

**ACETYLATION OF PLANTATION SOFTWOOD
WITHOUT CATALYSTS OR SOLVENTS**

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ABSTRACT

This study explored acetylation of wood of *Larix kaempferi* (Lamb.) Carr. and *Pinus sylvestris* var. *mongolica* Litv. without catalysts or solvents. Both wood samples were impregnated with acetic anhydride and subsequently heated to 120°C for different reaction durations (0.5-8 h) in the esterification reagent. The extent of acetylation was measured by weight percent gain (WPG), which varied from 12.0% to 21.7% and 13.6% to 22.3% for both wood species. The cell wall bulking and anti-shrink efficiency (ASE) started to increase faster and then increase slower with increasing reaction time. As the WPG reached 19.2% and 17.8% or more separately, ASE of both acetylated wood were above 50% in any RH conditions. FTIR, CP/MAS ¹³C NMR, and XPS studies produced evidences for acetylation of both wood species. The degree of acetylation of wood cell wall polymers increased with increasing WPG, but during the process degradation of lignin and acid hydrolysis of carbohydrates occurred.

KEYWORDS: Acetylation, plantation softwood, acetic anhydride, dimensional stability.

INTRODUCTION

As one of the most important renewable materials, wood continues to be used for many applications because of its many excellent material properties, such as a good strength-to-weight ratio, aesthetic appearance, and so on. However dimensional instability due to its hydroscopic behavior is one of the disadvantages of wood and wood products. Hence, to deal with such disadvantage many investigations have been carried out using different modification processes (Mai and Militz 2004, Esteves and Pereira 2009, Gérardin 2016). Chemical modification has the potential to improve properties of wood through formation of a covalent bond between a chemical

reagent and the wood structural polymeric constituents (Rowell 1983, Fuqua et al. 2012). One of the most researched technologies is the acetylation of wood with acetic anhydride. The properties of acetylated materials depend strongly on the wood species, the wood pre-treatment, reaction medium, reaction process conditions, and clean-up procedure (Hill 2005).

Acetylation has been generally accepted as a method to improve the dimensional stability, anti-weathering properties, and resistance to biodegradation of wood (Stamm and Tarkow 1947, Feist et al. 1991, Beckers et al. 1994, Ohkoshi et al. 1999, Sethy et al. 2012). The reaction converts the hydrophilic hydroxyl groups in the cell walls of the wood and the intercellular regions to hydrophobic ester groups (Rowell 1982). In particular, acetylation with acetic anhydride has received the most attention compared with other chemicals such as acetyl chlorides, thioacetic acid, ketene, etc. It can be performed with or without catalysts and solvents separately. Various catalysts such as pyridine, dimethyl amino pyridine, dimethyl formamide, potassium acetate, N-bromosuccinimide, etc. were used to increase the reaction rate during the reaction process (Hill et al. 2000, Li et al. 2009, Obataya and Minato 2009, Nagarajappa et al. 2016). However, the use of catalysts and swelling agents is not considered suitable for large-scale industrial processes (Hill 2005).

The acetylation of wood with acetic anhydride has been developed and commercialized within the last decade in Japan and the Netherlands (Rowell 2006, Mai 2010). Li et al. (2000) had acetylated wood using various anhydrides without catalysts and solvents through a three-step treatment under laboratory condition. In China, most studies on wood acetylation remained in the laboratory research stage. However, recently some researchers (Chai et al. 2015, 2017, Chu et al. 2016) have systematically carried out researches on wood acetylation technology using acetic anhydride without catalysts as well as solvents, and performed a pilot-scale study of acetylation of plantation wood using self-developed equipment. The acetylation process combined impregnation, heat treatment, and deodorization together, which also simplified the waste solvent recycle after wood acetylation. The research has shown that acetylated plantation poplar with weight percent gain (WPG) above 15% displayed good dimensional stability with anti-shrink efficiency (ASE) above 50%, and when acetylation temperature below 120°C, mechanical properties of acetylated wood were not significantly changed (Chai 2015).

