INFLUENCE OF NON-THERMAL MICROWAVE EFFECTS ON HEMP FIBER OBTANED BY MICROWAVE ASSISTED DEGUMMING

MINGWEI TIAN,[*,**,***] LIJUN QU,[*,**,***] SHIFENG ZHU[*,**] and GUANGTING HAN[**]

[*]*Research Center for Intelligent and Wearable Technology, College of Textiles and Clothing, Qingdao University, Qingdao, Shandong 266071, P.R. China*
[**]*State Key Laboratory of Bio-Fibers and Eco-Textiles, Qingdao University, Qingdao, Shandong 266071, P.R. China*
[***]*Collaborative Innovation Center for Eco-Textiles of Shandong Province, Qingdao University, Qingdao, Shandong 266071, P.R. China*
✉ *Corresponding authors: Lijun Qu, lijunqu@126.com*
Mingwei Tian, tmw0303@126.com

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Microwave-assisted heating degumming was successfully employed in hemp fiber extraction. This route was selected owing to the fact that it is a fast, green, high-efficiency and low-cost method. The mechanism of action was investigated and the results were compared with those obtained by the traditional water-heating method. The fibers treated by the two procedures were examined by X-ray photoelectron spectroscopy (XPS). Specifically, their C 1s spectra and the corresponding carbon and oxygen atomic concentration ratios (O/C) were analyzed. The results indicated that the O/C ratio gradually increases from 0.35 for untreated hemp to 0.49 for the microwave treated fiber, indicating that the lignin, which is mainly composed of the carbon component, was to a great extent removed from the fiber surface. It was concluded that the non-thermal effects of microwave radiation could accelerate the degumming process and its efficiency, as well as modify the surface composition and the structure of hemp fiber, compared with the conventional waterbath heating method.

Keywords: microstructure, oxidation, polymers, XPS, thermal properties

INTRODUCTION

Hemp fiber is considered to be one of the most inexpensive and readily available bast natural fibers, which has attracted research interest to its extraction, properties and application. Hemp fiber mainly consists of cellulose, hemicellulose and lignin, of which cellulose and hemicellulose are polysaccharides, while lignin is composed of complex polymers containing aromatic groups.[1] The extraction or the degumming process of hemp fiber from its raw bast lies at the basis of its further applications, thus, the chemical,[2] mechanical[3] and bio-enzymatic[4] routes have already been widely employed in hemp fiber extraction. Among these methods, waterbath heating is commonly applied to enhance the degumming reaction. Wang *et al.*[5] recommended a novel and effective heating method – microwave-assisted heating – to enhance the degumming of hemp fiber. Unlike conventional heating procedures by conduction and convection, microwaves heat the solution by radiation. The advantage of using microwaves consists in the fact that they are able to effectively penetrate into the solution and, therefore, can be absorbed uniformly by the solution, providing rapid and energy-efficient

heating along the degumming treatment.[6] The claimed effects of microwave irradiation include thermal and non-thermal ones. However, the existence of non-thermal effects is not well evidenced based on the chemical composition of the resulting hemp fibers. Herein, we treated hemp by an approach based on alkali-H_2O_2 bath assisted degumming, proposed by our research team.[2] During the extraction, two different heating modes, the traditional waterbath heating and the microwave assisted heating, were used as auxiliary procedures at the same temperature. Furthermore, the as-obtained fibers were characterized by XPS and the discrepancy between the samples was investigated.

EXPERIMENTAL

The original hemp bast used in our work was cultivated in Shandong, China. The diameter of the hemp bast bundles was around 100-200 μm. Two different auxiliary heating methods, the traditional waterbath heating and the microwave assisted heating, were employed to degum the hemp bast. A series of experiments were carried out to determine the final optimum conditions as follow: 1) waterbath assisted route: NaOH solution (5 g/L), $MgSO_4 \cdot 7H_2O$ solution (0.1 g/L), H_2O_2 solution (4 g/L), ATMP (Amino Trimethylene Phosphonic Acid) and magnesium chloride ($MgCl_2$) as H_2O_2 stabilizer (1.2 g/L), temperature: 99 °C, liquor ratio: 1:15, electronic thermostatic waterbath (LECHEN H-2, 800W, P.R. China) heated for 150 min; 2) microwave assisted route: NaOH solution (5 g/L), $MgSO_4 \cdot 7H_2O$ solution (0.1 g/L), H_2O_2 solution (4 g/L), H_2O_2 stabilizer ($MgCl_2$) (1.2 g/L), temperature: 99 °C, liquor ratio: 1:15, microwave reactor (Apex, EU Microwave Chemistry Technology, Shanghai, China) operated for 50 min at a power of 600 W. Other parameters were described in detail in our previous work.[2] In short, all the raw materials underwent acid pretreatment under the following conditions: H_2SO_4 solution (1 mL/L), temperature 50 °C, liquor ratio 1:15, waterbath heating for 60 min. The quantity of fibers was fixed to 10 g, and five replications of the experiments were performed. All the experiments were carried out according to ASTM E1755-01.

