ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

Carbohydrate Polymers 72 (2008) 657–663

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

A new process for the esterification of wood by reaction with vinyl esters

Mohamed Jebrane, Gilles Sèbe *

Unité Sciences du Bois et des Biopolymères, Université Bordeaux 1, INRA, CNRS, UMR US2B, 351 Cours de la Libération, Talence F-33405, France

Received 30 August 2007; received in revised form 27 September 2007; accepted 4 October 2007
Available online 12 October 2007

Abstract

A novel route to wood modification by transesterification of vinyl esters is developed in the current study. The reaction between varied saturated and unsaturated vinyl esters and the hydroxyl groups of maritime pine sapwood (*Pinus pinaster* Soland) was examined using potassium carbonate as a catalyst. The esterification of wood was investigated by weight percent gain calculations (WPG), Fourier-transform infrared spectroscopy (FTIR) and ^{13}C cross-polarization with magic-angle spinning nuclear magnetic resonance spectroscopy (^{13}C CP–MAS NMR). Differences in the rates of modification were noted, depending on the vinyl ester used, but relatively high yields were obtained in all cases. The infrared and NMR spectra of the different esterified samples were analysed in detail and the assignment of the signals corresponding to the grafted acyl groups confirmed that esterification occurred.

Keywords: ^{13}C CP–MAS NMR spectroscopy; Chemical modification; Esterification; FTIR spectroscopy; Vinyl ester; Wood

1. Introduction

Chemical modification has proven to be a very effective means of improving the material properties of wood (Hill, 2006; Hon, 1996; Rowell, 1983; Rowell, 2006). Among the many reactions examined, esterification using acid chlorides or anhydrides have received the most attention and have been reported to greatly improve a number of wood properties. The dimensional stability and fungal resistance of wood can be greatly enhanced if esterification is performed in the bulk of the material, e.g., if the cell walls are modified (Chang & Chang 2003; Hill & Jones, 1996; Hill et al., 2005; Iwamoto & Itoh, 2005; Iwamoto, Itoh, & Minato, 2005; Larsson, Brelid, Simonson, Bergman, & Nilsson, 2000; Li, Furuno, & Katoh, 2000; Prakash, Pandey, Ram, & Mahadevan, 2006; Rowell, 2003; Rowell, 2006). The photostability and weathering resistance of the wood surfaces can be also improved by such treatments (Chang & Chang, 2001a,b, 2003; Evans, 1998; Evans, Owen, Schmid, & Webster, 2002; Evans, Wallis, & Owen, 2000; Ohkoshi, 2002; Prakash et al., 2006). However, these esterification methods generate unwanted acidic by-products that can degrade wood. For example, the hydrochloric acid released after the reaction of wood with acyl chlorides catalyses the hydrolysis of holocellulose and leads to strength losses. Weaker acids are liberated when esterification is performed with acid anhydrides, but these are generally hard to remove from wood after the reaction and impart an undesirable odour to the wood and may cause strength losses or the corrosion of metal fasteners (Larsson Brelid, 2002; Li et al., 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.$_{[760\ \mathrm{mm\ Hg}]}$ = 21 °C). In this preliminary work, vinyl acetate was used as an acetylating agent, but if other vinyl esters were used, it is possible that a wide variety of acyl groups could be grafted in wood by this method.

---

* Corresponding author. Tel.: +33 (0)5 40 00 64 11; fax: +33 (0)5 40 00 64 39.
E-mail address: g.sebe@us2b.u-bordeauxl.fr (G. Sèbe).

0144-8617/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2007.10.001

In the present paper, the transesterification reaction between varied saturated and unsaturated vinyl esters and the hydroxyl groups of wood, using potassium carbonate as a catalyst, was investigated further. Reactions were performed on maritime pine sapwood sawdust (*Pinus pinaster* Soland), with dimethylformamide as a solvent. The chemical modifications were characterised by weight percent gain (WPG) calculations, FTIR and ^{13}C CP–MAS NMR spectroscopy.

2. Materials and methods

2.1. Chemicals

Vinyl propionate, vinyl butyrate, vinyl pivalate, vinyl decanoate, vinyl stearate, vinyl crotonate, vinyl methacrylate, vinyl cinnamate, vinyl benzoate, vinyl 4-*tert*-butylbenzoate, dimethylformamide (DMF) and potassium carbonate (K_2CO_3) were purchased from Sigma–Aldrich. DMF was previously dried over molecular sieve (4 Å).

