Comparison of Bio and Eco-technologies with Chemical Methods for Pre-treatment of Flax Fibers: Impact on Fiber Properties

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ABSTRACT

Flax fibers, available as fiber bundles, are commonly used as fiber reinforcement in composite materials as a substitute for glass fibers. Pre-treatments are often necessary for improving fiber-resin adhesion, and also to facilitate fiber elementarization, and to improve fiber ability to be implemented in mechanical processes limiting fiber damages.

This paper focuses on the impact of biotechnologies (effect of 2 different enzymes: a pectate lyase and a laccase) and of an ecotechnology (ultrasound with ethanol), compared to classical chemical pre-treatments (using aqueous NaOH and ammonia) on the final flax fiber bundle properties, before and after a carding process.

Fiber surface properties (wettability and/or zeta potential values), fiber elementarization and mechanical properties vary with the type of treatment (chemical nature of product and conditions used). Fibers elementarised using pectate lyase and ultrasound/ethanol have a hydrophilic surface and a high water absorption capacity, and are also of highest quality in terms of increased fineness. Treatment with NaOH yields the poorest fiber bundle tenacity. Laccase enzyme yields long thick hydrophobic fibers having very low water absorption capacity, and the most neutral surface charge.

Properties of flax fibers can be easily monitored using different pre-treatments resulting in fibers which would be suited for various final applications.

Keywords: Flax fiber pre-treatment, enzymes, ethanol ultrasound, wettability, tenacity, zeta potential

INTRODUCTION

Today there is an increase demand for natural fibers for the development of biocomposites, which may have application in various fields such as building, and automotive. The performance of current biocomposites is inadequate for most structural applications, and increasing the performance of these materials is essential if they are to gain widespread acceptance [1]. Natural fiber composites in automotive are generally made from scutched flax tows. These flax fibers, considered to be cheap technical fibers, are waste product of flax stem obtained after extraction of high quality linen fibers. The flax fibers are still in the form of fiber bundles linked by components such as pectin, lignin and hemicellulose [2]. The fineness of fiber bundles vary from 50 to 500 µm with a length varying from 100 to 1500 mm, while the fineness of the individual fiber varies from 15 to 35 µm and the length from 4 to 140 mm [2-4].

In order to improve mechanical properties of flax based composites, works have dealt essentially with improving the bulk physical and mechanical properties of the fibers themselves and improving the interface between the fiber and the matrix [1].

Short staple fibers [5] and chopped flax fibers have been used in composites, and the strategy has been to elementarize flax fibers to increase surface area of contact with the polymer matrix in composites [1]. For nonwoven based composites, longer fibers with adequate fineness are necessary to favour better mechanical entanglement of nonwoven webs and hence higher mechanical properties.

Various mechanical/chemical/biotechnological methods have been used for the pre-treatment of flax fiber bundles. Alkaline products such as treatment with NaOH, have not proved to be satisfactory for fiber quality [2], are not cost effective [6], and are not environmentally friendly. Biotechnological fiber modification using enzyme, provides a low environmental impact. In general most of the authors [7-9] show that pectinase used in acidic conditions weaken the treated flax fibers. The use of pectate lyase which acts in alkaline conditions was shown to maintain fiber strength [10]. Other enzymes such as laccases have been also used, alone or in combination with other enzymes or other chemical products for the biobleaching of flax fibers [11-14].

The potential use of a combined ultrasound/ethanol for extraction of flax fibers, has however, not yet been described in the literature. Ultrasound is an eco-technology being developed in the textile industry, and has already been used for enzymatic treatment for the bioscouring of cotton [15-16]. It would be worthwhile studying the impact of this ecotechnology for extraction of pectin from flax fibers. Alcohol was used by von Fellenberg [17] to extract pectin from vegetables leaf sources. Ethanol can be easily produced by biotechnology through certain fermentation process. A combined ethanol and ultrasound process would be an environmentally friendly method to extract flax fibers.

Thus, in this work we studied and compared the impact of biotechnological products (enzymes), of an ecotechnology (ultrasound with ethanol) and chemical treatments using aqueous NaOH and NH_3, on the final properties of flax fibers. The flax fiber bundle length, fineness, and tenacity have also been characterized. Moreover, the impact of an additional mechanical treatment called "carding" for further fiber separation was also studied. The fiber surface wettability and the surface charges which are important parameters determining adhesion between the flax fibers and the polymer matrix have also been characterized using wettability and zeta potential measurements and then compared to chemical composition of the resulting fiber bundles measured by chemical analysis. The study of the water uptake behavior of fibers was also necessary since swelling of fibers can lead to micro-cracking of the composite and, therefore, deteriorate mechanical properties.

EXPERIMENTAL

Raw Flax Fiber Bundles

Flax fibers selected for the study were scutched tows considered as by-products or flax waste obtained after removal of high quality linen fibers in flax stems. The flax fiber weight density was 1.49 g/cm^3.

Pre-Treatments

All pre-treatments (except with ethanol) were performed using the Washtec equipment, at constant rotation, at 50ºC during 40 minutes. The liquor ratio (ratio of weight of fiber compared to weight of water) LR 1/25 was used, and for each experiment the weight of flax fibers was set to 7g. Treatment with ethanol using ultrasound equipment was performed during 30 and 60 minutes respectively at 20°C.

All samples were then rinsed five times in distilled water after all pre-treatments.