The as-obtained fibers were labeled as “waterbath treated fiber” and “microwave treated fiber” by reference to the two different extraction procedures. Then, in order to investigate the surface elemental concentrations and the O/C ratios of both the hemp bast and the two types of resultant fibers, X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos AXIS His spectrometer, with a monochromatized AI KR X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms and a pass energy of 40 eV. The anode voltage and current were set to 15 kV and 10 mA, respectively. For peak synthesis, a Shirley type background was utilized.

RESULTS AND DISCUSSION

Figure 1 illustrates three typical survey spectra corresponding to untreated hemp, waterbath treated fiber and microwave treated fiber. Two characteristic peaks (O 1s and C 1s) appear at 530-535 eV and 284-290 eV, respectively, indicating that the main components of the samples are carbon and oxygen.

Furthermore, the high resolution C 1s spectra of the untreated hemp, waterbath treated fiber and microwave treated one are presented in Figure 2. The XPS analysis of hemp fiber reveals three C1 peaks at 285.0, 286.2 and 287.7 eV, which can be assigned to C-C, C-O and C=O, respectively. The C-C peak at 285.0 eV originates from impurities, such as lignin, extractive substances and fatty acids.

Also, it may be remarked that this peak gradually attenuates in intensity, while the intensity of the C-O peak enhances until it becomes the highest one in the spectrum of the microwave treated fiber. This result demonstrates that the microwave assisted extraction procedure was more effective in degumming the hemp bast.

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Table 1 lists the fitted results obtained for the O/C ratio and binding energy for each of the samples. It can be observed that the O/C ratio gradually increases from 0.35 to 0.49, indicating that the lignin, which is mainly composed of the carbon component, is to a great extent removed from the fiber surface. Furthermore, the intensity

of the C-C peak declines, while those of the other two peaks, corresponding to oxygen containing groups, increase simultaneously. The trend of the characteristic peaks is in agreement with the results obtained for the O/C ratio.

Considering the results obtained for the fibers extracted by the two procedures, it may be remarked that, compared with the fiber obtained by the waterbath treatment, that subjected to the microwave assisted degumming presents higher intensity peaks corresponding to C-O and C=O, indicating an efficient degumming process. Both heating procedures were carried out at the same temperature – of 99 °C, in other words, their thermal effects were the same and the samples could absorb heat from both waterbath and microwave radiation treatments. However, the different chemical composition of the resulting fiber might be an indication of the non-thermal effects of microwave radiation.