2.2. Wood treatment

Maritime pine sapwood (*P. 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. All chemical reactions were performed under a standard set of conditions, in a round-bottomed wide-mouthed flask equipped with a condenser and a calcium chloride drying tube. Reagent solutions consisting of 14 mmol vinyl ester/g dry wood, 0.15 g K_2CO_3 and 20 ml DMF were used throughout. The amount of vinyl ester 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). Each reaction was conducted with 1 g extracted sawdust, at 90 °C and for 3 h. All modified materials were subsequently extracted with water for 2 h, as above, to eliminate the catalyst K_2CO_3, then 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 any by-products). Samples were finally oven-dried at 105 °C for 16 h, and the weight percent gain (WPG) was calculated as follows: $\mathrm{WPG} = \frac{M_1 - M_0}{M_0} \times 100$, where M_0 and M_1 are the oven-dried weights of the sample, before and after esterification, respectively. The number of OH groups substituted in wood after each treatment was calculated from the WPG and the molecular weight of the adduct, assuming a 1:1 molar reaction between the vinyl esters and wood hydroxyl groups. The formula used accounts for the hydrogen atom transferred from wood to the vinyl alcohol (−1 in the formula):

$$\text{OH substituted (in mmol/g dry wood)} = \frac{(0.01 \times \mathrm{WPG})}{(\text{Molecular weight of adduct} - 1)} \times 1000.$$

2.3. Infrared spectroscopy (FTIR)

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 of 4 cm^{-1} (50 scans). In each case, 3% w/w of dry sawdust was dispersed in a matrix of KBr and pressed to form pellets.

2.4. ^{13}C CP–MAS NMR spectroscopy

Solid state ^{13}C CP–MAS NMR spectra of treated and unmodified samples 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. Sawdust 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

Transesterification is the process of exchanging the alkoxyl group of an ester compound by another alcohol. Since the reaction is an equilibrium, continuous removal of the alcohol produced is needed to obtain the desired ester in good yield. But with enol esters, the vinyl alcohol formed during the process tautomerizes to acetaldehyde and the equilibrium is naturally shifted towards the ester formation (Otera, 1993). The interchange reaction between alkoxyl (and/or phenoxyl) groups of wood and vinyl esters should therefore lead to the formation of esterified wood with acetaldehyde as a by-product (Fig. 1). Unlike carboxylic acids, acetaldehyde is a highly volatile compound that can be easily removed from wood after reaction (b.p.$_{[760\ \mathrm{mm\ Hg}]}$ = 21 °C).

The reaction between wood and vinyl acetate has been confirmed in a previous study, with potassium carbonate as a catalyst (Jebrane & Sèbe, 2007), but the feasibility of the reaction with other vinyl esters has not been demonstrated yet. Reactions performed here were derived from our previous investigations with vinyl acetate: DMF as a

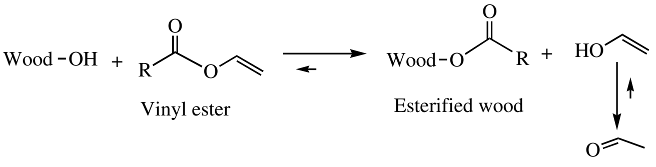
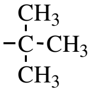
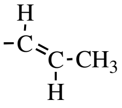
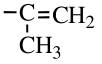
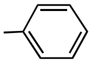
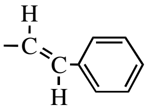
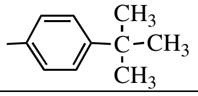


