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A comparative study on the acetylation of wood by reaction with vinyl acetate and acetic anhydride

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ABSTRACT

A comparative study on the acetylation of maritime pine wood by reaction with vinyl acetate (VA) and acetic anhydride (AA) has been undertaken. The reactivity of wood, cellulose and lignin with regards to VA or AA was examined using different techniques. The products dissolved in the reaction medium after acetylation of wood by the two different methods were analyzed by HPLC chromatography. Results suggested that the cellulose sites in wood were more attacked by VA than by AA in our experimental conditions. Besides, the unreacted cellulose sites of the AA-acetylated sample could be further esterified by vinyl propionate, which ^{13}C NMR signals could be differentiated from the acetyl signals. The esterified materials obtained after modification of isolated cellulose and lignin were also characterized by FTIR, ^{13}C CP-MAS NMR and ^{13}P NMR spectroscopy and compared. Results indicated that VA could acetylate both biopolymers, but they also showed that AA reacted more readily with lignin than VA. Moreover, FTIR spectroscopy revealed that unexpected side reactions concurrently occurred in lignin when VA was used. It is hypothesized that some C-acetylation also took place between VA and a number of lignin aromatic rings during the treatment.

1. Introduction

Wood esterification has been shown to be very effective in improving the material performances (Hon, 1996; Hill, 2006). In particular, wood acetylation with acetic anhydride has received the most attention and the acetylated product is now commercialized in Europe since 2007. Many studies have shown that the dimensional stability, fungal resistance, photostability and weathering of wood could be greatly enhanced by this treatment (Chang & Chang, 2001; Evans, Wallis, & Owen, 2000; Hon, 1996; Hill et al., 2005; Hill, 2006; Larsson Brelid, 2002; Larsson Brelid, Simonson, Bergman, & Nilsson, 2000; Ohkoshi, 2002). Other acetylation methods involving acetyl chlorides (Kumar, Dev, & Singh, 1991; Singh, Dev, & Kumar, 1981), thioacetic acid (Kumar et al., 1991; Singh, Dev, & Kumar, 1979), ketene (Hill, 2006; Rowell, Wang, & Hyatt, 1986) or more recently vinyl acetate (Jebrane & Sèbe, 2007), have been also proposed. Acetylated materials are produced in all cases but different reactions can lead to different performances, the benefits of the treatment depending strongly on the process conditions. For instance, the by-products generated by the different acetylation methods may have a variable impact on the material properties. With acetyl chloride as reactant, a strong acid – hydrochloric acid – is released, which catalyses the hydrolysis of holocellulose and leads to important strength losses of the material (Hill, 2006). A weaker acid – acetic acid – is liberated when acetylation is performed with acetic anhydride, but this compound is generally hard to remove from wood after reaction, imparting an undesirable odour to the wood and causing strength losses or the corrosion of metal fasteners (Larsson Brelid, 2002; Li, Furuno, & Katoh, 2000; Simonson & Rowell, 2000). Recently, wood has been successfully acetylated by a new method based on the transesterification of vinyl acetate (Jebrane & Sèbe, 2007). Acetylated wood was obtained under mild conditions and in high yield, with potassium carbonate as a catalyst. One clear advantage of this method is that the by-product released is acetaldehyde, which is non-acidic and can be easily removed from wood after reaction because of its low boiling point ($b.p._{[760\ mm\ Hg]} = 21\ ^{\circ}C$). But at this stage of the research, very little is known about the actual reactivity of vinyl acetate with regards to the different biopolymers in wood. Preliminary results suggested that vinyl acetate reacted more readily with cellulose than acetic anhydride (Jebrane & Sèbe, 2007), but further work is needed to clarify this point. Different reactivity between vinyl acetate and acetic anhydride could lead to differences in the final properties of the material, as was reported with starch (Huang, Schols, Jin, Sulmann, & Voragen, 2007).

In the present paper, a comparative study on the acetylation of wood by reaction with vinyl acetate (VA) and acetic anhydride (AA) is proposed. Wood, cellulose and lignin were acetylated by

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Table 1
Fraction of lignin and polysaccharides dissolved in the reaction medium after esterification with VA or AA.

Treatment	Fraction dissolved (%)[a]	Polysaccharide content (%)[b]						Lignin (%)[b]	Other (%)[c]
		Cellobiose	Glucose	Xylose	Galactose	Arabinose	Mannose		
VA	3.0	0.3	31.7	2.4	1.1	1.5	42.0	17.2	3.8
AA	2.5	1.4	0.2	2.5	3.5	0.5	2.4	88.5	1.0

[a] Weight percentage of biopolymers dissolved in DMF based on unmodified dry wood before modification.
[b] Weight percentage of sugars or lignin contained in the residue dissolved in DMF, based on initial dry weight.
[c] Weight percentage of unidentified products detected by HPLC.

