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Mixed acylation of Scots pine sawdust and impact on hydrophobicity

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Abstract

Acetic–fatty esters of Scots pine sawdust (SPS) were obtained by reaction of SPS with mixtures containing acetic–fatty anhydrides and no solvent or catalyst. Such mixtures were synthesized by reaction between a carboxylic acid and acetic anhydride. The global reaction of acetic anhydride and a fatty acid yields at equilibrium a mixture of five compounds: acetic–fatty anhydride, acetic anhydride, fatty acid, acetic acid and fatty anhydride. The influence of temperature, molar ratio, reaction time and length of the fatty chain on the esterification and on the ratio of grafted acetyl/fatty acyl was investigated. Static contact angles (CAs) with water were measured over 5 min. CA values were dependent on the fatty acyl content and independent of the acetyl content. The minimum ester content of the oleoyl group required to obtain permanent water repellency was 25 mmol kg⁻¹. Water vapour adsorption measurements indicated that in contrast to water repellency, hydrophobicity to water vapour was correlated with the total mass acyl content.

Keywords: *Acetylation, fatty acylation, hydrophobicity, mixed anhydrides, wettability, wood esters.*

Introduction

Wood, even if it is the most important renewable material, presents limiting factors such as: dimensional instability, susceptibility to biological degradation and photodegradation. When the use of less durable species such as fast-growth softwoods is considered, these limitations are considerably increased. Chemical modification of wood with linear carboxylic anhydrides is one of the potential methods for improving these properties and many reviews have been published in this field (Kumar, 1994; Norimoto, 2001). Using local non-durable species becomes attractive and the need for importing tropical wood is greatly reduced. The ecological benefit is evident.

The treatment of wood by acetic anhydride (acetylation) has been the most investigated and it has been shown that the dimensional stability (Stamm & Tarkow, 1947; Rowell *et al.*, 1987; Militz, 1991), decay resistance (Stamm & Baechler, 1960; Rowell *et al.*, 1987; Wang *et al.*, 2002; Hill *et al.*, 2006) and photostability (Dawson & Torr, 1992; Chang & Chang, 2001; Tolvaj & Mitsui, 2005) of such treated wood were enhanced. Recently, the

company Titanwood has started commercial production of acetylated wood (Nashery & Durbin, 2005).

Work with other linear-chain anhydrides has been relatively limited. Symmetrical carboxylic anhydrides, presenting aliphatic chain lengths from C2 to C7, have been investigated and their reactivity has been revealed to decrease owing to steric hindrance with the increase in the aliphatic chain (Hill & Jones, 1996; Dawson *et al.*, 1999; Li *et al.*, 2000; Chang & Chang, 2002). Improved dimensional stability has been highlighted as for acetylation, but it has been shown that the length of the fatty chain grafted on wood had no impact on the antishrink efficiency (ASE). Instead, ASE has been found to be a function only of the weight percentage gain (WPG; extent of chemical modification in mass) (Hill & Jones, 1996; Li *et al.*, 2000).

Mixed anhydrides, i.e. with two different carboxylic acid radicals, are reactive molecules that have seldom been investigated for reactions with wood constituents (Vaca-Garcia *et al.*, 1998; Vaca-Garcia & Borredon, 1999; Chemeris *et al.*, 2003). These unstable molecules are very reactive

and have the advantage of permitting the grafting of two acyl groups on wood. The acetic–fatty anhydrides enable a dimensionally stable treated wood to be obtained, showing better water repellency than acetylated wood (Magne *et al.*, 2003).

Because of their instability, the use of mixed anhydrides must be done *in situ*. Such reactive mixtures or media are obtained by reaction between a symmetrical anhydride (acetic) and a carboxylic acid yielding at equilibrium a mixed anhydride, two symmetrical anhydrides and two fatty acids (Peydecastaing *et al.*, 2009a).

The aim of this paper was to study the reactivity of mixed acetic–fatty anhydrides mixtures on wood and to evaluate the impact of the fatty chain grafted on the wettability of the mixed wood ester. Fatty acids from C8 to C18 were used as the aliphatic long chain. In contrast to previous studies, no solvent or catalyst was used. The heterogeneity of wood blocks is a handicap when focusing on the reactivity of the constituents of wood, and the reactivity can be limited by diffusion phenomena. Therefore, the reactivity of wood constituents was investigated using Scots pine sawdust (SPS). This method will yield information on the straight reactivity of mixed anhydrides towards wood constituents. Results obtained with SPS may be compared with results obtained in previous works on cellulose (Peydecastaing *et al.*, 2009b, c). The hydrophobic properties of these novel wood derivatives will be described by measuring the wettability of sawdust moulded pellets and by measurement of the sorption and desorption isotherms of the treated SPS.

Materials and methods

Chemicals and standards

Acetic anhydride and carboxylic acids: propionic (C3:0), octanoic (C8:0), capric (C10:0), lauric (C12:0), myristic (C14:0), palmitic (C16:0) and oleic (C18:1), of 99%+ purity were purchased from Sigma-Aldrich (France). Pentadecanoic acid (C15:0) was used as an internal standard in gas chromatography and was obtained from Fluka (France) (99% purity). Phosphoric acid, 85% solution in water, was purchased from Acros (France). Trimethylsulphonium hydroxide (TMSH) was obtained from Macherey-Nagel (France) as a 0.2 mol l^{-1} solution in methanol. *Tert*-butyl methyl ether (MTBE), high-performance liquid chromatography (HPLC) grade was purchased from Scharlau (Spain). All the chemicals were stored at 4°C before use.

Synthesis of the reaction media

Reaction media were prepared on a 300 ml scale. The appropriate amounts (molar ratio varying from 1:2 to 2:1) of fatty acid and acetic anhydride were added to a 500 ml glass reactor equipped with a condenser. Reactions were carried out at 100°C with mechanical stirring at 500 rpm for 1 h. The reaction media were analysed by reversed-phase HPLC (Peydecastaing *et al.*, 2008).

Scots pine sawdust esterification

SPS was Soxhlet extracted with ethanol during 8 h, dried overnight at 103°C, and then conditioned at 25°C and 60% relative humidity (RH) for 2 weeks to reach its equilibrium moisture content (EMC): 8.8%. Reactions were performed in 50 ml reactors equipped with a condenser. One gram of conditioned SPS was stirred at 350 rpm in 15 ml of reaction medium without catalyst at the desired temperature and for the required duration. After cooling down to about 80°C, 20 ml of ethanol were added to recover the soluble fraction. SPS esters were separated by filtration over fritted glass and purified by Soxhlet extraction with ethanol for 8 h. The purified product was then dried under vacuum at 70°C at least for 24 h and to constant weight.

Determination of the fatty acyl content

The method used was based on the transesterification of ester functions with TMSH followed by gas chromatography (GC) analysis. This technique has been developed for the determination of the ester content on cellulose esters and has been described in a previous paper (Peydecastaing *et al.*, 2009d). The conditions were optimized for wood and the ester content was determined as follows.