Enzymatic Treatments

Pectate lyase (Sourzyme L) and laccase (Denlite) enzymes commercialised by Novozymes (Denmark), were used separately. Scourzyme L acts against pectin, and has an optimal activity from 50ºC to 60ºC at pH 7.5 to 9.5. The concentration was set to 10ml/l and 20ml/l for 3 different pH values (7, 8.5 and 9).
Denlite, acts against lignin. It has an optimal activity at around 50ºC to 60ºC and a pH between 6 and 8. 1g/l and 5 g/l of Denlite at pH 6 were used.

Chemical Treatments

Two chemicals: aqueous sodium hydroxide (NaOH) and aqueous ammonia (NH_3) were used at pH 9 and 12. Drops of 0.1 M aqueous NaOH or NH_3 were added to distilled water until the pH reached the value of pH 9 or 12. The pH values of the aqueous solutions were measured using a pH meter.

Ultrasound/Ethanol Treatment

Ethanol was used more as a solvent because of its low environmental impact, aided by ultrasound to facilitate removal of unwanted matter on the cellulosic flax fiber.

Carding Operation

The carding of the fibers was achieved with a lab-scale roller carding machine. This machine is equipped with a feeding roller, a lickerin roller, a main cylinder with one worker/stripper double rollers and a single doffer.

Fiber/Fiber Bundle Properties Characterization

Fiber Tenacity

A certain amount of fiber bundles were parallelized (by combing), cut to 1 cm length, clamped at both extreme ends, and then subjected to increasing loads using a Pressley fiber strength tester, until the bundles broke. After the test, the mass of fibers was measured and the tenacity expressed in terms of breaking load divided by the fiber weight (strength per mass unit). The test was repeated five times for each treated flax fiber bundle.

Chemical Composition Determination

A method of selective dissolution described by Z. Jinqiu [18] was used to determine the quantity of each component (pectin, lignin, hemicelluloses and cellulose) present on the fibers. Different solvents were used and the weight loss after dissolution allowed the quantification of different components.

The method used is as follows:

-Weigh sample under controlled relative humidity and temperature (HR= 65%, and temperature =20°C)

-Dissolve pectin with an aqueous 0.1 mol.l^{-1} EDTA solution at room temperature, by stirring during 1 hour. The samples are drained and dried during 2 days at room temperature.

-Hydrolyse hemicelluloses using aqueous 4 mol.l^{-1} HCl solution at room temperature, for 1 hour with continuous agitation.

-Hydrolyse cellulose using aqueous 1 mol.l^{-1} H_2SO_4 for 24 hours.

-Degrade lignin in oven at 105ºC for at least 3 hours. The weight of the sample was measured after each hour until the weight was stabilised.

Fineness

Fiber fineness is defined by the separation degree expressing the number of fiber bundles contained in 1 mg of raw material [18]. The fibers were manually parallelized and cut to a length of 1 cm each. The fiber bundles were placed one by one on a balance with a clamp, until the weight of all fibers reached 1 mg. The number of fibers counted represents the separation degree *SD*.

Length

The length of the flax fiber bundles was measured with the WIRA equipment. One hundred randomly selected flax fibers were placed manually parallel to each other, with the extreme end of each fiber sealed in between strips of plastic. The set of sealed fibers was placed in the WIRA machine and fiber lengths analyzed. This experiment was repeated 4 times. A computer linked to the WIRA machine provided data in the form of cumulative frequency (%) plotted against different fiber length classes.

Swelling Test Using Optical Microscope

Swelling of fibers due to water absorption was observed with a microscope. Single fibers removed from fiber bundles were placed in parallel direction on a glass slide, and both ends of all fibers taped. The positions of fiber diameter measurements were marked with a cross using a waterproof pen (see *Figure 1*). The glass slide was then immerged in a beaker containing distilled water for one hour. Measurements of fiber diameter at the marked positions were carried before and after immersion in water. The percentage increase in fiber diameter due to swelling was determined on three different fiber samples, at three different positions.

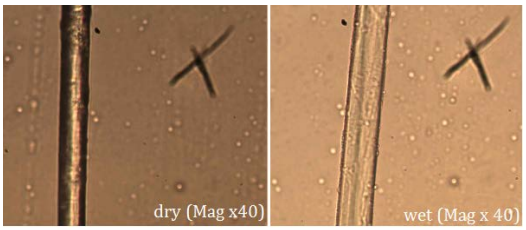

FIGURE 1. Microscopic views of a single flax fiber before (a) and after immersion in water for 1 hour (b)

Fiber Surface Properties Characterization

Fiber Wettability Was Characterised Using The Floating Test.

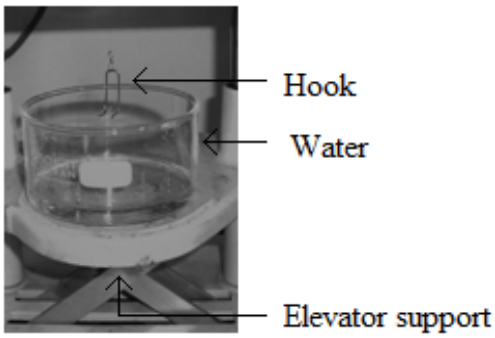

FIGURE 2. Wettability set-up, floating test.

