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Comparative determination of the grafting distribution and viscoelastic properties of wood blocks acetylated by vinyl acetate or acetic anhydride

Mohamed Jebrane[a], David Harper[b], Nicole Labbé[b], Gilles Sèbe[a,c,*]

[a] Université de Bordeaux, Laboratoire de Chimie des Polymères Organiques, IPB/ENSCBP, 16 Avenue Pey-Berland, F-33607 Pessac cedex, France
[b] Center for Renewable Carbon, The University of Tennessee, 2506 Jacob Drive, Agriculture Campus, Knoxville, TN 37996-4570, USA
[c] Centre National de la Recherche Scientifique, Laboratoire de Chimie des Polymères Organiques, 16 Avenue Pey-Berland, F-33607 Pessac cedex, France

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ABSTRACT

Extracted maritime pine sapwood blocks were acetylated to different weight gains with vinyl acetate (VA) and acetic anhydride (AA) and the samples were characterized with regard to their grafting distribution and dynamic viscoelastic properties. We found that the reaction with the VA/DMF/K_2CO_3 system was controlled by the diffusion of VA and/or K_2CO_3 (catalyst) within the solid wood blocks, and that this diffusion was somehow more difficult than the diffusion of AA. Fourier transform infrared (FTIR) spectroscopy was used to confirm the grafting and investigate the distribution of the acetyl moieties within the wood blocks. Whatever the acetylating agent used and the reaction time applied, we observed that the surface of the wood blocks was always more acetylated than the bulk. Some swelling of the cell walls also occurred, but the AA-acetylated blocks were always more swollen than the VA-acetylated ones at a given WPG. The viscoelastic properties of the samples were investigated by dynamic mechanical analysis (DMA). The temperature profiles of the storage modulus (E') and loss modulus ($\mathrm{Log}\, E''$) indicated that some plasticization occurred after acetylation and also confirmed that the cellulose sites in wood were more attacked by VA than by AA. Results also revealed that the softening, induced by the acetyl groups introduced in the substance matrix, was counterbalanced by some stiffening effect at high WPG, more particularly when VA was used. We hypothesized that some VA-acetylated material may have expanded into the cell wall micropores or lumen during reaction, leading to the limited swelling and increased stiffness observed.

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1. Introduction

Acetylation is one of the best methods to improve wood performances (Hill, 2006; Hon, 1996). The reaction can be performed by various means, but the treatment with acetic anhydride (AA) has been so far the most investigated and the corresponding product is now commercialized in Europe and Japan. Several studies have demonstrated that the treatment improves dimensional stability, fungal resistance, photostability and weathering of wood (Chang & Chang, 2001; Evans, Wallis, &, Owen, 2000; Hill, 2006; Hill, Forster, Farahani, Hale, Ormondroyd, & Williams, 2005; Hill & Jones, 1996; Hon, 1996; Larsson Brelid, 2002; Larsson Brelid, Simonson, Bergman, & Nilsson, 2000; Ohkoshi, 2002). More recently, we showed that wood could be also easily acetylated by an alternative method based on the transesterification of vinyl acetate (VA) (Jebrane, Pichavant, & Sèbe, 2011; Jebrane & Sèbe, 2007). One clear advantage of this approach is that the by-product released during reaction is acetaldehyde, which is non-acidic and can be easily removed from wood after reaction because of its low boiling point ($\mathrm{b.p.}_{[760\,\mathrm{mm\,Hg}]} = 21\,^{\circ}\mathrm{C}$). With AA, the acetic acid liberated is generally hard to remove from wood after reaction, which results in undesirable odors and causes strength loss or corrosion of metal fasteners (Larsson Brelid, 2002; Li, Furuno, & Katoh, 2000; Simonson & Rowell, 2000). Despite the apparent advantages of the VA method, the performances of the VA acetylated products could be very different from those obtained with AA, the benefits of the chemical treatments depend strongly on the process conditions. Our recent investigation indicated that the VA/DMF/K_2CO_3 and AA/DMF systems have a different reactivity with regard to wood components and also to the isolated polymers (Jebrane et al., 2011). Both of these systems allow for producing acetylated wood with similar yields but the cellulose sites in wood were more modified by VA than by AA under our experimental conditions. This result could have a significant impact on the final properties of the material, as could the diffusion of reactants when larger samples are treated. Up to now, our investigations were performed with wood

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* Corresponding author at: Université de Bordeaux, Laboratoire de Chimie des Polymères Organiques, IPB/ENSCBP, 16 Avenue Pey-Berland, F-33607 Pessac cedex, France. Tel.: +33 (0)5 40 00 64 11; fax: +33 (0)5 40 00 64 39.
E-mail address: gilles.sebe@u-bordeaux1.fr (G. Sèbe).

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sawdust as a starting substrate (so the diffusion phenomena were limited), but very little is known about the reaction of vinyl acetate within solid wood blocks.

