Conference Paper

Characterization of Cellulose Microfibrils Obtained from Hemp

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Received 4 July 2013; Accepted 2 October 2013

Academic Editors: R. Alagirusamy, R. Figueiro, H. Hong, and A. T. Marques

This Conference Paper is based on a presentation given by Anna Šutka at “International Conference on Natural Fibers—Sustainable Materials for Advanced Applications 2013” held from 9 June 2013 to 11 June 2013 in Guimarães, Portugal.

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Microfibrillated cellulose was extracted from hemp fibres using steam explosion pretreatment and high-intensity ultrasonic treatment (HIUS). The acquired results after steam explosion treatment and water and alkali treatments are discussed and interpreted by Fourier transform infrared spectroscopy (FTIR). Scanning electron microscopy (SEM) was used to examine the microstructure of hemp fibres before and after each treatment. A fibre size analyser was used to analyse the dimensions of the untreated and treated cellulose fibrils. SEM observations show that the sizes of the different treated fibrils have a diameter range of several micrometres, but after HIUS treatment fibres are separate from microfibrils, nanofibres, and their agglomerates.

1. Introduction

Hemp fibres have high strength, low density, and high sustainability; therefore they are used as reinforcement in composite materials. This usefulness of cellulose fibrils is because small fibrils have better mechanical properties than the individual macrofibres. Within their structure, small fibrils include more cellulose crystals, having a higher elastic modulus than fibres, which contribute to their increased strengths [1]. Microfibrillated cellulose (MFC) is cellulose fibril aggregates obtained through disintegration of the cell wall in cellulose fibres [2]. The diameter of MFC fibrils is usually at the range of 10–100 nm and can be up to several micrometres in length, depending on the preparation methods and material source [3].

This paper compares the preparation of cellulose micro- and nanofibers obtained from hemp bast fibres and shives using steam explosion and high-intensity ultrasonication treatments.

The steam explosion (SE) autohydrolysis is currently comprehensively studied as a promising green pretreatment technology [4, 5] to obtain microfibrils of cellulose and also to remove noncelluloses constituents—lignin, hemicelluloses, pectins, and waxes.

The high-intensity ultrasonication technique is an environmentally benign method and a simplified process that conducts fibre isolation and chemical modification simultaneously and helps significantly reduce the production cost of cellulose nanofibre and its composites [3]. HIUS creates cavitation and high vibrational energy in the suspension, resulting in the separation of hemp cellulose micro- and nanofibre bundles and agglomerates [6]. In the present work SE and HIUS will be combined to obtain MFC fibrils.

2. Materials and Methods

Dew-retted hemp fibres of local variety “Purini” and shives of local variety “Bialobrzieskie” grown on the experimental fields of the Latgalian Agriculture Research Center LLZC (Latvia, district Vilani) and sodium hydroxide (NaOH) (Commercial grade) are used in this research. Hemp fibres were prepared by cutting into uniform size of approximately 1–2 mm length, whereas shives were prepared by milling into uniform size of approximately 1–2 mm length. This size of fibers and shives allows steam explosion process and ultrasound treatment taking place in the chemical and physical processes to

FIGURE 1: Untreated and steam-exploded hemp fibers.

FIGURE 2: Ultrasonic-treated hemp fibers after steam explosion (F SE WA US).

penetrate deeper into the fibers in the inner layers. The samples variants under investigation are shown in Table 1.

2.1. Steam Explosion Treatment. Steam explosion treatment (SE) conditions are shown in Table 2. After SE treatment hydrothermal and alkali treatment follows that allows partial removal of constituents from hemp fibres including hemicelluloses, pectins/waxes, lignin, and oils covering the external surface of the fibres cell wall.

Severity parameter or the reaction ordinate R_0 can be expressed as

$$R_0 = t * \exp \left[\frac{(T - 100)}{14.75} \right], \quad (1)$$

where duration of the value of treatment time (t , minutes) and temperature (T , °C) express the SE severity against the base temperature T_{base} or reference = 100°C [7].

2.2. High-Intensity Ultrasonication Technique (HIUS). The fibres were suspended in distilled water and treated with ultrasound (ultrasonic processor UP 200 Hp, 200 W, frequency 26 kHz, amplitude 90%, sonotrode S26d14, Ø14 mm) (HIUS) for 45 min. HIUS produces very strong mechanical oscillating power, so cellulose fibrils can be isolated from cellulose fibres by the action of hydrodynamic forces of ultrasound [8]. In order to control the process temperature, the beaker with the cellulose fibres in water was put in a water bath with controlled temperature. The fibres and shives suspensions were filtered and dried at room temperature, while there is no change in mass.

TABLE 1: Sample variants under investigation.

Sample	SE	Water extraction	0.4% NaOH extraction	HIUS
F (fibers)	–	–	–	–
F SE WA	+	+	+	–
F SE WA US	+	+	+	+
S (shives)	–	–	–	–
S SE WA	+	+	+	–
S SE WA US	+	+	+	+

TABLE 2: Steam explosion treatment parameters.