A simple floating test described by Van Hazendonka [19] was used to characterize the wettability of treated flax fibers (see *Figure 2*). When a cylindrical fiber is placed horizontally at a liquid surface, it will float though its density exceeds that of the liquid, because gravitational forces are counteracted by interfacial forces. The interfacial forces which can be measured using water contact angle originate from surface

energy of solids in contact with water. Thus, in the case of a flax fiber with a very hydrophilic surface, water contact angle can reach 0°, and the fiber falls as its density (1.49) is greater than 1. However for flax fiber with hydrophobic surface (low surface energy) the high interfacial energy will prevent the fiber from falling (sinking). Fibers were placed horizontally onto a metallic hook at the surface of distilled demineralized water. The beaker containing the water was moved vertically up, until the fiber touched the water surface. The hook was removed gently, and the behavior of the fiber observed (floating or sinking) for 5 minutes. For fibers which sink, the time taken for the fiber to reach the bottom of the recipient was measured. For each treatment, the test was carried out on 5 single fibers.

Streaming Potential Measurements

The surface zeta potential was measured by streaming potential measurement using Zetacad equipment (France) at 25°C. A 0.001mol.l^{-1} of KCl electrolyte solution was used. 1 g of flax fiber was maintained in a cell while the electrolyte was forced to flow through the fibers at varying pressures. Before any zeta potential measurement, the sample was maintained in the electrolyte solution for 24 hours in order to reach equilibrium before making the measurement itself. Five measurements were carried out on each sample for pH values of the electrolyte solution varying from 3 to 10.

Indeed Bismarck et al. [20] has shown that there is a decrease in zeta potential of natural fibers with time which is due to water adsorption at the fiber surface, and swelling of fibers causes the transfer of the shear plane which excludes the diffuse point of the electric double layer from the mechanical or electrical interaction. Maintaining each fiber sample in the electrolyte for at least two hours ensures more static measurements.

Design of the Study

In the first part of this study (Part I), for each of the 5 products (Scourzyme, Denlite, aq. NaOH, aq. NH_3, and ethanol), varying treatment conditions (pH, duration, concentration) were used to study their impact on the fiber bundle tenacity and wettability properties. The aim of this first part of the work was to select optimum conditions for the 5 products, for minimum tenacity loss as well as least environmental impact (least amount of chemical or biochemical agent used, smaller duration time, neutral pH).

In part II, more detailed characterization of fibers treated with the 5 optimised processes were carried before and after a carding process: fiber bundle length, fineness, tenacity, as well as surface properties and chemical composition were determined.

The margin of error (p) for statistical analysis at 95% confidence level is indicated in each study. For most of studies, p<5%, which ensures the validity of our results.

RESULTS

PART I

Impact of Treatment Conditions on Fiber Bundle Tenacity and Fiber Wettability

Fiber Bundle Tenacity

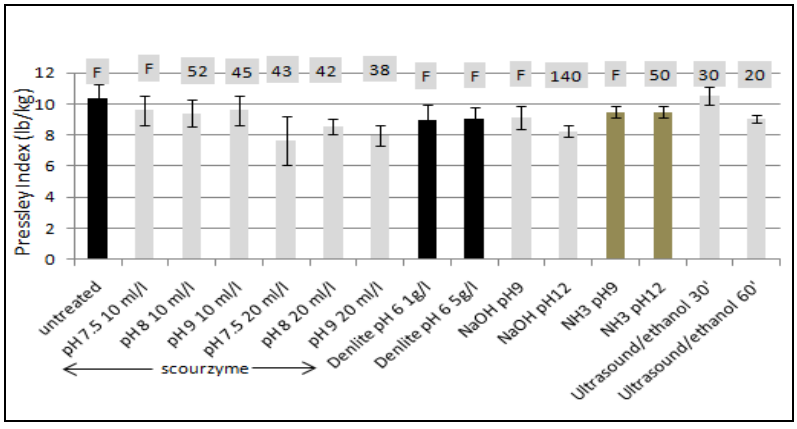

FIGURE 3. Tenacity (1b/kg) of flax fiber bundles. The wettability of fibers characterised using the floating test is expressed in terms of time taken in seconds for a floating horizontal fiber to fall down (to sink) when placed at the top of distilled water surface. 'F' in a grey square denotes that the fiber always floated.

Figure 3 shows the tenacity values of flax bundles as a function of different treatment conditions. Almost all treatments lead to a reduction in the bundle tenacity values compared to the untreated flax fiber bundles, depending on the treatment conditions. With Scourzyme at 10 ml/l and at 3 different pH values, the tenacity values (~9.4 to 9.6 lb/kg) are slightly lower than that of the untreated ones (~10.4 lb/kg). Higher concentration of Scourzyme (20 ml/l) leads to a considerable decrease in tenacity for all pH values: tenacity values are around 7.6 to 8 lb/kg.

Increase in pH from pH 9 to pH 12 with NaOH decreases the bundle tenacity. With aqueous ammonia-NH_3, no reduction in tenacity is observed for the same increase in pH.

With ethanol (using ultrasound), slight reduction in mechanical strength is observed for increase in treatment time from 30 to 60 minutes. However tenacity values for a treatment of 30 minutes are similar to those of the untreated flax fiber bundles. Increase in Denlite concentration does not lead to great reduction of tenacity.

