Characterizing Cellulosic Fibers from *Ulex europaeus*

Richard Celis,[a] Marco Torres,[b] Paulina Valenzuela,[c] Rolando Ríos,[a] William Gacitúa,[c] and Héctor Pesenti [a,d,]*

Information on the morphological and physical properties of biofibers is necessary to support the mechanical understanding of the biological design of plants, as well as for the development of new technology that adds value to non-traditional bioresources, such as those based on *Ulex europaeus* fibers. *Ulex europaeus* fibers were extracted through a chemical pulping process at 170 °C and with 40 g/L NaOH. The dimensions of the fibers produced were 0.97 ± 0.1 mm in length and 13 ± 2 µm in diameter. Pressed fiber paper sheets were made to evaluate their mechanical properties. Burst and tear indices of 1.2 mN/kg and 8.6 Nm^2/kg, respectively, were recorded. The values obtained did not compare well to fiber paper sheets from *Pinus radiata*, presumably due to the significant amount of non-structural elements of wood present in the samples and the lower length of *Ulex europaeus* fibers, which resulted in lower tensile strength. Additionally, nanoindentation tests were conducted to assess the hardness and elastic modulus of the fibers, obtaining average values of 0.84 GPa and 9.23 GPa for the stem, respectively. These values were significantly lower than those of industrial biofiber, perhaps due to the lower morphogenic maturity of *Ulex europaeus* fibers compared to other traditional sources of fiber.

Keywords: Biofiber; Ulex europaeus; Nanoindentation; Properties

Contact information: a: Instituto de Materiales y Procesos Termomecánicos, Universidad Austral de Chile, Valdivia; b: Instituto de Bosque y Sociedad, Universidad Austral de Chile, Valdivia; c: Centro de Biomateriales y Nanotecnología, Universidad del Bío-Bío, Concepción; d: Lab. de Superficies Funcionales, Universidad Austral de Chile, Valdivia;
** Corresponding author: lab.super.funcionales@gmail.com*

INTRODUCTION

Green materials have been garnering substantial attention in science and engineering because they offer interesting advantages such as renewability, recyclability, biodegradability, low density, high specific strength, and also some catalytic properties (Mohanty *et al.* 2000, 2002). Currently, natural fibers, or biofibers, extracted from plants or cellulose, are widely used for various technological applications. Nontraditional biofibers from renewable sources are a matter of great interest, particularly fibers from sources that have developed an intelligent functional system to adapt to a variety of different climatic and soil conditions (Huda *et al.* 2007).

Ulex europaeus (sometimes called gorse or furze) is a perennial shrub of the family Leguminosae, reaching approximately 5 m in height and native to central Europe. It has a high reproductive capacity and seeds presenting long latency periods, long vegetative growth seasons, and rapid growth. Moreover, it produces isoprene-based volatile biogenic compounds that make it a highly combustible plant (Boissard *et al.* 2001). This, in addition to its morphology of well-developed primary thorns, results in a lack of natural enemies. Therefore, it has adapted to a wide variety of ecosystems, making it one of the most aggressive species for native landscapes and agriculture in recent years. It has had a great economic impact on the world due to its expansion and difficult eradication (Gaynor and MacCarter 1981; Radclife 1986; Matthei 1995). Therefore, *Ulex europaeus* has become regarded a highly invasive and persistent plant. In spite of the control efforts, the gorse plant expands its coverage without difficulty.

On the other hand, some potential advantages of *Ulex europaeus* have become known because of its interesting content of organic macromolecules. Indeed, the first uses of this shrub were to provide protein to cattle, goats, and sheep (Bao *et al.* 1997). However, its most remarkable feature is the seeds, which contain a protein called *lectina Ulex europaeus*. This protein has been studied in medicine, immunology, and genetics, due to the recognition mechanisms that allow it to mimic or selectively combine itself with glyco-conjugates on the cell surface, producing agglutination or transport (Lis and Sharon 1986; Kennedy *et al.* 1995; Hamashin *et al.* 2003).

