

# Water-repellent acylated and silylated wood samples and their surface analytical characterization

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## Abstract

The interest for chemical modification of wood with the aim of preserving it from physical and biochemical deterioration is rapidly increasing. Among the possibilities, acetylation has a great potential for improving the dimension instability of wood against moisture and the durability of wooden objects. Recently, a new acetylating agent, isopropenyl acetate has attracted attention giving an improved acetylating method. By increasing the size of the acyl group, a positive effect on the wood hydrophobicity can be reached. The anhydrides, however, are less reactive. Another applicable surface modification is the silylation of wood that renders the wood surface hydrophobic.

In this paper, we report about the acylation and silylation of different wood samples. A new manufacturing process is tested in which low-value *Eucalyptus* wood is mixed acylated. The reagent mixture contains at least two kinds of acyl group. One of them is acetyl group; the other(s) can be user-defined. We also report about a silylation method, in which catalyst facilitates the chemisorption process. The extent of modification of the treated wood samples was evaluated by means of weight percent gain, ATR-FTIR, and pyrolysis-gas chromatography–mass spectrometry (Py-GC/MS). Methylene blue adsorption of selected samples was also studied. The result of analytical measurements was in agreement with that of wettability studies.

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## 1. Introduction

Chemical modification of wood exhibits a great potential for improving its properties, to increase the dimensional stability against moisture and bio-deterioration, increasing the service life and extending the applicability. Numerous reviews can be found on chemical modification of wood with a variety of chemicals [1,2]. Most of the research works have been devoted to acetylation. The technical acetylation uses acetic anhydride at 120–130 °C without catalyst. This reagent has the advantage that it is not toxic and not so expensive as other modifying chemicals. During this reaction, however, acetic acid is evolved as a side-product, which is difficult to remove from the wood.

Recently, a new acetylation agent for wood, isopropenyl acetate (IPA) has been applied for the modification. In this reaction (Fig. 1) catalysts are used, but high acetylation grade can be achieved even at lower temperature (80–110 °C) and only acetone will be released as side product [3–5].

Only few works were published about reagents with longer acyl groups for treating wood, although the longer acyl groups are expected to bring even more improved properties of wood for special applications or for wood polymer composites (WPCs). Chang and Chang [6] compared the light fastness of acetylated and butyrylated China fir wood. It was detected that the inhibition effect of butyrylation on the photo-yellowing of wood was superior to that of acetylation.

Another possible surface modification of wood is silylation. Silylation of wood aroused the interest because this reaction-type renders the surface hydrophobic efficiently (see e.g. [7,8]). Recently, several papers have been reported on silylation of wood [9–16]. However, it was revealed not long ago that

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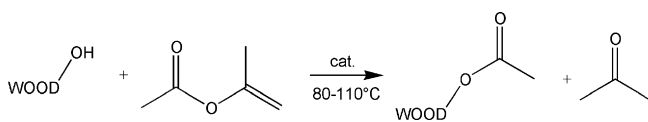


Fig. 1. The scheme of the reaction of wood hydroxyl groups with IPA.

direct silylation of wood by chlorosilanes might only result in physisorption of agents at room temperature [17].

In this paper, we report about the silylation and acylation of apple (*Malus sylvestris*) and eucalypt (*Eucalyptus globulus*, abbreviated as *Euca*) wood samples.

The crab apple is native in semi-natural woodlands in Britain and occurs also in different countries of Europe. The tree is too small to produce large timber, but the wood is of great value especially for carving.

The *E. globulus* is very advantageous in forestry due to its rapid growth and the high resistance to various pests and pathogens. It is ideal for pulp and paper but has not been widely used as a timber due to the inconvenience with its high water soaking, its low dimensional stability with very high swelling and shrinkage coefficients [18]. The market of eucalypti would quickly develop especially if its water repellence and dimension stability can be significantly increased. The urgent need to find successful ways and technologies for its uses of high quality justifies choosing *Euca* for our investigations.

The purpose of the present work is to show a solvent free acylation process [19] for wood that results in mixed acylated wood particles and leads to high weight percent gain. The effect of longer alkyl chains of acylation agent on the surface properties is also demonstrated. On the other hand, some novel silylating surface treatments are reported which are tested by water-uptake and contact angle measurements. Moreover, reactivity of wood sample is also investigated both in acylation and silylation reactions. The treated samples and the obtained surface layers are characterized using different analytical methods and the practical viability of the improved processes are estimated.