Wettability of Elementarized Fiber

Each manually elementarized flax fiber was tested. The behavior of a flax fiber (fall or float) at the water surface varied according to the treatment conditions.
The average time taken (in seconds) for a floating horizontal fiber to fall down (sink) when placed at the top of distilled water surface are indicated in the grey squares (see *Figure 1*), while 'F' in a grey square denotes that the fiber always floated. Fibers from fiber bundles treated with Scourzyme or with ethanol/ultrasound, fell. With Scourzyme treatment, the flax fiber falls at both concentrations of 10 ml/l and 20 ml/l, at both pH 8 and 9. At lower pH=7.5, the higher concentration of Scourzyme-20 ml/l gives good wettability results but it leads to a higher decrease in tenacity. The use of 10 ml/l of Scourzyme at pH 8 leads to higher rate of removal of hydrophobic components without considerable loss in tenacity and with minimum input of chemical products.

Varying concentrations of Denlite does not improve the hydrophilic properties of the fiber: the fiber never falls as in the case of the untreated flax fibers.

With chemical treatments using aqueous ammonia and NaOH, the fiber falls, that is, it becomes hydrophilic at pH 12 only, and not at pH 9. However, at pH 12, only NaOH yields a great reduction in tenacity.

With the eco-technological treatment with ultrasound/ethanol, rapid sinking takes place for both treatment times of 30 min. and 60 min. meaning that hydrophobic components are easily removed, but only the higher longer treatment time (60 min.) has a considerable effect on the tenacity loss. In general, treatments with ultrasound/ethanol or with scourzyme lead to hydrophilic fiber surfaces.

Denlite leads to a hydrophobic fiber surface, while the fiber surface properties vary with concentrations of aqueous NH_3 and NaOH used.

PART II
Effect of 5 different Chemical/Biotechnological/ Ecotechnological treatments before and after Carding on the Flax Fiber Properties

The five treatments yielding high tenacity values and the least environmental impact (least chemical and energy inputs) are shown in *Table I*. Their influence on fiber bundle length, fineness and tenacity before and after carding, was studied.

TABLE I. The five treatments carried before carding of flax fibers.

Products	pH	concentration	Duration	Temp.
Scourzyme	8	10ml/l	40 min.	50°C
Denlite	6	1 g/l	40 min.	50°C
NaOH	9		40 min.	50°C
NH_3	9		40 min.	50°C
Ultrasound+ethanol	30 minutes		30 min.	20°C

Flax Fiber Bundle Fineness, Length, and Tenacity

Flax Fiber Bundle Fineness

Flax fiber bundle fineness (measured by the separation degree-SD) before and after carding are shown in *Table II*. Before carding, Denlite and ethanol (with ultrasound treatment) lead to better separation of fibers (higher SD value). For treatments with Scourzyme, aqueous NaOH and ammonia, the separation degree seems to be similar to that of the untreated flax fibers.

However, after carding, separation degree (SD) of the flax fibers is higher in all cases. Even without any treatment, the separation degree is doubled with the mechanical separation by carding. With Scourzyme, though no increase in separation degree is observed before carding compared to the untreated ones, the separation degree reached after carding is high (SD=46) and is similar to that obtained with the combined ethanol/ultrasound ecotechnological process. Treatments with aqueous ammonia NH_3 (aq),

NaOH and Denlite do not increase the fiber fineness compared to the mechanical treatment alone (SD =34 for untreated fibers).

TABLE II. Separation degree (SD) of flax fiber bundles for different pre-treatments, before and after carding. The standard deviation values are presented by bar errors in *Figure 6*.

	Untreated	Scourzyme pH 8, 10ml/l	NaOH pH 9	NH_3 PH 9	Denlite PH 6, 1g/l	ultrasound + ethanol 30'
SD before carding	17	18	19	18	22	25
SD after carding	34	46	39	36	36	48

Flax Fiber Length

Data collected from the WIRA fiber length measuring apparatus, for the untreated flax fiber before and after carding are illustrated in *Figure 4*. It shows the cumulative frequency (%) for different fiber length classes.

Before carding, 65% of fibers exceed a length of 100 mm. After carding, only about 20% of fibers exceed 100 mm (see *Figure 4*).

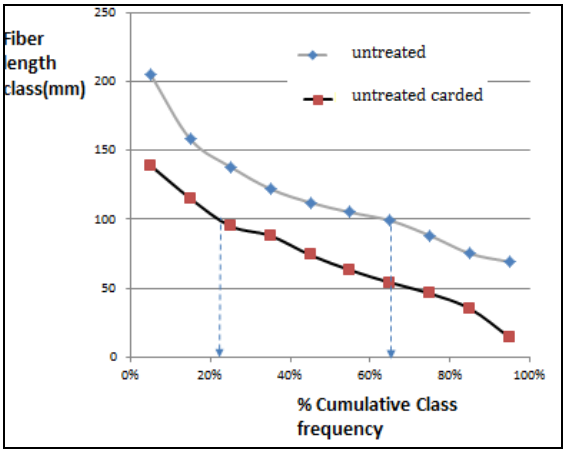

FIGURE 4. Cumulative frequency (%) plotted against fiber length class for the untreated flax fibers before carding (grey curve) and after carding (black curve).

Fibers were classified into four groups according to their length: small fibers (<50 mm); medium length fibers (50-100 mm) ; long fibers (100-150 mm) and ultra-long fibers (150-250 mm). The fiber length frequency bar charts are shown in *Figure 5*, for the five different treatments, before carding (grey bars) and after carding (black bars).