Therefore, in this paper we investigated and compared the grafting distribution and viscoelastic properties of wood blocks acetylated by VA and AA. Maritime pine sapwood blocks were acetylated at different weight percent gains by the VA and AA procedures, and the distribution of the grafting within the samples was analyzed by Fourier transform infrared (FTIR) spectroscopy and by performing swelling measurements. Dynamic mechanical analysis (DMA) subsequently investigated the viscoelastic properties of the acetylated samples.

2. Materials and methods

2.1. Materials and chemicals

Oriented maritime pine sapwood blocks (*Pinus Pinaster* Soland) of 20 mm × 20 mm × 5 mm and 10 mm × 2 mm × 30 mm (radial × tangential × longitudinal) were used as starting material. The size was selected for the distribution studies (FTIR and swelling analysis) and for the DMA analysis, respectively. Prior to use, all samples were extracted in a soxhlet apparatus with a mixture of toluene:ethanol (2:1/v:v) for 8 h then with water for an additional 8 h, to remove all extractives. The wood samples were then oven dried at 105 °C for 16 h and cooled to ambient temperature in a dessicator containing phosphorus pentoxide.

Vinyl acetate (VA), acetic anhydride (AA), dimethylformamide (DMF) and potassium carbonate (K_2CO_3) were purchased from Sigma–Aldrich. DMF was previously dried over molecular sieve (4 Å).

2.2. Esterification reactions

All chemical reactions were performed in a round-bottomed wide-mouthed flask equipped with a condenser and a calcium chloride drying tube. Reactions were conducted using reagent solutions consisting of 14 mmol of VA or AA/g dry wood, in 20 ml DMF. For the VA-acetylation, 1.1 mmol K_2CO_3/g dry wood was added to the medium, as a catalyst. Samples were pre-impregnated with the reagent solution by applying several vacuum/atmospheric pressure cycles, until sinking occurs. The reaction temperature was fixed at 100 °C and different reaction times were applied under gentle stirring. All modified samples were subsequently soxhlet extracted with a mixture of toluene:ethanol:acetone (4:1:1 v/v/v) for 8 h, to remove all non-bonded chemicals (DMF, unreacted compounds and by-products generated during the reaction). For the VA-acetylation, the samples were additionally extracted with water for 2 h (prior to the toluene:ethanol:acetone extraction) to eliminate the catalyst K_2CO_3. The wood blocks were finally oven-dried at 105 °C for 16 h and the weight percent gain (WPG) was calculated as follows: $\mathrm{WPG} = [(M_1 - M_0)/M_0] \times 100$, where M_0 and M_1 are the oven dried weights of untreated and acetylated blocks, respectively.

2.3. FTIR spectroscopy

Infrared absorption spectra of treated and unmodified samples were obtained with the potassium bromide technique (between 4000 and 400 $\mathrm{cm^{-1}}$), using a Perkin-Elmer Paragon 1000 PC FTIR spectrometer, at a resolution of 4 $\mathrm{cm^{-1}}$ (64 scans). In each case, the block sample was ground in a Wiley mill to pass a 35 mesh screen and 3% w/w of dry material was dispersed in a matrix of KBr and pressed to form pellets.

In addition, the distribution of the grafted acetyl groups within the 20 mm × 20 mm × 5 mm (radial × tangential × longitudinal) wood blocks was investigated by the attenuated total reflectance (ATR) technique. The samples were microtomed at different depths in the longitudinal direction of the blocks and each new microtomed surface was analyzed using an AVATAR 370 ThermoNicolet spectrometer. The diamond crystal of an ATR accessory was brought into contact with the area to be analyzed and 8 spectra at various locations were collected and averaged after normalization (64 scans). The peak height ratio of the 1735–1510 $\mathrm{cm^{-1}}$ vibrations (I_{1735}/I_{1510}) in the average spectrum was then calculated using a baseline constructed by extrapolating a line between the valleys at 1905 and 1554 $\mathrm{cm^{-1}}$.

2.4. Swelling measurements

The dimensional changes caused by the acetyl moieties grafted in the cell walls were measured in the radial and tangential directions of the 20 mm × 20 mm × 5 mm (radial × tangential × longitudinal) samples, using a digital caliper accurate to 0.025 cm. The radial and tangential swellings (Rad and Tan, respectively) after reaction, extraction and drying were then calculated as followed: $\mathrm{Rad} = [(R_1 - R_0)/R_0] \times 100$ and $\mathrm{Tan} = [(T_1 - T_0)/T_0] \times 100$, where R_0/R_1 are the radial dimensions and T_0/T_1 the tangential dimensions of the dry blocks before/after the treatment, respectively.

