International Journal of Biological Macromolecules 83 (2016) 117–125

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: www.elsevier.com/locate/ijbiomac

Molecular association of adsorbed water with lignocellulosic materials examined by micro-FTIR spectroscopy

Xin Guo[a], Yan Qing[a], Yiqiang Wu[a,*], Qinglin Wu[a,b,*]

[a] College of Material Science and Engineering, Central South University of Forestry & Technology, Changsha, 410004, China
[b] School of Renewable Natural Resources, Louisiana State University AgCenter, Baton Rouge, Louisiana, 70803, United States

ARTICLE INFO

Article history:
Received 24 September 2015
Received in revised form 8 November 2015
Accepted 16 November 2015
Available online 21 November 2015

Keywords:
Hydrogen-bonding
Hydrophilic groups
Moisture adsorption

ABSTRACT

For lignocellulosic materials, water adsorption is extremely important for its product performance. For gaining a deeper understanding of moisture adsorption mechanisms, the molecular interactions between adsorbed water and a typical lignocellulosic material (i.e., wood) were studied using in-situ microscopic Fourier transform infrared (micro-FTIR) spectroscopy and a specially designed sample cell. The spectral shifts of 1733 cm^{-1}, 1604 cm^{-1} and 1236 cm^{-1} and different spectra between the moist and dry spectra indicated that carbonyl C═O and C—O groups preferred to combine with water molecules to form hydrogen bonds. From component band analysis of the spectral range of 2900–3700 cm^{-1}, three peaks at 3178 cm^{-1}, 3514 cm^{-1} and 3602 cm^{-1} were identified and assigned to strongly, moderately and weakly hydrogen-bonded water molecules, respectively. According to the variation trend of these hydrogen-bonded water molecules, three sections were divided for the adsorption process. Furthermore, the molecular structure of water absorbed by hydrophilic groups of wood in each section was demonstrated.

1. Introduction

Lignocellulose is the most abundant renewable material on earth [1]. The material potential of lignocellulose is enormous and it has been used by humans for thousands of years. Traditional uses for lignocellulose include structural materials, hog fuel, and paper fibers [2–4]. With the progress of modern material science, lignocellulose can also be used as a raw material for biofuels, a variety of specialty chemicals and functionally versatile nano-objects [5,6]. Lignocellulosic materials are hygroscopic, and in view of both traditional and modern utilizations, absorbed water has an obvious influence on the properties, particularly the dimensions and mechanical properties of such materials [7]. Consequently, fundamental understanding of the molecular association of adsorbed water with lignocellulosic materials is of great importance.

The water adsorption characteristics are prime properties of lignocellulosic materials under different environmental conditions. Sorption isotherms have been analyzed and adapted to theories of sorption mechanisms as a layered adsorption or as cluster formation [8–11]. Traditional methods such as gravimetric sorption [12,13], laser interferometry [14], quartz crystal microgravimetry (QCM) [15], nuclear magnetic resonance (NMR) spectroscopy [16–18], dielectric relaxation spectroscopy [19], CT-Scanning [20,21], dynamic vapor sorption (DVS) [22] and Fourier transform infrared (FTIR) spectroscopy [23] have been employed to investigate the water adsorption. Though sorption isotherms of lignocellulosic materials such as wood have been analyzed, hydration structural changes are still unclear. Among these methods, FTIR shows some distinct advantages because it can provide information relating to the interactions between water and lignocellulosic materials at the molecular level and is more sensitive for carrying out observations of structural change [24]. In particular, micro-FTIR spectroscopy has the ability to visualize sample morphology, which enables the quantitative detection of selected areas [25]. Recently, micro-FTIR and a specially designed sample cell have been developed to investigate water adsorption, which can take in-situ spectra under strictly controlled humidity conditions, and enhance spectral resolution by reducing the interference of water vapor. Thus, this new approach has become an effective technique to demonstrate molecular association of adsorbed

---

* Corresponding authors at: College of Material Science and Engineering, Central South University of Forestry & Technology, Changsha 410004, China; School of Renewable Natural Resources, Louisiana State University AgCenter, Baton Rouge, Louisiana 70803, United States. Tel.: +86 73185623301/+1 2255788369; fax: +86 73185623301/+1 2255784251.
E-mail addresses: wuyq0506@126.com (Y. Wu), qwu@agcenter.lsu.edu (Q. Wu).

http://dx.doi.org/10.1016/j.ijbiomac.2015.11.047
0141-8130/© 2015 Elsevier B.V. All rights reserved.

water with lignocellulosic materials during the adsorption process.

The idea that moisture is adsorbed to specific sites on the material has also been advocated by many researchers. Haxaire et al. showed that infrared spectroscopy can help identify whether the hydroxyl groups are hydrogen bonded or not with water molecules [26]. Olsson et al. examined the association of water on pulp paper using FTIR spectra, and indicated that all the moisture-sorbing sites adsorbed moisture to the same relative degree [27]. A limited number of 1.0–1.3 adsorbed water molecules per hydroxyl group at relative humidity of below 100% were established for a number of hydrophilic materials [28]. Cellulose is the most important component in terms of its volume and effect on the characteristics of wood. For a model system of partly carboxymethylated cellulose, the specificity of moisture adsorption to hydroxyl and carboxyl groups was demonstrated [29,30]. However, few studies have been able to show the specific bonding of water molecules to these adsorption sites. Rautkari et al. claimed that there had to be an additional mechanism to exercise control over the equilibrium moisture content (EMC) of wood in addition to hydroxyl group [31]. Because of the different possibilities of hydrogen-bond formation in adsorption sites, the adsorbed water exists in a special form deviated from ordinary water and the interaction between lignocellulosic materials and water is very complicated, which deserves a more detailed investigation.

