Hydrophobicity of Mixed Acetic-Fatty Wood Esters

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ABSTRACT

Mixed acetic-fatty esters of Scots pine sawdust (SPS) were obtained after reaction between SPS and mixtures containing acetic-fatty anhydrides. No solvent or catalyst was used. 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 treatment conditions, 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. Measurement over 5 minutes of static contact angles (CA) with water permitted to evaluate the water repellency of esterified SPS. 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 (WR) was 25 mmol.Kg-1. Water vapor adsorption measurements indicated that contrarily to WR, hydrophobicity to water vapor was correlated to the total mass acyl content.

INTRODUCTION

Wood, even if it is the most important renewable material, presents limiting factors such as: dimensional instability, susceptibility to biological degradation and photo-degradation. Chemical modification of wood with linear carboxylic anhydrides is one of the potential methods for improving these properties. The treatment of wood by acetic anhydride has been the most investigated and it has been shown that the dimensional stability (Stamm and Tarkow 1947, Rowell, Simonson *et al*. 1987, Militz 1991) the decay resistance (Stamm and Baechler 1960, Rowell *et al*. 1987, Wang, Lin *et al*. 2002, Hill *et al*. 2006) and the photostability (Dawson and Torr 1992; Chang and Chang 2001; Tolvaj and Mitsui 2005) of such treated wood was enhanced. Symmetrical carboxylic anhydrides, presenting aliphatic chain lengths from C2 to C7, have been investigated and their reactivity has been revealed to decrease due to steric hindrance with the increase of the aliphatic chain (Hill and Jones 1996, Dawson *et al*. 1999, Li *et al*. 2000, Chang and Chang 2002). An improved dimensional stability has been highlighted as for acetylation but ASE has been found to be a function only of the weight percentage gain (WPG, extent of chemical modification in mass) (Hill and Jones 1996, Li *et al*. 2000). Mixed anhydrides, *i.e*. with two different carboxylic acid radicals

are reactive molecules that have been seldom investigated for reactions with wood constituents(Vaca-Garcia *et al*. 1998, Vaca-Garcia and Borredon 1999, Chemeris, Musko *et al*. 2003). These unstable molecules are very reactive and present the advantage to permit the grafting of two acyl groups on wood. The acetic-fatty anhydrides permitted obtaining a dimensionally stable treated wood showing better water repellency compared to acetylated wood (Magne *et al*. 2003). Our main objective in this work was to study the reactivity of mixed acetic-fatty anhydrides mixtures on Scots pine sawdust and to evaluate the impact of the fatty chain grafted on the wettability of the mixed SPS ester.

EXPERIMENTAL

Synthesis of the reaction mediums

Reaction mediums 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 during 1 hour. The reaction mediums were analyzed by reversed-phase HPLC (Peydecastaing *et al*. 2008).

Scots pine sawdust esterification

SPS was Soxhlet extracted with ethanol during 8 h, then dried overnight at 103 °C and then conditioned at 25 °C and 60% relative humidity (RH) during two weeks. Reactions were performed in 50 mL reactors equipped with a condenser. 1 g of conditioned SPS was stirred at 350 rpm in 15 mL of reaction medium without catalyst at the desired temperature and duration time. 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 and acetyl contents

In order to determine the fatty acyl content, we employed the method 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*. 2008). The acetyl content was determined by performing an alkaline hydrolysis followed by acidification and GC analysis of the acetic acid formed.

Contact angle measurements

Pellets (10 mm diam.) of the esterified products were obtained using a laboratory press (10 t) and a conventional pellet mold. 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 was measured with a goniometer (GBX Instruments, France), equipped with an automatic camera registering still images every 0.1 seconds. Contact angles were measured automatically using the triple point calculation method. Three specimens were used for each sample. Two contact angle measurements were done per specimen.

Dynamic vapour sorption (DVS) analysis

All experiments were performed on a DVS automated gravimetric vapor sorption analyzer (Surface Measurement Systems Ltd., London, UK). The DVS measures the

uptake and loss of vapour gravimetrically using a Cahn D200 recording ultra-microbalance with a mass resolution of ±0.1 µg. A sample size between 5 and 8 mg was used. Prior to being exposed to any water vapour the samples were dried at 0% relative humidity (RH) to remove any surface water present and establish a dry, baseline mass. Next, the samples were exposed to the following relative humidity profile: 0%, 10%, 20% … 90%, 80% … 0% RH. At each stage, the sample mass was allowed to reach equilibrium before the relative humidity was increased or decreased. All experiments were performed at 25.0 °C.