2.5. Dynamic mechanical analysis (DMA)

DMA experiments were conducted on wood blocks of 10 mm × 2 mm × 30 mm (radial × tangential × longitudinal) using a Perkin-Elmer Pyris Diamond Dynamic Mechanical Analyzer. The samples were attached at one extremity and subjected to a periodic strain at a frequency of 1 Hz, over a range temperature between −150 and 200 °C. The heating rate was 3 °C $\mathrm{min^{-1}}$ and the strain level 0.1%. Before each analysis, the samples were heated at 150 °C for 15 min and allowed to cool to ambient temperature in a desiccator containing phosphorus pentoxide. The storage modulus (E') and loss modulus ($\mathrm{Log}\,E''$) were then recorded as a function of temperature.

3. Results and discussion

Extracted maritime pine sapwood blocks of 20 mm × 20 mm × 5 mm (radial × tangential × longitudinal) were reacted with vinyl acetate (VA) and acetic anhydride (AA) for various reaction times, according to the general schemes presented in Fig. 1. 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 without catalyst in these conditions but the reaction with VA requires K_2CO_3). Preliminary experiments with wood blocks showed that the reactions were much slower than when sawdust was used. Hence, longer reaction times were applied with wood blocks.

The evolution with time of the WPG obtained after acetylation with VA and AA is presented in Fig. 2. As a comparison, the kinetics of the VA-acetylation of sawdust is also reported. With sawdust, the VA-acetylation is very fast during the first hour (WPG = 22.3% after 1 h), then it slows down and a WPG of 26.7% is obtained after 6 h. Any further increase in reaction time led to a concomitant decrease in WPG, most probably because some of the acetylated biopolymers increasingly dissolved in the reaction medium (Jebrane et al., 2011). The WPG of the wood blocks acetylated with VA increased progressively over time, to reach a plateau at about 21–22% after 36 h of reaction. The reaction is much slower than when sawdust was used, suggesting that the reaction rate with VA is controlled by

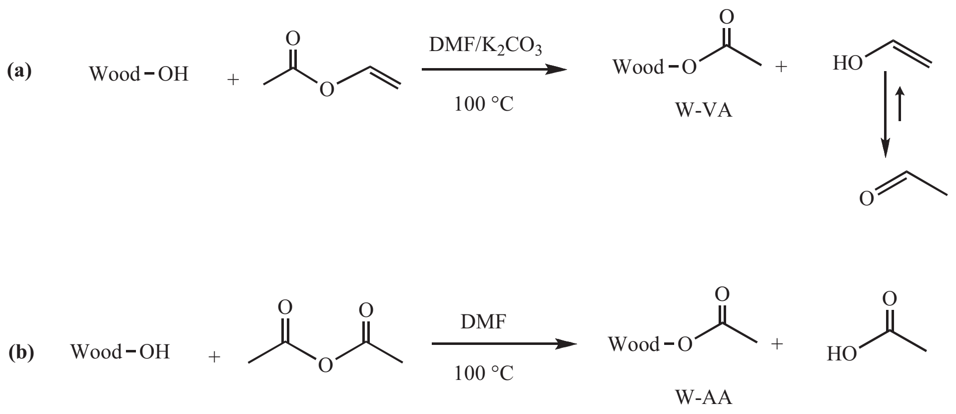

Fig. 1. General schemes for the acetylation of wood blocks by reaction with vinyl acetate (a) or acetic anhydride (b).

the diffusion of the reagents within the wood block, i.e. by the accessibility of the reactive sites to the reagents. A similar behavior has been already reported with AA (Hill, 2006; Hill, Jones, Strickland, & Çetin, 1998; Minato, 2004; Minato & Ito, 2004). However, significant differences are observed when the VA and AA treatments are compared. Within the first 6 h, the acetylation of wood blocks was much faster when AA was used, suggesting than that diffusion of VA and/or K_2CO_3 within the wood blocks was more difficult than the diffusion of AA. No such difference in reaction rate was evidenced when wood sawdust was esterified. Most probably, the progression of the reactive VA/K_2CO_3 complex within the blocks is delayed by the poor solubility of K_2CO_3 in DMF.