VA or AA and the differences between the two reaction processes were investigated. The products dissolved in the reaction medium after acetylation were analyzed by HPLC chromatography and the esterified solid materials were characterized by FTIR, ^{13}C CP-MAS NMR and ^{13}P NMR spectroscopy. The different reactivity of VA and AA with regards to wood biopolymers was discussed.

2. Materials and methods

2.1. Materials and chemicals

Maritime pine sapwood (*Pinus pinaster* Soland) was ground in a Wiley mill to pass a 0.5 mm screen. Prior to use, the sawdust was extracted in a Soxhlet apparatus with a mixture of toluene:ethanol (2:1, v/v) for 8 h, and then with water for an additional 8 h, to remove all extractives. Wood was then oven-dried at 105 °C for 16 h and cooled to ambient temperature in a desiccator over phosphorus pentoxide.

Maritime pine lignin was extracted from a thermomechanical pulp provided by the ISOROY company. The isolation procedure has been reported elsewhere (Gellerstedt, Pranda, and Lindfors, 1994). Cellulose was purchased from Whatman (CF11 fibrous cellulose powder).

Vinyl acetate (VA), vinyl propionate (VP), acetic anhydride (AA), dimethylformamide (DMF), potassium carbonate (K_2CO_3), 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, cellobiose, glucose, xylose, galactose, arabinose and mannose were purchased from Sigma–Aldrich. DMF was previously dried over molecular sieve (4 Å).

2.2. Esterification reactions

All chemical reactions were performed under a standard set of conditions, in a round-bottomed flask equipped with a condenser and a calcium chloride drying tube. For 1 g of dry starting material (wood, cellulose or lignin), solutions containing 14 mmol of VA, VP or AA and 20 ml of DMF were used. The amount of reagent used is based on an estimation of the concentration of hydroxyl groups in maritime pine, calculated from a formula described by Hill and Jones (1996). The VA- and VP-esterifications were performed at 90 and 110 °C respectively, with 1.1 mmol K_2CO_3/g of dry starting material as catalyst. The AA-acetylation was performed at 90 °C without catalyst, or at 100 °C with pyridine as catalyst (7 mmol/g dry wood). Reactions with wood were conducted for 6 h (VA and AA), or for 4 h (VP). Reactions with cellulose or lignin, were conducted for 3 h. After reaction, wood samples were Soxhlet extracted with a mixture of toluene:ethanol:acetone (4:1:1 v/v/v) for 8 h, to remove all non-bonded chemicals (i.e. unreacted compounds and by-products formed). When K_2CO_3 was used as catalyst, the samples were additionally extracted with water for 2 h (prior to the toluene:ethanol:acetone extraction), to eliminate the catalyst. Cellulose and lignin samples were rinsed several times with water and ethanol during the filtration process. All modified materials were finally oven-dried at 105 °C for 16 h, and the weight percent gain (WPG) was calculated as follows: $WPG = ((M_1 - M_0/M_0) \times 100)$ where M_0 and M_1 are the oven-dried weights of the sample, before and after esterification, respectively.

2.3. HPLC analysis of the biopolymers dissolved in the reaction medium

The biopolymers dissolved in the reaction medium after acetylation by VA or AA were analyzed by HPLC according to a general procedure described elsewhere, with minor modifications (Kaar, Cool, Merriman, & Brink, 1991). The liquid phase remaining after the treatment of 10 g of maritime pine sawdust was recovered and the liquid products (i.e. DMF, excess reactants and by-products formed) were eliminated by vacuum evaporation. The solid residue remaining was then dried and weighed (300 and 250 mg, with VA and AA, respectively) and the weight percentage of biopolymers dissolved in the reaction medium was evaluated ('Fraction dissolved' in Table 1). The polysaccharides present in the residue were then hydrolyzed to their sugar monomers by sulfuric acid: the solid residue was stirred in beaker with 9 ml (VA) or 7.5 ml (AA) of 72% sulfuric acid during 4 h at room temperature. 300 ml of deionized water were added and the mixture was refluxed for 4 h. The insoluble fraction (i.e. klason lignin) was filtrated out, rinsed, dried and weighed to evaluate the lignin content. The volume of the filtrate was adjusted to 500 ml by adding deionized water and neutralized until pH 7 with $Ba(OH)_2{\cdot}8H_2O$. After centrifugation at 10 °C for 20 min, the supernatant was concentrated and analyzed by HPLC for sugar analysis. The sugar were separated on a ThermoFinnigan HPLC system equipped with a BIO-RAD Aminex column (HPX-87P) and a Water 410 differential refractometer, at 85 °C, with dionized water as eluant and a flow rate of 0.6 ml/min. The different sugar concentrations were determined using standard solutions of cellobiose, glucose, xylose, galactose, arabinose, and mannose. The weight percentage of sugars contained in the initial residue ('polysaccharide contents' in Table 1) was then calculated, based on initial dry weight.