As known, plantation wood has played an increasing role in supply of wood products in China. The plantation area is 69.33 million ha with the stock volume of 2483 million m³ according to the 8th national forestry inventory of forest resources in China. Larch (*Larix kaempferi* (Lamb.)) Carr. and pine (*Pinus sylvestris* var. *mongolica* Litv.) are two important plantation tree species in northeast China. Both species have been widely used for outdoor applications because of their beautiful texture and natural decay resistance (Li 2006). Nevertheless, these species exposed to the outside environment tend to show problems related to warp deformation and cracks. Therefore, in this study through the combined acetylation process larch and pine plantation woods were esterified using acetic anhydride without solvents and catalysts at 120°C under different reaction durations to examine the changes of dimensional stability of both plantation softwoods. The esterified wood was analyzed by FTIR, ¹³C NMR, and XPS to reveal the reactivity of cell wall polymers to acetic anhydride. It is expected that the acetylation can improve their dimensional stability and resistance to fungi and by that adding potential value on larch and pine wood to be used more effectively in further wood markets.

MATERIAL AND METHODS

Materials

Two species were used in this study. Larch (*Larix kaempferi* (Lamb.) Carr.) and pine (*Pinus sylvestris* var. *mongolica* Litv.) were harvested from Qingyuan County in Liaoning Province and Suifenhe city in Heilongjiang Province separately, China. Larch and pine wood samples with dimensions of 30 × 20 × 20 mm (longitudinal × radial × tangential) were prepared from defect free wood and air-dried. The wood samples were acetylated using acetic anhydride (97% concentration, industrial grade, obtained from Shanghai Jiaohua Chemical. Co.) at various conditions.

Wood Acetylation

The wood samples were first oven-dried at 105°C to a constant weight. The oven-dried samples were placed into a stainless reactor and vacuumed for 30 min. Then, the acetic anhydride was introduced to the stainless reactor and the samples were submersed under a pressure of 0.7 MPa for 2 h at room temperature. The reactor was heated to 120°C and kept for 0.5 h, 1 h, 2 h, 4 h, and 8 h under a pressure of 0.1~0.3 MPa. After acetylation, the pressure of the stainless reactor was relieved, cooled to 30°C, and the reaction liquid removed. The acetylated wood samples were kept in the reactor and washed with running fresh water for 24 h to remove the unreacted acetic anhydride and acetic acid. The acetylated samples were then oven-dried until constant weigh.

Measurement of weight percentage gain, bulking and anti-swelling efficiency

Weight percentage gain (WPG), bulking and anti-swelling efficiency were used as essential parameters for characterization of acetylated wood. The WPG and bulking were calculated based on equations 1 and 2, respectively.

$$WPG = \frac{W_1 - W_0}{W_0} \times 100\% \quad (1)$$

$$Bulking = \frac{V_1 - V_0}{V_0} \times 100\% \quad (2)$$

where: W_0 and W_1 - oven-dried weights of samples before and after acetylation separately,
 V_0 and V_1 - oven-dried volume of samples before and after acetylation separately.

The volumetric anti-shrinking efficiency (ASE) was evaluated according to Chinese standard GB/T 1934.2-2009. During the test, the treated and untreated samples, 20 × 20 × 20 mm (L×T×R), were submersed in a distilled water bath at 20°C ± 2°C and measured every 72 h. Once the dimension changes of the samples were less than 0.02 mm, it was assumed that the samples had attained a constant volume and their dimensions in L (length), T (width) and R (thickness) directions were measured using screw micrometer. In addition, the relative humidity of 35%, 85%, and 98% were regulated by the magnesium chloride saturated salt solution, potassium chloride saturated salt solution, and potassium sulfate saturated salt solution in desiccators, respectively. The relative humidity of 65% is controlled by a constant temperature and humidity chamber. All samples were adjusted from oven dry to target humidity. The temperature during the experimental process was maintained at 20°C ± 2°C. Fifteen replications were tested for each treatment.