Sample preparation. A precise quantity of about 20 mg of treated SPS was introduced into a 2 ml vial. Then, 500 μl of 0.5 mmol l^{-1} pentadecanoic acid in MTBE and 250 μl of TMSH were added. The vial was hot-stirred for 60 min in a VorTemp 56 shaking incubator at 1200 rpm and 75°C. Once the sample had cooled down and the solid had been decanted, the formed fatty acid methyl esters (FAMES) in MTBE were quantified by GC.

Gas chromatography. The GC analysis was carried out using a Varian 3900 gas device equipped with a Varian 8400 autosampler, a split/splitless injector, a flame ionization detector (FID) and a Varian

CP7419 capillary column (50 m, 0.25 mm i.d., 0.25 μm film thickness). Helium was used as carrier gas, at a flow rate of 1.2 ml min⁻¹. The temperature of the injector used was set at 260°C and the split ratio at 1:20. The oven temperature was programmed as follows: 110°C for 4 min, then increased to 230°C at a rate of 15°C min⁻¹, then 230°C for 7 min. This enabled the separation of the corresponding FAMEs within 19 min. The temperature of the FID detector was set at 260°C. From the GC analysis the concentration of fatty acyl groups, C_f , can be determined.

Calculation of the ester content of fatty acyl groups in mol g⁻¹.

- C_f : concentration of the FAME in MTBE determined by GC (in mol l⁻¹)
- V_i : volume of internal standard (pentadecanoic acid) solution added to the analysed sample (in litres)
- m_i : mass of the SPS sample analysed in MTBE with TMSH (in grams).

Determination of the acetyl content. The acetyl content was determined by performing an alkaline hydrolysis followed by acidification and GC analysis of the acetic acid formed. Conditions were performed on commercial cellulose acetates and acetylated SPS and the optimal conditions are as follows.

Sample preparation. A precise amount of about 20 mg of treated SPS was weighed and introduced into a 2 ml vial. Then, 1000 μl of aqueous sodium hydroxide (0.5 N) and 500 μl of a 0.5 mmol l⁻¹ propionic acid solution in water were added. The vial was hot-stirred for 5 h in a VorTemp 56™ Shaking incubator set at 1200 rpm and 100°C. The sample was cooled down, 45 μl of H₃PO₄ was added and the vial was stirred at 1200 rpm for 10 min. Once the solid had been decanted, a small sample of the supernatant in the reaction mixture was analysed by GC.

Gas chromatography

The GC analysis was carried out as described above. Separation was achieved in a CP-Select CB for FFAP fused silica capillary column (CP7845, Varian; 25 m, 0.32 mm i.d., 0.25 μm film thickness). Helium was used as carrier gas, at a flow rate of 2.6 ml min⁻¹. The temperature of the injector used was set at 250°C and the split ratio at 1:100. The oven temperature was programmed as follows: 80°C for 1 min, then increased to 145°C at a rate of

20°C min⁻¹, then 250°C for 2 min. This enabled the separation of the acetic and propionic acids within 12 min. The temperature of the FID detector was set at 270°C. From the GC analysis the concentration of acetyl groups, C_2 , can be determined.

Calculation of the acetyl content in mol g⁻¹.

- C_2 : concentration of the acetic acid after saponification and acidification determined by GC (in mol l⁻¹)
- V_j : volume of internal standard (propionic acid) solution added to the analysed sample (in litres)
- m_j : mass of the treated SPS sample analysed (in grams).

Contact angle measurements

Pellets (10 mm diameter) of the esterified products were obtained using a laboratory press (10 t) and a conventional pellet mould at room temperature. Metal surfaces in contact with the sample were carefully cleaned to avoid pollutant sources. A drop (3 μl) of Milli-Q water was placed on the surface of the pellet and the static contact angle (CA) was measured with a goniometer (GBX Instruments, France), equipped with an automatic camera registering still images every 0.1 s. CAs were measured automatically using the triple-point calculation method. Three specimens were used for each sample. Two CA measurements were made per specimen.

Dynamic vapour sorption analysis

All experiments were performed on a dynamic vapour sorption (DVS) automated gravimetric vapour sorption analyser (Surface Measurement Systems, London, UK). The DVS measures the uptake and loss of vapour gravimetrically using a Cahn D200 recording ultra-microbalance with a mass resolution of $\pm 0.1 \mu\text{g}$. The RH around the sample was controlled by mixing saturated and dry carrier gas streams using mass flow controllers. The temperature was maintained constant ($\pm 0.1^\circ\text{C}$) by enclosing the entire system in a temperature-controlled incubator. The samples were stored in a desiccator. For each experiment SPS ester was immediately placed in the DVS under a continuous stream of dry (<0.1% RH) air. A sample size between 5 and 8 mg was used. Before being exposed to any water vapour the samples were dried at 0% RH to remove any surface water present and establish a dry, baseline mass. Next, the samples were exposed to the following RH profile: 0%, 10%,

20% ... 90%, 80% ... 0% RH. At each stage, the sample mass was allowed to reach equilibrium before the RH was increased or decreased. From the complete moisture sorption and desorption profile an isotherm was calculated using the DVS Advanced Analysis Suite v3.6. All experiments were performed at 25.0°C.

Results and discussion

Synthesis of the reaction media

The reaction between acetic anhydride and a fatty acid consists of two consecutive and equilibrated reactions (Peydecastaing *et al.*, 2009a) yielding at equilibrium a mixture of acetic acid, acetic anhydride, acetic–fatty anhydride, fatty acid and fatty anhydride (Figure 1). Reactions between acetic anhydride and oleic acid at ratios between 1:2 and 2:1 were conducted. The molar ratio of reagents in this work has been defined as fatty acid/acetic anhydride. From previous work it is known that the equilibrium state is reached in less than 15 min at 100°C (Peydecastaing *et al.*, 2009a). Therefore, all the mixtures prepared were then analysed after 1 h of reaction. The detailed compositions of all the treated media presented in this work have been described in a previous paper (Peydecastaing *et al.*, 2009b). However, for a better understanding of the reactivity of such media on SPS, it is noted that among the five entities constituting the reaction medium, the concentrations of the most abundant

reactive molecules (acetic anhydride and acetic–oleic anhydride) were relatively constant: $33.4 \pm 2.5\%$ and $24.0 \pm 2.8\%$, respectively, regardless of the molar ratio.

Synthesis and characterization of Scots pine sawdust esters

Owing to the low reactivity of carboxylic acids, especially in the absence of catalyst, only the three anhydrides present in the medium: acetic, acetic–fatty and fatty, are expected to react with SPS forming a mixed (acetic–fatty) SPS ester (Figure 2).

For the treated SPS samples the variations in the acetyl (ΔEC_2) and fatty (ΔEC_f) contents were determined and compared with an untreated reference of SPS. $\Delta EC = [(EC)_m - EC_u]$, where EC_m is the ester content of the chemically modified SPS and EC_u the ester content of the unmodified sample (blank).

The blank of untreated SPS after extraction was found to contain $917 \pm 11 \text{ mmol kg}^{-1}$ of acetyl content and $0.21 \pm 0.07 \text{ mmol kg}^{-1}$ of oleoyl content.