2.4. ^{31}P NMR analysis of lignin

Unmodified lignin and VA-acetylated lignin were analyzed by ^{31}P NMR spectroscopy, following the procedure developed by Argyropoulos (1994) and Granata and Argyropoulos (1995). 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane was used as a phosphitylating agent and cholesterol was used as internal standard.

After phosphitylation of lignin and cholesterol, the ^{31}P NMR spectra were recorded on a Bruker DPX-200 NMR spectrometer, at a frequency of 81.03 MHz. Chemical shifts were calibrated to the ^{31}P cholesterol signal at 144.9 ppm. The spectra were run in the conditions reported by Argyropoulos (1994).

2.5. FTIR spectroscopy

Infrared absorption spectra of treated and unmodified samples were obtained with the potassium bromide technique (KBr), using a Perkin-Elmer Paragon 1000 PC FTIR spectrometer, at a resolution

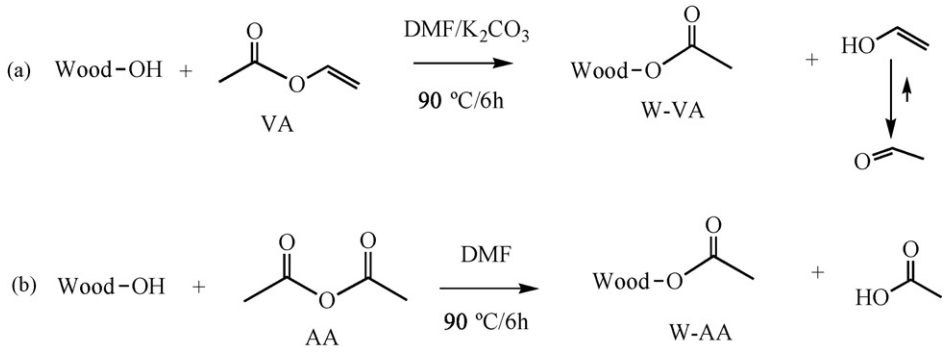

Fig. 1. General schemes for the acetylation of wood by reaction with vinyl acetate (a) or acetic anhydride (b).

of 4 cm^{-1} (50 scans). In each case, a small amount of dry material (wood: 3%, w/w; cellulose and lignin: 0.5%, w/w) was dispersed in a matrix of KBr and pressed to form pellets.

2.6. ^{13}C CP-MAS NMR spectroscopy

Solid-state ^{13}C CP-MAS NMR spectra were obtained at room temperature on a Bruker DPX-400 NMR spectrometer, using MAS rates of 4–8 kHz, at a frequency of 100.61 MHz. The sample was packed in MAS 4 mm diameter zirconia rotors. Chemical shifts were relative to tetramethylsilane used as an external standard. All the spectra were run for 15 h (25,000 scans).

3. Results and discussion

Extracted maritime pine sapwood sawdust was reacted with vinyl acetate (VA) and acetic anhydride (AA) according to the general schemes presented in Fig. 1. With VA, the vinyl alcohol formed during the process tautomerizes to acetaldehyde and the equilibrium is shifted towards the formation of acetylated wood. With AA, acetic acid is released as a by-product. Reactions with VA and AA were performed in the same conditions except that catalytic amounts of potassium carbonate were added in the case of the VA-acetylation. The AA-acetylation can be easily performed in DMF, without additional catalyst, but the reaction with VA is ineffective without K_2CO_3 (Jebrane & Sèbe, 2007). After 6 h of reaction, WPG's of 26.4 and 23.9% were obtained with VA and AA respectively, and the formation of ester bonds was confirmed by FTIR spectroscopy (Jebrane & Sèbe, 2007).