The samples modified to different weight gains were ground and analyzed by FTIR spectroscopy (Fig. 3). The grafting was confirmed in all cases, the intensity of the grafted acetyl group vibrations augmenting with increasing WPG with both VA and AA (see $\nu_{\mathrm{C-H}}$, $\nu_{\mathrm{C=O}}$, $\delta_{\mathrm{C-H}}$, $\nu_{\mathrm{C-O}}$, $\gamma_{\mathrm{C-H}}$ in Fig. 3 and the unidentified band at 600 cm^{-1}). The distribution of the grafted acetyl groups within the 20 mm × 20 mm × 5 mm (radial × tangential × longitudinal) wood blocks was also investigated. For these experiments, the samples were microtomed at different depths in the longitudinal direction of the blocks and each new microtomed surface was analyzed by FTIR-ATR spectroscopy (8 spectra at various locations were collected and averaged after normalization). The rate of acetylation at the different depths within the sample was then evaluated by calculating the peak heights ratio of the 1735–1510 cm^{-1} vibrations (I_{1735}/I_{1510}) in each averaged spectrum, and plotting this ratio as a function of the depth in the longitudinal direction of the sample (Fig. 4). In this method, the intensity of the carbonyl stretching vibration of the grafted acetyl group at 1735 cm^{-1} is actually normalized by the 1510 cm^{-1} vibration associated with the aromatic ring of lignin used as an internal standard (Glasser & Jain, 1993; Schultz & Glasser, 1986). The samples were analyzed up to the center of the block, which corresponds to a depth of about 2.5 mm in Fig. 4. Whatever the acetylating agent used and the reaction time applied, the wood blocks surface (depth = 0) was always more acetylated than the bulk, confirming that the esterification rates were strongly impacted by the diffusion of the reagents within the samples. Inside the blocks and for a given reaction time, the I_{1735}/I_{1510} ratio did not vary much with the depth, indicating that the bulk of the wood blocks were evenly modified in the longitudinal direction. Since the reactive solution penetrates into the wood cell walls through the longitudinally oriented lumen, the progression with time of the grafting in the bulk of the samples is similar whatever the depth (Fig. 5).

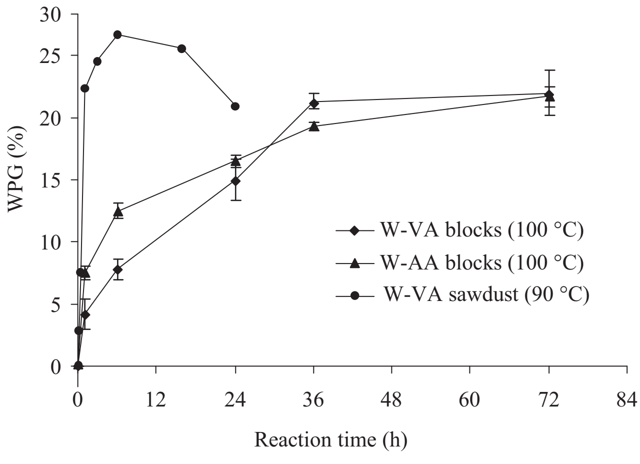

Fig. 2. Evolution with time of the WPG of the wood blocks acetylated by VA or AA (W-VA blocks and W-AA blocks, respectively). As a comparison, the VA-acetylation of sawdust is also reported (W-VA sawdust).

The difference between surface and bulk was particularly pronounced after acetylation with VA, the surface of VA-acetylated samples being generally more acetylated than the surface of the AA-acetylated ones, for a given reaction time (for instance, in Fig. 4 the surface is more acetylated by VA after 6 h than by AA after 24 h). This difference between VA and AA could be explained by the higher reactivity to cellulose of the VA/DMF/K_2CO_3 system compared with the AA/DMF one (Jebrane et al., 2011), more OH sites being potentially reactive with the first system. After 6 h of reaction with VA (WPG ~ 7–8%), the grafting is located mostly at the surface of the sample, the bulk being only slightly modified ($I_{1735}/I_{1510} \sim 1$ in the bulk). As a comparison, the acetylation with AA was faster (WPG ~ 7–8% after 1 h, instead of 6 h with VA) and the core of the AA-acetylated blocks was more modified ($I_{1735}/I_{1510} \sim 2$). This result confirms that the reaction with the VA/DMF/K_2CO_3 system is controlled by the diffusion of VA and/or K_2CO_3 within the wood blocks, and that this diffusion is somehow more difficult than the diffusion of AA. But after 24 h, the progression of the chemicals within the samples is such that the level of modification in the bulk of the VA-acetylated samples matched the level obtained with AA ($I_{1735}/I_{1510} \sim 4$ in both cases). This level increased further after 72 h reaction ($I_{1735}/I_{1510} \sim 6$), indicating that both reagents continued to diffuse within the samples and accessed novel reactive sites. But unlike what was observed at the surface, similar levels of modification were obtained with both VA and AA.

The chemical swelling of the samples, produced by the acetyl groups grafted within the wood cell walls, was measured as a function of reaction time (Fig. 6a) and as a function of WPG (Fig. 6b) in the radial and tangential directions of the 20 mm × 20 mm × 5 mm (radial × tangential × longitudinal) samples (Rad and Tan, respec-