Figure 3 shows the evolution of the grafting yield as a function of the temperature. The reactions were conducted during 1 h and with a molar ratio of 1.5. The highest increase in ester content of oleates ($\Delta EC_{18:1}$) and acetates (ΔEC_2) was obtained at 175°C with values of 57 and 2350 mmol kg^{-1} , respectively. These values can be described in terms of WPG as 1.5% for the oleoyl groups and 9.9% for the acetyl content, which are consistent values for

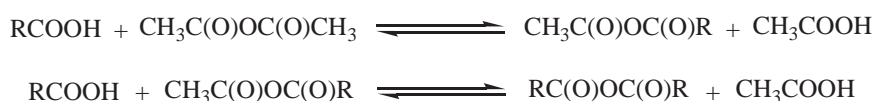


Figure 1. Consecutive reactions occurring when making react a fatty acid with acetic anhydride.

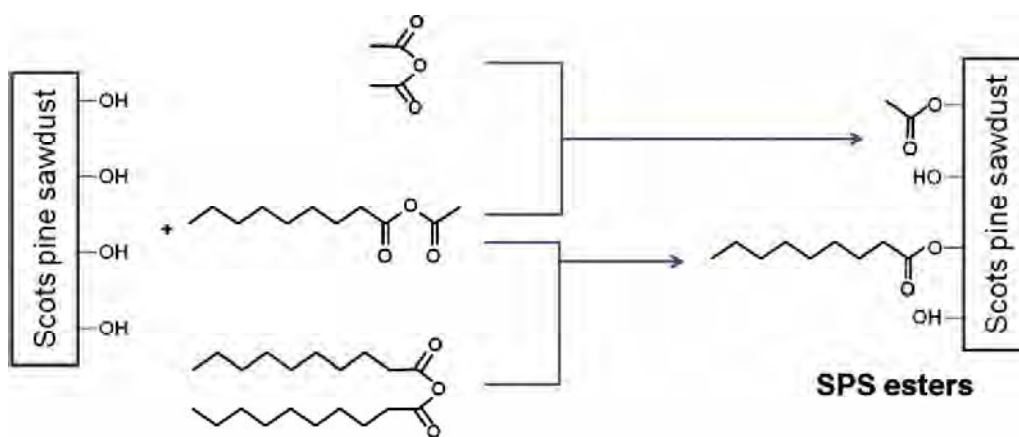


Figure 2. Esterification of Scots pine sawdust (SPS) treated by a mixture of acetic anhydride and a fatty acid.

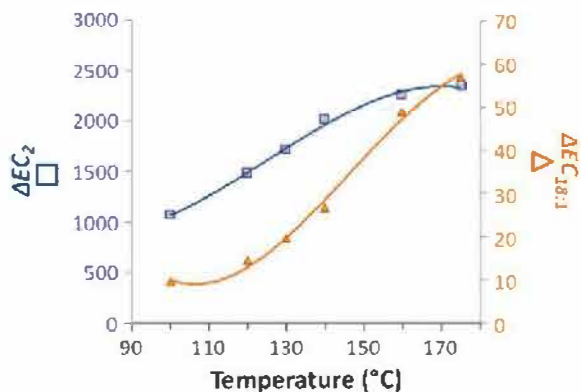


Figure 3. Influence of the reaction temperature on the acetyl and fatty acyl contents.

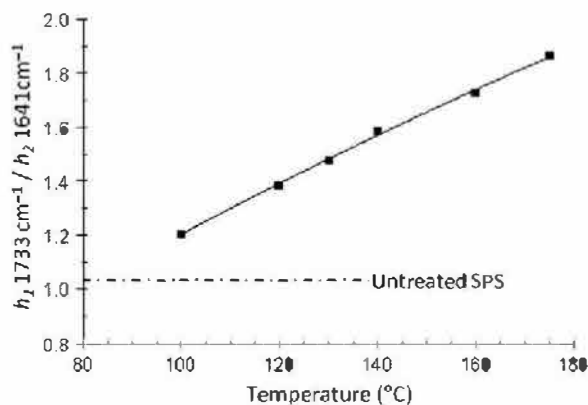


Figure 4. Ratio of two Fourier transform infrared bands transmission intensities of solvent extracted SPS treated at various temperatures. SPS = Scots pine sawdust.

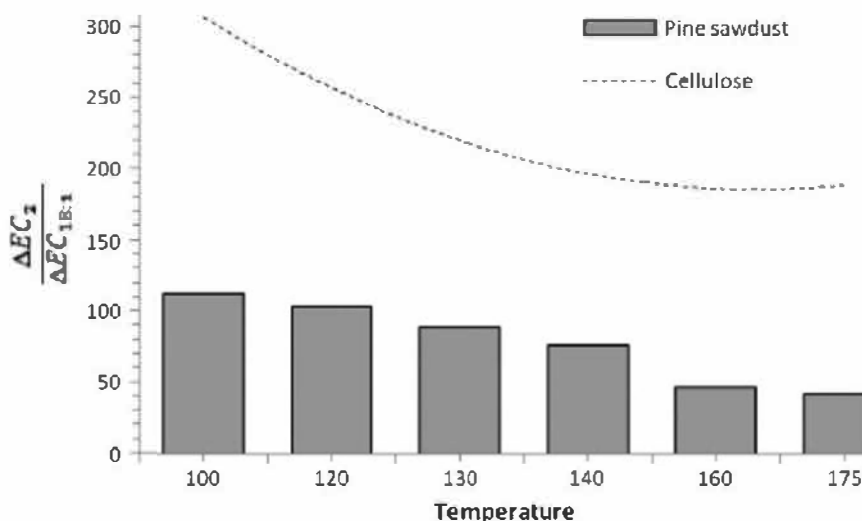


Figure 5. Influence of the reaction temperature of the treatment on the grafting ratio acetate/oleate. Molar ratio of 1.5.

SPS treated for 1 h without a catalyst or pretreatment. The individual acetyl and oleoyl contents obtained at 160°C are around two times and four times higher than those obtained at 100°C. These results highlight the fact that the esterification reaction is highly dependent on the temperature.

FTIR analysis was performed of the SPS samples treated at various temperatures. The ratio was calculated and plotted of the transmission intensities of the ester band at 1733 cm^{-1} and of a constant band characteristic of cellulose at 1641 cm^{-1} (Figure 4). The trends for the acetyl and oleoyl ester content followed the same tendency. These FTIR analyses also allowed confirmation that no residual carboxylic acids were present after extraction.

Even though Figure 3 may give the impression that the oleoylation and the acetylation follow parallel trends, in reality, the increase in temperature causes an enhancement of the global grafting but with amplified proportions of fatty chains (Figure 5). When changing the temperature from 100°C to 175°C, the ratio $\Delta EC_2 / \Delta EC_f$ diminishes, with values of 112 and 41, respectively.

One hypothesis that may explain the decrease in this ratio is that the composition of the reaction medium is dependent on the temperature. Nevertheless, as demonstrated in a previous report (Peydecastaing *et al.*, 2009a), the composition of the medium at equilibrium was scarcely dependent on the temperature. For the considered temperature, the variation in the composition would only be 3% at most. This small variation cannot account for a decrease of 50% in the substituents ratio.