Among other biobased products, gorse is defined as a lignocellulosic material (Jobson and Thomas 1964; Ligero *et al.* 2011), noting that cellulose is the most abundant polysaccharide in *Ulex*. Obtaining other organic components of technological importance such as xylan and other oligosaccharides (Ares-Peón *et al.* 2013) is an important area of research. Moreover, the possibility of generating bioethanol (Ares-Peón *et al.* 2013) has also been studied, and encouraging results were obtained.

Currently, the study on many lignocellulosic non-traditional biofiber resources including cornstover, kenaf, bagasse, ramie, palm fiber, jute, flax straw, barley straw, bamboo, cane, rice stubble, hemp, sisal, wheat straw, sorghum stalks, pineapple leaves, banana leaves and many more have revealed positive results with properties adequate for textile, composite, and industrial applications (Reddy 2005; John and Thomas 2008; Faruk *et al.* 2012; Brinchi *et al.* 2013). The properties of the natural cellulose fibers are determined by the source, maturity, and anatomical origin; these factors affect the cellulose quantity and fibril angle (Bledzki and Gassan 1999; Mohanty *et al.* 2001; Ververis *et al.* 2004). However, it has been noticed that the mechanical properties of composites materials with natural fiber fillers are determined by the preconditioning processes and length of fibers (Ververis *et al.* 2004). Evidently, natural short fibers of average size 0.24 to 0.5 mm are preferred since they provide a higher specific surface area (Mohanty 2001; Herrera-Franco and Valadez-Gonzalez 2005). Furthermore, the fibers are dispersed more homogeneously, increasing compatibility between the fiber and matrix. In order to continue to make progress, constant advances are made to understand and control the properties of natural fibers obtained from nontraditional sources, with very promising technological results (Reddy 2005; Jacob and Thomas 2008; Faruk *et al.* 2012).

Nontraditional *Ulex europaeus* biofibers from renewable sources can provide an interesting resource to supply the industrial technologies, nanotechnology, composite materials, and eco-efficient building materials as fillers or for reinforcement. However, there is limited information on structure and properties of *Ulex europaeus* fibers. Moreover, the adaptability, resilience, rapid growth, and the wide expansion around the world of "gorse" can turn it into a big reserve of raw material for the new technologies, being a motivating and challenging subject of study to gain a better and more comprehensive understanding of the structural behavior of the fiber for developing new engineering materials.

EXPERIMENTAL

Materials

Ulex europaeus of approximately 6 to 7 years of age was collected from Santa Rosa Experiment Station located in Cabo Blanco, Valdivia, Chile. The size of the specimens was reduced to 30-80 mm using a chipper and without discriminating by shape, size, or anatomy. Subsequently, the chips were reduced to less than 10 mm with a chipper machine model PZ-8 (PallMann; USA).

Stem morphology

Blocks of stem samples were treated with alcohol/glycerin/water (1:1:3 in volume) in boiling water for 2 h. Later, the specimens were cut with a knife along the radial and tangent planes, forming cubes about 10 mm in size. Finally, the hand microtome operating at 5 μm steps was used to prepare sections sufficiently fine for image analyses. The stem anatomy was determined with an Olympus SZ6145TR stereo light microscope (Japan) equipped with a digital camera model MD90 and digital imaging software (MshOt Microscopy Imaging Expert; Guangzhou, China). In addition, images of the morphology were obtained by scanning electron microscopy (SEM) with a LEO 420 Carl Zeiss (Germany) microscope in high vacuum at 20 kV on gold metallized surface.

Chemical composition

Quantitative determination of holocellulose, cellulose, and lignin was performed for *Ulex europaeus* stems following Poljak's method (1948), Kurschner-Hoffer cellulose method (1931), and the standard method of TAPPI T 222 om-88 (1988), respectively. Extraction in cold and boiling water with 1% NaOH, ethanol and toluene was also conducted according to the method set in TAPPI T 204 om-88 (1988) standard.