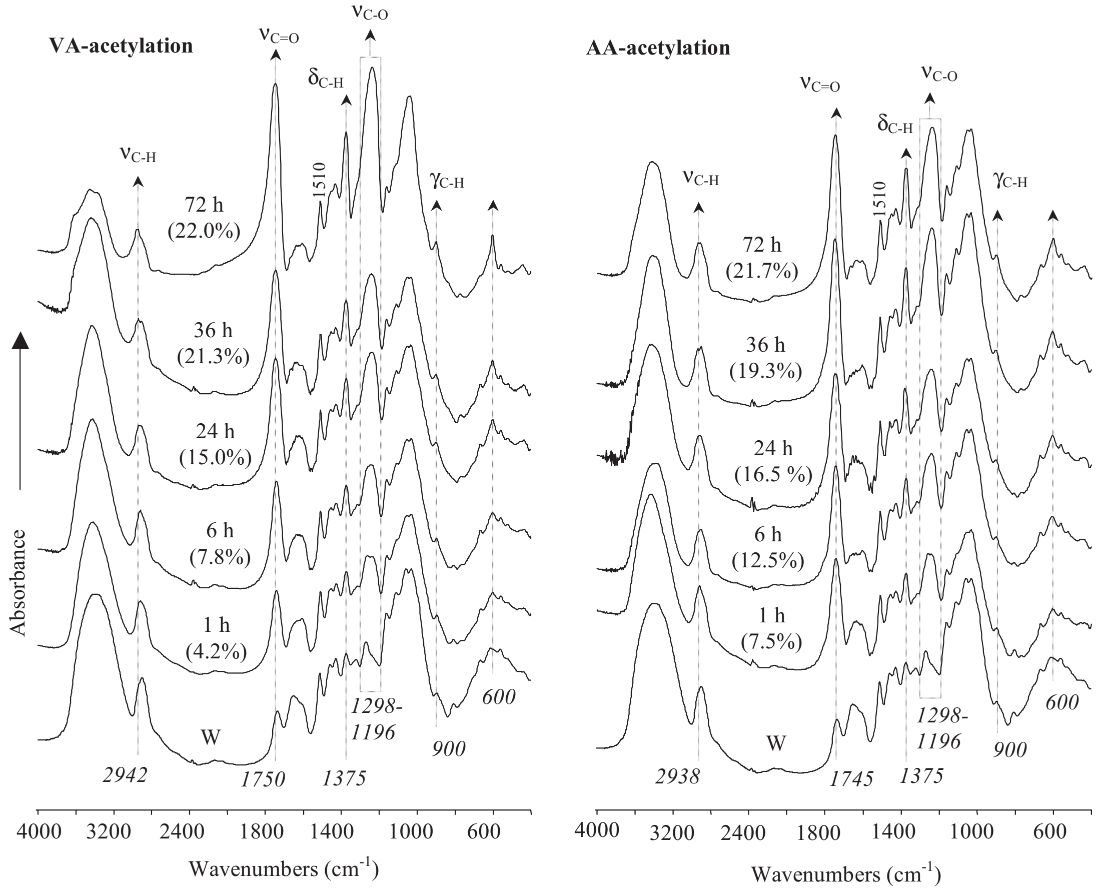

Fig. 3. FTIR spectra of wood blocks acetylated by VA or AA for 1, 6, 24, 36 and 72h (the WPG is given in brackets). Wood blocks were grinded and analyzed by the KBr technique (W, unmodified wood; ν, stretching vibration; δ, in-plane bending, γ, out-of-plane bending).

tively in Fig. 6). Whatever treatment used, the swelling was more important in the tangential direction of the samples, i.e. the grafting occurred preferentially in that direction within the cell walls. In all cases, the swelling increased with reaction time, indicating that the cell walls were increasingly modified. However, the acetylation with VA always produced a lower swelling at a given reaction time, even though the bulks of VA and AA-acetylated samples are equivalently modified after 24 h of reaction (Fig. 4). It has been previously demonstrated that VA/DMF/K_2CO_3 and AA/DMF systems have a different reactivity with regard to wood components (Jebrane et al., 2011), therefore VA and AA probably attacked different sites within the cell walls. The most likely possibility is that areas around the cell wall micropores or lumen are more acetylated in the VA-treated samples: the esterified material in these areas could expand into the micropores or lumen, hereby decreasing the voids volume and limiting the overall swelling of the sample. The chemical swelling induced by VA is limited during the first 24 h (i.e. when WPG $\leq$ 15% in Fig. 6b) but tends to increase drastically between 24 and 72 h. Surprisingly, the WPG increases only slightly between 36 and 72 h (WPG = 21 and 22%, respectively in Fig. 6b). A possible hypothesis for this observation is that the WPG calculation is not estimating properly the level of modification at high reaction times: some of the acetylated biopolymers may have dissolve in the reaction medium, leading to an underestimation of the WPG in samples treated for long periods (Jebrane et al., 2011). However, infrared results indicate that the bulk of the VA and AA-acetylated samples is equivalently modified after 72 h (Fig. 4), so more work is needed to clarify this point.