Another possible explanation for the decrease in the ratio could be that the vaporization of acetic

anhydride and acetic acid, whose boiling points are 116°C and 145°C, respectively, could also affect the composition of the reaction medium and shift the equilibrium. Nevertheless, this is not the case because the decrease in the ratio is linear in the range of temperature concerned. The third and most likely hypothesis would be that the energy of activation for the grafting of acetates is lower than for the grafting of oleates.

The values of the ratio of grafting tend to reach a plateau at 160°C. More acetyl groups are grafted than oleoyl groups on SPS because the mixture still contains acetic anhydride and the acetic-oleic anhydride can lead to the formation of both acetates and oleates. Moreover, the steric hindrance of the fatty chain can account for such a difference; reasonably, the acetyl group would be more able to reach hydroxyl functions in the cellulose microfibrils than the oleoyl group from the acetic-oleic and oleic anhydrides.

Comparing these results with the values of ratio obtained when treating cellulose in the same conditions in a previous work (Peydecastaing *et al.*, 2009b), the ratio of grafting is more important in the case of cellulose. The reactivity of cellulose pulp is lower than that of SPS; the accessibility of the hydroxyl groups towards the fatty acyl groups is more difficult because of the crystallinity of cellulose. Hydrogen bonds limit considerably the reactivity of cellulose without a pretreatment or swelling agent. The reactivity of lignins and hemicelluloses present in SPS is much higher than the reactivity of cellulose, which explains the higher reactivity of SPS compared with the reactivity of cellulose pulp.

Reaction time is also an important factor (Figure 6). When a mixture with a molar ratio of 1.5 is treated at

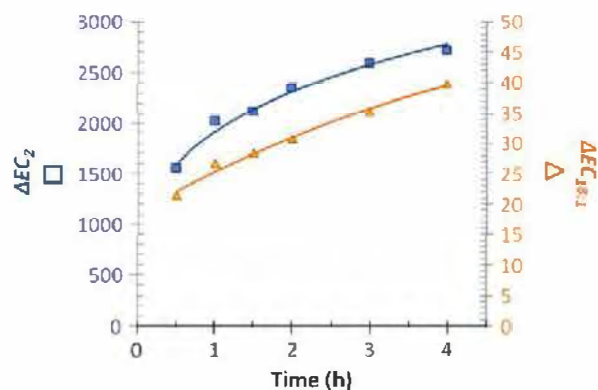


Figure 6. Influence of the duration of the treatment on the acetyl and oleoyl content. Reaction at 140°C.

140°C, the grafted acetate and oleate contents are multiplied by two when passing from 30 min to 4 h of reaction. But, surprisingly, the ratio of grafting (acetate/oleate) remains constant at a value of about 73 ± 3 for the duration of the reaction (Figure 7). Since the ratio of grafting is dependent on the temperature only and not on the reaction time, the hypothesis formulated above concerning the energies of activation is confirmed. Fatty acyl groups need more energy to react with hydroxyl groups. A limit to this ratio is reached regardless of the temperature. The limitation is due only to the steric hindrance encountered by the fatty compounds.

In the following experiments, the temperature and reaction time were kept constant (140°C, 1 h) and only the molar ratio reagents was varied. The plot of ΔEC_2 and $\Delta EC_{18:1}$ as a function of the molar ratio shows an increase of $\Delta EC_{18:1}$ with the molar ratio accompanied by a decrease in ΔEC_2 (Figure 8). It is

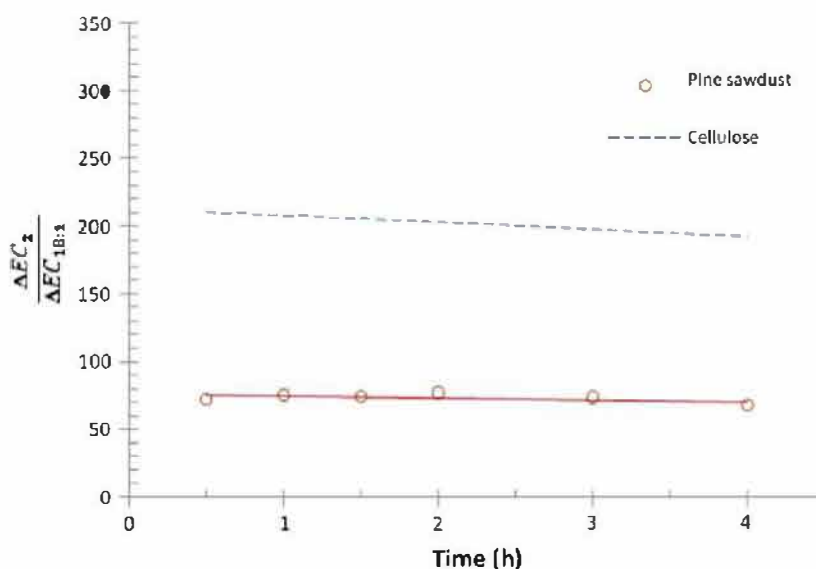


Figure 7. Influence of the reaction time on the grafting ratio acetate/oleate.

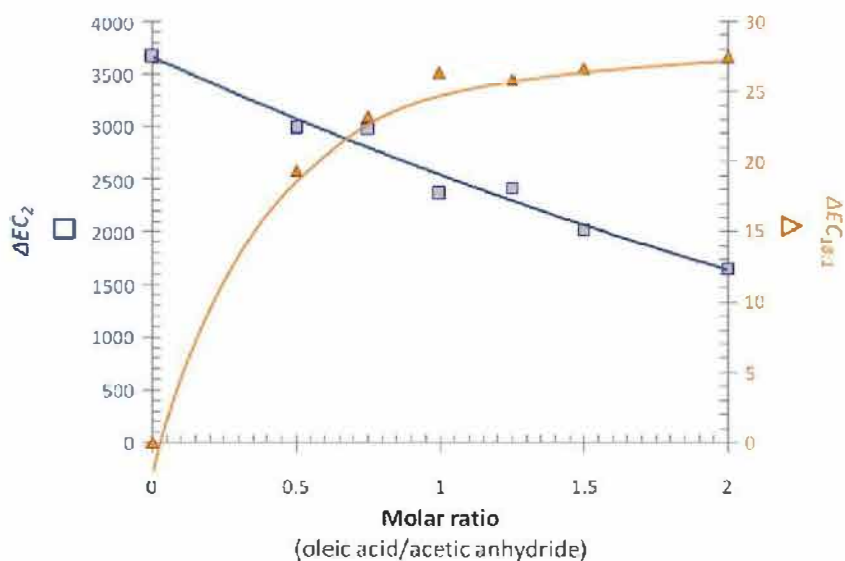


Figure 8. Influence of the molar ratio of the mixture on the acetyl and fatty acyl content.

important to note that a sample treated with pure acetic anhydride, i.e. a molar ratio of zero, presents a ΔEC_2 of 3664. This is the same order of magnitude as for acylation of SPS with a molar ratio of 0.5 with a ΔEC_2 of 3005. When the molar ratio increases, the concentration of reactive molecules tends to diminish to reach eventually the value of 0 for an infinite molar ratio (pure oleic acid). $\Delta EC_2 / \Delta EC_{18:1}$ decreases when the molar ratio of reagents increases (Figure 9). The theoretical value of $\Delta EC_2 / \Delta EC_{18:1}$ for a molar ratio of 0 (pure acetic anhydride) is infinite. This is why ΔEC_2 decreases with the molar ratio as the total concentration of molecules susceptible to acetylate SPS globally decreases. In contrast, $\Delta EC_{18:1}$ increases despite the diminishing of the total anhydride content in the mixture. This could

be explained by the fact that in a mixture of acetic anhydride and oleic acid the concentration of acetic-fatty anhydride remains constant, whereas the concentration of acetic anhydride diminishes (Peydecastaing *et al.*, 2009a). The concentration of oleic anhydride also increases, thus increasing in the mixture the concentration of molecules susceptible to forming fatty esters of SPS.

