitudinal orders of the cellulose crystals were, however, preserved as shown by the near constant high strength, position, and width of the (200) peak and of the (004) peak in the WAXS spectrum (Fig. 1).[49] As a result, this technique appears to be an environmentally benign alternative to the use of hydrolysis techniques for the production of cellulose whiskers with a relatively low hemicellulose and lignin content.

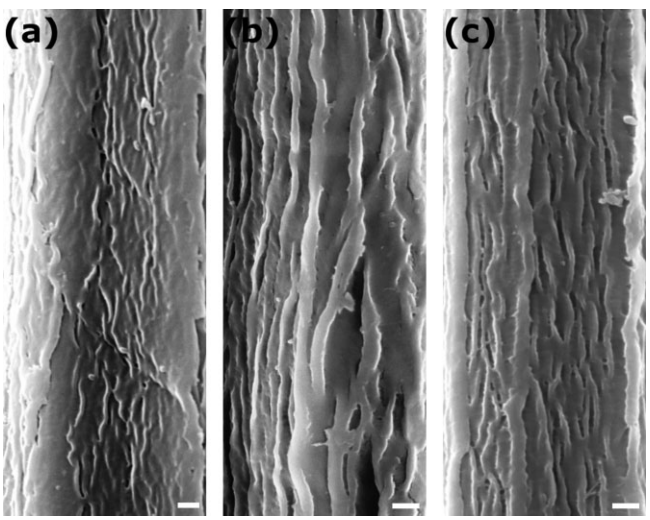

Figure 5 Scanning electron micrographs of the surface of Harakeke fiber after the (a) standard thermal, (b) combinative thermal-alkaline, and (c) combinative thermal-enzymatic-thermal treatment (*N.B.* all measurement bars are 1 µm).

CONCLUSIONS

WAXS, FTIR, and SEM were used to evaluate the effect of different fiber treatments used in isolation and combination on the microstructure and potential properties of Harakeke fibers. All of the treatments helped to break down the fiber bundle, enhance the primary fiber surface roughness, and remove some of the hemicelluloses and lignin. The most promising results were obtained via the thermal-alkaline treatment as it resulted in the thorough extraction of noncellulosic components. A novel and environmentally benign thermal-enzymatic-thermal treatment was shown to have the advantage of producing short whisker-like fibers with a high-cellulose content. In a future work, biocomposites will be produced with the fibers obtained via these treatments. Their mechanical properties will be assessed to further demonstrate the benefits of improving the interfacial area between the natural fiber and a polymer matrix.

The authors acknowledge and recognize Māori ownership, traditional knowledge, and the status of Harakeke under Article II of The Treaty of Waitangi. The authors also like to thank the late Dr. S. Jackson (Biological Sciences); Mr. D. Brown and Mr. T. Beri (Chemical and Process Engineering); Dr. K. Chapman (Forestry); and Mr. K. Stobbs, Mr. S. Amies, and Mr. M. Flaws (Mechanical Engineering). They also like to thank Dr. Kees Van Luijk (ex-WRONZ) for his participation to the project. Finally, they are indebted to the assistance of Dr. Sue Scheele whom kindly supplied raw Harakeke leaf from the New Zealand Flax Collection located at Landcare Research (Lincoln, New Zealand).

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