Before carding(grey bars), pre-treatments with the two enzymes (Scourzyme or Denlite) and with the aqueous NH_3, do not lead to significant decrease in frequency of long fibers (100-150 mm) and ultra long fibers (150-250 mm). After carding (see black bars), there is no longer any ultra-long fiber left in the case of untreated flax fibers. With a pre-treatment using Denlite and aq. NH_3, there is still some percentage (5-10%) of ultra-long fibers present after the carding process. These two pre-treatments would reduce fiber bundle breakage during carding process.

With the alkaline NaOH(aq) and the combined ethanol/ultrasound process, a significant reduction in fiber bundle length is observed after carding compared to the carded untreated ones. The frequency of small fibers (length< 50 mm) for these two treatments is very high: 55 % for the alkaline NaOH treatment and 45% for the ethanol/ultrasound process compared to 30% for the untreated flax fibers. With the alkaline NaOH(aq) treatment, all fibers are smaller than 100 mm, and no long or ultra-long fiber is present, after carding.

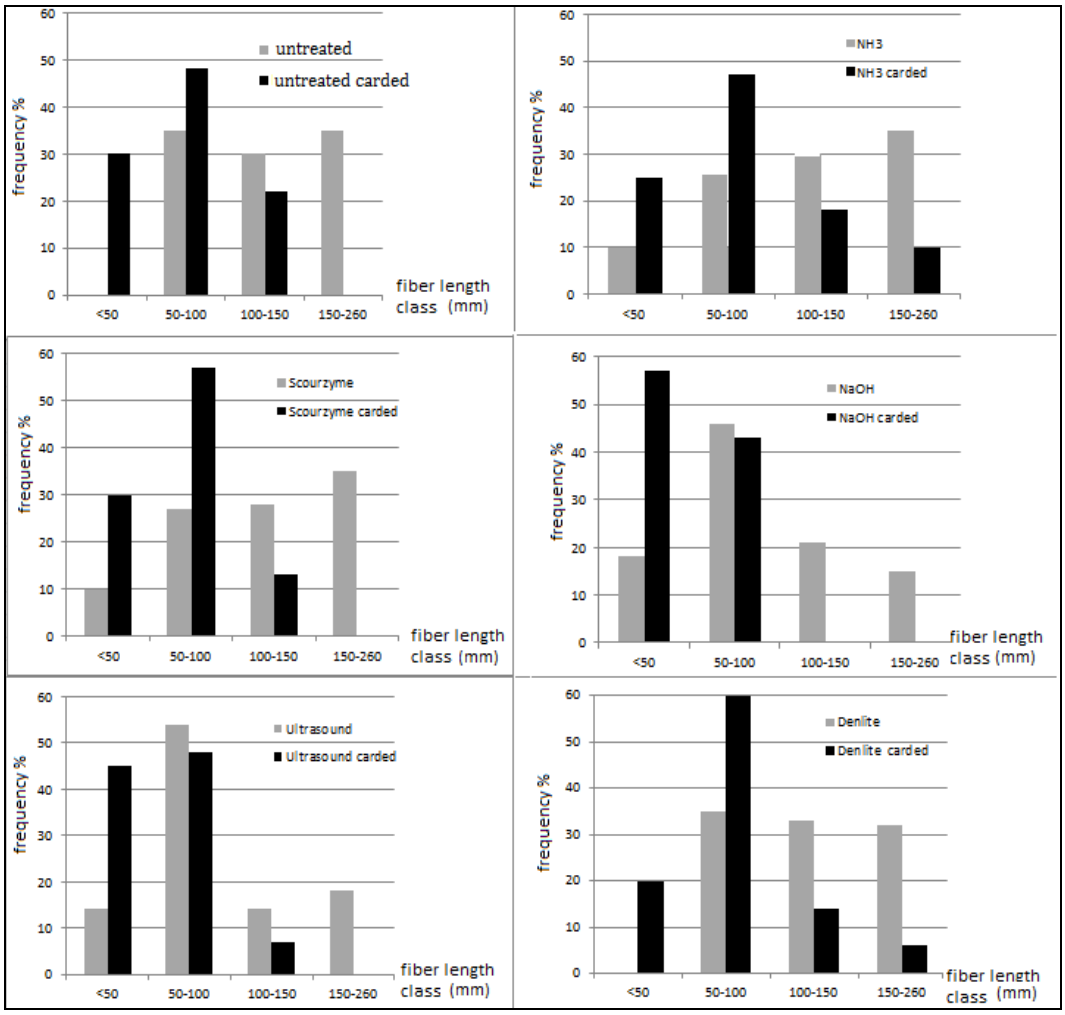

FIGURE 5. Frequency distribution of 4 different fiber length classes for the 5 different treatments, before carding (grey bars) and after carding (black bars).

Flax Fiber Bundle Fineness and Length

Fiber bundle fineness was plotted against fiber bundle average fiber length for the five different pre-treatments (see *Figure 5*). Indeed, even without any pre-treatment, carding leads to a considerable reduction in fiber bundle length and thickness. Pre-treatment with ethanol/ultrasound leads to the best elementarization of flax fiber bundles (shortest and finest). With NH_3(aq), Denlite and Scourzyme, there is a further increase in bundle fineness without reduction in bundle length compared to the untreated fibers. However, amongst these three products only Scourzyme leads to the finest fibers, reaching nearly the fiber fineness obtained with ethanol/ultrasound pre-treatment.

