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FTIR Studies of the Changes in Wood Chemistry from Wood Forming Tissue under Inclined Treatment

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Abstract

In order to investigate the chemical modifications of wood forming tissue from *Pinus koraiensis* under different stem inclined angle, the change was measured by Fourier Transform Infrared Spectroscopy (FTIR). The results showed that the relative intensities of absorption bands at 1510, 1457, 1232 and 1267 cm^{-1} increased significantly, whereas the relative intensities of absorption bands at 1739, 1371 and 1160 cm^{-1} decreased. The absorption peaks and quantitative analysis of lignin showed similar variation patterns in different inclined angle. However, the cellulose crystallinity calculated by spectrum information showed contradictory with early reports. The results indicated chemical variation was in wood forming tissue of inclined stems and it displayed correlation and similar change pattern.

Keywords: wood forming tissue; inclined treatment; FTIR; lignin; *Pinus koraiensis*

1. Introduction

Wood is an important resource and energy sources which is produced by the vascular cambium. Variations in the anatomy, morphology, and chemical constitution of wood are induced by the habitat of trees and affect the end utility properties. Conifers usually develop compression wood at the lower side of leaning stems or branches in response to the perception of gravity and/or to mechanical stimuli [1, 2, 3]. In comparison to vertical wood, compression wood is often characterized by a modified secondary cell wall structure, broader rings, rounder cells in cross section, and is composed of different polymers [4, 5, 6]. Compression wood formation is reported to be a process inducible by mechanical stress [4, 7, 8, 9, 10].

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Normally, FTIR has been widely used to detect and quantify the chemical composition of wood under different treatment [11, 12, 13, 14]. However, the spectrum of wood forming tissue and its relationship with inclined angle is still not clear. In this paper, the chemical composition of a 7-year-old sapling stem of *Pinus koraiensis* at different stem inclined angle was measured by FTIR. The cellulose crystallinity was calculated by FTIR spectrum. The acetyl bromide lignin content was also measured. In addition, the changes pattern of lignin and carbohydrate peaks with inclined angle was described. Understanding chemical changes in wood forming tissue will provide unique insights into wood formation.

2. Materials and methods

2.1Plant materials

Experiments were conducted from April to July, 2010 in a plot at Northeast Forestry University, China. 7-year-old Pinus koraiensis saplings (about 63 cm in height and 10.5 mm in diameter) were planted in plastic pots filled with a mixture of black soil and compost. The straight stems of sapling (three for each treatment) were artificially inclined to the south at 10^o, 30^o, 50^o, 70^o for three months and harvest on July 16. The saplings were grown vertically (0^o inclination) as controls. Wood forming tissue was obtained by first peeling a rectangular section of bark (outer cambium) from about 10 cm above the ground on the lower side of the inclined stems and straight stems, and then scraping the immature xylem with a fresh razor blade. Samples were kept frozen at all times at -80 ^{o}C until ground. The samples were quickly ground to a fine powder using a liquid N_2-chilled mortar and pestle. Samples were dried at -60 ^{o}C in a freeze vacuum concentrator. Equivalent tissue from three duplicates was mixed for testing.

2.2 Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra were measured by direct transmittance using the KBr pellet technique. Spectra were recorded using a Nicolet Magna-IR 560 E.S.P. spectrometer. Spectral data between 400-4,000 cm^{-1} were collected averaging 40 scans at a resolution of 4 cm^{-1}. Peak heights of absorption bands were measured by OMNIC software (Version 8.0, Nicolet Instruments Corporation, USA) according to previous methods [11].

2.3 Lignin Content Determination

Lignin content was determined via the acetyl bromide method [15,16].

3. Results and Discussion

3.1 FT-IR Analysis

Wood cell wall is main been consist of cellulose, hemicelluloses and lignin. Generally, O-H stretching absorption bends (around 3400 cm^{-1}) and C-H absorption bands (around 2927 cm^{-1}) have contributions from all these chemical components. So, the functional groups in fingerprint region between 2000-600 cm-1 always been used to distinguish differences. FTIR bands in fingerprint region of inclined wood forming tissue are shown in Fig. 1. The peaks in the fingerprint region are assigned in Table 1[11, 17, 18]. As shown in Fig. 1, FTIR spectra of wood forming tissue display significantly difference after inclined treatment. Especially, in inclined stem, the relative intensities of absorption bands at 1510, 1457, 1232 and 1267 cm^{-1} increased significantly, whereas the relative intensities of absorption bands at 1739, 1371 and 1160 cm^{-1} decreased. The lignin band at 1232 cm^{-1} was not visible in the spectra of upright sample.

The aromatic skeletal vibration at 1510 cm^{-1} significantly increased and it revealed that the content of aromatic compounds in bending wood cell walls increased when compared to the normal stem. As lignin is the main aromatic compound in a wood cell wall, so it can experience higher lignin deposition in the bending stem, which is one of the most chemical features found in compression wood. In addition, the peak at around 1265 cm^{-1} resulting from syringyl ring breathing and C-O stretching vibration in lignin and xylan may also account for the increase of lignin deposition in wood cell wall of bent stem.

The relative intensities of lignin characteristic bands increased with stem inclination up to 50°, whereas the relative intensities of carbohydrates bands decreased with stem inclination up to 50°, after which it did not increase further (Table 2). The rate of changes in absorption intensity was higher between inclination angles of 0° and 10°, after which the increase was very gradual.