During reaction, some of the biopolymers may be sufficiently acetylated to become soluble in the reaction medium. Accordingly, the products dissolved in DMF during the two different treatments were analyzed by HPLC chromatography: after vacuum elimination of the liquid products (i.e. DMF, excess reactants and by-products formed), the solid residue was hydrolyzed in acidic conditions and analyzed. The weight percentages of the different sugars detected in the hydrolysates after reaction are presented in Table 1. The lignin percentage was deducted from the acid insoluble fraction (klason lignin). The small fraction of unidentified products detected ('Other' in Table 1) was assigned to the acetic acid released after hydrolysis of the acetate groups. The amount of biopolymers dissolved in DMF during the acetylation process was slightly lower when AA was used (2.5%). The nature of these biopolymers was also very different depending on the reactant used. With AA, the major biopolymer detected in the hydrolysate was lignin (88.5%), which means that lignin acetates were mostly dissolved in the reaction medium. This trend is confirmed by the FTIR spectrum in Fig. 2b, which pattern resembles more of a pattern of acetylated lignin rather than a pattern of acetylated holocellulose (see Fig. 4). The characteristic vibrations of the grafted acetyl groups can be seen at 1750 cm^{-1} ($\nu_{(C=O)}$), 1377 cm^{-1} ($\delta_{(CH3)}$) and 1180–1300 cm^{-1} ($\nu_{(C-O)}$). This result suggests that AA reacted more readily with lignin than with the polysaccharides, and since only a residual amount of glucose was detected (0.2%), hemicelluloses were apparently more reactive than cellulose. This result is in agreement with the literature data, which indicates that the reactivity of the wood cell wall polymers to AA decrease in the order lignin > hemicelluloses > cellulose, both within the wood cell wall and with the isolated polymers (Efanov, 2001; Hill, 2006; Rowell et al., 1994). With VA on the other end, 79% of sugars were detected in the hydrolysate (mostly glucose and mannose, the main monomers found in the cellulose and hemicelluloses), indicating that esters of cellulose and hemicelluloses were mostly dissolved. This result in agreement with the FTIR spectrum in Fig. 2c, which pattern resembles the pattern of acetylated cellulose (comparison with spectrum in Fig. 3a). The lignin fraction was about 17.2%, which is close to the lignin ratio found in maritime pine (~25%). Accordingly, it is believed that lignin and polysaccharides within the wood structure have a similar reactivity with regards to VA, leading to ester concentrations in DMF reproducing the lignin/polysaccharides ratio found in wood.

Since the reactivity of the isolated wood polymers to VA has never been investigated, pure cellulose and lignin were also reacted with VA and analyzed by FTIR and NMR spectroscopy (reactions in

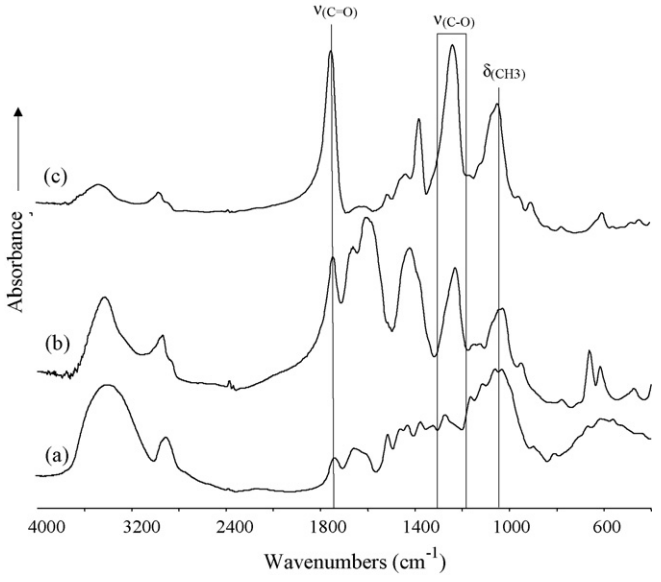

Fig. 2. FTIR spectroscopy of unmodified wood (a) and of the residue dissolved in DMF after acetylation with AA (b) or VA (c).