Fiber extraction

The stem chips went through the chemical pulping process steps as set in the laboratory protocol to obtain *Ulex europaeus* fibers. This thermochemical treatment consisted of mixing the fibrous material with a Mini-Mill (MK System Inc., USA) digester in an aqueous solution (40 g/L) of sodium hydroxide (NaOH), with a fiber release rate of at least 10%, *i.e.* kappa number less than 67. Then, heat was applied to remove the lignin binding the fibers of *Ulex* chips and achieve a high degree of delignification (Casey 1990).

The same process was employed to obtain fibers from *Pinus radiata*. The process was carried out under constant NaOH concentration, pressure, temperature, and time following the work on *Eucalyptus globulus* by Torres and Rodriguez (1991), as shown in Table 1. The purpose of this process was to form the least fiber bundles (bonded fiber packages) possible.

Finally, the process yielded a basis of about 75% NaOH, obtaining a kappa number of 22. The residues obtained for this experimental study were collected, treated and managed by the Environmental Management Unit (MIR) of Universidad Austral de Chile.

Table 1. Parameters for Obtaining Fibers by Chemical Pulping Process

Dry wood, *kg*	1
Maximum temperature, °C	170
Time until maximum temperature, *min*	65
Time at maximum temperature, *min*	120
Concentration NaOH, *g/L*	40
Hydromodule, *w/v*	4/1
Pressure, *MPa*	0.827

Fiber morphology

Images of *Ulex europaeus* fiber were obtained using a JEOL JSM-6610LV scanning electron microscope (SEM) (Japan) in low-vacuum mode (0.9 torr) at an accelerating voltage of 15 keV. JEOL MP-45030TDI's three dimensional image software provided the diameter of 30 *Ulex* fibers. An Olympus SZ6145TR stereo light microscope (Japan) equipped with a digital camera model MD90 and digital imaging software (MshOt Microscopy Imaging Expert; Guangzhou, China) was used to determine the length of 30 full continuous fibers that did not show evidence of significant damage.

Physicomechanical properties of fiber sheets

Fiber paper sheets of *Ulex europaeus* and *Pinus radiata* were manufactured according to standard procedures stated in TAPPI T 205 om-88 (1988) to assess pulps and fibers (Table 2). The rupture length was obtained on paper strips 15 mm wide and 160 mm long using an electro hydraulic mechanical testing machine from Thwing-Albert Instrument Company, USA, model 37-4, according to the standard method of TAPPI T 404 cm-92 (1992). Furthermore, resistance to tearing was evaluated with an Elmendorf Tearing Tester from Thwing-Albert Instrument, as specified in TAPPI T 414 om-88 (1988) standard. Finally, the burst index was measured with a tester machine by Mullen Testers (Chicopee, USA), model AH, following the method of TAPPI T 403 om-91 (1991) standard.

Table 2. Physical Characteristics of Gorse and Radiata Pine Paper Sheets

Type of Pulp	*Ulex europaeus*	*Pinus radiata*
Moisture content wet basis, *%*	5.49	6.07
Grammage, *g/m²*	60	60
Caliper, *mm*	0.12	0.12

Nanoindentation

Three random samples of gorse stem were collected from the splintered material to perform the nanoindentation studies, and these were used to obtain cubes of about 5 mm^2. The specimens were dried in an oven for 3 h at 70 °C to remove moisture. Subsequently, the dry specimens were placed in capsules to be embedded in epoxy resin. Similarly, *Ulex europaeus* fibers were thermally dried in order to select sets of fibers with a clip and analyze them under a Leica EZ4HD stereo digital microscope (Wetzlar, Germany). The sets of fibers were placed on adhesive tape to align them parallel to the force of the indenter and to avoid movement when the epoxy resin was applied. The adhesive tape with the fiber sets were placed in rubber molds and the epoxy resin was applied to continue the impregnation process. The prepared samples of gorse stem and fibers were placed in a muffle furnace at 60 °C for 24 h for polymerization, and then placed at room temperature for an additional 24 h. Once cured, the test specimens were trimmed with a razor blade and sectioned at 250 nm thickness with a Leica RM2265 rotary microtome (Wetzlar, Germany), using a glass and diamond knife to obtain a smooth surface of indentation according to the technique employed by Jakes *et al.* (2007).