In this work, we used the micro-FTIR technique to study the molecular association of adsorbed water with a typical lignocellulosic material (i.e., wood) during the adsorption process. The objective of this study was to demonstrate the molecular structure of water absorbed by hydrophilic groups of the typical lignocellulosic material according to the assignment of absorbance bands.

2. Material and methods

2.1. Sample preparation

A 5-to 7-year-old ginkgo biloba tree was obtained from Hebei province in China. The samples were taken from the main stem and no compression wood was present in the area of the samples. Transverse sections, 5 mm by 5 mm by 10 μm thick, were prepared by a microtome from these samples. Then, these sections were fixed to two microscopic glass slides and air dried. Prior to doing the experiment, the microtomed wood sections were annealed at 102 ± 3 °C in the oven for a minimum 3 h.

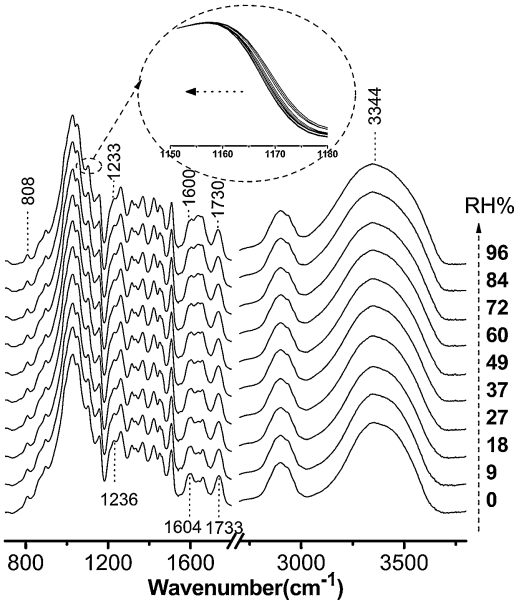

Fig. 2. Micro-FTIR spectra of wood at various RH levels. The arrow means the RH is increasing from 0 to 96%.

2.2. Microscopic Fourier Transform Infrared (micro-FTIR) spectroscopy equipment

Fig. 1 shows a schematic design of the experimental apparatus. The central part is a Nicolet IN 10^{TM} micro-FTIR spectrometer (Thermo Electron Scientific Instruments, Madison, WI, U.S.A.), which is equipped with a liquid-nitrogen-cooled mercury-cadmium-telluride (MCT) detector. An aperture is placed on the optical path after the objective and defines the area of the sample over which the IR spectrum is collected. After the aperture, the IR beam is focused onto the MCT detector.

The sample was deposited onto the bottom of a specially designed sample cell, which was composed of two ZnSe plates with a thickness of 2 mm. Before each experiment, the sample cell was dried with nitrogen gas for 12 h. The relative humidity (RH) around the sample was adjusted by mixing streams of water-saturated N_2 and dry N_2, which was monitored by a flow rate meter (Alicat scientific, Tucson, AZ, U.S.A.). Once the RH arrived at a desired value, it was kept stable at the same level for a further 60 min. The resulting RH was measured by a hygrometer (Center 310, Center Technology Corp., New Taipei, Taiwan) near the exit point of the sample cell. The whole experiment was performed at room

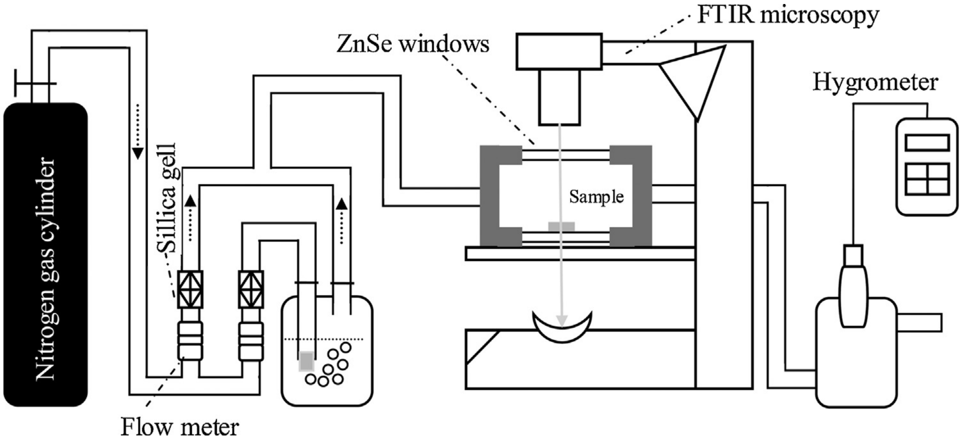

Fig. 1. Schematic diagram of the experimental apparatus.