Fourier transform infrared (FTIR) analysis

FTIR spectra of treated and untreated wood were collected with a spectrometer Spectrum GX FTIR (Perkin-Elmer Inc., USA), equipped with a deuterated triglycine sulfate (DTGS) detector. Each spectrum was recorded in the region of 4,000-400 cm^{-1} by an average of 32 scans at a resolution of 4 cm^{-1} . The samples were chopped into small sticks, grinded and sieved (100 ~ 120 mesh). Then it was blended with potassium bromide (KBr) and compressed at a pressure of 8.5 $\text{tons}\cdot\text{cm}^{-2}$ to prepare a tablet. Three spectra were taken from each sample and the presented FTIR spectra were average value spectra.

CP/MAS ^{13}C NMR analysis

The treated and untreated wood was ground into powder and sieved (≥ 200 mesh). The wood powder was analyzed by Solid-state CP/MAS ^{13}C NMR. The spectra were recorded on a Bruker AV 400 spectrometer at a frequency of 75.5 MHz. Chemical shifts were presented relative to tetramethylsilane (TMS) as an external standard. Acquisition time is 0.026 s with number of transients of about 1600. All the spectra are run with a relaxation delay of 2 s, contact time of 1 ms and spectral width of 300 Hz. Spinning rates are 5 KHz. Chemical shifts are expressed in parts per million.

XPS analysis

Small wood chips of size $5 \times 5 \times 1$ mm were cut with a cutter blade from untreated and treated wood radial surface. X-ray photoelectron spectroscopy (XPS) measurements were performed on Thermo Scientific ESCALAB 250Xi spectrometer using a monochromatic Al $K\alpha$ X-ray source ($h\nu = 1486.6$ eV) with a power of 150 W. The high-resolution spectra were collected at a pass energy of 20 eV with a step of 0.1 eV using for quantitative measurements of binding energy and atomic concentration. XPS peak software (Vision 4.1) was utilized in the data processing. Chemical bond analysis of the carbon and oxygen was accomplished by fitting the C1s and O1s peaks, and then de-convoluting them into four and two sub-peaks, respectively.

RESULTS AND DISCUSSION

Variation of weight percentage gain and bulking

Low-temperature acetylation is not applicable to large-scale industrial acetylation, because it is a time-consuming process. In this study, the acetylation of wood was carried out at 120°C for 0.5-8 h. Fig. 1 and 2 depict the relationships between WPG as well as bulking values of acetylated samples and reaction time. As apparent from the Fig. 1, increasing the reaction time caused an increase in WPG values for both species. An average weight gain of 12.0% and 13.6% was achieved in a reaction time of 0.5 h for larch and pine wood separately. This results are higher than that of acetylated radiata pine without catalyst (Sethy et al. 2012), mainly because of different acetylation processes. After 8 h reaction time, an average weight gain of 21.7% and 22.3% was achieved for both species. While, the reaction rate of esterification was faster in first four hours for both species.

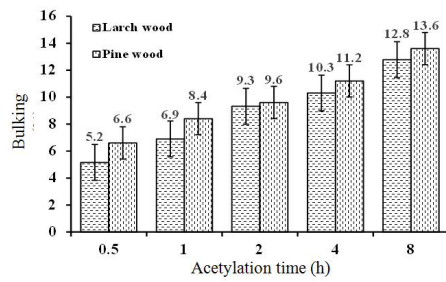
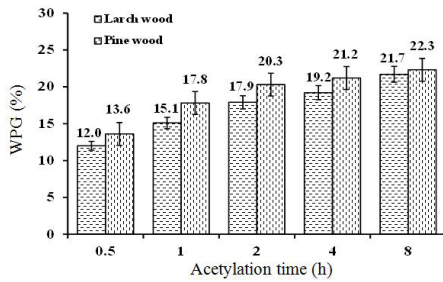


Fig. 1: Average weight percent gain (WPG) values of species as function of acetylation (%). Fig. 2: Average bulking values of species as function of acetylation.