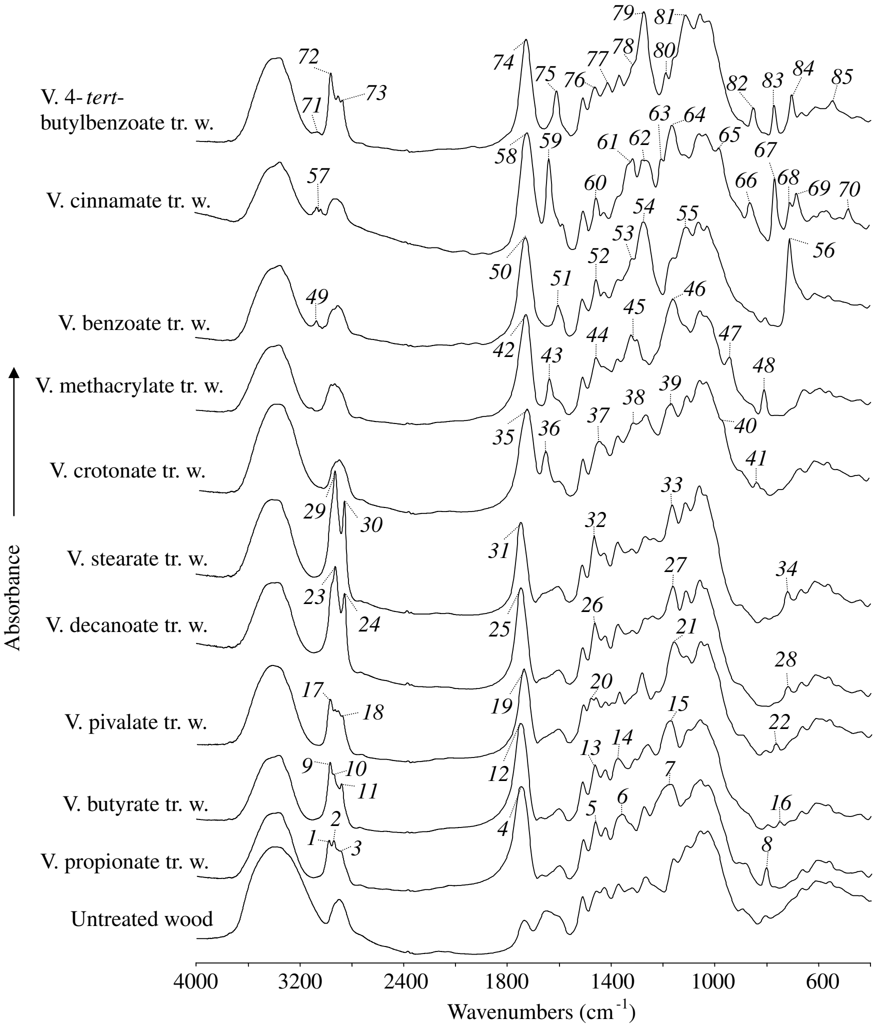
Fig. 1. Esterification of wood using the transesterification reaction between wood hydroxyl groups and vinyl esters.

solvent, 90 °C, 3 h and 1.1 mmol K_2CO_3/g dry wood. The vinyl esters used and the weight percentage gains (WPG) obtained after reaction are presented in Table 1. The number of OH groups substituted in wood after each treatment is also reported (in mmol/g dry wood) assuming a 1:1 molar reaction between the vinyl esters and wood hydroxyl groups. Relatively high WPG's were obtained in all cases, indicating that a significant amount of chemicals remained bounded to wood after reaction and extensive extraction with appropriate solvents. Differences in the rates of modification were, however, noted depending on the vinyl ester used, but since no statistical analysis was done only general trends will be discussed. With saturated vinyl esters, the rate of OH groups substituted decreased with increasing molecular weight of the reactant, probably because of differences in the kinetics of diffusion within the wood cell walls. A similar trend was observed with the aryl-containing vinyl esters. Several kinetics studies performed with acetic anhydride demonstrated that reactions with wood were controlled by the diffusion of the reagent within the material (Hill, Jones, Strickland, & Çetin, 1998; Minato, 2004; Minato & Ito, 2004). Lower kinetics of diffusion are therefore logically expected when the vinyl esters are bulkier. But the type of substituent (R group in Fig. 1) probably also affects the reactivity of the carbonyl group, especially when saturated and unsaturated reactants are compared. The difference in reactivity noted between vinyl crotonate and vinyl methacrylate can not been explained at present.

Table 1
Weight percentage gains (WPG) and substitution rates obtained after the transesterification of different saturated and unsaturated vinyl esters with wood hydroxyl groups

Vinyl esters [$CH_2{=}CH{-}O{-}CO{-}R$]	—R	WPG (%)	OH groups substituted (mmol/g dry wood)
Vinyl propionate	$-CH_2-CH_3$	23.6	4.2
Vinyl butyrate	$-CH_2-CH_2-CH_3$	30.0	4.3
Vinyl pivalate	 $-C(CH_3)_3$	15.2	1.8
Vinyl decanoate	$-CH_2(CH_2)_7CH_3$	49.6	3.2
Vinyl stearate	$-CH_2(CH_2)_{15}CH_3$	52.2	2.0
Vinyl crotonate	 $-CH{=}CH-CH_3$	16.8	2.5
Vinyl methacrylate	 $-C(CH_3){=}CH_2$	24.8	3.6
Vinyl benzoate		46.5	4.5
Vinyl cinnamate		46.3	3.6
Vinyl 4-*tert*-butylbenzoate		31.8	2.0