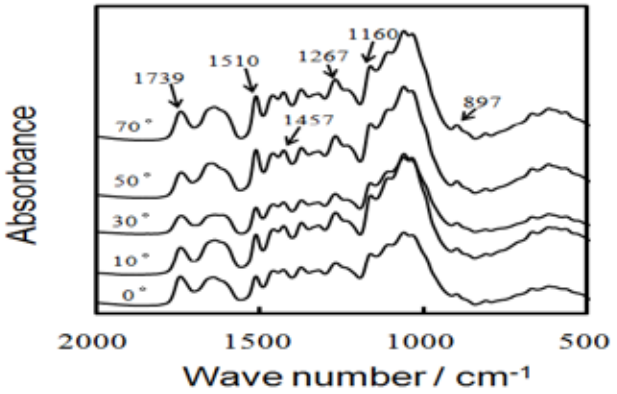

Fig.1 FTIR spectra of wood forming tissue from *P. koraiensis* samples under different inclination

Table 1. Assignment of major absorption IR spectra peaks in wood forming tissue

Wave number (cm^{-1})	Band assignment
1739	C=O stretching in unconjugated ketone
1640	C=O stretching vibration in conjugated carbonyl of lignin
1510	Aromatic skeletal vibrations
1457	CH_2 deformation stretching in lignin and xylan
1425	Aromatic skeletal combined with C-H in-plane deforming and stretching
1371	Aliphatic C-H stretching in methyl and phenol OH
1320	C1-O vibrations in S derivatives, CH in-plane bending in cellulose I and cellulose II
1267	Syringyl ring breathing and C-O stretching in lignin and xylan
1160	C-O-C asymmetric stretching in cellulose I and cellulose II
1059	C-O stretching vibration (cellulose and hemicellulose)
1034	C-O stretching vibration (cellulose , hemicellulose and lignin)
897	C1 vibration

Table 2. Relative intensities of characteristic peaks for carbohydrates and lignin for inclined samples

Inclined angle(°)	I_{1739}	I_{1371}	I_{1160}	I_{1510}	I_{1457}	I_{1267}
0	6.000	2.667	3.556	4.500	0.889	1.944
10	4.120	2.240	3.240	4.941	1.960	2.480
30	3.824	2.235	3.235	4.680	1.824	2.765
50	3.037	2.148	3.037	5.556	1.741	2.741
70	3.931	2.034	3.103	4.897	1.690	2.621

3.2 Inclined treatment affects cellulose crystallinity in the wood forming tissue

The physical and mechanical properties of polymers are profoundly dependent on the degree of crystallinity [19]. The ratio of peak intensity at 1425 and 897 cm^{-1} (I_{1425}/I_{897}) and I_{1372}/I_{2925} in FT-IR spectra of wood samples was used to examine the crystallinity of celluloses in wood samples [20]. The results show that all the relative crystallinity index of the stem subjected to mechanical bending treatment increased compared to the control sample (Fig 2). The rate of I_{1425}/I_{897} shows obviously increased with stem inclined to 30°, after which it decreased slightly. In addition, the rate of I_{1372}/I_{2925} shows tiny increased with stem inclination. However, these results are contradictory to early reports which consider that compression wood will be induced via machine bend and lower crystallinity of cellulose is a feature of compression wood. The reasons need to investigate in further experiments.

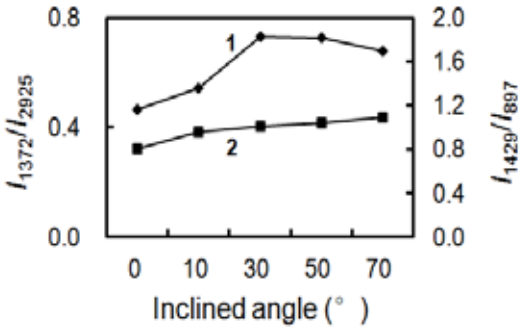

Fig. 2 Changes in crystallinity of wood forming tissue under inclined treatment.

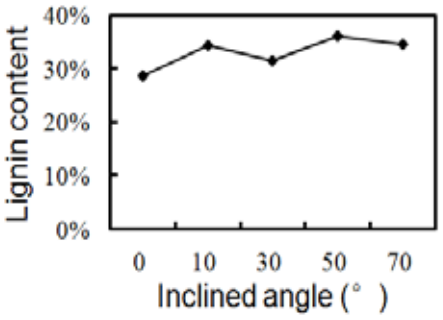

Fig. 3 change of lignin content of wood forming tissue under inclined treatment.

Acetyl bromide lignin content was measured at the different inclined angle (Fig.3), and on the whole, lignin content increased during bending treatment when compared to an upright stem. The lignin content increased sharply with stem inclinations up to 50°, after which it decreased slightly. Observations from FTIR analyses also indicated that the changes pattern of lignin content under different inclined angle. The changes pattern is similar to results of experiments in Japanese cypress (*C. obtusa*) [6], indicating that the degree of development of compression wood reaches a limit at 30-50°.

4. Conclusion

FTIR spectroscopy was used to examine changes of chemical components of wood forming tissue response to stem inclined treatment. The relationship between the changes of chemical components and inclined angle was also investigated. The intensities of carbohydrate peaks decreased with stem inclination up to 30-50°and increased slightly. Simultaneously, the intensities of lignin peaks increased up

to 30-50°and decreased slightly. The wood tissue with compression wood feature was produced under inclined treatment and this show markedly in 30-50°. The results indicate that FTIR can be used for qualitative and semi-quantitative analysis on wood forming tissue in compression wood cell wall formation.

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