Finally, the nature of the fatty chain was varied by preparing different mixtures from acetic anhydride and fatty acids bearing saturated aliphatic chains from C8 to C16 at a molar ratio of 1.5 (Figure 10).

The plot of the ester contents as a function of the chain length (Figure 10) shows a decrease in the number of grafted fatty chains (ΔEC_f) when the number of carbon atoms of the aliphatic chain

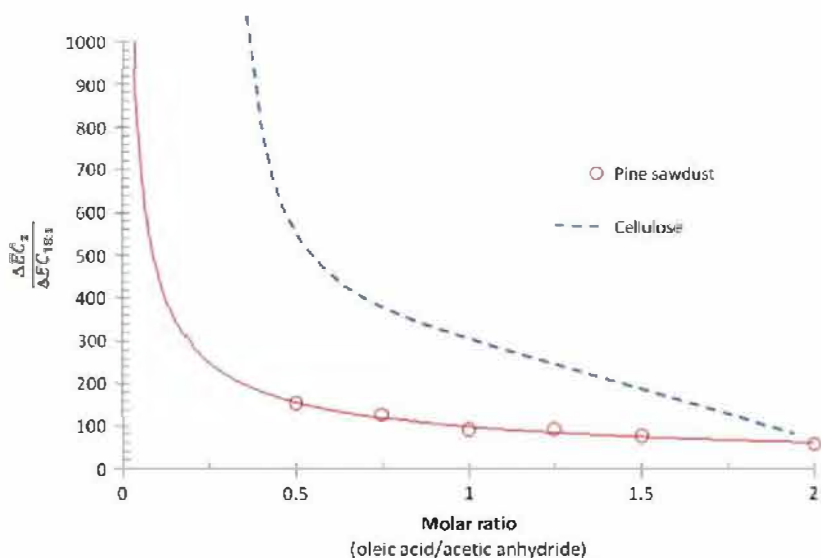


Figure 9. Influence of the molar ratio of the mixture on the grafting ratio acetate/oleate.

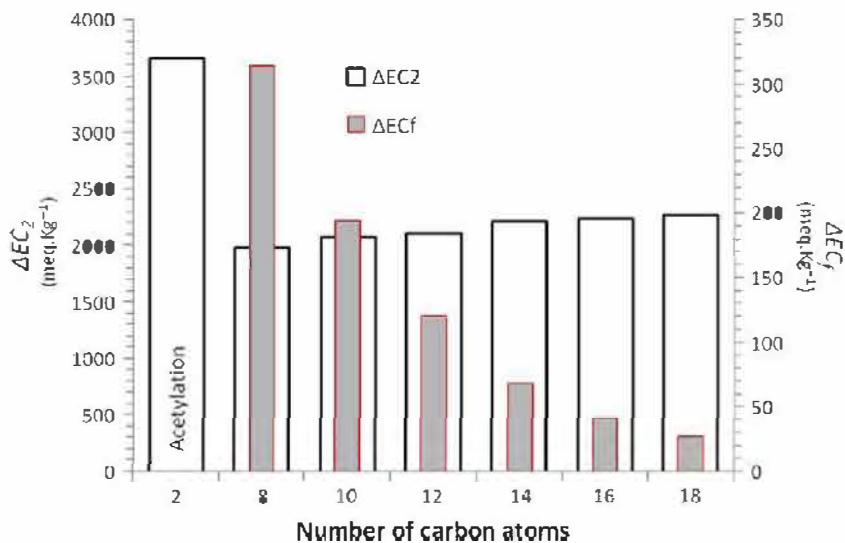


Figure 10. Influence of the aliphatic chain length on the acetyl and fatty acyl content.

increases. This can be explained by the steric hindrance encountered by the bigger molecules and by the presumed increase in the activation energies of the reaction of esterification with the length of the fatty chain. ΔEC_2 keeps approximately the same value and seems to be independent of the fatty acid used for the mixture synthesis. However, a slight increase in its value with fatty chain length was noted; this was due to the higher reactivity of the mixed anhydride. Indeed, the increase in the fatty chain length makes the mixed anhydride more asymmetrical and therefore more reactive (Arni *et al.*, 1961). The ratio of grafting (Figure 11) is therefore correlated with the difficulty in grafting fatty molecules; the steric hindrance of the fatty chains favours the grafting of acetyl groups.

Wettability of mixed Scots pine sawdust esters

Water repellency prevents or slows down the rate at which liquid water is absorbed by a material. It may therefore be correlated with the water CA measured at a certain point in time. In the case of SPS, it was necessary to make an object with a regular smooth surface. In this work, static CAs with water were measured on pellets moulded from the treated SPS samples.

First of all, the CAs of untreated SPS samples were determined, and an average value of $39 \pm 4^\circ$ was found at the initial time (0 s). The drop after deposition was totally absorbed by the material in less than 3 s. Untreated SPS can therefore be considered highly hydrophilic. The CAs of water drops deposited on the pellets prepared from SPS

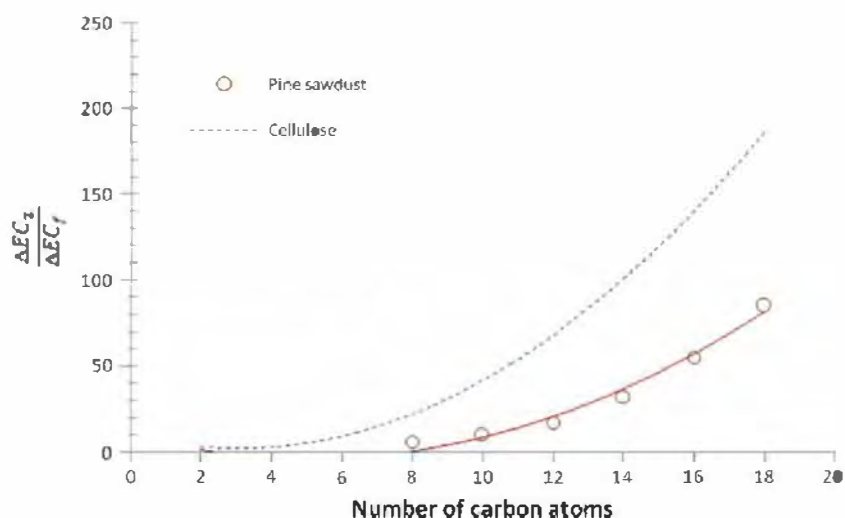


Figure 11. Influence of aliphatic chain length on the grafting ratio acetate/oleate.