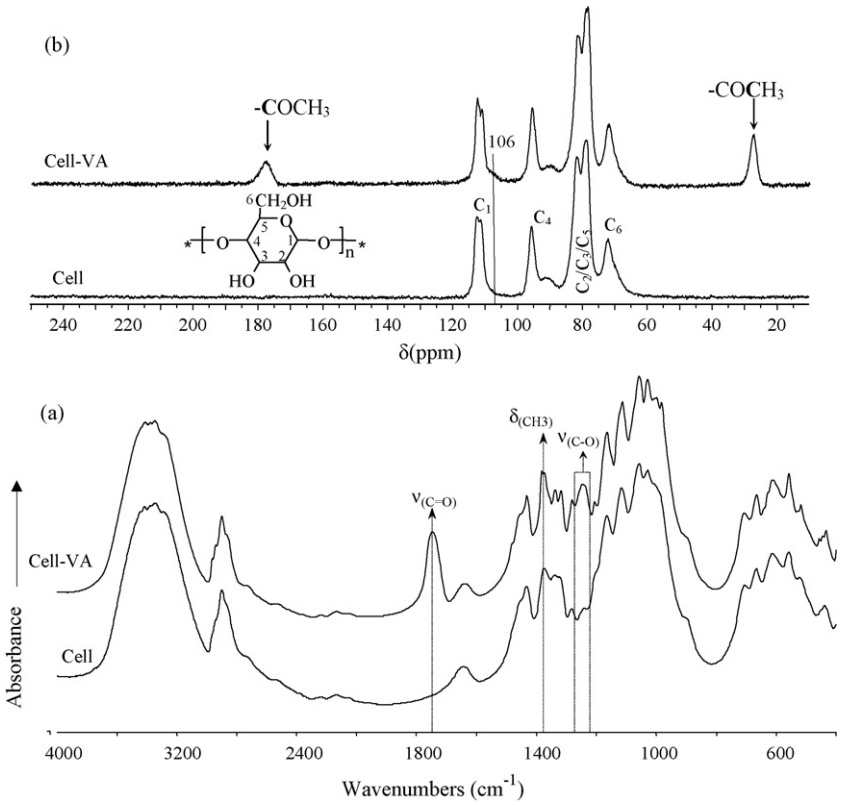

Fig. 3. FTIR spectrum (a) and ^{13}C CP-MAS NMR spectrum (b) of cellulose before (Cell) and after reaction with VA (Cell-VA) (insoluble fraction).

the same conditions than with wood but for 3 h instead of 6 h). After reaction, the insoluble fractions were filtered and weighed: weight losses of 10.4% and 17.2% were measured with cellulose and lignin, respectively, indicating that part of the material was dissolved in the reaction medium, most probably in the form of esters (cellulose and lignin acetates). The FTIR and ^{13}C CP-MAS NMR spectra of VA-treated cellulose (insoluble fraction) confirmed the introduction of acetyl functions after the treatment (Fig. 3). The signals of the grafted acetyl groups in the FTIR spectrum are observed at 1745 cm^{-1} ($\nu_{(C=O)}$), 1373 cm^{-1} ($\delta_{(CH3)}$) and 1220–1270 cm^{-1} ($\nu_{(C-O)}$), and in the ^{13}C CP-MAS NMR spectrum at 27 and 178 ppm. The chemical shifts corresponding to the different carbons of cellulose are directly assigned on the NMR spectrum (C_1, C_2, C_3, C_4, and C_6). The shoulder at 106 ppm has been assigned to the upfield shift expected after acetylation of the OH at the C_2 position (Dicke, 2004; Yoshimoto, Itatani, & Tsuda, 1980). No obvious differences between the FTIR and NMR spectra of cellulose acetylated by VA or AA were detected.

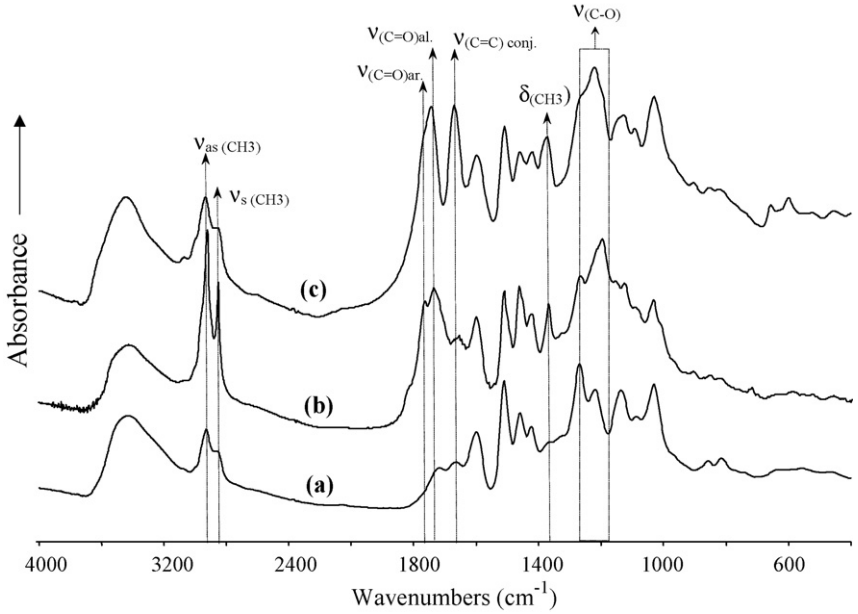

Fig. 4. FTIR spectra of lignin before (a) and after reaction with AA (b) or VA (c) (insoluble fraction). s, symmetric; as, asymmetric; ar., aromatic; al., aliphatic, conj., conjugated.

