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Effects of Extraction Methods on the Morphology and Physico-Chemical Properties of Spanish Broom (*Spartium junceum* L.) Fibres

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Abstract

Spanish Broom fibers are very interesting natural material for textile and technical applications. Spanish Broom elementary fibers are arranged in bundles and bound by lignin and pectins. Any industrial utilisation of Spanish Broom requires the separation of the fibers from the woody core of the branches (known as vermenes), which is achieved by different methods: mechanical, chemical and biological. In this work, two different extraction methods (mechanical and physico-chemical) for obtaining Spanish Broom fibers were compared. The chemical and physical properties of Spanish Broom fibers are reported. Fibers extracted by the physico-chemical method showed a content of lignin and pentosans lower than those extracted mechanically. Both the mechanically and physico-chemically extracted fibers were observed by scanning electron microscopy (SEM), and the tensile properties of the fibres extracted are discussed. Spanish Broom fibers extracted by the physico-chemical method have better tensile properties than fibers extracted mechanically.

Key words: *cellulose, spanish broom fibres, fibre extraction, biomaterials.*

Introduction

In recent years, several studies of natural fibres such as flax [1, 2], hemp, sisal [3, 4] and jute [5, 6] as reinforcement for composite materials have been carried out. Natural fibres present important advantages, such as low density, appropriate stiffness and mechanical properties, as well as high disposability and renewability [7, 8]. Moreover, they are recyclable and biodegradable [9].

In addition to these traditional fibres, Spanish Broom (*Spartium junceum* L.), a dicotyledonous perennial shrub, is an important fibre with numerous advantages: it is flexible, abundantly available and biodegradable. With these advantages in mind, we explored the potential of Spanish Broom fibres for various applications (textile, paper, and composite materials). Interest in this species has been recently extended to technical applications as reinforcements in the automobile industry [10].

Spartium junceum L. is a small shrub found in Mediterranean countries [11]. In Italy it grows spontaneously and is very widespread. It is even more abundant in central and southern Italy, where it is a typical part of the landscape. This plant usually grows at the sides of country roads in areas exposed to sunlight [12, 13]. Traditional applications of Spanish Broom fibres include textiles and cordage. As a matter of fact, the name Spartium is from the Greek word sparton meaning “broom”, alluding to brooms which used to be made of the esparto grass plant (ref. genus Spartium) [14].

Cortical fibres of Spanish Broom are multiple elementary fibres (ultimates) arranged in bundles. The elementary fibres are obtained through partial removal of the binding materials (lignin and pectins) that hold the single cells together by different methods, such as mechanical, chemical and biological. Each method has its own advantages and drawbacks, which influence the amount and quality of fibre obtained. Fibre quality is influenced by the presence of vegetable waste on the surface, as well as by the fibre length and properties. The mechanical method is the one most typically employed. Nevertheless, its efficiency in removing vegetable components from the surface of the fibre bundle is poor. Instead, chemical procedures allow to obtain a higher amount of fibre bundle than the mechanical methods. In the present study, the influence of the mechanical and physico-chemical fibre extraction methods on chemical composition, morphology and tensile properties was investigated.

Materials and methods

Materials

Spanish Broom was obtained from a research field at Calabria University, Arcavacata di Rende (CS), Italy. The Spanish Broom was used without any pretreatment or purification.

Fibre extraction

The physico-chemical process

Spanish Broom fibres were extracted by the physico-chemical process reported in the World Patent “Physical chemical process for production of vegetable fibres” [15], in which Spanish Broom fibre branches were chemically treated using 15% sodium hydroxide solution at 100 °C for 15 min. The fibres extracted were washed with distilled water until a state of neutrality was achieved, and then the fibres were put in an autoclave for compression in air for 3 h at 120 °C and a pressure of 10 atmospheres, followed by rapid decompression of the system [16]. Finally, the fibres were brushed to make them suitable for chemical and morphological analysis. Before testing, the fibres were dried at 105 ± 5 °C for 24 h.

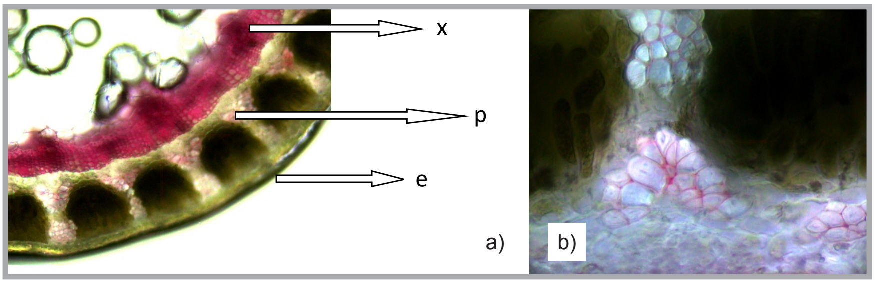

Figure 1. Cross-section of Spanish Broom vermenes (a); e - epidermis; p - phloem; x - xylem. Cross section of Spanish Broom bundles (b).

