

Application of ATR Infrared Spectroscopy in Wood Acetylation

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ABSTRACT

Acetylation is a chemical modification of wood to enhance its properties. IR-spectroscopy is a useful technique for proofing chemical bondings in wood and the Attenuated Total Reflection (ATR) Infrared Spectroscopy technique was applied as an easier technique over other IR-spectroscopies. In this research, different degrees of acetylation, weight percentage gains (WPGs) in beech and pine mini-stakes were achieved by using acetic anhydride. Acetylated samples were analyzed by applying an Attenuated Total Reflection (ATR) Infrared Spectroscopy technique. Comparison of the acetylated samples with non-acetylated woods showed that hydroxyl groups (O-H) were diminished at wave numbers of about 3,354-3,328 cm^{-1} due to the substitution of hydrophobic acetyl groups in cell wall polymers. A strong peak appeared at wave numbers of about 1,733-1,728 cm^{-1} in beech and 1,737-1,728 cm^{-1} in pine due to the carbonyl (C=O) stretching of acetyl groups. The magnitude of the bands increased with raising the weight percentage gains (WPGs). The methyl deformation of the acetyl groups induced at wave number 1369 cm^{-1} caused by the stretching of C-H in polysaccharides. There was also a clear increase in the magnitude of the wave numbers at about 1234-1226 cm^{-1} in beech and 1236-1226 cm^{-1} in pine due to the stretching of C-O and carbonyl deformation in the ester bonds during the acetylation of lignin.

Keywords: Acetylation, Acetyl groups, Attenuated total reflection, Infrared Spectroscopy, Beech, IR spectroscopy.

INTRODUCTION

Wood as an engineering material is a biopolymer and is composed of highly elongated cells whose walls have complex and multilayered structures. It is constituted of three main polymers- cellulose, lignin and hemicelluloses- known as cell wall polymers. Cellulose is a chain polymer and forms microfibrils, which are embedded in a matrix, composed of amorphous hemicelluloses and lignin. These biopolymers determine the physical, mechanical and chemical properties of the wood. Hydroxyl groups in the polymers are important functional groups and perform a major role in the wood properties. Water exchange (sorption/desorption processes) with the surrounding

environment, reaction with enzymes of fungi or bacteria and the influence of ultraviolet light are the best means of indicating their importance in the physical, mechanical and chemical properties of wood as well as its bio-resistance. Improving those properties and protecting wood against relative humidity, biological agents, UV and weathering are of great technical importance. Wood modification is a new approach to improve its properties. Chemical modification is one of the methods that alter basically the chemical structure of wood.

Acetylation is known as a chemical modification technique by which OH groups of wood cell wall polymers are substituted by acetyl groups [7, 8, 9, 11, 20]. Figure 1 shows a typical reaction between the acetic

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anhydride and OH groups of the wood cell polymers during the acetylation. Due to the acetylation, the cell wall polymers become hydrophobic and blocked against biological enzymes and UV light. It cannot react with water due to the substituted hydrophobic acetyl groups [7, 8, 9, 20]. Also, its mechanical properties become improved due to the increased hydrophobicity. Consequently, the chemical structure of the cell wall polymers becomes altered and indistinguishable for the enzymes of biological degraders; such as fungi and bacteria [11, 12, 21].

Many studies have been carried out on the chemical wood modification, especially acetylation and its influences on wood properties such as bioresistance [9, 11, 12, 13], water repellency [2, 16, 20] and mechanical properties [7, 8]. There are also a few reports concerning the chemical structure of the acetylated wood [14, 15, 22].

Different methods are used to study wood chemistry, such as wet chemistry. Since they are actually tedious and time consuming, finding rapid and easy methods to be used and techniques is of great concern. Infrared spectroscopy is a rapid technique to determine chemical changes in the acetylated wood. During acetylation, the chemical substitution of hydrophilic OH groups by hydrophobic acetyl groups occurs in cellulose, hemicelluloses and lignin and it changes the typical spectra in the wood (Figure 1). Therefore, IR-spectroscopy is a good tool to

proof any chemical changes in the wood cell wall polymers qualitatively.