The viscoelastic properties of the samples acetylated by VA or AA were investigated by dynamic mechanical analysis (DMA). For these experiments, wood blocks of 10 mm × 2 mm × 30 mm (radial × tangential × longitudinal) were modified with VA or AA for 6 and 12 h, to produce samples with moderate (8–9%) and high (18–20%) WPG, respectively. Fig. 7 shows the temperature profiles of the storage modulus E' and loss modulus E'' obtained for the unmodified and esterified samples strained at a frequency of 1 Hz. For unmodified wood (W), the loss modulus response ($\mathrm{Log}\,E''$) reveals three relaxation processes labeled α, β and γ and assigned respectively to the micro-Brownian motions of the lignocellulosic polymers in the non-crystalline regions ($\sim$180 °C), to the motions of lignin and/or lignin-hemicellulose complexes plasticized with residual moisture ($\sim$25 °C) and to the motion of the methylol groups of the lignocellulosic polymers in the non-crystalline regions (~ -90 °C) (Jiang & Lu, 2009; Kelley, Rials, & Glasser, 1987; Obataya, Norimoto, & Tomita, 2001; Sugiyama, Obataya, & Norimoto, 1998). After acetylation with VA or AA, three relaxation processes were again detected but significant differences were noted in the temperature profiles compared with unmodified wood. Whatever the chemical used, a strong increase in the intensity of the α transition was observed, indicating that the mobility of the lignocellulosic polymers in the wood cell walls increased at that temperature. It is believed that the introduction of bulky acetyl groups reduced the cohesive forces between the main chains of the matrix substance and facilitated their backbone motion as was reported by Sugiyama et al. (1998). The dramatic decrease in E' associated with the α transition in both VA and AA-acetylated samples is consistent with the occurrence of large-scale segmental motions at high temperature (Kelley et al., 1987). Hence, some internal plasticization occurred after wood acetylation, causing a reduction of the energy required to initiate chain mobility.

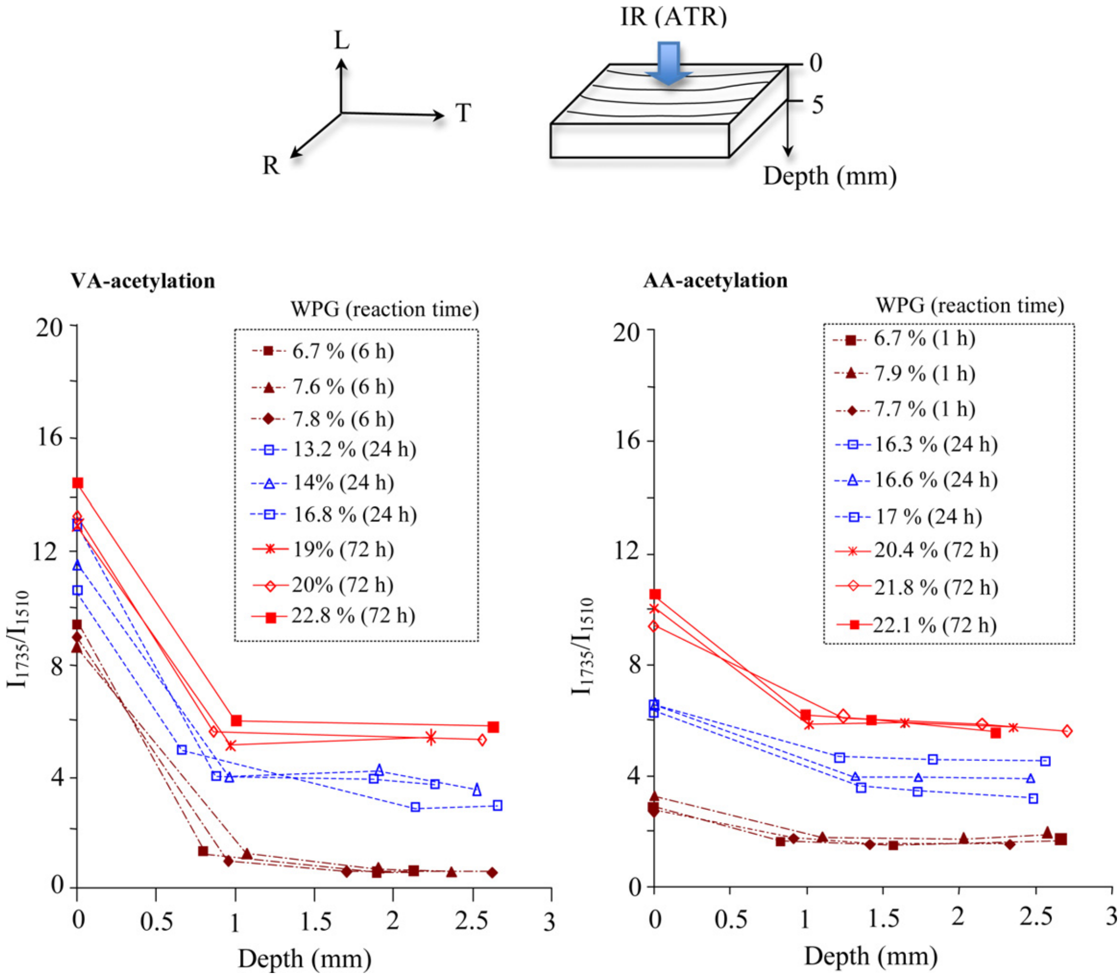

Fig. 4. Peak heights ratio I_{1735}/I_{1510} at different depths in the longitudinal direction of the samples acetylated by VA or AA.