Table 1. Chemical composition (in%) of Spanish Broom fibres obtained by mechanical and physico-chemical processes.

Kind of fibre	Cellulose, %	Pentosans, %	Lignin, %	Pectins, %	Ash, %	WAXS, %
Vermenes	44.5 ± 0.2	16.3 ± 0.1	18.5 ± 0.3	13.3 ± 0.1	4.0 ± 0.2	3.4 ± 0.1
Mechanical process	66.9 ± 0.1	7.2 ± 0.3	11.7 ± 0.2	12.0 ± 0.2	1.0 ± 0.1	1.2 ± 0.1
Physico-chemical process	91.7 ± 0.1	4.1 ± 0.3	3.2 ± 0.4	0.0 ± 0.0	1.0 ± 0.2	0.0 ± 0.0

The mechanical process

Spanish Broom fibres were mechanically extracted from the branches. All samples were passed through the machine two or three times until no green components were seen on the cortical surface of the bundle. After that, the fibres were hand brushed to make them suitable for chemical and morphological analysis.

Fibre composition

The pectin content was determined by the colorimetric method using a carbazole reagent [17], in which 0.5 g of Spanish broom fibres were treated with a 0.05 N sodium hydroxide solution for 30 minutes at 25 °C, and then sulphuric acid was added. After cooling, carbazole was added, and after 25 min. the absorbance at 520 nm was read. The concentrations of pectins were calculated using galacturonic acid as standard. The pentosan content was determined according to TAPPI T 223 hm 84 (1984) [18]. They are transformed by boiling 3.85 N hydrochloric acid to furfural, which is collected in the distillate and determined colorimetrically with a orcinol-ferricchloride reagent. The lignin content was determined according to TAPPI T222 om-02 (2002) [19]. In this method of determination, lignin (also known as "Klason lignin") is defined as constituent fibres insoluble in 72% sulphuric acid. The content of cellulose was determined with an anthrone reagent [20, 21], in which fibres were boiled (at 100 °C) with a mixture of nitric/acetic acid (1:8, v/v) for 1 h to remove the lignin and hemicelluloses. After centrifugation, the fibres were treated with 67% sulphuric acid. The amount of cellulose was then determined spectrophotometrically (Spectrophotometer: UV/VIS, Jasco, Milan, Italy) at 620 nm using cold anthrone.

Morphological structure

A LEO 420 scanning electron microscope (SEM) was used to observe the morphological features of untreated Spanish Broom and the fibres obtained. The specimens to be observed were mounted on conductive adhesive tape, sputter coated with gold-palladium and analysed.

FT-IR spectroscopy

FTIR spectra were obtained with a Bio-rad spectrophotometer using KBr disks. All spectra were registered from 4000 to 400 cm^{-1}, with a resolution of 4 cm^{-1} and 32 scans.

Physical structure

The physical structure of the fibres in terms of the percentage of crystallinity was determined with a Philips PW 3710 diffractometer using Cu-K$_\alpha$ radiation.

Tensile properties

The tensile properties of the fibres in terms of the tenacity and percentage of breaking elongation were determined, according to UNI EN ISO 5079, at room temperature (20 °C) and 65% relative humidity using an Instron 6021/5500 tensile testing machine. About 100 fibres were tested, and the average and standard deviations are reported.

Results and discussion

Fibre extraction

Figure 1.a shows an optical micrograph of a transversal section of a Spanish Broom branch, on which we can observe, from the outside to the inside of the branch, the epidermis, the phloem (cellulosic cells) and the xylem (lignified cells). As seen from ***Figure 1.b***, Spanish Broom fibres are arranged in bundles of single cells called "ultimates" or "elementary fibre", which are bound together by non-cellulosic substances (lignin,