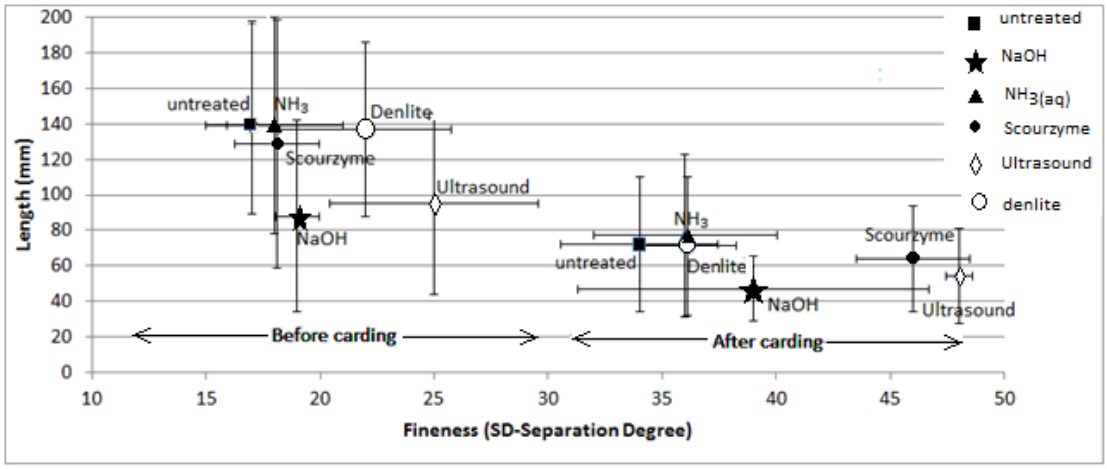

FIGURE 6. Fiber fineness and length variation before and after carding process for the five different pre-treatments.

Flax Fiber Bundle Tenacity

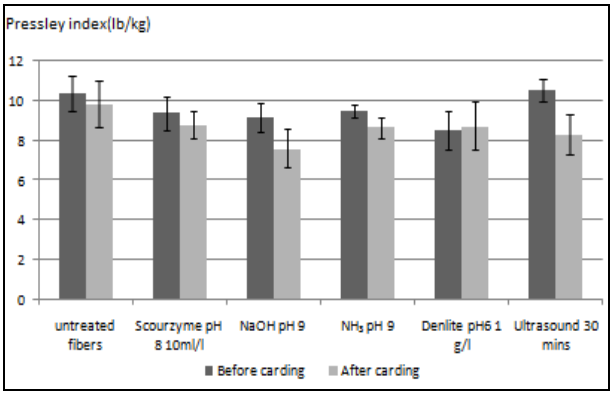

FIGURE 7. Flax fiber bundle tenacity for different pre- treatments before and after carding. The standard deviation values are presented by bar errors.

The variation of the flax fiber tenacity before and after carding is presented in the *Figure 7*. Without carding, the chemical/and biotechnological treatments lead to a slight reduction in tenacity. No reduction in tenacity is observed for the flax fibers treated using the ethanol/ ultrasound.

However after carding, tenacity values of flax fibers subjected to all treatments (except NaOH) are similar and are around 9 lb/mg. These values are however slightly lower than that of the untreated carded flax fibers. With ethanol (+ultrasound), though a very big decrease (21 %) in mechanical strength is observed after carding, the average tenacity is similar to those with chemical/biotechnological treatments (except with NaOH).

With Denlite, the tenacity values before and after carding are similar, which means that Denlite treatment would limit fiber breakage during carding. Alkaline treatment with NaOH leads the highest loss in tenacity.

Flax Fiber Surface Properties Compared to Water Absorption and Chemical Composition

The water absorption, chemical composition, wettability of the fibers subjected to the five different treatments, are presented in part A of the *Table III*. For further comparison, water absorption capacity and wettability of the fibers were also measured by varying treatment conditions of the 5 treatments (see part B of the *Table III*).

Chemical Composition

The chemical composition of fibers (before carding) having been subjected to each of the five different treatments was determined by dissolving each component present on the fibers using different chemicals described in section 2.2.

For the untreated flax fiber, 2% of pectin and 4% of hemicelluloses were measured. The quantity of lignin could not be quantified, probably because it might be present in very small quantity (was null) since the flax fibers had been subjected to a physical pretreatment using at the scutching stage to yield the raw waste fibers.

Pectin is completely removed by all pre-treatments except ethanol (with ultrasound). However, hemicelluloses are also removed with certain pre-treatments: a decrease from 4% to 2% is observed with aqueous NaOH and a lower decrease to 3% with Denlite and aqueous NH_3 (see *Table III*). Treatment with ethanol does not remove any hemicellulose, and there is still 1% of pectin present.

The untreated flax fibers have a higher swelling capacity than the treated flax fibers. An average of 18% increase in fiber diameter is observed for the untreated

TABLE III. Chemical composition, wettability and swelling capacity of the fibers having been subjected to 5 different treatments.