Variants	Temperature °C	SE parameters			$\log R_0$
		Pressure bar	Time min		
Fibres (“Purini”)	235	32	3		3.97
Shives (“Białobrzskie”)	235	32	3		3.97

2.3. Fourier Infrared Spectroscopy (FTIR). Fourier transform infrared (FTIR) spectra of the samples under investigation were recorded in KBr pellets by Spectrum One (Perkin Elmer, UK) FTIR spectrometer in the range of 4000–400 cm^{-1} (resolution: 4 cm^{-1}). About 2 mg of sample was crushed into powder. The fibre or shive particles were then mixed with KBr and pressed into a disc about 1 mm thick.

FIGURE 3: Untreated, steam-exploded, and ultrasonic-treated hemp.

FIGURE 4: Size distribution of steam-exploded and ultrasonic-treated hemp fibers and shives diameter.

2.4. Scanning Electron Microscopy (SEM). SEM micrographs of fibres surface were taken using a scanning electron microscope VEGA Tescan 5136M (Czech Republic—UK). Prior to SEM evaluation, the samples were coated with gold by means of a plasma sputtering apparatus.

2.5. Static Image Analysis. CorelDRAW Graphics Suite X6 software was used to measure the diameters of fibres and shives from two dimensional images obtained from SEM micrographs.

3. Results and Conclusions

This study shows that there are substantial differences on the isolation of hemp microfibrils after various treatments (alkali treatment, steam explosion, and ultrasonic treatment),

TABLE 3: Diameters of fibers and shives particles after SE and HIUS treatments.

Diameter nm	Fibers (F SE WA US)	Shives (S SE WA US)
Average	125.2	24.0
Max	777.8	60.0
Min	24.4	8.9

surface morphology, physical properties, and chemical composition of microfibrils.

The cellulose microfibrils made by steam explosion and HIUS treatment were light and dark brown depending on treatment conditions and severity parameter, still indicating the presence of residual organic substrates, including a small amount of lignin.

SEM is used to characterize properties of hemp fibers and shives such as fiber diameter, diameter distribution, fiber orientation, and morphology. Figures 1, 2, and 3 show SEM micrographs of untreated, steam-exploded, and ultrasonic treated hemp fibres. From micrographs we can see differences of surface morphologies and fibril sizes. SEM showing the presence of the individual cellulose micro- and nanofibres obtained from hemp on steam explosion together with ultrasonication is used. Rest of the samples did not show formation of MFC fibrils which could be explained by insufficient and uneven capacity of steam explosion treatment to form fibrils.

Shorter and finer fibrils were observed from the micrographs of shive S SE WA US sample (Figure 3), a combination of SE and HIUS treatments; however, fibrils were not individual but agglomerate during the sample drying process affected by the strong intermolecular hydrogen bonding [3].

Size distributions of the diameter of nanofibres obtained from shives (S SE WA US) and fibers (F SE WA US) by image analysis are compared in Figure 4. From these results, hemp fibers were found to have diameters ranging from 20 to 700 nm with average value ~ 125 nm, whereas shives range from 9 to 60 nm with average value 24 (Table 3). From Figure 4 we can see that nanofibres obtained from shives have more uniform distribution of diameters than nanofibres obtain from bast fibers.

FIGURE 5: FTIR spectra of untreated, steam-exploded, and HIUS-treated hemp fibres (F) and shives (S).

Infrared Fourier spectroscopy allows revealing modifications of main structures; noncellulose compounds through identification of carboxylic acids and esters found in pectin, lignin, and waxes were found in cellulose microfibrils [9]. The hemp fibres showed characteristic peaks at 1737 cm^{-1} (unconjugated C=O in hemicellulose) and 1638 cm^{-1} (absorbed O-H or carbonyl band) (Figure 5(a)). IR bands of hemp shives are found at 1738 cm^{-1} (unconjugated C=O in hemicellulose), 1635 cm^{-1} (absorbed O-H or carbonyl band), 1508 cm^{-1} (aromatic rings of lignin), and 1251 cm^{-1} (acetylated hemicellulose) (Figure 5(b)) [10, 11]. After SE, water and alkali extraction corresponding peaks are decreasing. HIUS treatment improves the extraction of lignin as evidenced by the disappearance of peak at 1508 cm^{-1} .

4. Conclusions

Hemp cellulose microfibrils are individualized from bast fibres and shives using steam explosion, hydrothermal and alkali treatment and high-intensity ultrasonication. Results of this study have shown that SE treatment combined with following hydrothermal and 0.4 wt.% NaOH treatment allows partial removal of constituents from hemp fibres. SEM observations show that the sizes of the different treated fibrils have a diameter range of several micrometres. It can be seen that after HIUS treatment fibres are separate from microfibrils, nanofibres, and their agglomerates. FTIR analysis showed differences between the spectra for the untreated, steam-exploded, and ultrasound-treated hemp fibres and shives. Further work should be performed in order to avoid agglomeration of microfibrils due to and after ultrasonic treatment for further nanotechnological processing.

Acknowledgment

This work has been supported by the European Social Fund within the project “support for the implementation of doctoral studies at Riga Technical University.”

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