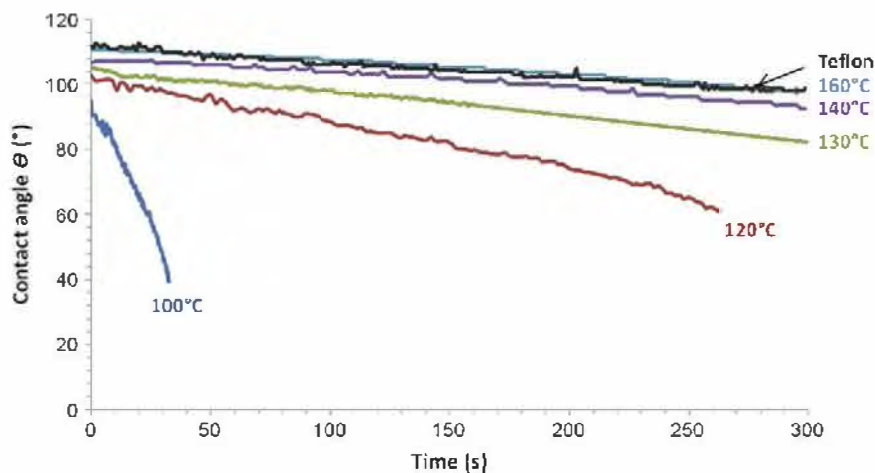


Figure 12. Water contact angles of mixed acetic–oleic Scots pine sawdust esters treated at various temperatures.

samples, treated at various temperatures with a molar ratio of 1.5 for 1 h, were then measured. The evolution of the CA as a function of time is shown in Figure 12. Although all the samples show high CA values ($>95^\circ$) at the initial time, some of them saw their CA value decrease after a few seconds. The sample treated at 100°C , for example, can be considered as wettable compared with the samples treated at temperature higher than 120°C . From a treatment temperature of 140°C , the moulded pellets of SPS esters present high water repellency with CA values of 105° and 109° at 140°C and 160°C , respectively. The CA values were measured for 5 min, and for the samples treated at 140°C and 160°C there was a slight decrease in the CA values, but no absorption of the water drop. Evaporation of the water drop due to the heat from the light may explain this decrease. Therefore, an experiment was set up with a non-porous tablet of Teflon. As the slope of the line was identical to those of SPS esters, it was concluded that this decrease was effectively induced by the measurement conditions.

A plot of the CA values measured after 1 min of contact with the pellets as a function of the temperature is also indicated in Figure 12. Considering the ester content values of these SPS esters, their water repellency is dependent on the grafting. Since the acetyl and fatty contents both increase, it is difficult to determine whether the increased water repellency is dependent on the fatty content or on the total grafting. The same observation was made with the samples treated at 140°C with acetic–oleic anhydride mixture (molar ratio of 1.5) during different reaction times (Figure 13).

The water repellency of the sample treated at molar ratios between 0 and 2 (at 140°C for 1 h) was studied. A molar ratio of 0 correspond to acetylation. Figure 14 shows the CA of these samples as a

function of time. The acetylated sample (molar ratio = 0) did not show water repellency even if its total ester content was higher than that of all the other samples. Its CA at the initial time was $52 \pm 2^\circ$ and the water drop was absorbed in less than 4 s, the same as for untreated sample. The high acetyl content does not give water repellency to the treated SPS. The literature reports acetylated wood blocks presenting CA values of 98° (Hill & Jones, 1996). However, these values were measured just after the deposit of the water drop and no information is given on the “permanent” character of this property. Moreover, the reported sample has an acetyl content of about 5700 meq kg^{-1} , which is higher than the value in the present study (3500 meq kg^{-1}).

The wettability of the samples decreases with the molar ratio of the mixture used for the treatment. The SPS samples treated with mixtures with molar ratios from 1.25 to 2 can be qualified as highly water repellent. Their initial content angles are between 105° and 110° and no absorption of the water drop by the material is observed in 5 min of measurement. These results are interesting as there is no correlation between the wettability of the samples and their total

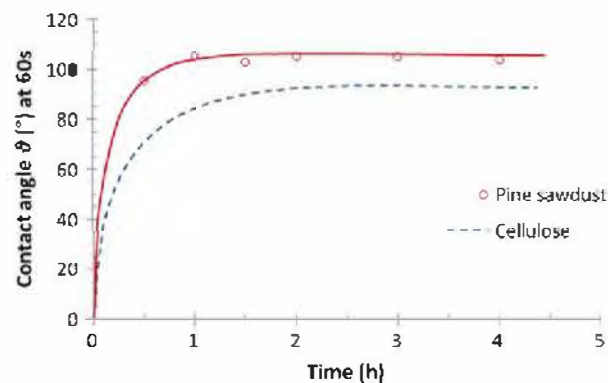


Figure 13. Water contact angles measured at 60 s of mixed acetic–oleic Scots pine sawdust esters treated at various reaction times.

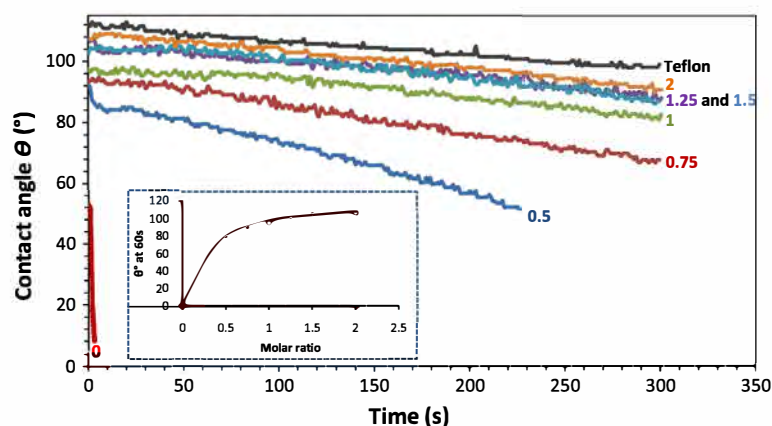


Figure 14. Water contact angles of mixed acetic-oleic Scots pine sawdust esters treated at molar ratios (oleic acid/acetic anhydride) between 0 and 2, where 0 corresponds to acetylation.

ester contents. ΔEC_2 decreases with the molar ratio, while $\Delta EC_{18:1}$ increases. This seems to indicate that the water repellency of the treated samples depends only on the fatty acyl content. The acetate content seems therefore to have no influence on the water repellency of the pellets. To confirm this hypothesis the CA values after 1 min of measurement were plotted as a function of the fatty content added by the treatment (Figure 15). A good correlation can be clearly observed ($R^2 = 0.961$). In contrast, no correlation was found with the acetyl content. This indicated that by grafting fatty chains to a low extent on SPS, an important water-repellent character can be given to the material. A threshold at 25 mmol kg^{-1} fatty acyl content for the SPS esters is highlighted in Figure 15.

The impact of the aliphatic chain on the water repellency of the treated SPS is shown in Figure 16. Although the grafting is higher for the short chains, with ratios acetyl/fatty acyl of 6 in the case of C8 and 76 in the case of C18:1, the CA values are more or less identical.