As Fig. 2 shows, the bulking values of larch and pine woods increased to 12.8% and 13.6% for 8 h at 120°C. In the oven-dry condition, the volume of acetylated wood increased because the wood cell wall was swollen with the introduction of bulky acetyl groups. In the same acetylation reaction condition, pine wood showed higher esterification rate than that of larch wood.

Variation of anti-swelling efficiency

Fig. 3 displays anti-swelling efficiency (ASE) values of acetylated samples. It is apparent that the ASE of both acetylated wood species increased with increasing time. ASE of larch and pine woods increased rapidly below 4 h to 58.4% and 72.9% for 4 h at 120°C, respectively. However, the ASE values of larch and pine for 8h were 61.2% and 75.3% resp. The increasing of ASE from 4 to 8 h was 5.1% and 3.3% for both species, which were significantly lower than those of the first 4 h. It is concluded that dimensional stabilization is closely related to the cell wall bulking (Hill 2005).

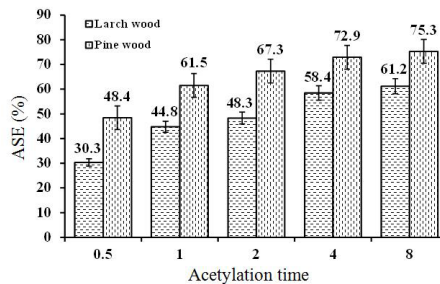


Fig. 3: Average anti-swelling efficiency (ASE) values of species as function of acetylation.

As shown in Fig. 4, ASE of acetylated samples decreased with relative humidity (RH) increasing at the same WPG, and at the same RH condition ASE increased with WPG increasing. When the WPG of acetylated larch and pine woods reached 19.2% and 17.8%, ASE of acetylated wood were above 50% in any RH conditions. The modified wood proved a better dimensional stability. This is because the wood is swollen to some extent due to the volume occupied by bonded acetyl groups. Thus when the modified wood is exposed to conditions of high RH, it shows a lower rate of swelling compared with the untreated wood.

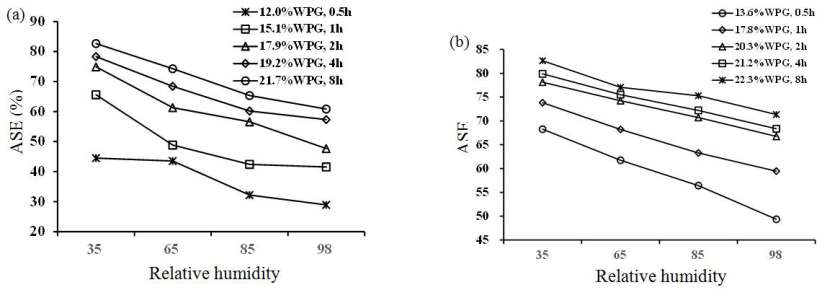


Fig. 4: The anti-swelling efficiency (ASE) of the samples under different relative humidity conditions: (a) Larch wood; (b) Pine wood.

Fourier transform infrared (FTIR) analysis

FTIR spectroscopy was used to characterize the chemical changes of wood before and after acetylation. The assignments of the characteristic IR absorption peaks in wood are listed in Tab. 1.

Tab. 1: Assignments of absorption IR spectra bands in wood (Mohebbi 2008, Faix 1991, Pandey and Pitman 2003, Li 2003).

Peak number	Wavenumber (cm ⁻¹)	Assignments and remarks
1	3349	O-H stretching vibration
2	2900	C-H stretching vibration
3	1738	C=O stretching in xylan
4	1607	C=C in aromatic ring in lignin
5	1508	C=C in aromatic ring in lignin
6	1452	C-H deformation in lignin and carbohydrates
7	1369	C-H deformation in cellulose and hemicellulose
8	1263	Guaiaacyl nuclei in lignin
9	1221	Syringyl ring in lignin and C-O stretching in xylan
10	1029	C-O stretch in cellulose and hemicellulose

The IR spectra of untreated and acetylated samples, normalized at the highest intensity peak at 1029 cm⁻¹, are shown in Fig. 5.