All the modified samples were characterised by FTIR spectroscopy. The characteristic vibrations of the grafted acyl groups can be identified by numbers on the different spectra (Fig. 2). The assignments of the different vibrations bands in Table 2 were obtained both by compiling literature data (Silverstein, Bassler, & Morill, 1991) and comparing the different spectra. From the spectra of vinyl decanoate and vinyl stearate treated wood, it was possible to precisely identify the asymmetrical and symmetrical stretching vibrations of the methylene groups, which are numerous with these reactants (ν_{as} and ν_s at about 2940 and 2850 cm^{-1}, respectively). Stretching vibrations of the methyl groups were obtained with samples treated by vinyl pivalate and vinyl 4-*tert*-butylbenzoate (ν_{as} and ν_s at about 2970 and 2880 cm^{-1}, respectively) and the $=C-H$ stretching vibrations with samples treated by vinyl benzoate, vinyl cinnamate, and vinyl 4-*tert*-butylbenzoate (ν [$=C-H$] at about 3060 cm^{-1}). This last band was only observed in the aryl-containing esters. The most characteristic band in all spectra was the carbonyl stretching vibration, which emerged at about 1750 cm^{-1} in the samples with saturated acyl groups. Because of the conjugation with the alkene groups or aromatic rings, this value shifted to 1720 cm^{-1} with unsaturated esters. The spectra of these samples displayed $C{=}C$ stretching vibrations in the 1600–1650 cm^{-1} region. The band was particularly strong with vinyl cinnamate treated wood (*59* in Fig. 2) because the conjugation of the alkene with the aromatic ring amplifies the absorption of the alkene (Silverstein et al., 1991). The interpretation of the bands in the fingerprint region is trickier, but a number of acyl vibrations have been identified. The band at about 1460 cm^{-1}, observed in all methyl and methylene containing esters, was assigned to both CH_2 scissoring and CH_3 rocking modes (δ_s and δ_{as}, respectively), which generally overlap (Silverstein et al., 1991). Its intensity was stronger with vinyl decanoate and vinyl stearate treated samples, because of the high number of methylene moieties with these compounds. The bands that emerged in the same area with vinyl benzoate and vinyl cinnamate treated wood (*52* and *60* in Fig. 2) and at 1414 cm^{-1} with vinyl 4-*tert*-butylbenzoate treated wood (*77* in Fig. 2), have been assigned to some $C{=}C$ stretching vibrations of the aromatic ring. The scissoring vibrations of the methyl groups (δ_s [CH_3]) were identified in the 1360–1375 cm^{-1} region, only in those samples with short acyl chains (i.e. wood treated by vinyl propionate and vinyl butyrate). The corresponding band was also identified in the spectrum of acetylated wood, in our previous study (Jebrane & Sèbe, 2007). All the samples esterified with compounds containing unsaturated acyl groups displayed an absorption band at about 1315 cm^{-1}, which was assigned to in-plane $=C-H$ bending



V. propionate tr. w. *1*: 2980; *2*: 2945; *3*: 2887; *4*: 1749; *5*: 1463; *6*: 1360; *7*: 1174; *8*: 805. **V. butyrate tr. w.** *9*: 2967; *10*: 2940; *11*: 2879; *12*: 1748; *13*: 1463; *14*: 1375; *15*: 1172; *16*: 750. **V. pivalate tr. w.** *17*: 2972; *18*: 2879; *19*: 1739; *20*: 1479; *21*: 1160; *22*:767. **V. decanoate tr. w.** *23*: 2927; *24*: 2856; *25*: 1748; *26*: 1463; *27*: 1162; *28*: 719. **V. stearate tr. w.** *29*: 2925; *30*: 2853; *31*: 1747; *32*:1463; *33*: 1163; *34*: 718. **V. crotonate tr. w.** *35*: 1726; *36*: 1654; *37*: 1444; *38*: 1314; *39*: 1168; *40*: 970; *41*: 836. **V. methacrylate tr. w.** *42*: 1727; *43*: 1636; *44*: 1457; *45*: 1314; *46*: 1161; *47*: 944; *48*: 810. **V. benzoate tr. w.** *49*: 3066; *50*: 1726; *51*: 1601; *52*: 1455; *53*: 1315; *54*: 1272; *55*: 1108; *56*: 708. **V. cinnamate tr. w.** *57*: 3046; *58*: 1718; *59*: 1634; *60* : 1452; *61*: 1321; *62*: 1266; *63*: 1201; *64*: 1160; *65*: 980; *66*: 860; *67*: 765; *68*: 706; *69*: 681; *70*: 481. **V. 4-*tert*-butylbenzoate tr. w.** *71*: 3068; *72*: 2962; *73*: 2873; *74*: 1727; *75*: 1610; *76*: 1463; *77*: 1414; *78*: 1312; *79*: 1273; *80*: 1189; *81*: 1113; *82*: 853; *83*: 772; *84*: 705; *85*: 548.