## 2. Experimental

### 2.1. Chemicals

The following chemicals were used: (a) silylating agents: chlorotrimethylsilane (CTMS) (Merck,  $\geq 99\%$ ), octadecyltrichlorosilane (OTS) (Merck,  $\geq 98\%$ ), dichlorodiphenylsilane (DPS) (Fluka,  $\geq 98.5\%$ ) and dichlorodimethylsilane (DDS) (Fluka,  $\geq 98\%$ ). (b) Acylating agents: isopropenyl acetate (99%), propionic acid (99%), hexanoic acid (99%) and undecanoic acid (99%) were purchased from Fluka. (c) Wettability test liquids: ion exchanged water (Millipore,  $18.2 \text{ M}\Omega \text{ cm}$ ), aqueous solution of methylene blue (Reanal, bacteriological grade) of  $6 \times 10^{-3} \text{ g/L}$  concentration; ethanol (Merck, 99.9%), tetrahydrofurfuryl alcohol (THFA) (Fluka, 98%); *n*-heptane (Merck, 99%). (d) Triethylamine base (TEA) (Fluka, 99.5%) for silylation and *p*-toluenesulfonic acid monohydrate (Fluka, 99%) for acylation as catalysators.

### 2.2. Wood samples

For preliminary swelling studies of silylated wood, Apple wood (*Malus sylvestris*, from Hungary) was cut into  $15 \text{ mm} \times 15 \text{ mm} \times 40 \text{ mm}$  pieces in parallel with the fibres (radial direction) and then silylated.

For reactivity studies, wood chips of *Euca* were obtained from Portugal. The *Euca* chips were air-dried (ca. 90% dryness) and then ground at the Laboratory of Wood and Paper Chemistry of Åbo Akademi University. The sample was further ground in our laboratory and then sieved. The obtained chips had 0.25–0.60 mm diameter and 1.4–6.0 mm length. This fraction was divided into separate portions to carry out four different acylation and three silylation procedures.

### 2.3. Silylation in solution

#### 2.3.1. Apple wood pieces (macroscopic plates)

The treatment was adapted from [20]. One vol% *n*-heptane solutions of CTMS, DDS, DPS and OTS were prepared, respectively. It has to be noted that constant volume fractions can be used in these experiments because according to our former experience (e.g. [9,12]), 1 vol% concentration of silylating agent is high enough to reach the maximum surface concentration on the wood surface thus variation of the molar ratio can only cause negligible difference in the measurable contact angles. Each wood sample was immersed in saturated gaseous TEA for 10 min (see also [21]) then kept in the silanizing solution of 20 ml at room temperature (in a fumehood) for 10 min. Then the samples were rinsed with pure *n*-heptane and air-dried.

Another series of samples were prepared based on the method in [21], silylation of apple wood samples were also carried out in the presence of trace amount of TEA (ca.  $10^{-3} \text{ M}$ ) with 1 vol% *n*-heptane solution of OTS for 2 h as mentioned above. After the treatment, the samples were rinsed with pure *n*-heptane and air-dried.

In certain cases, ultrasonication was applied during the silylation for improving the surface treatment (sample OTSu). The ultrasonic treatment was applied in every second 20-min-long periods (as alternating sections) in order to avoid significant heating of the reaction media, but other parameters of the treatment were identical with those carried out in the presence of TEA.

For the sample treated in two steps (2st, as two steps), OTS-treated samples (OTSu) were silanized again with the 1 vol% *n*-heptane solution of CTMS under the same conditions as in the first step for 60 min in the presence of TEA base (ca.  $10^{-3} \text{ M}$ ). It is assumed that this second step improves the efficiency of the treatment by silylating the (possible polymerized) precursors and the un-reacted ligand groups.

#### 2.3.2. *Euca* chips (sawdust)

For the treatment of *Euca* sawdust (similarly to apple wood samples), 1 vol% *n*-hexane solutions of DDS, DPS and OTS were prepared, respectively. Fifteen grams amount of *Euca* sample were stirred in the silanizing solution of 100 ml under continuous stirring at room temperature for 2 h in the presence

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