The transition related to the residual moisture at about 25 °C was not observed anymore in acetylated wood, probably because of the reduced hygroscopicity engendered by the treatment (a significant amount of hydroxyl groups are replaced by the more hydrophobic acetyl moieties). On the other hand, a new β transition emerged at about 50 °C, its amplitude varying depending on the acetylation method. This transition was more intense in VA-acetylated samples and increased with increasing WPG (Fig. 7). It has been assigned in the literature to the micro-Brownian motion of the modified cellulose main-chains in the amorphous regions of wood (Nakano, 1994; Nakano & Nakamura, 1986). Therefore, the stronger amplitude obtained for the β transition in VA-acetylated samples shows good agreement with our previous experiments, which suggested that the cellulose sites in wood were more attacked by VA than by AA (Jebrane et al., 2011). In the low-temperature range, the γ transition at about −90 °C slightly shifted to lower temperatures after acetylation with both VA and AA. This downshift was assigned to the substitution of a significant amount of methylol groups by the acetyl moieties after reaction, the relaxation processes of these two side-chains overlapping in the low-temperature region (Morooka, Norimoto, Yamada, & Shiraishi, 1983; Nakano, 1994; Obataya, Minato, Tomita, 2001; Obataya, Norimoto, et al., 2001; Scandola & Ceccorulli, 1985).

Over the entire range of temperature, the storage modulus (E') of the acetylated samples with moderate WPG (∼8–9%) was significantly lower than that of unmodified wood, the decrease being more accentuated after acetylation with AA (Fig. 7). This softening of the material after acetylation can be assigned to an increase in the free volume induced by the breakdown of intra-molecular bonds in the viscoelastic regions of the material, i.e. in the lignin-rich regions (Nakano, 1994; Obataya, Furuta, & Gril, 2003). However, when the WPG is further increased (∼18–20%), the storage modu-

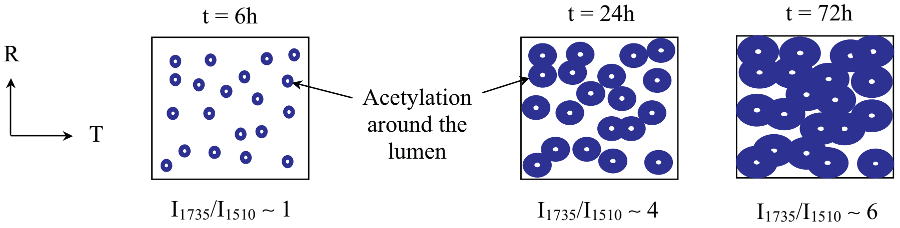

Fig. 5. Schematic representation of the progression with time of the VA-acetylation in the bulk of the samples (I_{1735}/I_{1510} is obtained from the average of 8 spectra collected at various locations).

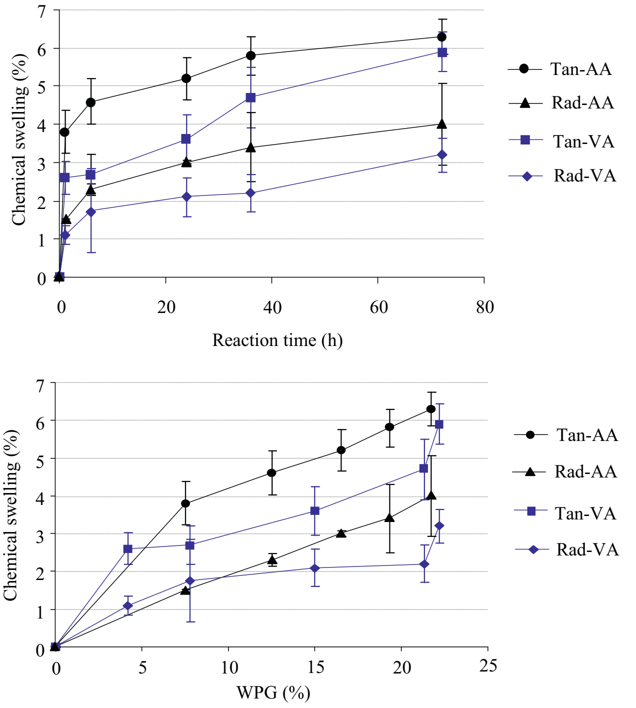

Fig. 6. Evolution with time (a) and with WPG (b) of the chemical swelling in the radial and tangential directions of the wood blocks after acetylation with VA or AA.

lus (E') is also increased and the difference between unmodified and acetylated wood diminishes. With VA, this increase is such that the highly modified acetylated sample (WPG = 19.6%) is stiffer than the unmodified one in the range of temperature between −90 °C and 145 °C. It is believed that at high WPG, the former softening effect is counterbalanced by some stiffening effect, which increased with increasing WPG. A similar antiplasticizing effect has been already observed with acetylated samples in wet conditions (Obataya, Minato, et al., 2001). As suggested earlier, it is possible that after a certain level of modification some esterified material expands into the cell wall micropores or lumen, leading to a decrease in the voids volume and an increase in stiffness. The higher values obtained for E' with the VA-acetylated samples could result from a higher esterification of the areas in the vicinity of the micropores and/or lumen in that case.