Attenuated Total Reflection (ATR) Infrared Spectroscopy is a rapid technique that is used for solid or powdered wood [10]. It is much easier to use than typical FTIR spectroscopy by preparing small pellets with KBr. In this study, ATR-IR spectroscopy was applied as rather a simple and easy technique over FTIR spectroscopy to distinguish the chemical alteration in beech and Scots pine wood due to the acetylation by using powdered acetylated samples.

MATERIALS AND METHODS

Acetylation

Small stakes of beech (*Fagus sylvatica*) and Scots pine (*Pinus sylvestris*) wood were prepared in 100 mm×10 mm×5 mm bits and dried at 60°C to achieve uniform moisture content in the specimens. About ten mini-stakes were dried at 103±2°C to calculate the initial dry weights of the specimens. The moderately dried mini-stakes were placed in a closed stainless steel cylinder as a reactor and pre-vacuumed for effective penetration by the chemical. Acetic anhydride as a reacting agent was mixed with acetic acid and pumped into the cylinder. Acetic acid was used to reduce the reaction rate. Afterwards, the mixture was heated up to 120°C for 180

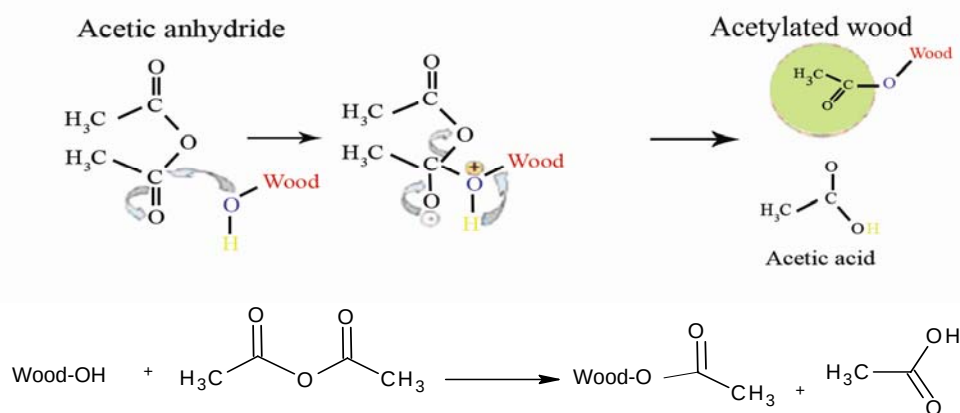


Figure 1. Acetylation reaction of wood.

minutes to reach different weight percent gains (WPGs) according to Table 1. Thereafter, the acetylated samples were washed in water to remove the acetic acid that was formed as a by-product during the acetylation reaction. Specimens were dried at $103\pm2^\circ\text{C}$ to determine dry weight and calculate the weight gained by acetylated samples after acetylation (Equation 1).

$$\text{WPG (\%)} = (W_{\text{act}} - W_{\text{unt}}) / W_{\text{unt}} \times 100 \quad (1)$$

Where: W_{PG} , W_{unt} and W_{act} indicate the weight percentage gain and dry weights before and after the acetylation, respectively.

IR Spectroscopy

Attenuated Total Reflection (ATR) Infrared Spectroscopy has an advantage over other methods. It is a very easy and rapid technique due to using solid material (as solid wood or its powder) [10]. For this purpose, dried samples were milled and passed through a sieve with mesh 40. IR spectra were collected directly from the wood powder on to a detector prism using a Bruker Vectra 22 FTIR Spectrometer equipped with a DuraSampleIR IITM detector. All spectra were taken at a spectral resolution of 4 cm^{-1} between wave number range $5,000\text{--}600\text{ cm}^{-1}$.

Sample and background were scanned with 60 scans. The background spectra were collected using an empty collector. A rubber band method was used for baseline correction. The band for CO_2 was removed to make a suitable baseline correction. Collection of data and baseline correction were carried out by OPUS software [10, 11].

RESULTS AND DISCUSSION

Table 1 shows the weight percentage gains (WPGs) that were obtained during different reaction conditions of the acetylation.

