Fibers and Polymers 2013, Vol.14, No.3, 423-427 DOI 10.1007/s12221-013-0423-x

Effect of Alkali and Silane Treatments on Mechanical and Thermal Behavior of *Phormium tenax* Fibers

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(Received January 13, 2012; Revised July 27, 2012; Accepted August 16, 2012)

Abstract: The effect of different treatments on the mechanical (tensile), thermal behavior (TGA), FTIR, and morphology of *Phormium tenax* fibers has been studied with the aim to investigate methods to improve their compatibility with polymer matrices. Applied treatments included sodium hydroxide (NaOH), silane (APTES, 3-aminopropyltriethoxysilane), and the combined application of silane treatment after NaOH. The effectiveness of the treatments in the removal of non-structural matter from the fibers was confirmed by FTIR investigation and TGA measurements, suggesting also that the alkali treatment has a strong effect on their thermal behavior. The study of tensile properties of the fibers performed using Weibull statistics indicates that the tensile properties are somewhat reduced by chemical treatment. The morphological investigation of treated fibers through scanning electron microscopy indicates that silane treatments, both on raw fibers and on alkalized ones, result in limited fiber degradation.

Keywords: New Zealand flax (*Phormium tenax*), Treatments, Tensile properties, Thermal analysis, Morphology

Introduction

The ever-growing environmental awareness requires the development of the next generation of materials and processes to be inspired by principles of sustainability, ecoefficiency, and green chemistry. The depletion of petroleum resources coupled with the disposition of stricter environmental regulations are acting synergistically to create a strong stimulus for new materials and products, whose use would produce the lowest 'carbon footprint'. In this regard, 'green' composites made of renewable agricultural and forestry feedstock can represent a suitable alternative to glass fiber reinforced composites, providing potential value-added source of income to the agricultural community [1]. In this context, together with the more traditional plant fibers increasingly used as reinforcement for polymer composites such as jute, flax, hemp, sisal, and coir, other fibers may generate some interest, in view of their potential for this application [2].

In particular, New Zealand flax, more correctly referred to as *Phormium*, is a monocotyledon plant belonging to the *Agavaceae* family indigenous to New Zealand and Norfolk Island. There are two distinct species of New Zealand flax: *Phormium tenax* (also known as harakeke) and *Phormium cookianum* (also known as wharariki), the key difference being the way their seedpods grow. Phormium represented an important resource in Maori life. *Phormium* leaves are traditionally used in the Maori culture for making plaiting mats and containers, while the extracted fibers have been used for making fishing nets, ropes, baskets, and cloaks [3]. During the last few years, several papers have been published concerning the use of *Phormium tenax* fibers as potential reinforcement in both thermoplastic and thermosetting matrices [4-8], but only a few studies regarding the tensile behavior of technical fibers can be found [9,10].

In general, the properties of plant fiber composites can be improved in terms of interfacial adhesion and resistance to moisture absorption using suitable chemical treatment [11]. However, the mechanical and thermal effect of treatment on fiber modification is still quite poorly known, especially on leaf-extracted fibers, which have been less used in products for the textile industry, from which the procedures most commonly applied on plant fibers, such as sodium hydroxide treatment, originate. A substantial difference is recognized between primary treatments (e.g., alkali), and secondary treatments, such as the application of organosilanes [12]. While the former are mostly devoted to the removal of non-structural matter from the fibers, the latter appear capable of providing protective coating to the fibers, furthermore improving their adhesion to the polymer matrix. On *phormium* fibers, deacetylation by means of alkali treatment has been tried, which resulted in the additional removal of some of the xylans by applying 5 % of sodium hydroxide for 4 h, considerably reducing the water uptake of the composites with no detectable effect on mechanical properties [13].

In this work, alkali and organosilane treatment, and a combination of them have been applied on *phormium* fibers in preparation for their introduction in a polymer matrix with the aim of contributing to the definition of an optimized chemical treatment for these fibers.

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Experimental

Materials and Treatments

Phormium tenax (harakeke) technical fibers were collected from New Zealand. Leaves were stripped and the hanks of fiber were washed and then paddocked and scutched [6,8,9].

Alkali Treatment

The fibers were mercerized in a 10 % wt. sodium hydroxide (NaOH) solution at room temperature for 2 h, washed with water to remove any traces of alkali on the fiber surface, and neutralized with 1 % acetic acid solution, then dried in oven at 80 °C for 48 h. The above concentration of sodium hydroxide has been frequently used on leaf-extracted plant fibers, such as sisal, in the view of providing a fast and effective treatment to remove non-structural matter without resulting in a too extensive degradation of fiber cellulose [14,15].