RESULTS AND DISCUSSION

Synthesis of the reaction mediums

The reaction between acetic anhydride and a fatty acid consists in two consecutive and equilibrated reactions (Peydecastaing *et al*. 2008) yielding at equilibrium a mixture of acetic acid, acetic anhydride, acetic-fatty anhydride, fatty acid and fatty anhydride. The detailed compositions of all the treated mediums presented in this work have been described in a previous paper (Peydecastaing *et al*. 2008). However, for a better understanding of the reactivity of such mediums on SPS, we will remind that among the five entities constituting the reaction medium, the concentration of the most abundant reactive molecules: acetic anhydride and acetic-oleic anhydride were relatively constant: 33.4% ± 2.5% and 24.0% ± 2.8% respectively regardless of the molar ratio.

Synthesis and characterization of SPS esters

Due 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 anhydrides are expected to react with SPS in order to form a mixed (acetic-fatty) SPS ester (Figure 1).

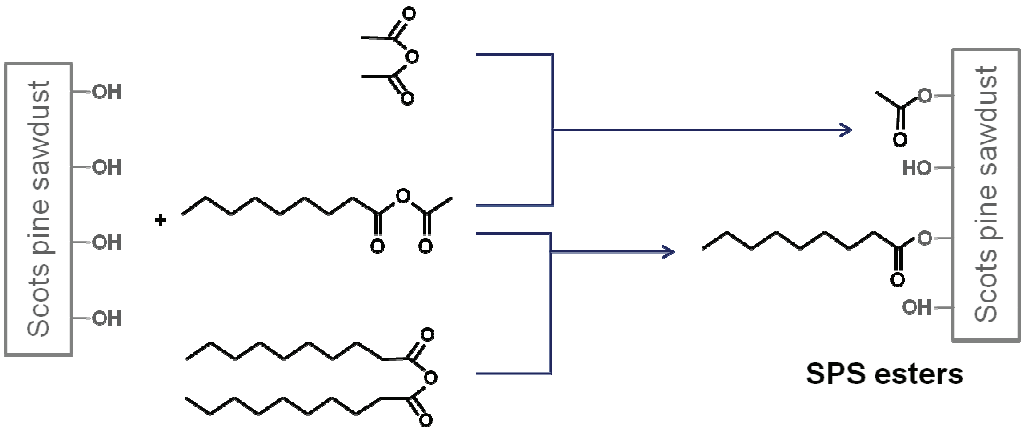

Figure 1: Scots pine sawdust esterification by mixed anhydride mixtures

We determined for the treated SPS samples the variations of the acetyl (ΔEC_2) and fatty (ΔEC_f) contents compare to an untreated reference of SPS. ΔEC=(EC_m-EC_u) were 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 was found to contain 917±11 mmol.kg-1 of acetyl content and 0.21±0.07 mmol.kg-1 of oleoyl content. Figure 2 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.

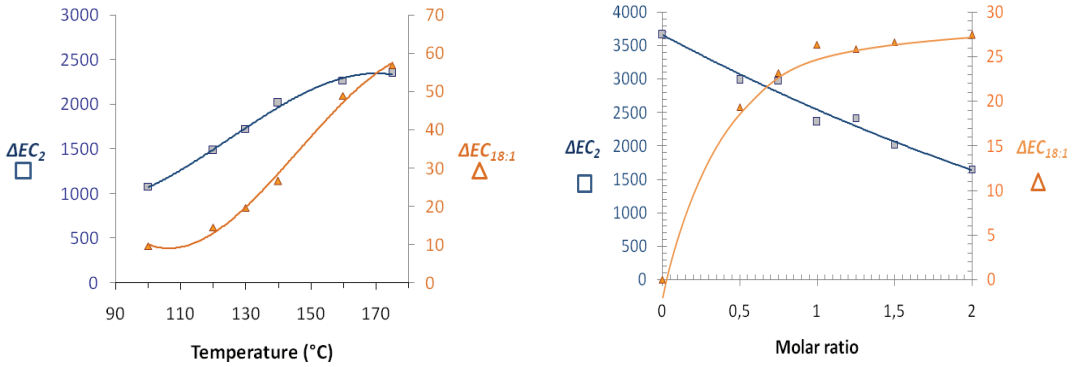

Figure 2: Influence of the reaction temperature and molar ratios on the acyl contents