The IR spectra of untreated beech and pine wood are shown in Figure 2. A strong OH bond vibration was seen at $3,500\text{--}3,300\text{ cm}^{-1}$ (1) relating to the water absorbed in the wood and a prominent C-H stretching vibration around $2,881\text{ cm}^{-1}$ (2). There were many well defined peaks in the finger print region of $1,800\text{--}600\text{ cm}^{-1}$. The peaks in the wood were assigned as un-conjugated C=O stretching in xylan at $1,724\text{ cm}^{-1}$ (3); conjugated C-O stretching at $1,587\text{ cm}^{-1}$ (4); aromatic skeletal vibration at $1,500\text{ cm}^{-1}$ (5); C-H deformation in lignin and carbohydrates at wave numbers $1,450\text{ cm}^{-1}$ (6) and $1,417\text{ cm}^{-1}$ (7); C-H deformation in cellulose and hemi-

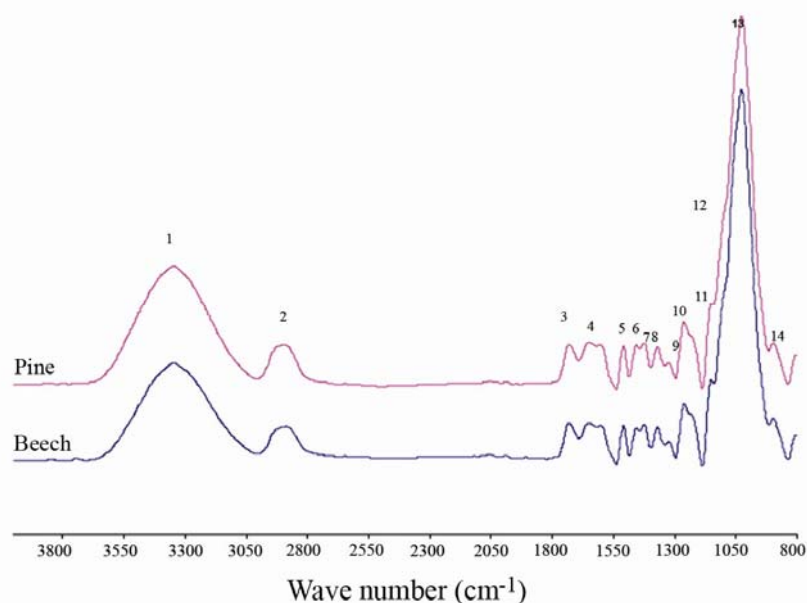


Figure 2. IR spectra of non-acetylated.

**Table 1.** Acetylation conditions and weight percentage gains (WPG) in acetylated wood.

Reaction conditions		Weight Gains (%)	
Acetic acid (%)	Acetic anhydride (%)	Beech	Scots Pine
-	-	0	0
75	25	1.84	2.43
50	50	6.72	9.13
25	75	8.33	10.12
0	100	17.43	19.46

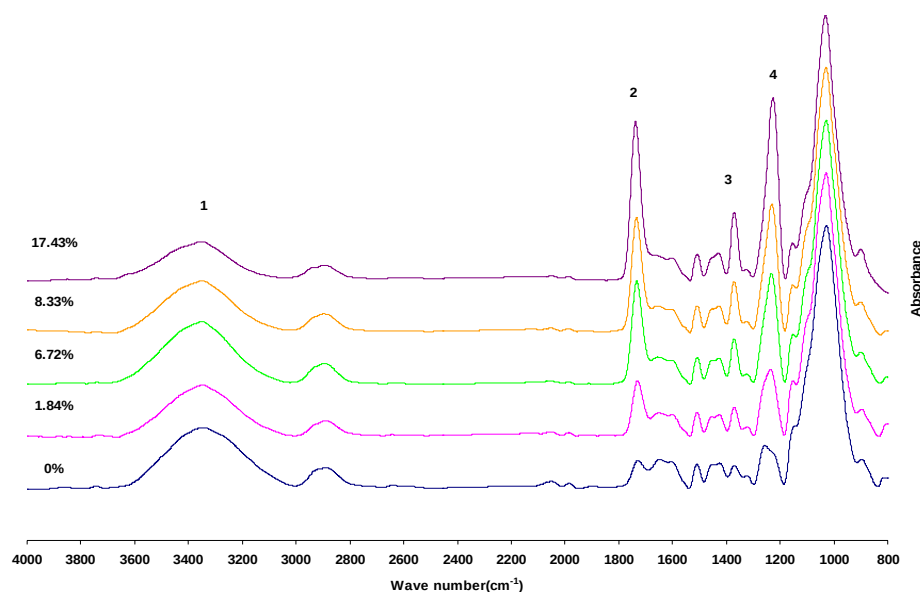
celluloses at $1,369\text{ cm}^{-1}$ (8); C-H vibration in cellulose and $\text{C}_1\text{-O}$ vibration in syringyl derivatives at $1,319\text{ cm}^{-1}$ (9); syringyl ring and C-O stretching in lignin and xylan at wave number $1,226\text{ cm}^{-1}$ (10); C-O-C vibration in cellulose and hemicellulose at $1,151\text{ cm}^{-1}$ (11); aromatic skeletal and C-O stretch at $1,116\text{ cm}^{-1}$ (12); C-O stretch in cellulose and hemicelluloses at wave number $1,024\text{ cm}^{-1}$ (13) and C-H deformation in cellulose at 892 cm^{-1} (14).