Fig. 2. FTIR absorbance spectra of wood, before and after esterification using different vinyl esters (V., vinyl; tr. w., treated wood).

vibrations (δ [=C—H]). For the out-of-plane bending mode (γ [=C—H]), different frequencies are expected in the 700–1000 cm^{-1} region, depending on the substitution pattern of the grafted alkene or aryl group (Silverstein et al., 1991). One band is expected at about 890 cm^{-1} for wood treated by vinyl methacrylate (geminal configuration), at 960–980 cm^{-1} for wood treated by vinyl crotonate and vinyl cinnamate (transconfiguration) and at 800–860 cm^{-1} for wood treated by vinyl 4-*tert*-butylbenzoate (para-disubstituted aryl). These bands were identified in Fig. 2 as *47* (vinyl methacrylate treated wood), *40* (vinyl crotonate treated wood), *65* (vinyl cinnamate treated wood) and *82* (vinyl 4-*tert*-butylbenzoate treated wood), respectively. Two other bands were expected with vinyl benzoate and vinyl cinnamate treated wood, at 730–770 and 680–720 cm^{-1} (mono-substituted aryl). These bands were identified as *68* and *69* in the spectrum of vinyl cinnamate treated wood, but the involvement of band *67* (instead of the *68* or instead of the *69*) cannot be excluded. With the vinyl benzoate treated sample, only one vibration was detected (*56*), but since the band is broad at the base, it could account for the two expected frequencies. The C—O stretching vibrations of esters generally consists of two coupled asymmetric vibrations: the strong O—(C=O) absorption at 1150–1300 cm^{-1} and the weaker C—O(C=O) one at 1000–1150 cm^{-1}. Only the first one was detected in most spectra, at about 1160 cm^{-1} (wood treated by vinyl propionate, vinyl butyrate, vinyl pivalate, vinyl decanoate, vinyl

Table 2
Assignment of the FTIR vibrations associated with the grafted acyl groups in wood after esterification with different vinyl esters

Vibration bands	Absorption range (cm^{-1})	Assignments[a]
49, 57, 71	3068–3046	ν [=C—H]
1, 9, 17, 72	2980–2962	ν_{as} [CH_3]
2, 10, 23, 29	2945–2925	ν_{as} [CH_2]
3, 11, 18, 73	2887–2873	ν_s [CH_3]
24, 30	2853–2856	ν_s [CH_2]
4, 12, 19, 25, 31, 35, 42, 50, 58, 74	1749–1718	ν [C=O]
36, 43, 51, 59, 52, 60, 75, 77	1654–1601	ν [C=C]
5, 13, 20, 26, 32, 37, 44, 76	1479–1452	δ_{as} [CH_3] and δ_s [CH_2]
6, 14	1375–1360	δ_s [CH_3]
38, 45, 53, 61, 78	1312–1321	δ [=C—H]
7, 15, 21, 27, 33, 39, 46, 54, 55, 64, 79, 81	1272–1108	ν [C—O]
40, 47, 56, 65, 68, 69, 82	706–970	γ [=C—H]
16, 22, 28, 34	805–718	δ_{as} [CH_2]
8, 41, 48, 62, 63, 66, 67, 70, 80, 83, 84, 85	–	Not assigned

[a] ν, stretching vibration; δ, in-plane bending; γ, out-of-plane bending; as, asymmetrical; s, symmetrical.

stearate, vinyl crotonate, vinyl methacrylate, vinyl cinnamate) or 1270 cm^{-1} (wood treated by vinyl benzoate and vinyl 4-*tert*-butylbenzoate). Such a difference between the esters of aromatic acids and the other esters is in agreement with the literature data (Silverstein et al., 1991). The additional vibration detected at about 1110 cm^{-1} in the spectra of vinyl benzoate and vinyl cinnamate treated wood (*55* and *81*, respectively) was assigned to the second C—O stretching vibration. Finally, the bands observed in the 720 cm^{-1} region of the samples treated by vinyl butyrate, vinyl pivalate, vinyl decanoate and vinyl stearate, were assigned to the methylene rocking vibrations expected with long acyl chains (δ_{as} [CH_2]). The infrared vibrations that could not be assigned at this stage of the study are reported in Table 2. Some of them could be associated with the ring torsion of the aryl group (bands *67*, *83* and *84*).