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 SPS treated 1 hour without a catalyst or pretreatment. These results highlight the fact that the esterification reaction is highly dependent on the temperature. Besides, we performed FTIR to confirm that no residual carboxylic acids were present after extraction. Even though Figure 2 may give the impression that the oleoylation and the acetylation follow parallel trends, in reality, the increase of the temperature causes an enhancement of the global grafting but with amplified proportions of fatty chains. The ratio $\Delta EC_2/\Delta EC_f$ is divided by about three passing from 112 at 100 °C to 41 at 175 °C. The steric hindrance of the fatty chain can account for such a difference; reasonably the acetyl group would present more ability to reach hydroxyl functions in the cellulose microfibrils than the oleoyl group from the acetic-oleic and oleic anhydrides. Reaction time is also an important factor. When treated at 140 °C a mixture with a molar ratio of 1.5, the grafted acetate and oleate contents are multiplied by two when passing from 30 min to 4 hours of reaction. But surprisingly the ratio of grafting (acetate/oleate) remains constant at a value of about 73±3 during the whole duration of the reaction.

Since the grafting is dependent on the temperature only and not on the reaction time, the energies of activation needed to make react fatty acyl and acetyl groups are different. Fatty acyl groups need more energy to react with hydroxyl groups. In the following experiments, the temperature and reaction time were kept constant (140 °C, 1 h) and we only varied the reagents molar ratio. 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 of ΔEC_2 (Figure 2). It is important to note that a sample treated with pure acetic anhydride, i.e. a molar ratio of zero, presents a ΔEC_2 of 3664. When the molar ratio increases, ΔEC_2 decreases as the total concentration of molecules susceptible to acetylate SPS globally decreases. On the contrary, $\Delta EC_{18:1}$ increases despite the diminishing of the total anhydride content in the mixture. This could be explained by the fact that the concentration of acetic-fatty anhydride remains constant and oleic anhydride is formed whereas the concentration of acetic anhydride diminishes (Peydecastaing *et al*. 2008). Finally, we varied the nature of the fatty chain by preparing different mixtures form acetic anhydride and fatty acids bearing saturated aliphatic chains from C8 to C16 at a molar ratio of 1.5. A decrease of the number of fatty chains grafted (ΔEC_f) when the number of carbon atoms of the aliphatic chain increases was observed. This can be explained by the steric hindrance encountered by the bigger

molecules and by the presumed increase of the activation energies of the reaction of esterification with the length of the fatty chain.

Wettability of mixed SPS esters

Water repellency prevents or slows down the rate at which liquid water is absorbed by a material. It may therefore be correlated to the water contact angle measured at a certain time. In the case of pine sawdust, it was necessary to make an object with a regular smooth surface. In this work, static contact angles (CA) with water were measured on pellets molded from the treated SPS samples. First of all, we determined the CA of untreated SPS samples and found an average value of 39°±4 at initial time (0 s). The drop after deposited was totally absorbed by the material in less than 3 s. Untreated SPS can therefore be considered as highly hydrophilic. We then measured the CA of water drops deposited on the pellets prepared from all the treated SPS samples. The evolution of the CA as a function of time was followed as for example in the case the SPS samples treated at various molar ratios (Figure 3).

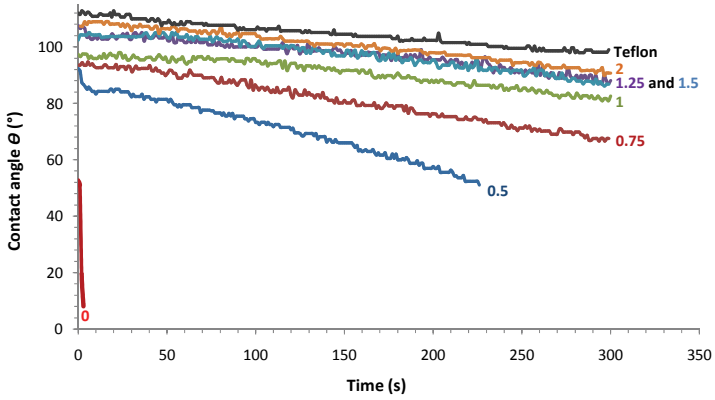

Figure 3: Water contact angles of mixed acetic-oleic SPS esters treated at molar ratios (oleic acid/acetic anhydride) comprised between 0 to 2. 0 corresponds to acetylation.

We can note that the sample acetylated does not present water repellency even if its total ester content is higher than that of all the other samples. The SPS samples treated with mixtures with molar ratio from 1.25 to 2 can be qualified as highly water repellent with content angles comprised between 105 and 110° after five minutes of measurement. This seems to indicate that the water repellency of the treated samples depends only on the fatty acyl content. In order to confirm this hypothesis we plotted the CA values after 1 min of measurement as a function of the fatty content added by the treatment (Figure 4).