PART A						
TREATMENTS	**Untreated**	**Scourzyme 10 ml/l at pH8**	**NaOH pH9**	**NH_3 pH9**	**Denlite 1g/l pH6**	**Ultrasound Ethanol 30'**
Separation degree SD (Before->after carding)	17 -> 34	18 →46	19 →39	18 → 36	22 → 36	25 → 48
Chemical composition						
Pectin (%)	2	0	0	0	0	1
Hemicelluloses (%)	4	4	2	3	3	4
Lignin (%)	0	0	0	0	0	0
Increase in fiber diameter due to water absorption (microscopy)	18%	9%	16%	16%	9%	16%
Wettability (time before sinking in sec.)	FLOATS	FALLS(58s)	FLOATS	FLOATS	FLOATS	FALLS (26s)
PART B						
TREATMENTS		**Scourzyme 20 ml/l at pH9**	**NaOH pH12**	**NH_3 pH12**	**Denlite 5g/l pH6**	**Ultrasound Ethanol 60'**
Increase in fiber diameter due to water absorption (microscopy)		15%	5%	5%	2%	24%
Wettability (time before sinking in seconds (s))		FALLS	FALLS(140s)	FALLS(50s)	FLOATS	FALLS(20s)

fiber. The water absorption capacity of fiber bundles seem to depend on the type of treatment. For treatments with the two enzymes, Scourzyme and Denlite: the water absorption is divided by two (9%), half of that of the untreated fibers. With the chemicals (aqueous NH_3, and NaOH at pH 9), the water absorption (16%) is only slightly below that of the untreated flax fiber value (18%), though pectin is completely or partially eliminated. However as pH is increased (from pH 9 to 12-see part B of *Table II*), the swelling ability of fibers is decreased from 16% to 5% for both chemicals.

With Denlite, considerable reduction in water absorption is observed.

For the ecotechnological treatment with ethanol, increasing treatment time with ultrasound increases the swelling capacity from 16% to 24% which is above the water absorption capacity of the untreated flax fibers. At both treatment times (30 and 60 min), the fiber sinks which indicates a hydrophilic fiber surface.

Streaming Potential Results

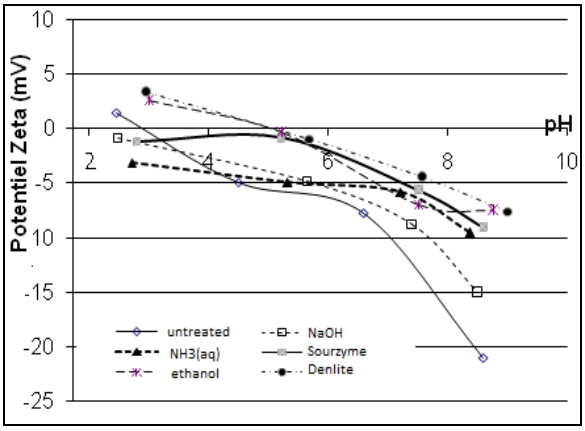

FIGURE 8. Zeta potential (mV) as a function of pH values for flax fibers with 5 pre-treatments.

Zeta potential measurements were carried on carded fiber bundles. The zeta potential curves of the 5 treated samples presented in *Figure 8* show a similar overall trend as a function of pH, but at pH> 7 these values differ significantly. For the untreated fiber, a significant increase in negative zeta potential values is perceived at pH>7. For fibers treated by the alkaline products (aqueous NaOH and NH_3) zeta values are less negative. Those treated by enzymes (Denlite or Scourzyme and the ultrasound/ethanol)) have zeta values more close to zero.

DISCUSSION

Five treatments using two enzymes (Scourzyme, Denlite), two chemicals (aq. NaOH and NH_3) and an ecotechnology (ethanol/ultrasound) were selected on the basis of minimum flax fiber bundle tenacity loss after treatment as well as least environmental impact generated. Tests carried out before and after mechanical carding shows that both fiber bundle length and fiber thickness decrease considerably after carding. However the extent of decrease depends on the type of pre-treatment used. Use of Scourzyme (a pectate lyase) or of the combined ethanol/ultrasound leads to highest degree of elementarisation, though with Scourzyme, fiber bundles are the finest and longest. Treatment with the alkaline NaOH leads to the highest reduction in fiber bundle length and tenacity.

The chemical composition of fibers (before carding) having been subjected to each of the five treatments were determined. Results show that the pectin content at the flax fiber surface has a considerable impact on the swelling ability of flax fibers. Pectin has a high water absorption capacity and can form a hydrogel on prolonged contact with water. The untreated flax fiber with 2% of pectin has the highest swelling capacity (18% increase in fiber diameter). For treatments with the two enzymes, Scourzyme and Denlite, the water absorption is divided by two (9%), probably due to the absence of pectin at the extreme surface.

With the chemical treatments (aqueous NH_3, and NaOH at pH 9), though pectin is completely or partially eliminated, the water absorption (16%) is only slightly below that of the untreated flax fiber (18%). These chemicals would most probably penetrate the fiber structure, break intermolecular hydrogen bonds between cellulosic chains, and thus increase the amorphous regions and hence the water absorption capacity of fibers. The swelling ability of fibers is however decreased from 16% to 5% for both chemical treatments when pH is increased from pH 9 to 12. This may be due to conformational changes of the cellulosic chains [21] at high pH (pH12), as in the case of mercerization process. The chemicals would also react with the free –OH ends of cellulose chains (in amorphous regions), forming an alkali cellulose with NaOH, and a complex cellulose compound with aqueous ammonia. As NH_3 or NaOH is allowed to evaporate, new hydrogen bonds are formed which results in a new pattern of hydrogen cross-linking and hence conformational changes (a sort of mercerisation). However, mercerizing would theoretically lead to an increase in cristallinity and hence an increase in fiber tensile strength. Indeed, the higher decrease in tenacity of flax fiber bundles at pH 9 with NaOH (compared to aqueous NH_3), can be explained by the higher quantity of hemicellulose eliminated with NaOH (see *Table III*).