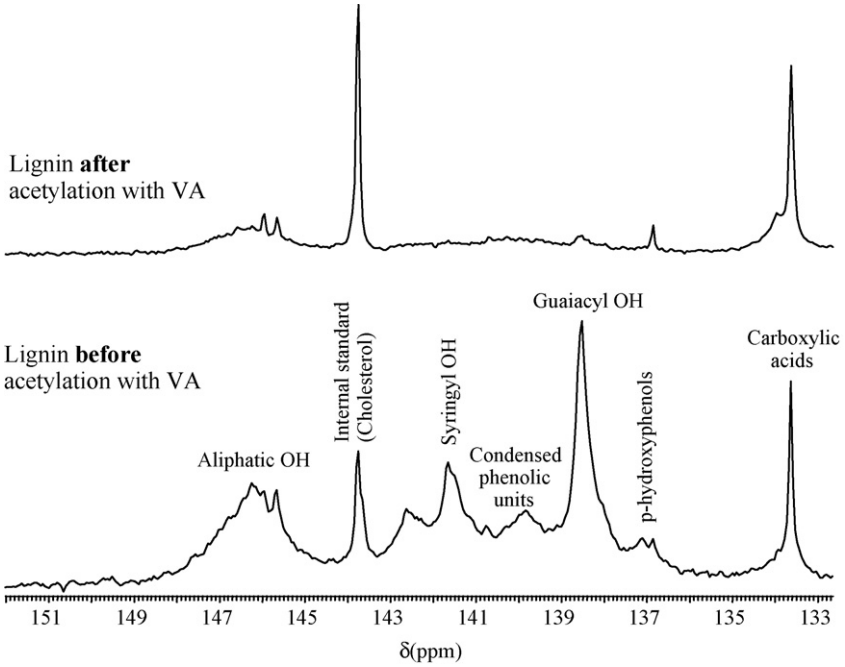

Fig. 5. ^{31}P NMR spectra of phosphitylated lignin before (bottom) and after acetylation with VA (top).

The VA-acetylation of lignin was also confirmed by FTIR spectroscopy. But this time, differences were noted when the spectra of VA- and AA-acetylated lignin were compared (Fig. 4). The characteristic vibrations of the grafted acetyl groups were easily identified in both cases. After acetylation of the aromatic and aliphatic OH in lignin, two carbonyl stretching vibrations are observed at 1760 and 1740 cm^{-1}, respectively, in line with the literature data (Glasser & Jain, 1993). The two bands are more differentiated in the spectrum of AA-acetylated lignin, suggesting that different aromatic/aliphatic acetyl ratios are obtained with AA and VA. The $\delta_{(CH3)}$ can be seen at 1373 cm^{-1} and the ν_{C-O} in the 1175–1260 cm^{-1} region of both spectra, but differences in the shapes and intensities are noted. The ν_{C-O} and C–H stretching vibrations of the methyl group ($\nu_{s\ (CH3)}$ and $\nu_{as\ (CH3)}$ at 2850 and 2940 cm^{-1}) are particularly strong in the case of AA-acetylated lignin, indicating that lignin was much more attacked by AA after 3 h of reaction. This result can be explained by differences in the kinetics of reaction when VA or AA is used, the reaction with AA being generally faster than with VA (Huang et al., 2007). But the unusual vibration observed at 1670 cm^{-1} in the spectrum of VA-acetylated lignin (Fig. 4c), suggests that other reactions occurred in that case. This band is typical of conjugated carbonyl stretching vibrations (Silverstein, Bassler, & Morill, 1991). An explanation could be that benzoyl moieties are produced with the VA/DMF/K_2CO_3 system, by C-acetylation of a number of lignin aromatic rings (i.e. the acetyl group is directly attached to an aromatic carbon). Similar Friedel-Crafts acylations have been proven between aromatic systems and enol esters, with aluminium chloride as catalyst (Rothman & Moore, 1970). Such reactions are generally catalysed by Lewis acids, but recent studies have shown than DMF complexes (such as the I_2/DMF complex) could be also very effective (Guenadil, Aichaoui, Lambert, McCurdy, & Poupaert, 2008). Maybe in lignin, the DMF/K_2CO_3 complex concurrently catalyses the C-acylation of some phenyl propane units, which could be activated by the presence of the many electron-donating groups on the aromatic ring (+M effect of hydroxyl, methoxyl or acetoxyl groups). Additional work is needed to clarify this point.