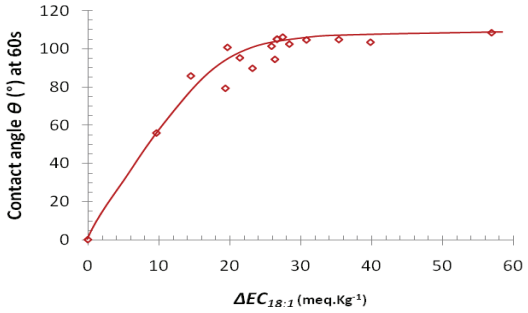

Figure 4: Water contact angles of mixed acetic-oleic SPS esters as a function of the oleoyl content

A correlation can be clearly observed. On the contrary no correlation was found with the acetyl content. This definitely indicated that by grafting fatty chains in low extent on pine sawdust, an important water repellent character can be given to the material. A threshold at 25 mmol.Kg-1 of fatty acyl content for the SPS esters is highlighted in Figure 4.

Water vapor 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 equilibrium moisture content. In this work we will consider hydrophobicity as the capacity of SPS to adsorb water in vapor form. Eight of the treated samples were selected to be analyzed by dynamic vapor sorption with water. We aimed to evaluate the influence of the extent of grafting and of the nature of the fatty chain. We selected samples representative of the whole range of variation of these parameters (Table 1).

Table 1: Hydrophobicity parameters

Sample	ΔEC_2	ΔEC_f	ΔEC_{total}	Δ acyl fraction (total) (g/Kg)
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

The sorption isotherms of these samples are gathered in Figure 5.

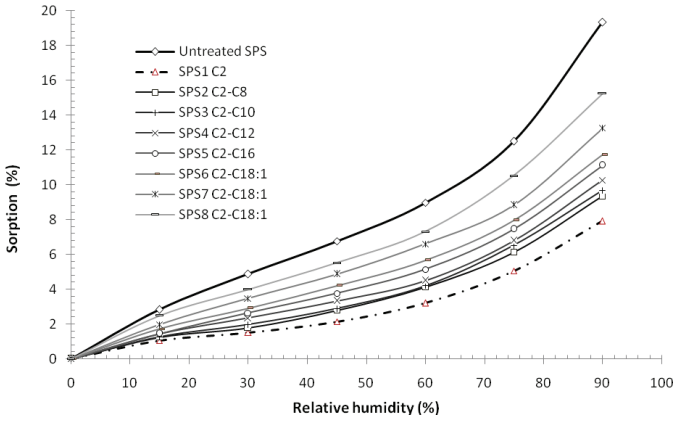

Figure 5: Dynamic vapor sorption analysis of samples described in Table 1

The values of equilibrium moisture content are spread in a wide range due 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 is less hydrophobic that this sample containing only C2 aliphatic chains. This surprising fact seems to be in contradiction with the values of CA. Indeed, all the acetic-fatty SPS samples exhibited permanent hydrophobicity whereas the acetylated

sample did not. Let us remind 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 6).

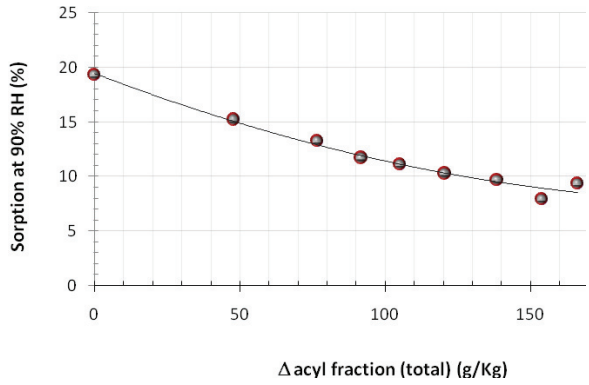

Figure 6: Influence of the acyl groups content on the hydrophobicity of esterified sawdust

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 is expressed. Hill and co-workers (Hill and Jones 1996) demonstrated that the anti-shrink efficiency of Corsican pine was dependent on the weight percentage gain. The latter is a parameter equivalent to the mass acyl content. These interesting results indicate that the water repellency and the ability to adsorb vapor water are two different concepts.

CONCLUSIONS

Mixed Scots pine sawdust 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 nature of the fatty acid, and the conditions of treatment. The contact angle 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 contact angles values of such mixed SPS esters were comprised between 90° and 110°. In the case of acetic-oleic SPS esters the minimum fatty acyl content to reach water repellency is 25 mmol.Kg-1. Equilibrium moisture content has been demonstrated to be dependent on the mass acyl proportion, contrarily to the water repellency. The nature of the substituent had no impact in the studied domain. The use mixed anhydride mixture permit to obtain chemically modified substrates able to show both hydrophobicity and water repellency.

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