Silane Treatment

The fibers were treated in a 2 % wt. silane (3-Aminopropyl) triethoxysilane (APTES) solution, prepared in a mixture 40/60 (w/w) for 45 min, washed with water to remove residual chemicals then dried in oven at 80 °C for 48 h. The same silane treatment procedure was also applied in fibers that were alkali-treated previously. The percent of silane applied in literature is normally 1 %, although normally followed by application of other chemicals, such as dycumil peroxide for further bleaching [16] or executed for longer times (6 h in [17]). Here, the percent is doubled to reduce the time of application. The coding of the different sets of fibers is reported in Table 1.

Tensile Tests

Phormium tenax technical fibers were mounted on a slotted testing tab according to ASTM D 3379-75. Tensile tests were carried out at room temperature on a Lloyd dynamometer LR 30 K equipped with a 20 N cell with an accuracy of 0.5 %. Fibers were tested at a gauge length of 10 mm in displacement control and at a cross-head speed of 1 mm/min. Fifty fibers were tested for each batch. *Phormium tenax* fibers show a polygonal shape, as described already in [9]. To simplify the evaluation of the tensile strength, the section of each fiber was considered to be perfectly circular. Fiber diameter was calculated through optical microscopy observations as the average of five apparent diameter measurements taken at different locations along the fibers. The values obtained with relevant standard deviations are listed in Table 2.

Table 1. Coding of the different fiber categories studied

Material code	Chemical treatment
Ph-raw	Untreated
Ph-NaOH	NaOH
Ph-Sil	APTES
Ph-NaOH-Sil	NaOH+APTES

Table 2. Fiber diameters with standard deviations

Material code	Diameter (μm)
Ph-raw	183.6±47.0
Ph-NaOH	152.8±43.5
Ph-Sil	157.7±53.4
Ph-NaOH-Sil	154.1±50.3

The data obtained for the tensile properties of the fibers can be represented by a two-parameter Weibull [18] equation, which expresses the cumulative density function of the strength of the fibers as:

$$F(\sigma_f) = 1 - \exp\left[1 - \left(\frac{\sigma_f}{\sigma_0}\right)^{\alpha}\right]$$

where α is the Weibull modulus and σ_0 is a location parameter. The same function was applied for the evaluation of cumulative density function of the elastic modulus, in which σ_f and σ_0 were replaced by E_f and E_0.

Scanning Electron Microscopy (SEM)

A morphological investigation on the untreated and treated *Phormium tenax* fibers was performed with a field emission scanning electron microscope (FESEM) Zeiss, model Supra 25 in order to see the effect of the chemical treatments on the modification of their surface properties along their length.

Thermogravimetric Analysis (TGA)

Thermogravimetry (TG) and differential thermogravimetry (DTG) techniques were utilized to analyze the thermal stability of *Phormium tenax* fibers. The measurements were performed using a thermobalance TG/DTA Seiko Exstar 6300 in nitrogen atmosphere (250 m*l*/min) in the temperature range 30-900 °C at a heating rate of 10 °C/min. Sample weights of about 10 mg were placed in a platinum pan. Two tests for each material were performed.

Fourier Transform Infrared Spectrometry (FTIR)

Fourier transform infrared spectrometry (FTIR) was carried out on *Phormium tenax* fibers in order to observe the effect of the treatments on the surface. IR spectra of the fibers were recorded using a Jasco FTIR 615 spectrometer in the frequency range 4000-500 cm^{-1}, operating in ATR (attenuated total reflectance) mode.