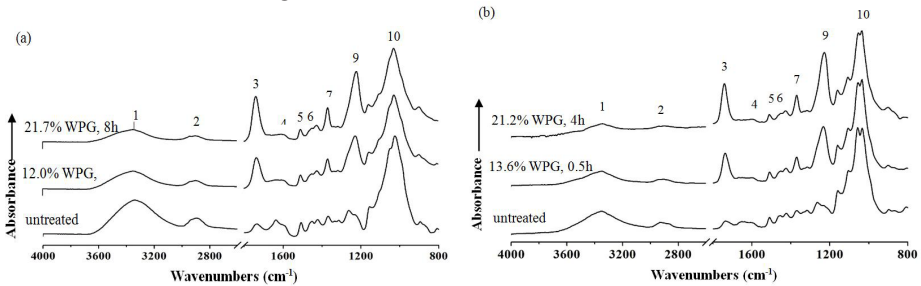


Fig. 5: FTIR spectroscopy of untreated and acetylated samples: (a) Larch wood; (b) Pine wood.

Bands in the 3800–2750 cm^{-1} region are assigned to the hydroxyl and methylene/ methyl stretching vibrations separately. For both acetylated larch and pine woods there was a decrease in the intensity of the absorbance at approximately 3349 cm^{-1} with increasing WPG. This indicated the exchange of OH groups (WOOD–OH) into acetyl groups (WOOD–O–C(=O)–CH₃). The intensity of the bands near 1738 cm^{-1} , 1369 cm^{-1} , and 1221 cm^{-1} , assigned to C=O vibration of the non-conjugated acetylcarbonyl groups in xylan, C–H bending vibrations in cellulose and hemicelluloses, and syringyl ring and C–O stretching in lignin and xylan (Mohebbi 2008, Faix 1991, Pandey and Pitman 2003), showed obviously increases after acetylation, indicating that cellulose and hemicelluloses of wood cell wall polymers were acetylated during the acetylation. In addition, the intensity of peak at 1263 cm^{-1} related with guaiacyl nuclei in lignin decreased and it disappeared with increasing reaction time, which indicated the acetylation of lignin occurred. It may be related with the reactivity of the wood cell wall polymers to acetic anhydride, in combination with reachability due to submicroscopical cell wall features that the order of acetylation in solid wood is lignin > hemicelluloses > cellulose (Rowell 1982). Furthermore, the slight decreases of the intensity in the bands at 1607 cm^{-1} , 1508 cm^{-1} , and 1452 cm^{-1} , related to the aromatic skeletal vibration in syringyl and guaiacyl lignin as well as the asymmetric C–H deformation in lignin (Faix 1991, Li 2003), suggested that lignin may degrade to a certain amount. It is more apparent for the acetylated larch and pine woods for 8 h and 4 h at 120°C. Similar results were obtained by Fodor et al. (2017) with acetylated hornbeam wood. It can possibly be explained that acetic acid as a by-product is formed during the acetylation process, and then some parts of lignin dissolve in the treatment media.

CP/MAS ¹³C NMR analysis

As shown in Fig. 6, evolution of CP/MAS ¹³C NMR spectra recorded the changes in polymeric structural constituents of untreated and acetylated larch and pine woods for different reaction time.

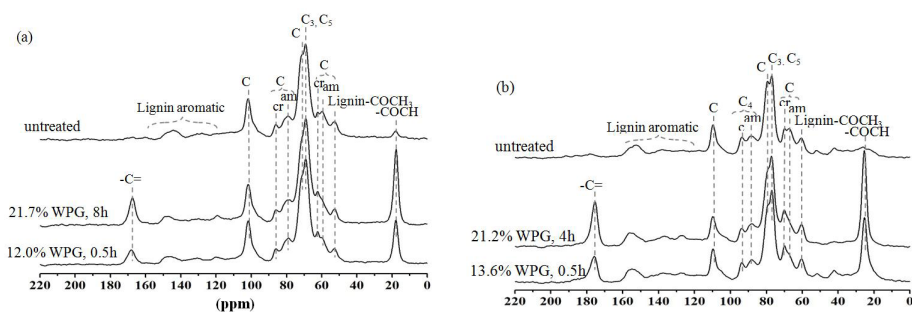


Fig. 6: ¹³C NMR spectra of untreated and acetylated samples: (a) Larch wood; (b) Pine wood.