Indeed, enzymes such as Scourzyme (pectate lyase) or Denlite (laccase) which are bigger molecules (than the NaOH, or NH_3, or ethanol), would not have easy access to the space in between cellulose polymer chains: these would not modify the internal 3-D structure of the cellulose, and have no action on the hydrolyis of cellulosic chains. Scourzyme causes lysis of pectin only. However, the swelling ability increases from 9% to 15 % as the concentration of Scourzyme and the pH are increased because of reasons described previously (combined effect of lysis of pectin by scourzyme, and hydrolyis of hemicelluloses by alkaline pH9).

With Denlite, increasing concentration from 1 g/l to 5g/l leads to a considerable reduction in water absorption from 5% to 2%. Simultaneously a special phenomenon was observed: the fiber bundles became very rigid as if a kind of coating was deposited at the flax bundle fiber surface. This coating would surely

consolidate fibers in the fiber bundles and would also lead to a smaller reduction in tenacity. The very hydrophobic surface and very low swelling ability may be due to the formation of a water resistant material in the presence of the laccase enzyme.

With ethanol, though 1% of pectin is still present for the treatment time of 30 minutes, the fiber swelling capacity is similar to the untreated flax fibers (with 2% pectin). Moreover, the treated fiber has a hydrophilic surface. Indeed pectin is composed of high methoxy pectin (DE: degree of esterification > 50%) and low methoxy pectin (DE: degree of esterification < 50%). The latter one can be linked to other low methoxy pectin through Ca^{2+} ions. The combined ethanol/ultrasound would lead perhaps to elimination of the high methoxy pectin in ethanol leaving the more hydrophilic low methoxy pectin at the fiber surface. This would result in an increase in the flax fiber surface energy and wettability. It is also probable that ethanol/ultrasound loosens the polymeric pectin (1%) and hemicellulose without eliminating them. This loosening of the polymeric chains would lead to a better separation of fibers during the carding process (Separation degree is the highest=48). .

As far as the zeta potential values are concerned, these seem also to be related to the content of pectin at the extreme surface. Thus at high pH values, the most negative zeta potential values of the untreated flax fibers can be explained by the high content of pectin (2%). Pectin contains carboxylic groups, and at pH>7, the carboxylic groups become dissociated, resulting in negative zeta potential. As pectin is removed, cellulose and hemicellulose polymers containing predominantly hydroxyl groups (-OH), are mostly exposed to water. This would explain the less negative zeta potential values (at pH>7) for the treated flax fibers. Indeed previous works [23] show that zeta potential values of fibers containing hydroxyl groups (eg. cotton -cellulose) are less negative than those of fibers containing both carboxylic and hydroxyl (-OH) groups (eg. polyester). However this phenomenon alone cannot explain all the results because with NaOH though all pectin is removed, negative zeta potential values at pH>7, is higher than that of scourzyme for example, where all pectin is equally completely removed. Indeed, at pH 9, as the NaOH chemical can more easily penetrate inside the cellulosic fiber and break hydrogen bonds between cellulosic chains in the crystalline regions of the cellulose: a greater number free hydroxyl groups are present, and would lead to more negative zeta potential values.

The zeta curve for Denlite is quite particular with no plateau observed. The hydrophobic coating formed would more probably result in a surface where the hydroxyl groups of the cellulosic chains are less available.

CONCLUSION

Varying degree of flax fiber bundle fineness and length can be obtained after a carding process, depending on the type of pre-treatment (ecotechnological/biotechnological or chemical) used. Use of Scourzyme (a pectate lyase) or of the combined ethanol/ultrasound leads to highest degree of elementarization, though with Scourzyme, fiber bundles are the finest and longest.

The bulk properties (tenacity and swelling capacity) and surface properties of the treated flax fibers seem to depend on the type of each pre-treatment. More particularly, the degree of elimination of biopolymers at the fiber/fiber interface, and the modification of individual fiber crystallinity depends on the type of pre-treatment. Elimination of hemicelluloses in addition to pectin by NaOH at the fiber/fiber interface reduces fiber bundle tenacity though there is an increase in fiber cristallinity (lower swelling of fibers) at higher pH (12).

The choice of treatment will depend on the properties of end-product.

Fibers elementarized using Scourzyme and ultrasound are hydrophilic and have high water absorption which varies with conditions: duration, pH and concentration of product used. Fibers elementarised with alkaline treatments (NH_3 and NaOH) are hydrophobic, but on increasing the pH, the fiber surface becomes hydrophilic (higher surface energy) and the flax fiber also absorbs less water. Denlite seems also interesting compared to the untreated one, giving long hydrophobic fibers having very low water absorption capacity (up to 2% of swelling), despite the total removal of pectin during the treatment.

According to different applications we can choose different treatments, and also modify water absorption, which is one of the main disadvantages on composites applications [22] by varying the pre-treatment product and conditions.

The work carried here can also be applied to other natural fibers**.**

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