Results and Discussion

Tensile Properties

In Table 3 the tensile properties of raw and treated fibers are reported: here, the conventional method of diameter measurement for calculation of cross-sectional area was considered [9]. Excluding some slippage at the beginning of

Table 3. Ultimate tensile stress and Young's modulus of raw and treated fibers (experimental data and Weibull distribution parameters)

	Weibull				Experimental			
	σ (MPa)		E (MPa)		σ		E	
	Mean	St dev	Mean	St dev	σ_0 (MPa)	α	E_0 (MPa)	α
Ph-raw	282.1	154.8	6770	4970	326.8	1.62.44	8879	2.8242
Ph-NaOH	170.3	89.3	6670	3330	193.1	2.0296	7553	2.1276
Ph-Sil-NaOH	127.1	77.0	5319	3348	144.6	1.4477	5960	1.8430
Ph-Sil-NaOH	139.0	74.9	5523	2764	159.3	1.7337	6248	2.1876

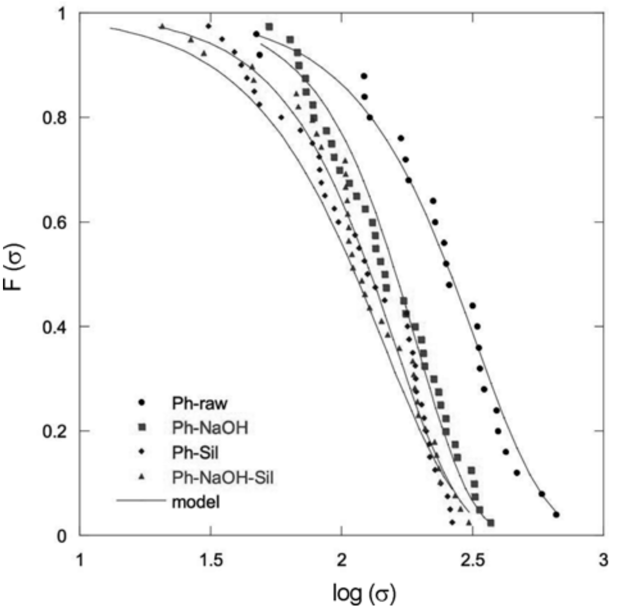

Figure 1. Weibull stress distribution of raw and treated fibers.

the test, phormium fibers exhibit the single linear elastic deformation until failure with no plastic deformation, which is typical of vegetable fibers and has been observed already in [6] on raw phormium fibers.

Phormium fibers exhibited variability in tensile strength and Young's modulus, which is also quite common to natural fibers. It needs to be noticed, however, that the effect of the large variability in diameters is predominant on the values obtained for stress and modulus. The values obtained by mechanical characterization were statistically analyzed using a two-parameter Weibull distribution. A single set of parameters for each property (i.e. tensile strength and Young's modulus), σ_0–E_0 and α, which simultaneously fits all the data, was obtained. Figure 1 shows the Weibull distributions for tensile strength of raw and treated phormium fibers. This two-parameter Weibull distribution provides a reasonable approximation of experimental data for mechanical properties. The Weibull modulus and location parameters (which are characteristic values of the distribution) for each property (tensile strength and Young's modulus) of the investigated systems are compared with the mean experimental values (Table 3). A clear reduction of the tensile properties is observed through all three treatments on values comparable between them.

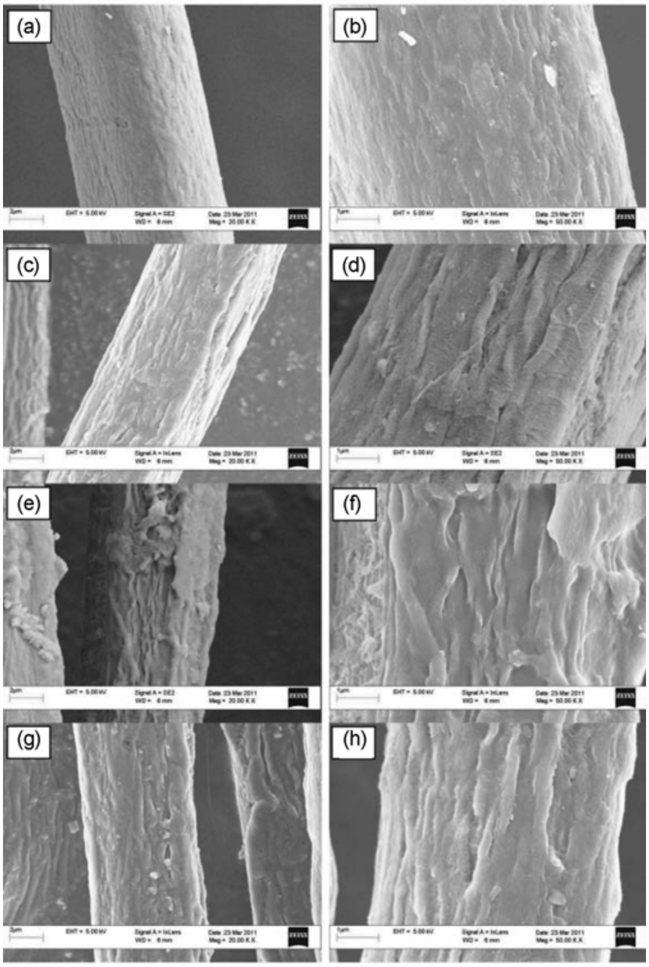

Figure 2. Morphology of raw and treated fibers observed by scanning electron microscopy; (a,b) untreated, (c,d) NaOH treated, (e,f) silane treated, and (g,h) (NaOH+silane) treated.

