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RESEARCH ARTICLE

Characterization of spectra of lignin from midribs of tobacco at THz frequencies

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Abstract The functions of the chemicals are closely related with their compositions and structures. In this paper, we report the characterization of different lignin in the midribs of tobacco leaves using terahertz (THz) time-domain spectroscopy in the frequency range of 0.3 to 2 THz. These lignins are extracted from tobacco leaves grown in different regions. Lignin in midribs of tobacco leaves from the south region and the north region show distinctively different refractive indexes and absorption coefficients at THz frequency. The differences at THz range are found to be correlated with their chemical compositions, which are obtained by way of X-ray micro-analysis. This clearly verifies that it is possible to employ THz time-domain spectroscopy as a tool for identifying the functions of the chemicals and analyzing their chemical compositions.

Keywords terahertz (THz) spectroscopy, lignin, X-ray microanalysis, midribs of tobacco, scanning electron microscope (SEM)

1 Introduction

Terahertz (THz) lies in the frequency range of 0.1–10 THz (i.e., 3.33–333 cm^{-1}). In recent years, because of the development of compact, reliable and highly sensing spectroscopic systems based on ultra-fast laser, the techniques of THz electromagnetic waves have been employed in many fields, including imaging [1,2], deoxyribonucleic acid (DNA) sensing [3], diagnosis of skin cancer [4], the inspection of illegal drugs [5], mainstream cigarette smoke [6], biological materials in a liquid phase [7], bimolecular sensing [8], inline monitoring [9], medicine [10], etc. THz spectroscopy of biopolymers, such as wheat starch [11], protein [12], midribs of tobacco [13,14], brain tissue [15], etc., has also been reported. The absorption spectra of THz can provide rich information on the collective mode of biomolecules lying in the range of THz. In this work, THz spectroscopy is used to detect the absorption of THz wave by lignin extracted from midribs of tobacco leaves.

Lignin, which is a natural bio-polymer, is very abundant in vascular and wood plants and is just next to fiber in the world. Lignin is used in many fields such as construction [16] and oil field chemicals [17] because of its powerful functions. The most important function of lignin, as part of dietary fiber, is to protect human beings from cancer such as colon cancer because some types of lignin such as lignin F has anticancer and antitumor properties [18,19]. Therefore, it is of critical importance to determine the relationship between lignin's function and its chemical composition. The absorption spectra in the range of THz frequencies could give information on the structure of lignin as well as the relationship between its function as medicine and its chemical composition, because the absorption at THz frequencies is very sensitive to the structures of substances. In this work, the absorption spectroscopy of lignin is measured by THz time-domain spectroscopy (TDS). Lignin is extracted from the midribs of tobacco leaves. The optical properties of lignin are characterized at the range of 0.3–2.0 THz and its relationship with elemental composition is discussed.

2 Experiments

Extraction and purification of lignin in the midribs of tobacco leaves is the same as described in Ref. [13]. Lignin 2 and lignin 4 from midribs of tobacco are from Chongqing and Nanyang, respectively. The setup of the THz spectroscopy system is similar to the one employed by Shi and

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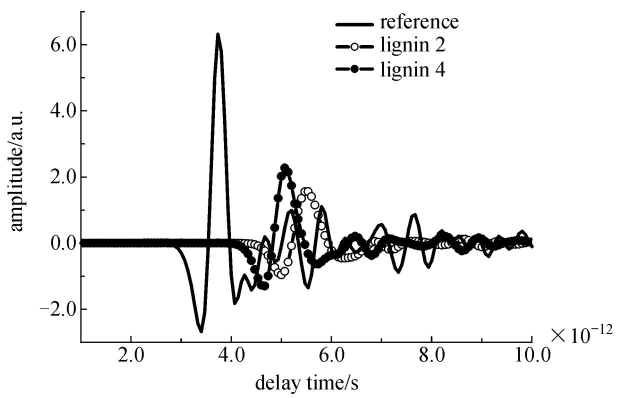
Zhao [20]. The powder of lignin 2 and 4 is pressed under a pressure of 18 MPa to form sample pellets with a diameter of 13 mm and a thickness of 0.682 and 0.694 mm, respectively. The THz absorption spectra of the two sample pellets are measured under a temperature of 20.4°C and moisture of 20.4% at the frequency range of 0.3–2.0 THz. Furthermore, scanning electron microscopy (SEM, Hitachi S-4800) is used to measure the surface appearance and microanalysis of the two samples.

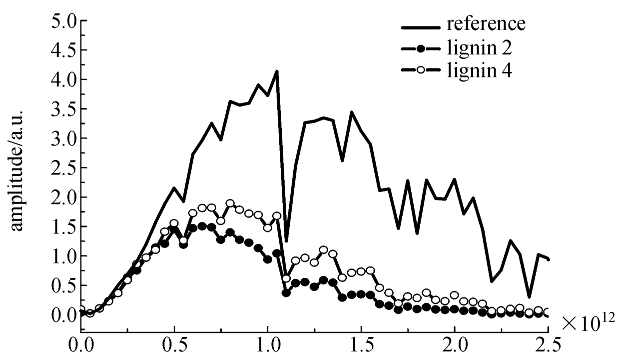
3 Results and discussion

3.1 Results of THz spectra of lignin 2 and lignin 4

Time-domain waveforms of a reference pulse and pulses after transmission of two samples are shown in Fig. 1(a). After transmission of samples, THz temporal waveforms show a time delay of a few picoseconds and a large amplitude change. The delay time of lignin 2 and lignin 4 are 1.80 and 1.34 ps respectively. These waveforms are processed by fast Fourier transform (FFT) and their frequency spectra are shown in Fig. 1(b). Refractive indexes and absorption coefficients can be obtained by comparing phases and amplitudes of the reference pulse and sample pulse. The refractive indexes of lignin 4 are apparently lower than those of lignin 2 as shown in Fig. 2(a). The refractive indexes are mostly flat across the measured THz range, and the average values are 1.77 and 1.31 respectively at the frequency range of 0.3–2.0 THz.