The modified samples were also characterised by ^{13}C CP–MAS NMR spectroscopy (Fig. 3). The carbons of the grafted acyl groups were assigned directly on the spectra, according to the nomenclature given on the left of each spectrum. In unmodified wood, the dominant pattern corresponds to the carbons of cellulose: C_1 (108 ppm), C_4 crystalline (92 ppm), C_4 amorphous (86 ppm), $C_2/C_3/C_5$ (75 and 78 ppm), C_6 crystalline (68 ppm) and C_6 amorphous (65 ppm) (Attala, Gast, Sindorf, Bartuska, & Maciel, 1980; Attala & VanderHart, 1999; Gilardi, Abis, & Cass, 1995; Kim & Newman, 1995; Sterk, Sattler, & Esterbauer, 1987). The carbons of the hemicelluloses are expected in the same region, but since they resonate in the form of a broad background they are hidden by the strong cellulose signals (Gilardi et al., 1995; Kim et al., 1995; Sterk et al., 1987). The chemical shift at 59 ppm corresponds to lignin methoxy groups and the broad signal between 145 and 160 ppm to aromatic rings of lignin. After esterification, the carbons of the grafted moieties were clearly identified in all spectra, confirming the success of the reaction. The small signal observed at 23–24 ppm in most spectra, was assigned to the methyl carbon of the acetyl groups found in hemicelluloses (Gilardi et al., 1995; Kim et al., 1995). The shoulder at 175 ppm in the spectrum of vinyl crotonate treated sample probably corresponds to the carbonyl of these same acetyl groups, which resonates downfield of the conjugated carbonyl *a*. The chemical shifts at 53 ppm with vinyl benzoate and vinyl cinnamate treated wood were identified as spinning sidebands arising from the benzoyl group (identified by varying the spinning velocity). A decrease in the intensity of the signal at 65 ppm was noted in most spectra, indicating that cellulose and/or hemicelluloses were modified to some extent. The decrease seemed to be stronger after reaction with the smaller reactants like vinyl propionate and vinyl crotonate. It was even stronger with vinyl acetate (Jebrane & Sèbe, 2007). The $C_2/C_3/C_5$ region was also modified in some cases (with wood treated by vinyl propionate, vinyl butyrate and vinyl acetate mostly).

4. Conclusions

The objective of the present study was to investigate the feasibility of esterifying wood, based on a novel reaction between vinyl esters and wood. The interchange reaction between alkoxyl (and/or phenoxyl) groups of wood and varied saturated and unsaturated vinyl esters was examined and results indicated that wood was esterified in high yield. During the reaction, vinyl alcohol is formed as a by-product and then tautomerizes to acetaldehyde. Hence, the transesterification equilibrium is naturally shifted towards the ester formation. The number of OH groups substituted in wood was found to decrease with increasing molecular weight of the reactant, probably because of differences in the kinetics of diffusion within the wood cell walls. The grafting of the acyl moieties was confirmed by weight percent gain calculations (WPG), FTIR spectroscopy and ^{13}C CP–MAS NMR analysis. The signals corresponding to the grafted acyl groups in the different spectra were thoroughly assigned. This transesterification method has a clear