The indentation tests were performed on a nanoindenter Hysitron TriboIndenter TI-900 (USA), equipped with *in situ* scanning probe microscopy (SPM) imaging technology and a diamond Cube-Corner tip of pyramidal shape with a curvature radius of approximately 100 nm, enabling a load displacement resolution of 50 nN and 0.1 nm, respectively. The charge-discharge cycles for the middle lamella and S_2 were defined as set by Valenzuela *et al.* (2012). The nanomechanical responses were activated on the surface of the *Ulex europaeus* fiber by a gradual increase of the displacement of the indenter tip for 5 s, up to a maximum load of 100 μN. Later, the load remained constant for 60 s, followed by a progressive withdrawal of the tip for 5 s. The remaining indenter stage, at the point of maximum load, was conducted in order to minimize the effect of the fluent deformation on the discharge to obtain a more precise calculation of the elastic modulus of the material (Bhustan and Li 2003).

The hardness and elastic modulus were estimated from the recorded curve of load (P) applied and the penetration depth (h) of the nanoindentation test, as stated by Oliver and Pharr (2004). The hardness (H) of the material studied was obtained by dividing the maximum load (P_{max}) of the indenter by the contact area (A_c) of the tip. The recorded data on the P-h curve also provided the P_{max} values, maximum penetration depth (h_{max}), and slope (S) from the initial section of the unloading curve. An analysis of these factors made it possible to estimate the reduced or effective (E_r) modulus based on the Sneddon ratio (Sneddon 1965), whose data were calculated according to the relationship of the Berkovich indenter (Fischer-Cripps 2006). Hence, the Cube-Corner tip was sharper, with an angle of θ = 35.26° (Fischer-Cripps 2006). The effective elastic modulus, which includes the mechanical behavior of the two materials involved in the displacement during the indentation test, was calculated. The analysis of the results from the data recorded by indentation was performed using R v3.0.1, the free software programming language and environment for statistical computing and graphics (Gentleman and Ihaka 2014).

RESULTS AND DISCUSSION

Chemical Composition

The physicochemical and mechanical properties of the stem are associated with natural factors (Huda *et al.* 2007), which are reflected in the proportion of holocellulose (cellulose and hemicellulose), lignin, and content of extractives (Rowell *et al.* 2005; Komuraiah *et al.* 2014; Moriana *et al.* 2014). In this study, *Ulex europeaus* exhibited component values (Table 3) typical of hardwood specimens **(**Rowell *et al.* 2005**)**. Cellulose was the main component of gorse, accounting for 47.5% of the wood dry weight and showing an interesting fiber yield. On the other hand, the hemicellulose content was about 22.2%, which is normal for deciduous plants. In this sense, it is important to note that the solubility in water-alkalis was about 21.6%, exhibiting highly soluble sugars and other polysaccharides, which can be regarded as indicative of an important soluble hemicellulose content, being much higher than those in average hardwoods, demonstrating a great capacity for the degradation and production of organic alcohols, acid, acetone, gases, and other novel products (Agbor *et al.* 2011). Moreover, the low-mass, soluble components can be a source of problems in the chemical production process of fibers, even affecting the properties of the products, especially in paper. The lignin content was normal, exhibiting a value of about 24.5%. Extractable compounds were 6.7%, which was very high compared with other traditional sources; this can be directly related to the high contribution of components that are involved in the biological metabolism, as energy reservoirs, or in the defense mechanism of *Ulex europaeus* against microbial attacks or other biological enemies (Rowell *et al.* 2005; Koch 2006). Also, the ashes were high, about 1.46%, a value considered normal for stem shrubs (Viana *et al.* 2012).