In the spectra, two noticeable signals at 19.9 and 170.1 ppm, which were assigned to a methyl and carbonyl carbon of the acetyl group of acetylated wood separately (Ohkoshi and Kato 1997a, b), increased in the intensity within creasing WPG indicating the substitution of the cell wall polymeric OH groups. Signals between 50 and 120 ppm are assigned to different carbohydrates carbon atoms (C₁, C₂, C₃, C₄, and C₆) (Boonstra et al. 1996, Jebrane et al. 2011, Yang et al. 2014). Compared with untreated wood, the intensity of signals at 71.1 ppm for C₂ and 59.9 ppm for amorphous C₆ decreased obviously with increasing WPG for both species. This result implied that acetylation at C₂ and C₆ have occurred in carbohydrates of acetylated larch and

pine wood. There was no significant change observed at other carbons. Regarding the lignin, methoxyl groups of syringyl and guaracyl lignin units are detected at 52.7 ppm, and aromatic carbons appear between 120 and 160 ppm. The broad signal at 143.5 ppm related with C₄/C₄, in nonetherified VI for the untreated wood shifted to 147.1 ppm connected with C4 in etherified G units after acetylation (Holtman et al. 2004). The result indicated the lignin was acetylated, which was consistent with the results of FTIR analysis. While, in the case of larch, its intensity decreased with increasing WPG, and it was more pronounced for acetylated wood for 8 h at 120°C. Therefore, lignin of acetylated wood degraded during the process.

XPS analysis

XPS survey spectra of untreated and acetylated larch and pine woods are shown in Fig. 7. The XPS spectra revealed that carbon and oxygen atoms are the major elements in the untreated and acetylated samples, which occur at approximately 284 and 533 eV separately, while some weaker signals associated with the existence of N, Ca, S, Si, and Cl are also present.

The detail O, C moieties and O/C ratios for untreated and acetylated wood are reported in Tab. 2. As shown, the percentage of carbon atoms decreased with acetylation time increasing, while the percentage of oxygen atoms increased. In comparison with untreated wood, the oxygen to carbon (O/C) ratios of acetylated larch wood increased from 0.27 to 0.45, corresponding values of 0.25 to 0.39 for pine wood samples. In principle, the O/C ratio of cellulose, which is made up of β-D-glucopyranose units, is calculated as 0.83. Hemicellulose, which is mainly represented by glucuronoxylans, has an O/C of approximately 0.8. The contribution of lignin is more complex due to its complicated molecular structure. The theoretical value of O/C for lignin is approximately 0.33 (Inari et al. 2006). The O/C ratio of extractives, which are mainly composed of lipophilic compounds, is estimated to be 0.1 (Inari et al. 2011). Therefore, the high polysaccharide content can be reflected by high O/C ratio. In this study, the increase in O/C ratio could be attributed to the introduction of acetyl groups and the increase of the relative content of carbohydrates resulting from the degradation of lignin and the dissolution of extractives.

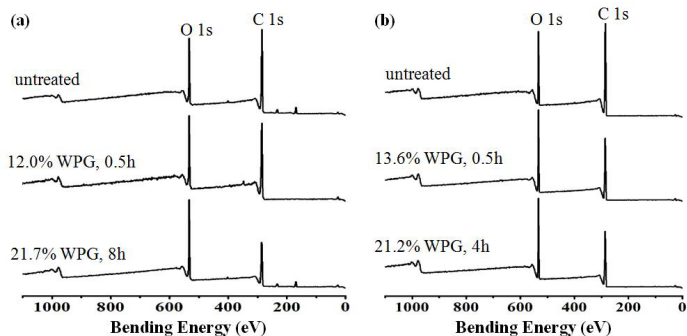


Fig. 7: XPS survey spectra of untreated and acetylated samples: (a) Larch wood; (b) Pine wood.