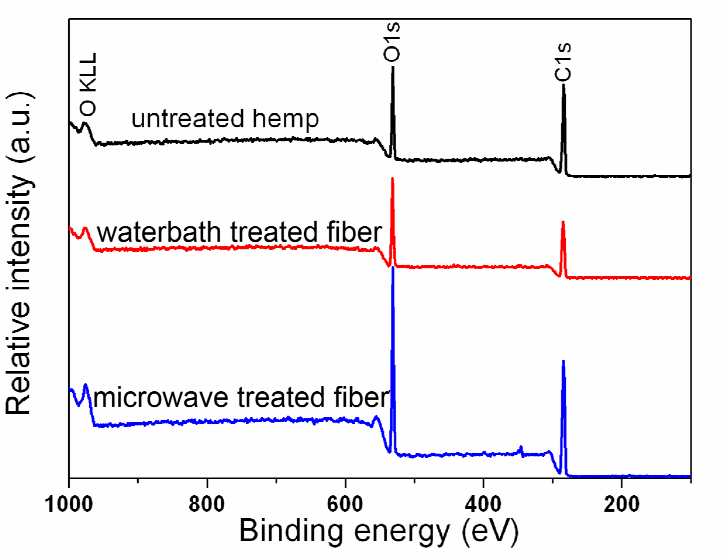
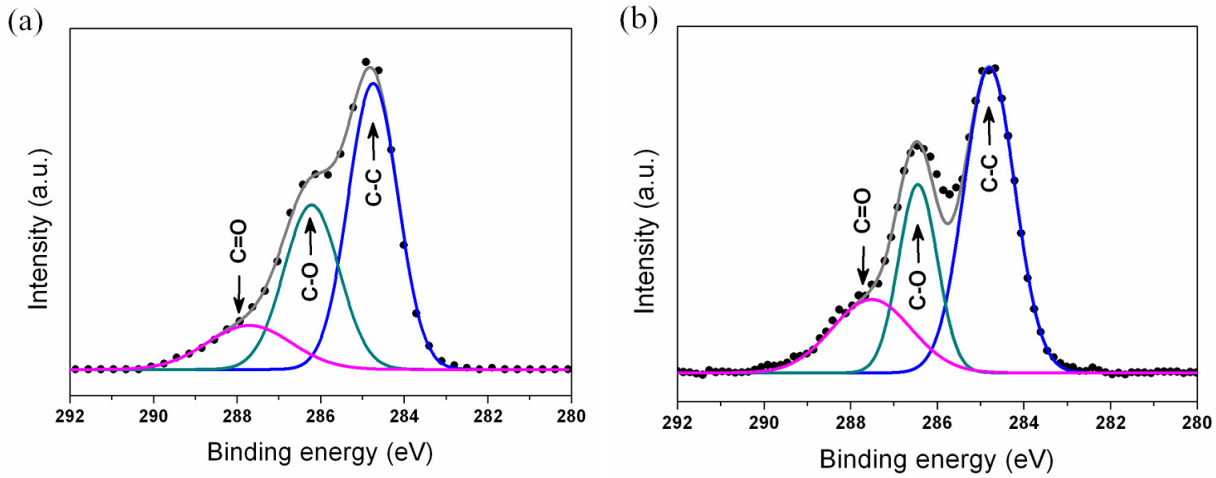


Figure 1: X-ray photoelectron spectroscopy (XPS) of hemp samples



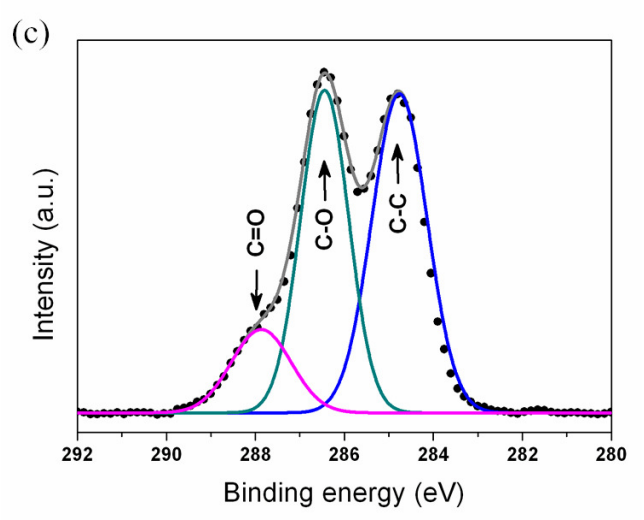


Figure 2: High resolution C 1s spectra, with component fitted carbon region, for (a) untreated hemp, (b) waterbath treated fiber and (c) microwave treated fiber

Table 1
XPS analysis of samples

Material	O/C ratio	Binding energy (eV)		
		C-C (285.0)	C-O (286.2)	C=O (287.7)
Untreated hemp	0.35	57.8	34.8	7.4
Waterbath treated fiber	0.41	53.0	35.3	11.7
Microwave treated fiber	0.49	46.3	40.6	13.1

CONCLUSION

In the present short communication, we report on a novel procedure of microwave-assisted heating degumming of hemp bast for the purpose of fiber extraction. We have analyzed untreated hemp bast, waterbath treated fiber and microwave treated fiber by XPS characterization. The results indicated that all the samples mainly contained carbon and oxygen, but the O/C ratio increased upon the treatments. Thus, the minimum one was recorded for the untreated hemp, while the maximum was reached for the microwave radiation treated fiber. These findings indicate that the microwave assisted procedure can improve the efficiency of the degumming process, due to the non-thermal effects of microwave raditation.

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