Table 3. Chemical Composition of Gorse (*Ulex europaeus*) Stem

Main compounds	Dry-wood percentage
Holocellulose	69.7
Cellulose	47.5
Lignin	24.5
Total extractable compounds	6.7
Materials	Dry-wood free from extractable base percentage
Cold water (soluble)	3.0
Boiling water (soluble)	5.4
NaOH (1%)	21.6
Ethanol / Toluene	3.2
Ash	1.46

Wood Characteristics

The morphological characteristics of the gorse stem used in this study are illustrated in Fig. 1, showing a cross-section of well-defined anatomy (Fig. 1a) highlighting a white dendritic network composed of a cluster of conductive elements in earlywood and diagonal to the reticular formation in latewood (Fig. 1b) (Skipper 1922; Gartner 1995; Schweingruber *et al.* 2011). It is also possible to see narrow and diffuse growth rings, with thin rows of flattened fibers, together with vascular tracheids or marginal parenchyma (semi-ring porous). Thin parenchyma spokes in rigid walls of fibers, which may be defined as a simple structure of homocellular procumbent cells in a biseriate system (Schweingruber *et al.* 2011), are shown in Fig. 2.

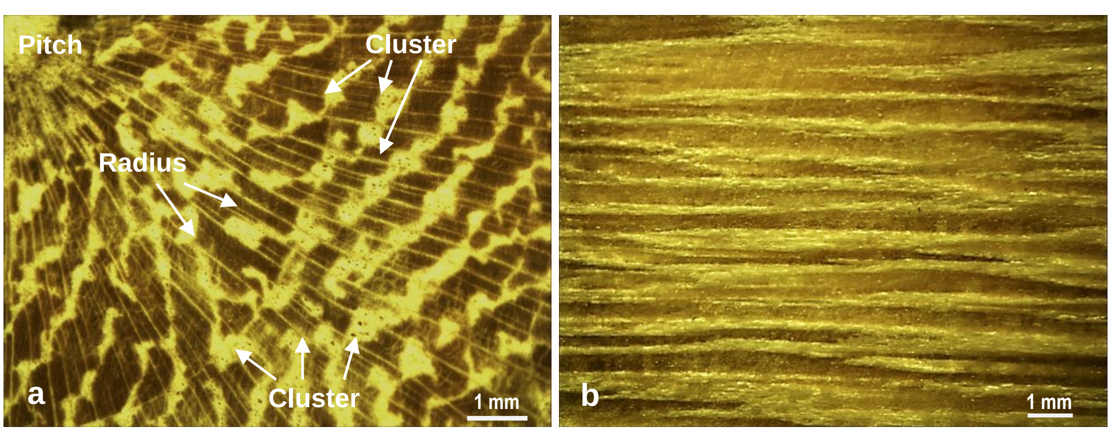

Fig. 1. Optical microscope images of the stem of *Ulex europaeus*. (a) radial cross-section and (b) radial section of overlapping fibers cemented together by pectin

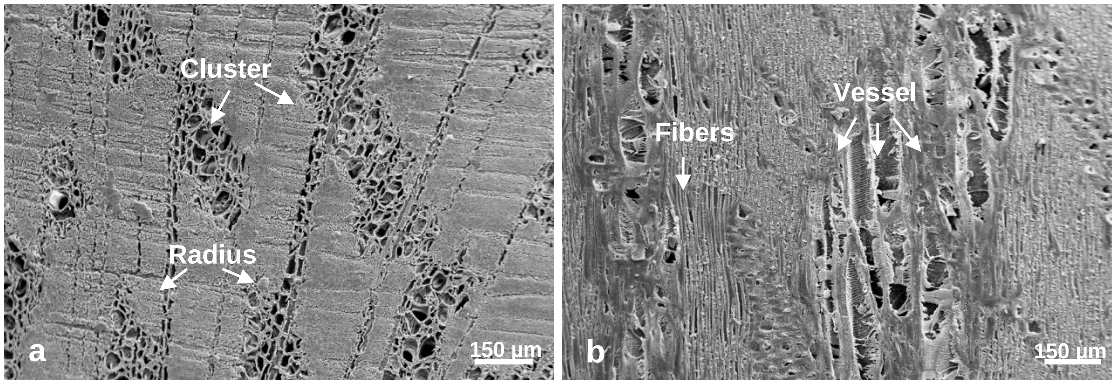

Fig. 2. SEM images of gorse (*Ulex europaeus*) stem. (a) Cross-section, radius, and cluster of conductive elements and (b) radial section, fibers, and conductive elements

