

New transesterification reaction between acetylated wood and tetramethoxysilane: A feasibility study

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Abstract

Novel transesterification of acetylated maritime pine sapwood (*Pinus pinaster* Soland) reaction was performed with tetramethoxysilane (TMOS) in presence of dibutyltin oxide as a catalyst. Transesterification was confirmed by weight percent gain calculations (WPG), infrared spectroscopy (FTIR) as well as ¹³C and ²⁹Si NMR CP-MAS analysis. The results showed that transesterification indeed occurs via exchange of acetate groups from acetylated wood and methoxysilane groups from TMOS. The effect of temperatures and reaction time upon transesterification efficiency was also investigated. © 2005 Elsevier Ltd. All rights reserved.

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1. Introduction

Wood has many technical advantages such as high specific strength and stiffness, good toughness, low processing energy, renewability and is aesthetically pleasing. However, it has some disadvantageous properties in comparison with other materials, such as dimensional instability when exposed to various moisture contents, biodegradability, photosensitivity and flammability. For these reasons, it is necessary to improve properties and performance of these naturally produced products by alteration or chemically modifications of their components.

A number of reviews dealing with the chemical modification of wood have been published [1,2,14,19,22,23].

Most of the chemical modification reactions are carried out in order to improve the dimensional stability or bio-resistance of wood. Many type of reactions have been studied of which the most useful are reactions with epoxides, anhydrides or isocyanates [3,10,23].

The most favoured modification reaction involves the acetylation of wood with acetic anhydride. It has been reported that physical and chemical properties of wood has been improved by acetylation [2,10,11,14,23,30]. Reacted acetate provides dimensional stability by bulking the cell wall polymers and reduces further swelling when wood comes into contact with water. In addition to that, acetylation also provides biological resistance [2,14,23,30].

For improving wood properties, particularly flame resistance and wood preservation, inorganic substances have been put forward, such as silicate and boron compounds [20,21,24,32]. It has been reported that silicate compounds have been suggested as promising chemicals for impregnation and fixation of wood forming gels [15].

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In the past, various types of silicon compounds were applied to wood. The sol–gel process of alkoxy silanes [8,25], the grafting of chlorosilanes [37], organo-functional silanes [28], trimethylsilyl derivatives [26] and hydride terminal silicon compounds [27] were carried out. The aim of last three treatments was to create a covalent bonding between wood hydroxyl groups and an organic function of the organosilicon compound, for preventing leaching. Two literature reviews about silicon compounds treatment of wood have been recently published [17,18].

In polymer science, it has been reported that an exchange reaction between ester groups of ethylene-co-vinyl acetate (EVA) and an alkoxy silane in presence of dibutyltin oxide (DBTO) as catalyst is possible [4–6,34]. Reactants such as tetraalkoxy silanes were used in the temperature range between 100 and 180 °C. Tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS) were treated with model esters while tetrapropoxysilane (TPOS) was reacted with ethylene-co-vinyl acetate (EVA). Crosslinking of EVA by TPOS using DBTO as a catalyst is a transesterification reaction and involves the exchange of acetate groups from EVA and propoxy silane groups from TPOS, each silane alkoxy groups being exchangeable [4–6,34].

The objective of the present study was to investigate the feasibility of a transesterification reaction between acetylated wood and tetramethoxysilane in the presence of DBTO as catalyst. The proof of transesterification reaction was obtained by FTIR and CP-MAS (Cross Polarisation Magic Angle Spinning) NMR spectroscopies.

2. Material and methods

2.1. Preparation of wood flour

Maritime pine sapwood was ground using a hammer mill and sieved to a size of 40 mesh. Following that, the wood flour was extracted with the standard solution (4/

1/1, v/v, toluene:acetone:ethanol) using a Soxhlet extractor for 8 h, then with deionised water for an additional 8 h to remove the extractives. Extracted wood flour was oven-dried at 105 °C overnight. Oven-dried wood flour was transferred to a desiccator containing phosphorous pentoxide, and allowed to cool to room temperature.

2.2. Chemicals

Tetramethoxysilane (TMOS), pyridine (Py), dimethylformamide (DMF), acetic anhydride (AA) and dibutyltin oxide (DBTO) were supplied from Aldrich and used without further purification. Chemical reactants were characterised by NMR spectroscopy and their carbons were assigned as follows (Fig. 1): AA: ^{13}C NMR (100.6 MHz, CDCl_3), 21.5 (b') and 166.1 (a') ppm. TMOS: ^{13}C NMR (100.6 MHz, CDCl_3), 50.8 (c') ppm; ^{29}Si NMR (39.7 MHz, CDCl_3), –78.3 ppm.

2.3. Acetylation of wood flour

Extractive free Maritime pine flour (*Pinus Pinaster* Soland) (WF) was used as a starting material for acetylation reaction. In a round bottom flask equipped with a condenser and a magnetic stirrer, 50 g of sawdust, 7 mmol Py/g of dry wood, 14 mmol AA/g of dry wood and 200 ml of DMF were introduced. The reaction mixture was heated at 100 °C for 6 h. At the end of the reaction, the modified samples were placed in a Soxhlet apparatus for solvent extraction, with the standard 4/1/1 mixture (toluene:acetone:ethanol) for 8 h and subsequently oven dried overnight at 105 °C. The samples were transferred to a desiccator containing phosphorus pentoxide until cool and weight gain levels were calculated.

Weight percent gain (WPG) was calculated according to

$$\text{WPG}(\%) = \frac{W_{t1} - W_{t0}}{W_{t0}} \times 100$$

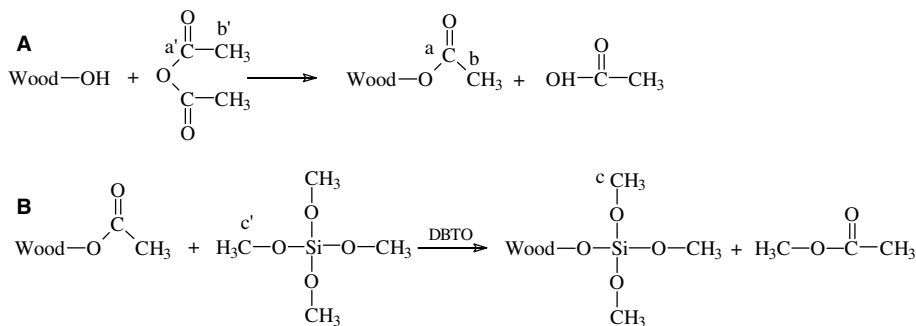


Fig. 1. (A) Acetylation of wood with acetic anhydride (AcWF) and (B) transesterification between AcWF and TMOS.

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