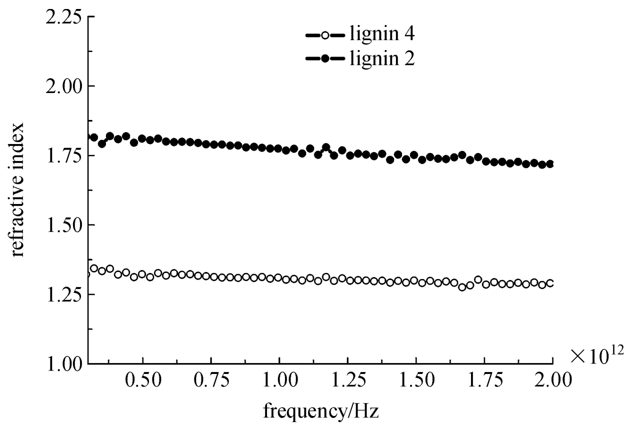


(a)

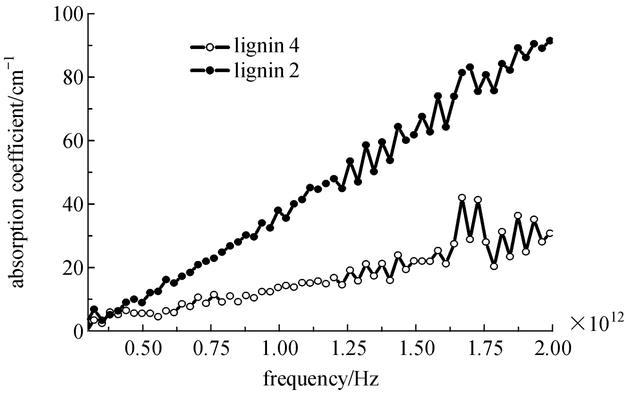


(b)

Fig. 1 Spectra of time-domain and frequency of lignin 2 and lignin 4. (a) Time-domain pulses of reference and after transmission of the two samples; (b) frequency spectra of the two samples



(a)



(b)

Fig. 2 Spectra of refractive index and absorption coefficient of lignin 2 and lignin 4. (a) Spectra of refractive index; (b) spectra of absorption coefficient

The absorption coefficients of the two samples are illustrated in Fig. 2(b). A big difference can be observed between them. Fitting of these absorption coefficients yields two lines with distinct slopes $Y = -16.94968 + 5.43528\times10^{-11}X$ for lignin 2 and $Y = -4.03737 + 1.8025\times10^{-11}X$ for lignin 4, respectively. The origin of the absorption coefficient differentials will be discussed in the next section.

3.2 Microanalysis of lignin 2 and lignin 4

The microanalysis of the two samples are measured by SEM (Hitachi S-4800, H was not detected) and the results of microanalysis (the surface appearance of two samples are not shown) are listed in Table 1. The results show that the elementary composition is similar. However, there is some difference in the contents of various elements. Furthermore, Al was only detected in lignin 4, not in lignin 2.

Table 1 Element composition and mass fraction of lignin from different distributes

samples	mass fractions (w%)					
	C	O	N	S	Cl	Al
lignin 2	69.95	24.80	4.41	0.43	0.41	–
lignin 4	73.99	20.74	3.78	0.39	0.91	0.20

Note : "–" for "not detected"

3.3 Discussion

The differences of THz spectra of various lignins come from their chemical compositions. There is no signature absorption peaks from lignin at the frequency range of 0.3–2.0 THz due to the complexity of its molecule. However, the numbers of units and covalent bonds, linkage types between atoms, conformations, and effects of inter- and intra-molecular, etc., are all different in different lignin. There is no specific molecular structure for lignin because each molecule has its own collective modes. The absorption of THz waves from lignin is the result of total absorption of all molecules. The data of absorption from different lignin can be fit for a line with different slope. This shows that THz wave is very sensitive to the chemical compositions and little changes of element compositions can lead to large changes in THz absorption. The differences of elemental compositions of lignin in the present work are from the varieties of tobacco and growth surroundings, etc.

4 Conclusions

In conclusion, the THz properties of lignin including refractive indexes and absorption coefficients are measured by THz time-domain spectroscopy. We have found that refractive indexes and absorption coefficients from different lignins are significantly different due to their chemical compositions. The results indicate that absorption in THz frequency is very sensitive to the chemical composition of lignin. A new method to detect the chemical composition of lignin is developed and could find application in distinguishing special functional lignin as anticancer or antitumor agents in pharmaceutical researches and clinical practices.

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