Additionally, multiple scalariform foraminate vessels (Figs. 2a and 3b) and well-developed tracheids (uniseriate and opposite) can be observed (Fig. 3a). Indeed, some differences in the characteristics associated with elements in the gorse stem can be attributed to climatic and soil conditions endured by the plant. As can be seen in Fig. 3, the fibers are present in high density between the conductive elements with an average fiber length of 970 ± 100 µm and an average fiber diameter of 13 ± 2 µm.

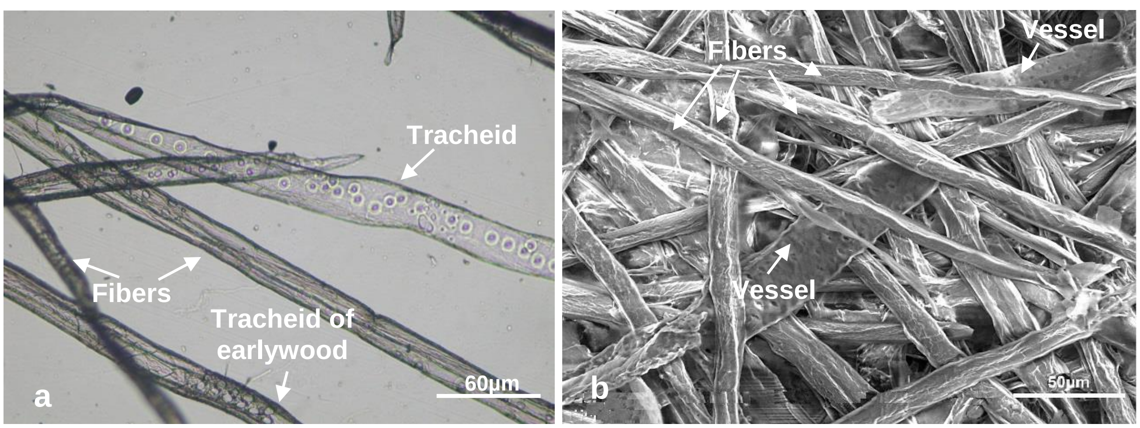

Fig. 3. (a) Optical microscope image of the fibers and tracheids, and (b) SEM image of fibers and vessels.

On the other hand, fibril angles range from 5 to 8°, by direct optical microcopy was observed. These values influence the mechanical properties of the fiber system (Bergander and Salmén 2002).

Physicomechanical Properties

Among the experimentally calculated physical properties, pressed gorse fiber paper exhibited an average density of 0.46 g/cm^3, which is less than the approximate average density of 0.52 g/cm^3 for pressed *Pinus radiata* fiber paper. This can be attributed to the high presence of conductive elements in the low density stem, such as vessels, parenchyma, and young tracheids, which decrease the weight of *Ulex europaeus* fiber paper.

Table 4. Physicomechanical Properties of Gorse and Radiata Pine

Test	*Ulex europaeus*	*Pinus radiata*
Density, g/cm^3	0.46	0.52
Tensile strength, *kg*	1.8	3.9
Tearing resistance in 4 sheets, *kg*	12.4	32.0
Maximum explosion strength in 2 sheets, *MPa*	0.14	0.49

Likewise, the mechanical properties of pressed fiber paper sheets of gorse were much lower than those of the fiber paper made of *Pinus radiata*, reaching a tensile strength of 1.8 kg (Table 4). This is because the length of gorse fiber is about 3 to 4 times shorter than that of *Pinus radiata*. Moreover, there are a significant number of tracheids and vessels in the fiber paper of gorse that influence the final values of its properties (Table 5).