In order to identify which type of hydroxyl groups in lignin reacted with VA, the lignin samples (acetylated and control) were characterized by ^{31}P NMR spectroscopy after phosphitylation with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane. The method allows detecting the different type of hydroxyl groups present in lignin after derivatization of the labile protons with a phosphitylating agent (Argyropoulos, 1994; Granata & Argyropoulos, 1995). The ^{31}P NMR spectra of phosphitylated lignin, before and after acetylation with VA, are presented in Fig. 5. The signals corresponding to the different types of hydroxyl groups are assigned directly on the figure. Cholesterol was used as an internal standard. As expected with softwoods, the starting maritime pine lignin is in majority composed of phenolic units of the guaiacyl type; but aliphatic hydroxyl groups are also present. After the treatment with VA, the signals of the guaiacyl, syringyl and condensed phenolic units were strongly reduced, indicating that most of the phenolic OH were acetylated. Only some p-hydroxyphenol units remained unreacted. Acetylation of aliphatic sites was only partial since some aliphatic OH remained accessible to the phosphitylating agent (signals in the 145–148 ppm region). The OH of the carboxylic acid groups were apparently not affected by the VA-treatment.

Since only a residual amount of glucose is detected in the reaction medium after acetylation of wood with AA, we can assume that the cellulose sites were moderately modified in that case (Table 1). With VA on the other hand, 31.7% of glucose were detected in the reaction medium, suggesting that cellulose was significantly attacked (cellulose acetates are soluble in DMF at high degree of substitution). The ^{13}C CP-MAS NMR results in our preliminary experiments seem to agree with this interpretation (Jebrane & Sèbe, 2007). To confirm this trend, we envisaged esterifying further the unreacted cellulose sites of the AA-acetylated sample, using the vinyl ester method. Since the samples acetylated by AA or VA cannot be easily differentiated by the FTIR or ^{13}C CP-MAS NMR methods, vinyl proprionate (VP) was selected instead of VA, as second acylating agent. A similar reactivity between VA and VP is anticipated, and the propionyl groups grafted in AA-acetylated wood should be easily discriminated from the acetyl groups by ^{13}C CP-MAS NMR spectroscopy (Fig. 6). To make sure that most of the sites susceptible of reacting with AA in wood are acetylated, stronger reaction conditions were employed: the AA-acetylation was performed at 100 °C (instead of 90 °C), and with pyridine as a catalyst. In these condi-

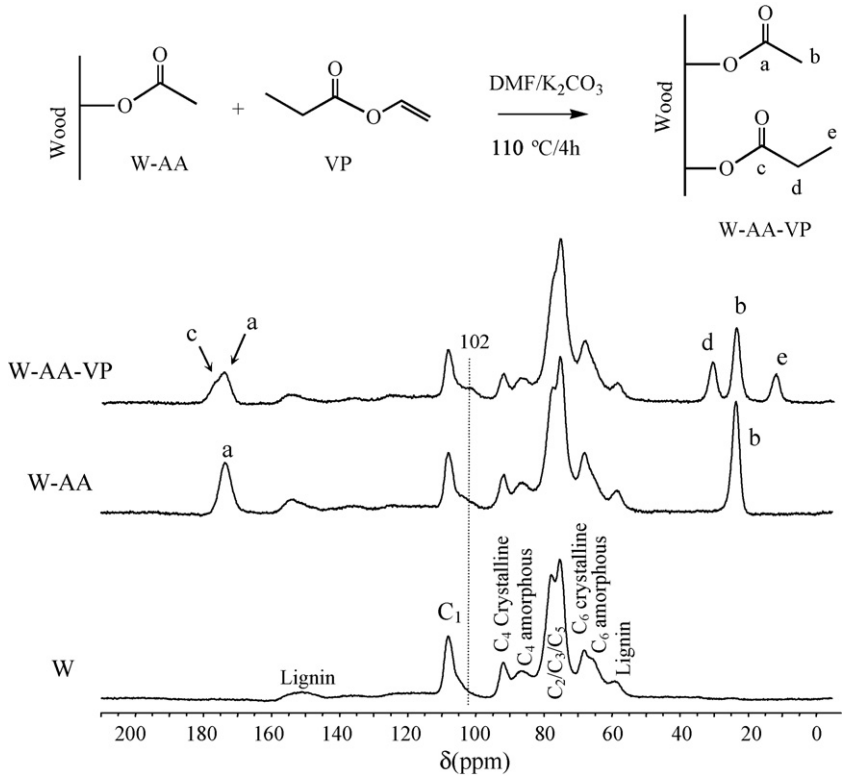

Fig. 6. ^{13}C CP-MAS NMR spectra of unmodified wood (W) and AA-acetylated wood, before and after reaction with VP (W-AA and W-AA-VP, respectively).