IR spectra in the acetylated beech and pine wood are shown in Figures 3 and 4. It was revealed that, at wave numbers between $3,500\text{-}3,300\text{ cm}^{-1}$ (1), the intensities were

decreased due to the acetylation. This peak is assigned for OH stretching of absorbed water to the wood cell wall polymers [4, 18]. It indicates that the number of OH groups was decreased due to the substitution of the acetyl groups during the acetylation in both woods. Many reports have shown that acetylation improves water repellency in the wood due to decreased OH groups [14, 20].

There are prominent peaks in the finger print region (wave numbers $1,800\text{-}600\text{ cm}^{-1}$) whose magnitudes were increased due to acetylation caused by raised WPGs. An assigned peak (2) at wave number $1,724\text{ cm}^{-1}$ is related to an un-conjugated C=O stretch in xylan [19, 22]. The magnitude of this peak was increased by raised WPGs in both woods (Figures 3 and 4). This peak has been shifted slightly to higher wave numbers ($1,737\text{-}1,730\text{ cm}^{-1}$) in the acetylated wood (Table 2).

As shown in Figures 3 and 4, another peak (3) at wave number $1,369\text{ cm}^{-1}$, which has been assigned for C-H deformation in cellulose and hemicelluloses, was increased due to the acetylation [1, 3, 17, 19]. Its magnitude was also increased by the raised WPGs in the acetylated beech and pine wood.

**Figure 3.** IR spectra of acetylated Beech wood.

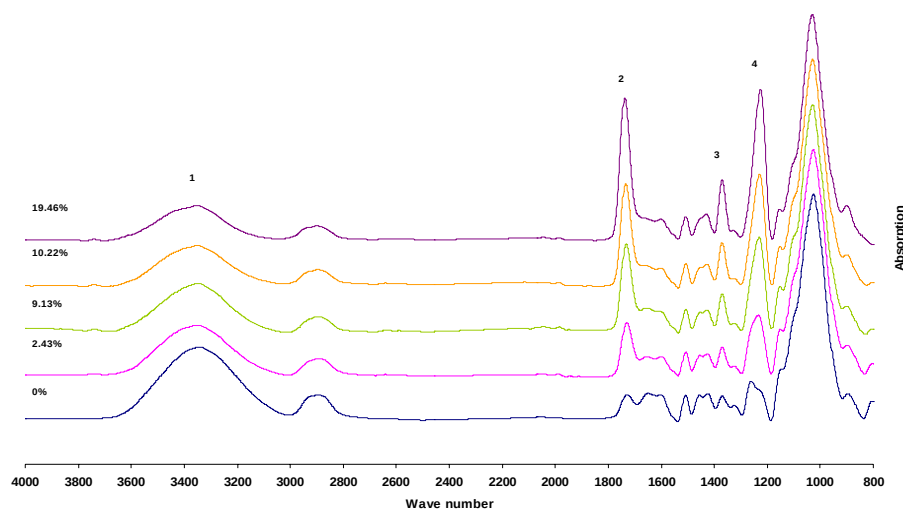


Figure 4. IR spectra of acetylated Scots Pine wood.

Another prominent peak (4) at wave number $1,226\text{ cm}^{-1}$ was increased in both acetylated beech and pine wood. This peak has been assigned for C-O stretching and C=O deformation in lignin and xylan [5, 6, 19]. The magnitude of this peak was increased by the raised WPGs. This peak has slightly been shifted to other close wave numbers ($1,236\text{--}1,226\text{ cm}^{-1}$) due to the acetylation in both woods (Table 2).