Tab. 2: The O, C moieties and O/C ratios for untreated and acetylated samples.

Species	Acetylation	Atomic (%)						Atomic ratio
		O	C	C ₁	C ₂	C ₃	C ₄	O/C
Larch	Untreated	20.30	76.37	51.59	18.16	4.44	2.18	0.27
	12.0% WPG, 0.5h	22.46	76.85	41.93	24.86	5.76	4.30	0.29
	21.7% WPG, 8h	30.14	66.57	28.18	27.34	4.91	6.14	0.45
Pine	Untreated	19.67	79.93	49.43	25.00	2.35	3.15	0.25
	13.6% WPG, 0.5h	26.83	73.04	34.03	29.85	3.83	5.33	0.37
	21.2% WPG, 4h	28.17	71.32	31.97	28.83	3.43	7.09	0.39

The C_{1s} signal can be resolved into four types of carbon atoms corresponding to different functional groups, expressed as C₁, C₂, C₃, and C₄, with increasing binding energy, as shown in Fig. 8. The C₁ component corresponding to carbon atoms bonded only with carbon or hydrogen atoms, which mainly arises from lignin and wood extractives (Kamdem et al. 1991). The C₂ component corresponding to carbon atoms bonded with one oxygen atom, which has been shown to be mainly derived from cellulose and hemicelluloses (Kamdem et al. 1991, Wang et al. 2009). The C₃ represents carbon atoms bonded to a carbonyl or two non-carbonyl oxygen atoms, which is assigned to cellulose (Popescu et al. 2016).

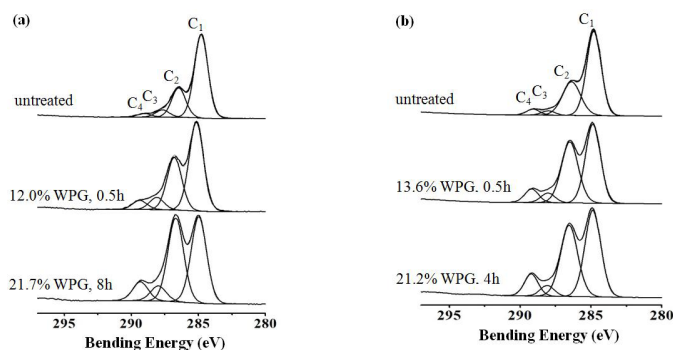


Fig. 8: XPS high resolution C_{1s} spectra of untreated and acetylated samples: (a) Larch wood; (b) Pine wood.

The C₄ represents carbon atoms linked to one carbonyl and one non-carbonyl oxygen atoms (Inari et al. 2006). As shown in Tab. 2 and Fig. 8, C₁ and C₂ components were the major constituents of C_{1s} for untreated and acetylated samples. The C₁ contribution decreased implying the degradation of lignin and the dissolution of extractives. The C₂ signal increased indicating the acetylation of carbohydrates. In addition, the C₄ signal increased indicating the wood acetylation occurred.

CONCLUSIONS

Larch and pine woods were impregnated with acetic anhydride without solvents and catalysts, and then heated in the solvent at 120°C for different reaction durations (0.5–8 h). Weight percent

gain and cell wall bulking were increased with increasing the reaction time indicating the introduction of bulky acetyl groups into the cell wall. In the first 4 hours, acetylation reaction rate was significantly faster than the latter reaction rate. ASE of acetylated larch and pine woods increased to 58.4% and 72.9%. FTIR indicated acetylation of carbohydrates and lignin of wood cell wall polymers occurred, but lignin degraded in the acetylation to a certain extent. This trend was further confirmed by ^{13}C NMR and XPS. It was found though ^{13}C NMR analyses that acetic anhydride was found to react at the carbohydrates C2 and C6 positions in acetylated wood. XPS experiments provided quantitative data about functional groups, which revealed the relative content of carbohydrates increased in the acetylated wood, but carbohydrates also underwent acidic hydrolysis as the reaction time increasing.

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