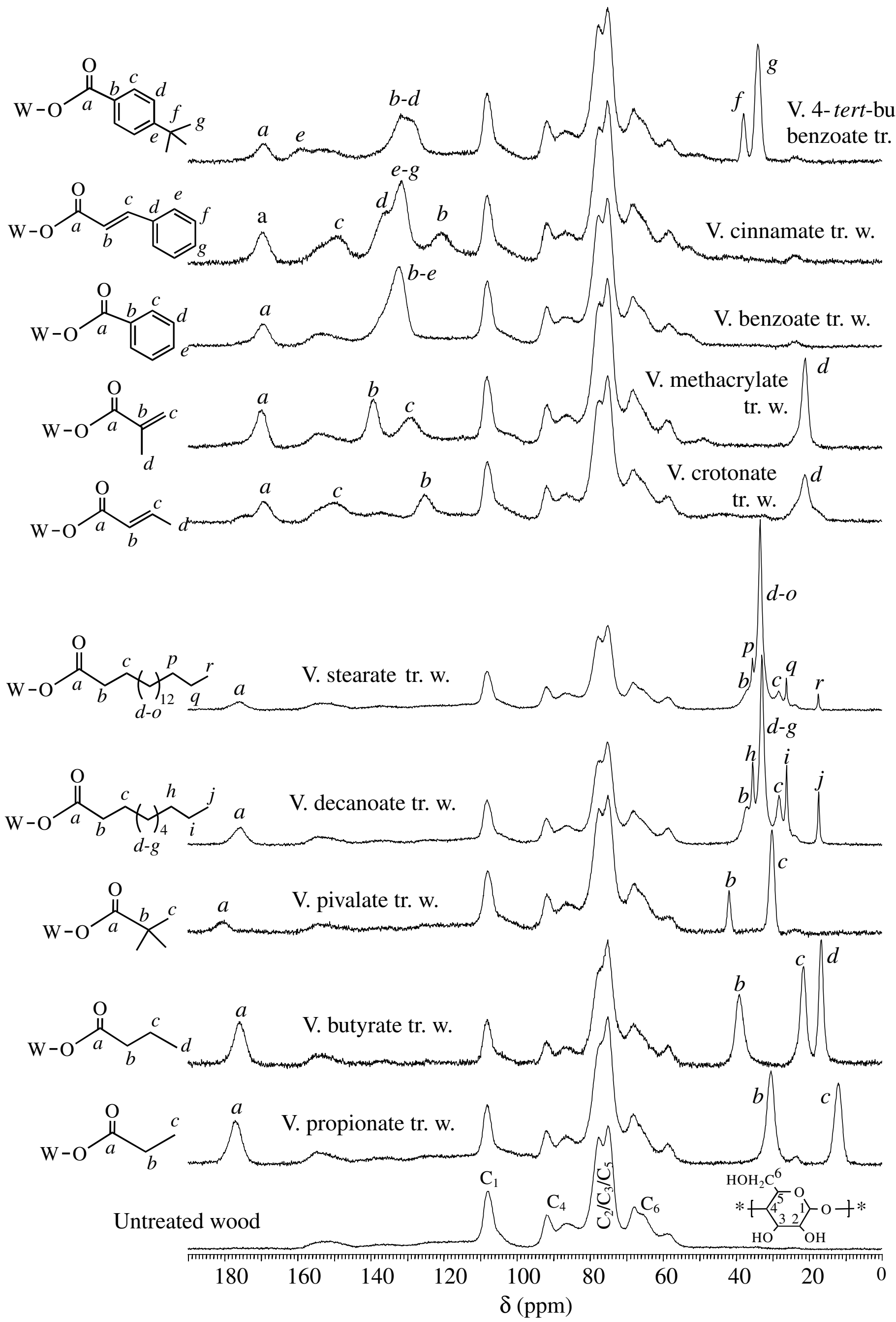


Fig. 3. ^{13}C CP–MAS NMR spectra of wood, before and after esterification using different vinyl esters (V., vinyl; tr. w., treated wood).

advantage compared with the classical esterification route from acid chlorides or anhydrides: since the acetaldehyde produced as a by-product is a non-acidic compound with a low boiling point, and its removal from wood is easy, wood degradation is limited. Moreover, the catalyst used for this reaction (potassium carbonate) is a mild catalyst and the temperature employed is relatively low (90 °C). Although these preliminary experiments were performed in DMF, a solvent-free process cannot be ruled out in other conditions. Further investigations are however needed to first clarify the reaction mechanism.

Acknowledgements

The authors gratefully acknowledge the Agence Nationale de la Recherche (ANR) that financially supported this work.

References

Attala, R. H., Gast, J. C., Sindorf, D. W., Bartuska, V. J., & Maciel, G. E. (1980). High resolution magic angle sample spinning^{13}C NMR of solid cellulose I. *Journal of the American Chemical Society, 102*(9), 3251–3252.

Attala, R. H., & VanderHart, D. L. (1999). The role of solid state ^{13}C NMR spectroscopy in studies of the nature of native celluloses. *Solid State Nuclear Magnetic Resonance, 15*, 1–19.

Chang, S.-T., & Chang, H.-T. (2001a). Comparisons of the photostability of esterified wood. *Polymer Degradation and Stability, 71*, 261–266.

Chang, S.-T., & Chang, H.-T. (2001b). Inhibition of the photodiscoloration of wood by butyrylation. *Holzforschung, 55*(3), 255–259.

Chang, H.-T., & Chang, S.-T. (2003). Improvements in dimensional stability and lightfastness of wood by butyrylation using microwave heating. *Journal of Wood Science, 49*, 455–460.

Evans, P. D. (1998). Weather resistance of wood esterified with dicarboxylic acid anhydrides. *Holz Roh- und Werkstoff, 56*(5), 294.

Evans, P. D., Wallis, F. A., & Owen, N. L. (2000). Weathering of chemically modified wood surfaces. Natural weathering of Scots pine acetylated to different weight gains. *Wood Science and Technology, 34*, 151–165.