tions, a WPG of 20.5% was measured, which is slightly less than the WPG obtained in the former conditions (23.9%). More esterified biopolymers were probably dissolved in the reaction medium due to the harsher conditions. Since VP is bulkier than VA, a lower reactivity is anticipated. Accordingly, the second esterification with VP was performed at 110 °C instead of 90 °C (the reaction time was limited to 4 h). A 3% increase in weight was measured after the VP-treatment, which corresponds to a total WPG of about 25% based on the unmodified dry starting material (i.e. before the AA treatment). The ^{13}C CP-MAS NMR spectra of AA-acetylated wood, before and after reaction with VP, are presented in Fig. 6. The carbons of cellulose and lignin are assigned directly on the spectra (the carbons of hemicelluloses are hidden by the strong cellulose signals). The carbons of the grafted acetyl moieties in AA-acetylated wood are easily identified at 174 ppm (a) and 23 ppm (b). The decrease in the intensity of the signal at 65 ppm indicates that cellulose was partially acetylated by AA, at the C_6 amorphous position. The degree of substitution of cellulose is probably too low to induce a partial solubilisation of cellulose acetates in the reaction medium (Table 1). After the treatment with VP, additional chemical shifts corresponding to the grafted propionyl groups emerge at 176 ppm (c), 30 ppm (d) and 12 ppm (e), confirming that a significant number of OH sites in AA-acetylated wood were further esterified. The changes in the intensity of the cellulose signals observed in the 70–80 ppm region indicate that cellulose reacted at the C_2 and/or C_3 position. The shoulder that emerged at 102 ppm has been assigned to the upfield shift expected after esterification of the OH at the C_2 position (Jebrane & Sèbe, 2007). A decrease in the intensity of the signals of the acetyl functions is also observed after the VP-treatment. At the end of the reaction, the intensity of the c, d and e signals is only slightly lower than the intensity of the a and b signals, suggesting that the amount of propionyl functions in wood is higher than what the 3% weight increase predicted. It is believed that some concomitant solubilisation of esterified biopolymers occurred during the VP-treatment. After propionylation of the cellulose OH at the C_2 and/or C_3 positions (cellulose being already acetylated by AA at the C_6 position), some cellulose esters (mixed acetates and propionates) could have dissolved in the reaction medium, leading to a loss in acetyl moieties. Maybe some deacetylation also occurred by ester/ester interchange reactions between the acetyl functions in wood and the propionyl functions of VP. Similar transesterification reactions have been previously evidenced between acetylated wood and methyl benzoate, with dibutyltin oxide as a catalyst (Özmen, Çetin, Tingaut, & Sèbe, 2006).

4. Conclusions

In conclusion, we have found that the VA/DMF/K_2CO_3 and AA/DMF systems have a different reactivity with regards to wood components and also to the isolated biopolymers, when the reactions are performed in the same conditions. Both of these systems allow to prepare acetylated wood in similar yield, but the HPLC analysis of the products dissolved in the reaction medium after acetylation suggested that cellulose sites in wood were more attacked by VA than by AA, which confirms our previous hypothesis (Jebrane & Sèbe, 2007). This trend was further confirmed by an additional experiment, when we envisaged esterifying the unreacted cellulose sites of the AA-acetylated sample with vinyl propionate (VP). VP was found to react at the cellulose C_2 and/or C_3 position in AA-acetylated wood but the treatment also induced the loss of a number of acetyl moieties. This was assigned to the solubilisation of some cellulose esters during the VP-treatment and/or a partial deacetylation by ester/ester interchange reaction. Experiments with isolated lignin and cellulose indicated that VA could acetylate both biopolymers, but results also showed that AA reacted more readily with lignin than VA in our experimental conditions. Moreover, FTIR spectroscopy revealed that unexpected side reactions concurrently occurred when VA was used. An explanation could be that benzoyl moieties are produced with the VA/DMF/K_2CO_3 system, by C-acetylation of a number of lignin aro-

matic rings. Further investigations are however needed to clarify this point.

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