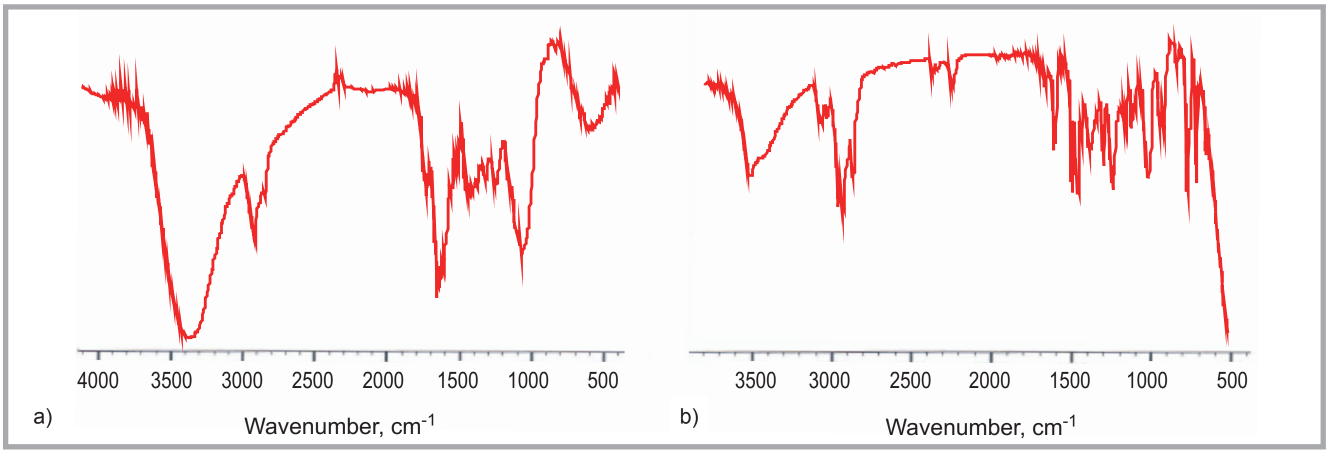

Figure 2. *FTIR spectra of Spanish Broom obtained by the mechanical (a) and physico-chemical processes (b); [26, 27].*

Table 2. Cristallinity of Broom fibres after the physico-chemical and mechanical processes.

Sample	Cristallinity, %
Broom fibres after physico-chemical process	69
Broom fibres after mechanical process	55

Table 3. Tensile properties of Spanish Broom obtained by the mechanical and physico-chemical processes.

Properties	Tenacity, cN/tex	Strain at break, %
Mechanical process	32.6 ± 1.8	4.2 ± 1.3
Physico-chemical process	35.9 ± 1.6	5.8 ± 1.7

hemicellulose and pectic substances) [14, 22, 23]. Any industrial utilisation of Spanish Broom requires the separation of fibres from the rest of the vermenes. Traditionally, mechanical methods have been employed to obtain fibre from Spanish Broom. These methods are quick, but they affect fibre quality (including the length and stiffness),which is generally an important property for the textile and yarn industry [24]. For this reason we suggest the physico-chemical process as an alternative method to obtain softer fibres of high quality. In addition, this process is fast, and the conditions can be easily controlled.

Fibre composition

The chemical composition of fibres extracted by different methods is reported in ***Table 1***. Both extraction methods reduced the content of non-cellulosic substances (lignin, pentosans, pectins and waxs), suggesting that the part of these substances which makes fibres stiff has been removed. Of the two different methods, the physico-chemical method appeared the most effective. In fact, this method deprotonated pectins, partially depolymerised lignin, and the cellulose content is higher than that obtained by the mechanical method.

FTIR spectroscopy

According to the chemical analysis, FT-IR spectra highlighted significative differences between the mechanical and physico-chemical processes with respect to fibre composition.

Vibrations at 1734 cm^{-1} in relation to free COOH groups of polygalacturonic acid and those at 1410 and 1615 cm^{-1} in relation to the ionised carboxyl groups [25] that are present in pectins can be observed in the spectra of Spanish Broom extracted mechanically. Vibrations of the aromatic skeleton of lignin at 1600, 1500 and 820-850 cm^{-1} are also present (***Figure 2.a***) [26, 27].

Variations in the spectra of fibre physico-chemically extracted were observed. Pectin vibrations at 1734 cm^{-1} disappeared, indicating that the pectin had been completely removed, and a reduction in the intensity band with respect to lignin and hemicellulose was observed (***Figure 2.b***)

Morphological structure

Scanning electron microscopy (SEM) showed the influence of the two different extraction methods on fibre morphology. ***Figures 3 - 4*** show SEM micrographs of fibre bundles obtained by the mechanical and physico-chemical methods. Like all other lignocellulosic sources, Spanish Broom bundles obtained by a mechanical procedure have a thick layer of deposits on the surface mostly composed of lignin, pectins and hemicellulose, which protect cellulose fibres inside (***Figure 3***). Physico-chemical treatment removes most of the surface material, resulting in fibres that have a relatively clean and smooth surface (***Figure 4.a - 4.b***).