Evans, P. D., Owen, N. L., Schmid, S., & Webster, R. D. (2002). Weathering and photostability of benzoylated wood. *Polymer Degradation and Stability, 76*, 291–303.

Gilardi, G., Abis, L., & Cass, A. E. G. (1995). Carbon-13 CP/MAS solid-state NMR and FT-IR spectroscopy of wood cell wall biodegradation. *Enzyme and Microbial Technology, 17*, 268–275.

Hill, C. A. S., & Jones, D. (1996). The dimensional stabilisation of corsican pine sapwood by reaction with carboxylic acid anhydrides. *Holzforschung, 50*(5), 457–462.

Hill, C. A. S., Jones, D., Strickland, G., & Çetin, N. S. (1998). Kinetic and mechanistic aspects of the acetylation of wood with acetic anhydride. *Holzforschung, 52*(6), 623–629.

Hill, C. A. S., Forster, S. C., Farahani, M. R. M., Hale, M. D. C., Ormondroyd, G. A., & Williams, G. R. (2005). An investigation of cell wall micropore blocking as a possible mechanism for the decay resistance of anhydride modified wood. *International Biodeterioration & Biodegradation, 55*, 69–76.

Hill, C. A. S. (2006). *Wood modification: Chemical, thermal and other processes*. Chichester: John Wiley and Sons.

Hon, D. N.-S. (1996). *Chemical modification of lignocellulosic materials*. New York: Marcel Dekker.

Iwamoto, Y., & Itoh, T. (2005). Vapor phase reaction of wood with maleic anhydride (I): Dimensional stability and durability of treated wood. *Journal of Wood Science, 51*, 595–600.

Iwamoto, Y., Itoh, T., & Minato, K. (2005). Vapor phase reaction of wood with maleic anhydride (II): Mechanism of dimensional stabilisation. *Journal of Wood Science, 51*, 601–606.

Jebrane, M., & Sèbe, G. (2007). A novel simple route to wood acetylation by transesterification with vinyl acetate. *Holzforschung, 61*(2), 143–147.

Kim, Y. S., & Newman, R. H. (1995). Solid state^{13} C study of wood degradated by brown rotfungus Gloephyllum trabeum. *Holzforschung, 49*(2), 109–114.

Larsson Brelid, P., Simonson, R., Bergman, O., & Nilsson, T. (2000). Resistance of acetylated wood to biological degradation. *Holz Roh- und Werkstoff, 58*, 331–337.

Larsson Brelid, P. (2002). The influence of post-treatments on acetyl content for removal of chemicals after acetylation. *Holz Roh- und Werkstoff, 60*, 92–95.

Li, J.-Z., Furuno, T., & Katoh, S. (2000). Chemical modification of wood by anhydrides without solvents or catalysts. *Journal of Wood Science, 46*, 215–221.

Minato, K. (2004). Application of a modified rate equation to the acetylation of wood. *Journal of Wood Science, 50*, 455–458.

Minato, K., & Ito, Y. (2004). Analysis of the factors influencing the acetylation rate of wood. *Journal of Wood Science, 50*, 519–523.

Ohkoshi, M. (2002). FTIR-PAS study of light-induced changes in the surface of acetylated or polyethylene glycol-impregnated wood. *Journal of Wood Science, 48*, 394–401.

Otera, J. (1993). Transesterification. *Chemical Reviews, 93*, 1449–1470.

Prakash, G. K., Pandey, K. K., Ram, R. K. D., & Mahadevan, K. M. (2006). Dimensional stability and photostability of octanoylated wood. *Holzforschung, 60*, 539–542.

Rowell, R. M. (1983). Chemical modification of wood. *Forest Products Abstracts, 6*(12), 363–382.

Rowell, R. M. (2006). Acetylation of wood: Journey from analytical technique to commercial reality. *Forest Products Journal, 56*(9), 4–12.

Silverstein, R. M., Bassler, G. C., & Morill, T. C. (1991). *Spectrometric identification of organic compounds* (5th ed.). New York: John Wiley and Sons.

Simonson, R., & Rowell, R. (2000). A new process for the continuous acetylation of lignocellulosic fiber. In *Proceedings of the 5th Pacific Rim bio-based composites symposium* (pp. 190–196). Canberra: Department of Forestry, The Australian National University.

Sterk, H., Sattler, W., & Esterbauer, H. (1987). Investigation of lignocellulosic materials by the carbon-13 N.M.R. C.P.–M.A.S. method. *Carbohydrate Research, 164*, 85–95.