Table 5. Mechanical Properties of Gorse and Radiata Pine Paper Sheets

	Ulex europaeus	*Pinus radiata*
Tensile index, *kNm/kg*	20.9	43.5
Burst index, *mN/kg*	1.2	4.1
Tear index, *Nm^2/kg*	8.6	21.2

The significant weakening of the mechanical properties in the sheets of pressed *Ulex europaeus* fiber was primarily due to: (a) significant amount of non-structural wood elements present in the sheets; (b) less morphogenic maturity of gorse fibers when compared to *Pinus radiata*; and (c) lower length of the fibers of *Ulex europaeus* that causes decreased resistance to breakage and deteriorates the quality of the fiber paper sheets.

Results of Nanoindentation

Figure 4a shows the xylem elements of *Ulex europaeus*, where the fibers submitted to nanoindentation are concentrated. Likewise, Figure 4b shows an image of the fibers scanned with the same indenter tip, where it is possible to see a thick secondary wall (S_2) between a thin primary wall (S_1) and a scarce tertiary wall (S_3) with a small lumen in the center.

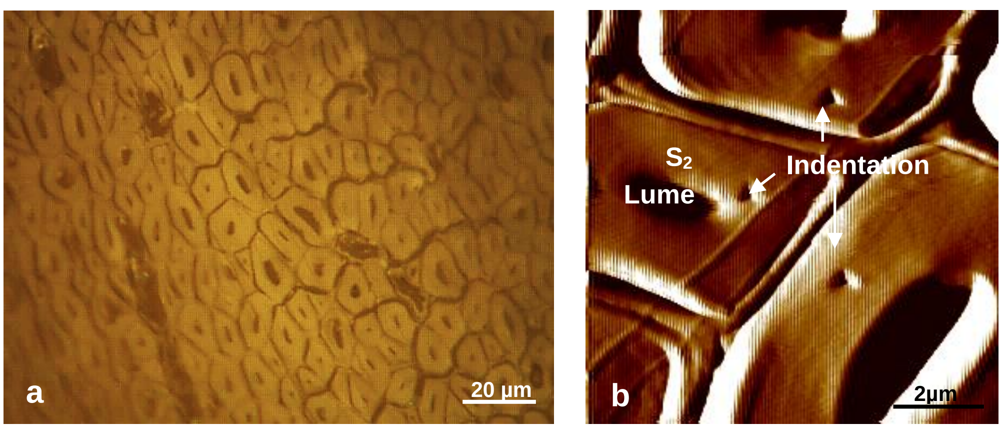

Fig. 4. Cross-sectional images of the stem: (a) overview of all bonded fibers through optical microscopy, and (b) AFM view of indented S_2 lamellas

The image in Fig. 5a shows the group of fibers, fixed by epoxy resin and a surface smoothed using a rotary microtome, in which the process of indentation was performed. The isolated fiber with imprints of the Cube-Corner tip in the secondary wall (S_2) is shown in Fig. 5b.

The verification of the area where the imprints of the indenter were carried out is a very important task for displaying the homogeneity of the mechanical characterization of the fiber, because the longitudinal elastic modulus and the projected area of the imprint are highly dependent on the focus of the microfibril angle (Yu *et al.* 2011). With respect to the mechanical properties, the hardness (H) of *Ulex europaeus* fiber, especially if measured in the S_2 layer, is an important parameter that is also directly related to the resistance to permanent plastic deformation of the materials. Then, the nanoindentation hardness is defined as the maximum load (P_{max}) of the indentation divided by the projected contact area (A_c) of the indenter. The average values of hardness (H) obtained from the stem fibers and fibers in epoxy resin were slightly different, 0.284 GPa and 0.245 GPa, respectively. The standard deviations of the data were 0.079 and 0.112, respectively. It is not surprising that these values may be influenced by the fibrils.