Physical structure

The physical structure of Spanish Broom fibres in terms of the percentage of cristallinity is reported in ***Table 2***, and ***Figure 5*** shows a diffractogram of Spanish Broom fibres, in which one can observe that Spanish Broom fibres extracted by the physico-chemical or mechanical process have a very similar diffraction pattern; however, the cristallinity of the fibres increased with the physico-chemical treatment. This is understandable as the cellulose content increased, whereas the amorphous hemicellulose content decreased with the physico-chemical process [28, 29]. This is in agreement with the FTIR and chemical analyses.

Tensile properties

The mechanical properties of Spanish Broom fibres extracted by the two different methods are reported in ***Table 3***. The strain at break and tenacity of physico-chemically extracted fibres were higher than those of mechanically extracted fibres. These data indicate that products made from physico-chemically extracted fibres are more flexible and softer to the

Figure 3. *SEM micrograph of a fibre bundle obtained by the mechanical process.*

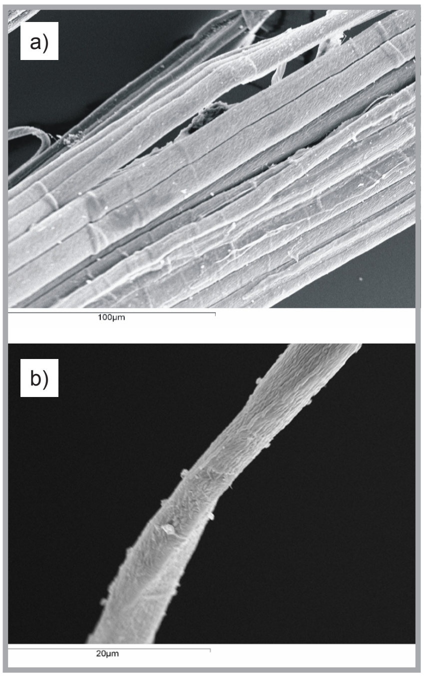

Figure 4. *SEM micrograph of a fibre bundle (A) and elementary fibre (B) obtained by the physico-chemical process.*

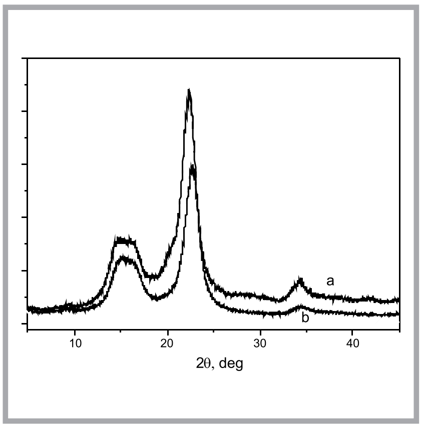

Figure 5. *X-ray diffractogram of (a) broom fibres after the physico- chemical process and (b) the mechanical process.*

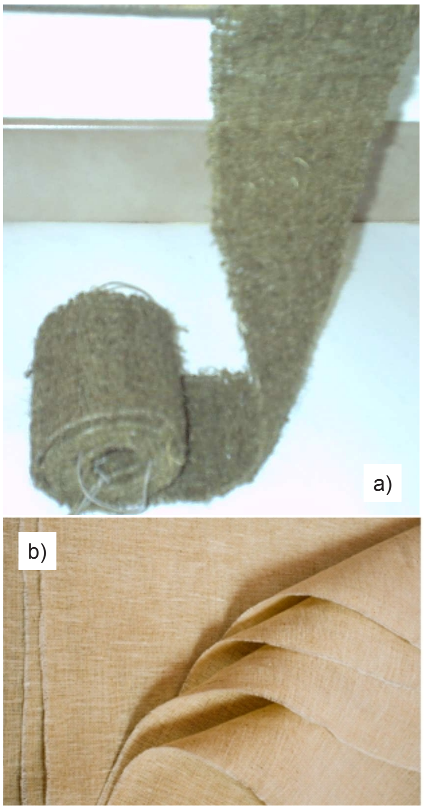

Figure 6. *Spanish Broom fabrics made from mechanically extracted fibres (a) and from physico-chemically extracted fibres (b).*

touch than products from mechanically extracted fibres, as shown in ***Figure 6***.

Conclusion

In this study, two different extraction methods were employed to obtain fibre from Spanish Broom branches. The physico-chemical process used in this study produces significant differences in the chemical composition of the fibre: pectins are depronated, and lignin is partially depolymerised. On the other hand, by mechanical extraction, fibres are embedded in a matrix mainly composed of pentosans, pectins and lignin, as confirmed by the chemical and morphological analyses. This fact has to be taken into account when we choose to use Spanish Broom in industrial applications (textile, composite manufacturing).

In conclusion, comparing the two different extraction methods, it can be seen that the physico-chemical treatment completely removes non-cellulose substances from the fibre surface, thus improving the tensile properties.

Acknowledgments

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