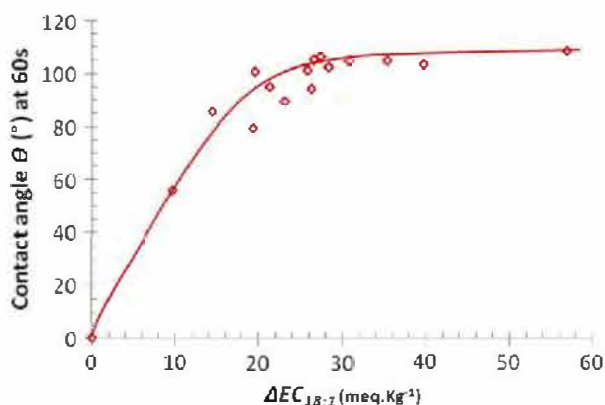


Figure 15. Water contact angles of mixed acetic-oleic Scots pine sawdust esters as a function of the oleoyl content.

Water vapour adsorption

Hydrophobicity is a concept related to the affinity of a material with water. There is no absolute scale for hydrophobicity. However, there are quantitative parameters directly related to these concepts, e.g. the EMC. In this work, hydrophobicity was considered as the capacity of SPS to adsorb water in vapour form.

Eight of the treated samples were selected to be analysed by DVS with water. The aim was to evaluate the influence of the extent of grafting and of the nature of the fatty chain. Samples representative of the whole range of variation of these parameters were selected (Table I). The sorption isotherms of these samples are gathered in Figure 17. The values of EMC are spread in a wide range owing to the significant differences among all the samples. The sample that shows the highest hydrophobicity is the acetylated sawdust (SPS1). Any of the samples containing grafted fatty chains are less hydrophobic than this sample containing only C2 aliphatic chains. This surprising fact seems to be in contradiction with the values of CA.

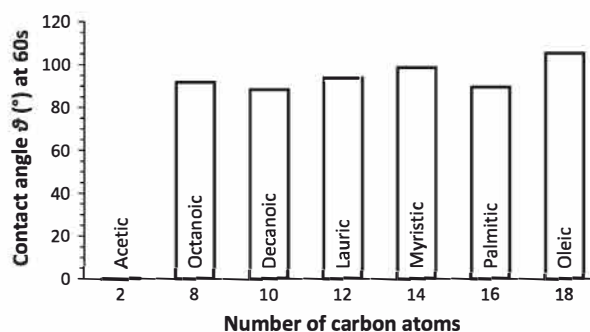


Figure 16. Water contact angles of mixed acetic-fatty Scots pine sawdust esters measured at 60 s. A synthesized SPS acetate sample is also shown.

Table I. Acyl contents of treated samples selected for dynamic vapour sorption analyses.

Sample	ΔEC_2	ΔEC_f	ΔEC_{total}	Δ Acyl fraction (total) ($g\ kg^{-1}$)
SPS1 C ₂	3664	–	3664	154.0
SPS2 C ₂ -C ₈	1981	314	2295	166.3
SPS3 C ₂ -C ₁₀	2075	194	2269	138.5
SPS4 C ₂ -C ₁₂	2108	121	2229	120.6
SPS5 C ₂ -C ₁₆	2245	41	2286	105.2
SPS6 C ₂ -C _{18:1}	2018	27	2045	91.9
SPS7 C ₂ -C _{18:1}	1649	28	1677	76.7
SPS8 C ₂ -C _{18:1}	1079	10	1089	48

Indeed, all the acetic-fatty SPS samples exhibited permanent hydrophobicity, whereas the acetylated sample did not. Remember that the water repellency is dependent only on the ΔEC_f . In this case, the hydrophobicity measured with the DVS device does not depend on the fatty acyl content. Instead, it depends exclusively on the total acyl content expressed on a mass basis (Figure 18). Other correlations were explored (in function of the molar acetyl content, or the molar fatty acyl content), but none of them was satisfactory. This is not the first time that this type of correlation was expressed. Hill and Jones (1996) demonstrated that the ASE of Corsican pine was dependent on the WPG. The latter is a parameter equivalent to the mass acyl content. These results indicate that water repellency and the ability to adsorb water vapour are two different concepts.

Finally, comment is made on recent works on the esterification of guaiacol and glucose as lignin and cellulose model compounds by mixed acetic-oleic anhydride mixtures. Lyon *et al.* (2008) did not find any evidence of the grafting of fatty chains and concluded that the process claimed by Magne *et al.*

(2003) was reduced to a pure acetylation of the substrates. The analytical method used to characterize the chemically modified model compounds (MAS-DEC, [¹³C]NMR) is evidently not adapted to the characterization of low degrees of substitution. In such cases, specific analytical methods are required (Peydecastaing *et al.*, 2009d). The claim by Lyon *et al.* (2008) that the water repellency of modified wood observed by Magne *et al.* (2003) was due to remaining free fatty acids is false. As demonstrated in the present study, a small amount of grafted fatty chains compared to acetyl groups enables permanent water repellency to be attained.

Conclusions

Mixed SPS esters bearing acetyl and fatty acyl groups can be synthesized by reaction in a medium prepared from acetic anhydride and a fatty acid without the use of any solvent or catalyst. The relative proportion of the acetyl and fatty acyl groups grafted on SPS can be controlled by an appropriate selection of the molar ratio of the initial reagents, the

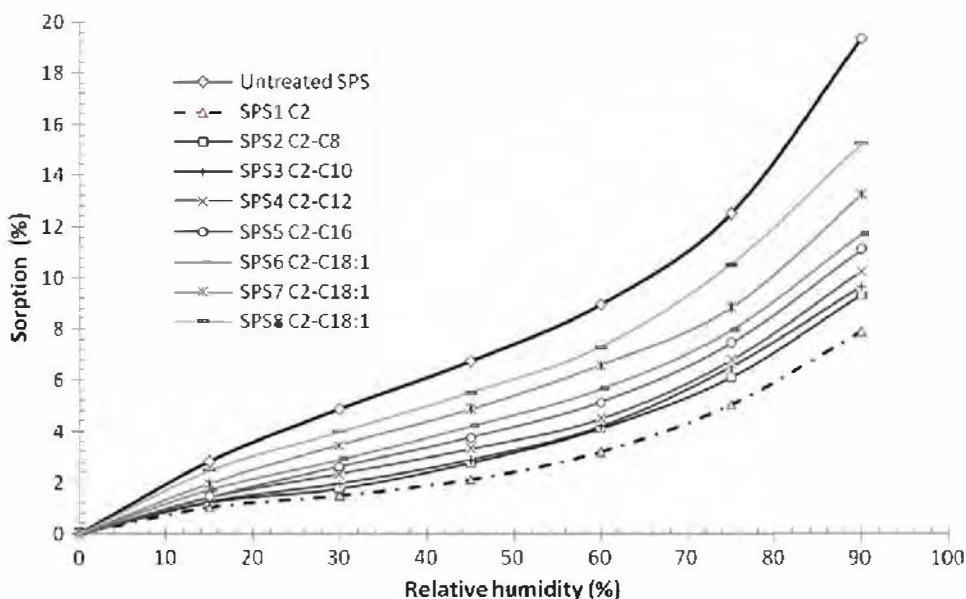


Figure 17. Dynamic vapour sorption analysis of samples described in Table I. SPS = Scots pine sawdust.