4. Conclusions

In conclusion, the graft distribution and dynamic viscoelastic properties of wood blocks acetylated by VA or AA were compared and significant differences between the two methods were noted. We have found that the diffusion of the reagents within the wood blocks was more difficult when the VA/DMF/K_2CO_3 system was used, most probably because the progression of the reactive VA/K_2CO_3 complex is delayed by the poor solubility of K_2CO_3 in DMF. This analysis was supported by the infrared data, which indicated that the surface of the VA-acetylated blocks was much more acetylated than the bulk. Whatever the treatment used, the grafting was found to provoke the chemical swelling of the cell walls, but the AA-acetylated blocks were always more swollen than the VA-acetylated ones at a given WPG. We believe that, because of the different reactivities of the VA/DMF/K_2CO_3 and AA/DMF systems (in particular with regard to cellulose), different sites are attacked within the cell walls. The regions modified by VA could be inclined to expand into the voids of the structure (i.e. the micropores and/or the lumen), hereby limiting the overall swelling of the samples. This hypothesis shows good agreement with the DMA results, which

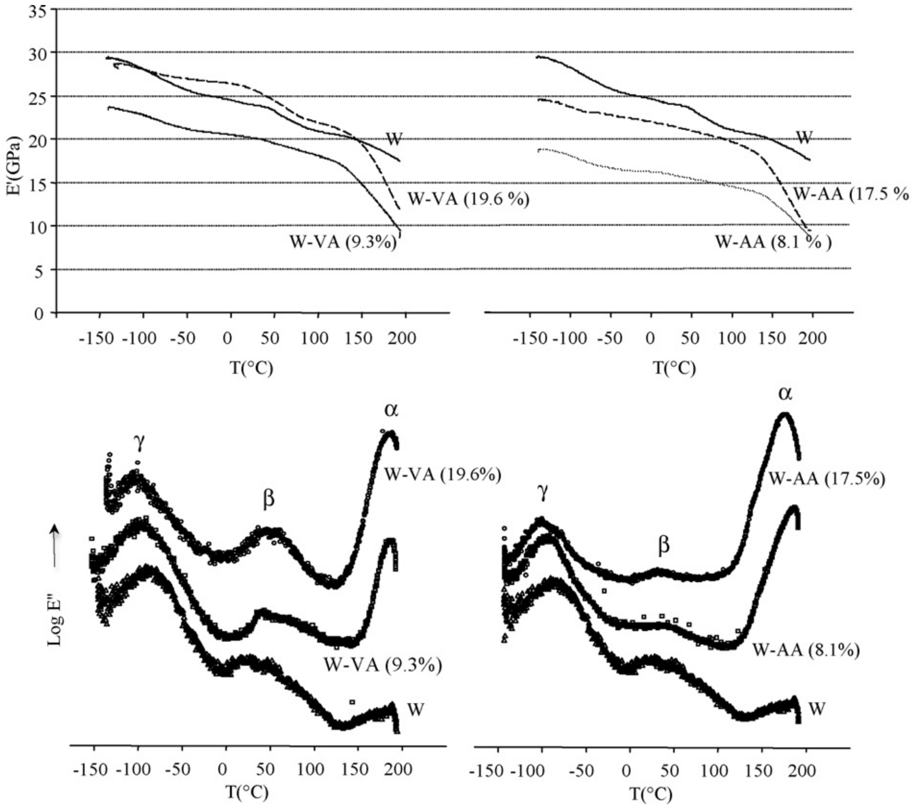

Fig. 7. Temperature profiles of the storage modulus (E') and loss modulus (Log E'') obtained for the unmodified blocks (W) and for the samples esterified by VA (W-VA) or AA (W-AA), at a frequency of 1 Hz.

revealed that the plasticization engendered by the VA treatment was strongly counterbalanced by some stiffening effect at high WPG (with AA, this effect existed but was more limited): this stiffening could result from the decrease in voids volume within the matrix substance after the esterification of cellulose-rich regions. The temperature profile of the loss modulus (Log E'') actually confirmed that the cellulose sites in wood were more attacked by VA than by AA. In any case, we showed that the grafting distribution and dynamic viscoelastic properties of the acetylated wood blocks depend strongly on the acetylation method employed. For instance, a comparatively stiffer material was obtained when wood blocks were acetylated by VA instead of AA. Therefore, the acetylation with VA shows promise as a way to improve wood performances and could be considered as a serious alternative process in the near future.

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