CONCLUSION

This research demonstrates the applicability of ATR-spectroscopy as a useful technique to proof acetyl bonding in wood cell wall polymers due to the acetylation.

As was expected from the acetylation reaction, the number of the acetyl groups bearing C=O (carbonyl) and C-H bonds (in the

Table 2. Wave numbers and their assignments in acetylated wood.

Peak number	Wave numbers in different weight gains (cm ⁻¹)										Assignments
	Beech					Scots Pine					
	Non-acetylated	1.84%	6.72%	8.33%	17.43%	Non-acetylated	2.43%	9.13%	10.12%	19.46%	
1	3342	3346	3346	3352	3354	3346	3348	3350	3348	3348	OH stretching (bonded) [4, 10]
2	1730	1730	1713	1733	1737	1730	1730	1733	1735	1735	C=O stretching in acetyl groups, increased due to acetylation in xylan [21, 22]
3	1369	1369	1369	1369	1369	1369	1369	1369	1369	1369	C-H deformation in CH ₃ from acetyl groups due to acetylation in hemicelluloses and cellulose [3, 17, 19, 1]
4	1259	1236	1230	1228	1226	1259	1234	1230	1228	1226	Stretching of C-O & C=O deformation in the ester bond formed during acetylation [19, 1, 5, 6]



methyl group) should be increased in the cell wall polymers and their intensities should be raised due to the acetylation. ATR-IR spectroscopy- here revealed that all the cell wall polymers- hemicellulose, cellulose and lignin-were acetylated during the acetylation. Therefore, this study proves the substitution of the hydrophobic acetyl groups in the wood cell wall polymers.

Substitution of the acetyl groups decreases the number of functional OH groups in the cell walls. It is well known that functional OH groups in the wood cell wall polymers react with surrounding water. As a result, any increase of absorbed water causes swelling in the wood and its composites. The substitution of the hydrophobic acetyl groups in the cell wall constituents restricts the absorption of water and the wood becomes sequentially water repellent, which is of great technical interest in to the wood industry.

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کاربرد طیف سنجی زیر قرمز انعکاسی در استیلاسیون چوب

ب. محبی

چکیده

استیلاسیون روشی برای اصلاح شیمیایی چوب به منظور افزایش ویژگیهای آن است. طیف سنجی زیر قرمز، تکنیک قابل استفاده‌ای برای تأیید انجام پیوندهای شیمیایی در چوب است. طیف سنجی زیر قرمز تضعیف شده انعکاسی (ATR IR) به عنوان روشی ساده نسبت به سایر طیف سنجی‌های زیر قرمز به کار برده شد. با استفاده از انیدرید استیک، شدت‌های مختلفی از استیلاسیون (درصد افزایش وزن، WPG) در باریکه چوب‌های راش و کاج به دست آمدند. نمونه‌های استیل شده با استفاده از طیف سنجی زیر قرمز تضعیف شده تجزیه و تحلیل شدند. مقایسه نمونه‌های استیل شده و نشده نشان داد که طیف گروه‌های هیدروکسیلی (OH) در عدد موجهای $3328-3354\text{ cm}^{-1}$ به دلیل جایگزینی گروه‌های آب‌گریز استیل در بسپارهای دیواره سلولی کاهش یافت. یک پیک قوی در عدد موج $1728-1733\text{ cm}^{-1}$ در چوب راش و $1728-1737\text{ cm}^{-1}$ در چوب کاج بر اثر کشش گروه کربونیل (C=O) ناشی از گروه‌های استیل پدیدار شد و بزرگی طیف پیوندها با افزایش درصد افزایش وزن (WPG) بیشتر گردید. تغییر شکل گروه‌های متیلی ناشی از گروه‌های استیل در عدد موج 1369 cm^{-1} به دلیل کشش پیوندهای C-H در پلی ساکاریدها افزایش یافت. همچنین افزایشی در بلندی پیک عدد موجهای $1226-1234\text{ cm}^{-1}$ در چوب راش و $1226-1226\text{ cm}^{-1}$ در چوب کاج وجود داشت که ناشی از تغییر شکل پیوندهای C-O و کربونیل ناشی از پیوندهای استری در طی استیلاسیون لینگین بود.