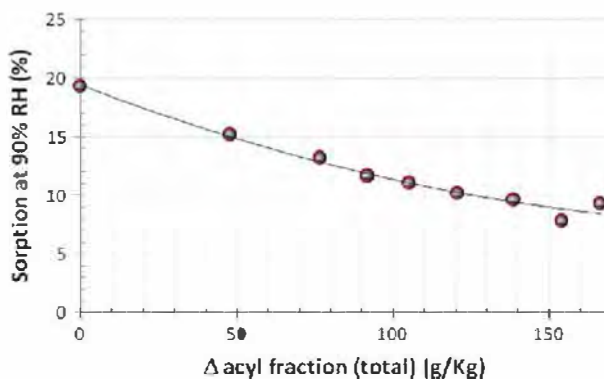


Figure 18. Influence of the acyl groups content on the hydrophobicity of esterified sawdust. RH =relative humidity.

nature of the fatty acid and the conditions of treatment.

The CA of SPS acetate is null, indicating that water repellency depends only on the fatty acyl content in the studied range of esterification. Mixed acetic–fatty SPS esters shaped into pellets could exhibit water repellency at low fatty contents. The CA values of such mixed SPS esters lay between 90° and 110°. In the case of acetic–oleic SPS esters the minimum fatty acyl content to reach water repellency was 25 mmol kg⁻¹.

The EMC has been demonstrated to be dependent on the mass acyl proportion, in contrast to the water repellency. The nature of the substituent had no impact in the studied domain.

The mixed anhydride mixture use here enabled chemically modified substrates to be obtained that showed both hydrophobicity and water repellency.

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References

Arni, P. C., Gray, J. D. & Scougall, R. K. (1961). Chemical modification of wood. I. Use of trifluoroacetic anhydride in the esterification of wood by carboxylic acids. *Journal of Applied Chemistry*, 11, 157–163.

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

Chang, H.-T. & Chang, S.-T. (2002). Moisture excluding efficiency and dimensional stability of wood improved by acylation. *Bioresource Technology*, 85, 201–204.

Chemeris, M. M., Musko, N. P., Salin, B. N. & Konshin, V. V. (2003). Synthesis of cellulose esters in a trifluoroacetic acid medium. *Efiry Tsellyulozy i Krakhmala: Sintez, Svoistva, Primenenie, Materialy Yubileinoi Vserossiiskoi Nauchno-Tekhnicheskoi Konferentsii s Mezhdunarodnym Uchastiem, 10th, Suzdal, Russian Federation, May 5–8, 2003* (pp. 108–115).

Dawson, B. & Torr, K. (1992). Spectroscopic and color studies on acetylated radiata pine exposed to UV and visible light. *FRI Bulletin*, 176 (Chemical Modification of Lignocellulosics), 41–51.

Dawson, B. S. W., Franich, R. A., Kroese, H. W. & Steward, D. (1999). Reactivity of radiata pine sapwood towards carboxylic acid anhydrides. *Holzforschung*, 53, 195–198.

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

Hill, C. A. S., Hale, M. D., Ormondroyd, G. A., Kwon, J. H. & Forster, S. C. (2006). Decay resistance of anhydride-modified Corsican pine sapwood exposed to the brown rot fungus *Comiophora puteana*. *Holzforschung*, 60, 625–629.

Kumar, S. (1994). Chemical modification of wood. *Wood and Fiber Science*, 26, 270–280.

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

Lyon, F., Thevenon, M. F., Pizzi, A., Tondi, G., Despres, A., Gril, J. & Rigolet, S. (2008). In: *Wood preservation by a mixed anhydride treatment: Using simple models of polymeric wood compounds for an ¹³C NMR investigation*. International Research Group on Wood Protection IRG 39, Istanbul, Turkey, May 25–29, 2008.

Magne, M., El Kasmi, S., Dupire, M., Morard, M., Vaca-Garcia, C., Thiebaud-Roux, S., et al. (2003). Method for treating lignocellulosic materials, in particular wood and material obtained by said method. WO084723.

Militz, H. (1991). The improvement of dimensional stability and durability of wood through treatment with non-catalyzed acetic-acid anhydride. *Holz als Roh- und Werkstoff*, 49, 147–152.

Nashery, K. & Durbin, G. J. (2005). Impregnation process. WO2005077626.

Norimoto, M. (2001). Chemical modification of wood. In D. N. S Hon & N. Shiraiishi (Eds.), *Wood and Cellulosic Chemistry* (2nd ed.) (pp. 573–598). New York: Marcel Dekker.

Peydecastaing, J., Vaca-Garcia, C. & Borredon, E. (2008). Quantitative analysis of mixtures of various linear anhydrides and carboxylic acids. *Chromatographia*, 68, 685–688.

Peydecastaing, J., Vaca-Garcia, C. & Borredon, E. (2009a). Consecutive reactions in an oleic acid and acetic anhydride reaction medium. *European Journal of Lipid Science and Technology*, 111, 723–729.

Peydecastaing, J., Vaca-Garcia, C. & Borredon, E. (2009b). Reactivity of mixed acetic–fatty anhydride mixtures toward cellulose. *Cellulose* (in press).

Peydecastaing, J., Vaca-Garcia, C. & Borredon, E. (2009c). Hydrophobicity of mixed acetic–fatty cellulose esters. *Cellulose* (in press).

Peydecastaing, J., Vaca-Garcia, C. & Borredon, E. (2009d). Accurate determination of the degree of substitution of long chain cellulose esters. *Cellulose*, 16, 289–297.

Rowell, R. M., Simonson, R. & Tillman, A. M. (1987). *A process for improving dimensional stability and biological resistance of lignocellulosic material*. European Patent EN 0213252 B1.

Stamm, A. J. & Baechler, R. H. (1960). Decay resistance and dimensional stability of five modified woods. *Forest Products Journal*, 10, 22–26.

- Stamm, A. J. & Tarkow, H. (1947). Dimensional stabilization of wood. *Journal of Physical and Colloid Chemistry*, 51, 493–505.
- Tolvaj, L. & Mitsui, K. (2005). Light source dependence of the photodegradation of wood. *Journal of Wood Science*, 51, 468–473.
- Vaca-Garcia, C. & Borredon, M. E. (1999). Solvent-free fatty acylation of cellulose and lignocellulosic wastes. Part 2. Reactions with fatty acids. *Bioresource Technology*, 70, 135–142.
- Vaca-Garcia, C., Thiebaud, S., Borredon, M. E. & Gozzelino, G. (1998). Cellulose esterification with fatty acids and acetic anhydride in lithium chloride/N,N-dimethylacetamide medium. *Journal of the American Oil Chemists' Society*, 75, 315–319.
- Wang, C.-L., Lin, T.-S. & Li, M.-H. (2002). Decay and termite resistance of planted tree sapwood modified by acetylation. *Taiwan Linye Kexue*, 17, 483–490.