Morphological Investigation

SEM micrographs enable the observation of the effect of treatment on fiber surface. In particular, the alkali treatment

(Figure 2(c),(d)) exposes the cellulose microfibers with respect to what is observable on the untreated ones (Figure 2(a),(b)). In general terms, silane treatment (Figure 2(e),(f)) appears, as reported for example in [19], to provide a smoother fiber surface for introduction in a polymer matrix. However, when combined treatment is applied, the presence of discontinuities and porosities in the order of a micron can still be encountered (Figure 2(g),(h)).

Thermogravimetric Analysis

TGA and derivative (DTG) curves of untreated and treated fibers are shown in Figure 3. It can be observed that after treatment with the alkali solution the thermal stability of the phormium fiber decreased slightly, while the organosilane (APTES) treatment improved the thermal stability of phormium fiber significantly. Decomposition of the untreated phormium fibers shows several stages, indicating the presence of different components that decompose at different temperatures. The initial weight losses can be attributed to the evaporation of moisture on the surfaces of these materials: the alkali treated fibers have shown a reduced weight loss, indicating that alkali treatment removes a part of the adsorbed molecules like fats and waxes [12]. Almost all of the chemisorbed water is found to be given off at 120 °C for all the four samples.

The two main peaks are related to the hemicellulose and cellulose decomposition. The rate of degradation due to the cellulose decomposition in inert atmosphere reaches its peak at 344 °C for untreated fiber, while the peak of maximum degradation rate becomes maximum at 333 °C, 353 °C, and 367 °C, for alkali, alkali-silane, and silane treated phormium fiber, respectively (as revealed by DTG curve). The shoulder in the DTG curve of silane treated fiber below 320 °C can be attributed to the grafted silane on the surface of the fibers.

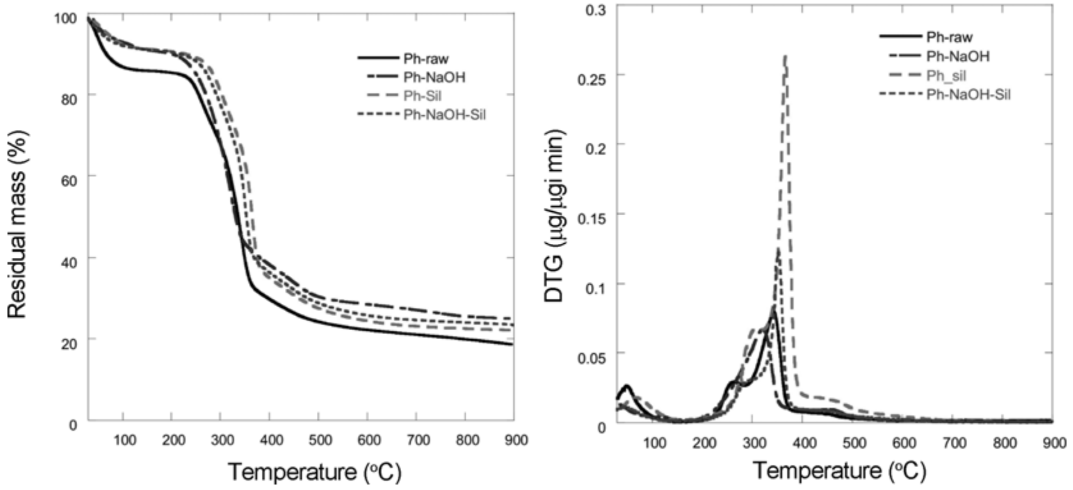

Figure 3. Thermogravimetric behavior of raw and treated fibers.