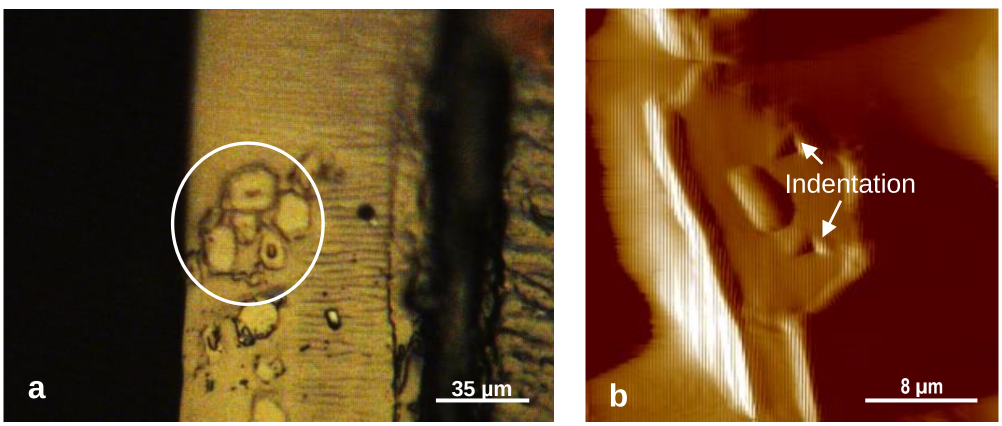

Fig. 5. Cross-sectional images of the fibers of *Ulex europaeus* resin: (a) optical microscopy view of the fiber assembly, and (b) overview of indented S_2 lamellas by AFM.

The evaluation of elasticity required a statistical analysis of normality through the Shapiro-Wilk and Kolmogorov-Smirnov tests, using the data obtained from the *P-h* curves to establish a representative average value for the fiber elasticity (Fig. 6).

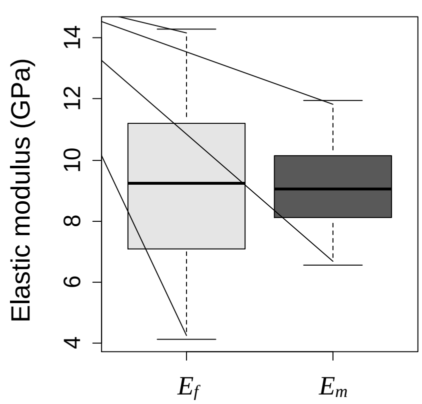

Fig. 6. Tukey diagram of gorse's elasticity. Comparison of data on the elasticity of wood, E_w, and fiber in its dispersed form, E_f

Based on this estimated result, an average value of 9.05 GPa, with a standard deviation of 1.3, was obtained for the measurements of the stem fiber. In contrast, the value for the fiber dispersed in epoxy resin was 9.23 GPa, with a standard deviation of 2.7. From a simple analysis of Fig. 6, it is possible to observe that the average elasticity values present in both the stem and epoxy supports were similar. The stem had more uniform statistics regarding the distribution of the plotted data, while in the other case there was a greater dispersion of the measured values.

CONCLUSIONS

1. Through this experimental study, it was possible to provide more data for the enhancement of *Ulex europaeus* as an interesting renewable source of biomass. Furthermore, the material meets the requirements of a functional system to adapt to a variety of different weather and soil conditions.
2. This perennial Leguminosae shrub has a simple anatomy, with narrow, faint rings of growth, conducting elements, and is a good non-traditional source biofiber, having an average fiber length of 970 ± 100 μm and a diameter of 13 ± 2 μm. This can be defined, from the viewpoint of a composite material, as a short fiber.
3. The fibers of *Ulex europaeus* have poor mechanical properties compared to the fibers of *Pinus radiata*. This can be attributed to the immaturity, fibril angles, and fiber length of gorse, as well as to the conductive elements that contribute negatively to the mechanical strength of the pressed fiber paper sheets.
4. The hardness and elastic modulus values for the fiber in the stem, obtained by nanoindentation from the cells of the intermediate wall, were 0.284 GPa and 0.245 GPa, respectively; however, the values for the isolated fiber were 9.23 GPa and 9.05 GPa, respectively. The mean values were similar, but showed a greater dispersion of statistical data in the case of isolated fibers, which can be caused by the conditions in sample preparation. The process for obtaining the fibers, *i.e*. hot soda, did not affect the nanomechanical properties of the middle lamella of the fiber, as observed in the hardness and elastic modulus values of the two measurement methods tested: stem and fixed in resin.

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