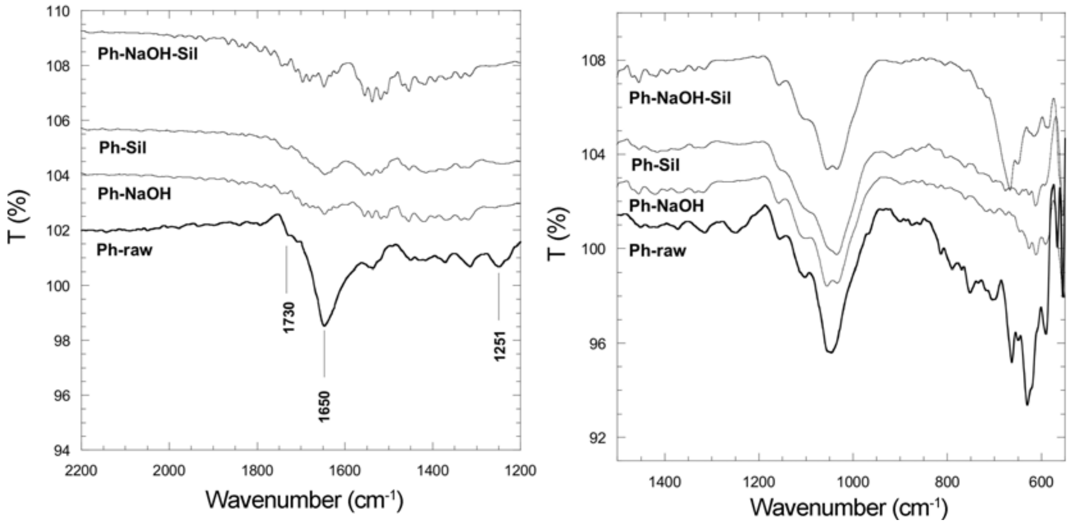

Figure 4. FTIR spectra of raw and treated fibers.

Spectroscopic Characterization

ATR-FTIR spectra for untreated and treated phormium fibers are reported in Figure 4. The untreated fiber shows bands at 3450 cm^{-1} due to the -O-H stretching. The peak at 1735 cm^{-1} is attributed to the C-O stretching of the carbonyl groups (>C=O) in hemicellulose. The changes in the FTIR spectrum of the alkali treated fibers are the absence of the characteristic peaks at 1730 cm^{-1} (C=O stretching in xylan) and 1251 cm^{-1} (C-O stretch vibration), which are both associated with hemicellulose and lignin. This effect has been reported previously in the literature and discussed as characteristic of the alkaline treatment of lignocellulosic materials [20]. Another band is also visible at 1650 cm^{-1} identified with the band assigned to lignin. From the change in intensity of these lignin bands, it is plausible to assume that the alkaline treatment is able to remove almost all of the lignin in Harakeke fiber.

FTIR spectra do not clearly show the effect of silane on the transmittance bands. Peaks should be present at 766 cm^{-1} and 847 cm^{-1} due to Si-C stretching bond [17]. The interaction between the silane and fiber cellulose appears also weak (peaks have been revealed elsewhere for Si-O-Cellulose and -Si-O-Si- bonds at 1200 and 1135 cm^{-1}, respectively [21]). It is suggested that this is due to the prevalent hydrolyzing of silane, so that the silane concentration on the phormium fiber surfaces is too small to be detected by FTIR [22]. The clearest effect of the silane treatment is its capacity to increase the intensity of the peaks at 1525 cm^{-1}, which is characteristic of C=C stretching [23].

In general, it may be suggested that the effect of silane treatment on phormium fibers is quite significant, though not at the levels shown on other plant fibers, for example on jute [17]. Of course, the definitive assessment of this effect can only be observed when treated fibers are inserted in a polymer matrix.

Conclusion

This study of effect of alkali, silane treatment, and a combination of the two on the tensile, thermal (TGA), FTIR, and morphology of *Phormium tenax* fibers suggested that treatment does result in a reduction of the tensile properties of the fibers, though is likely to have some benefits on the introduction of them in a polymer matrix. In particular, the alkali treatment strongly modifies the thermal behavior of the fibers, being particularly effective in the removal of non-cellulosic matter. In contrast, the use of silane results in limited fiber degradation: it appears nonetheless that most part of the silane applied is hydrolyzed rather than active on phormium fibers. The significance of the results lies in giving information towards the optimisation of treatment on these fibers with the idea of providing an effective interface with polymer matrices producing conversely an amount of damage to the fibers as limited as possible.

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