Annals of Warsaw University of Life Sciences – SGGW
Forestry and Wood Technology No. 110, 2020: 5-8
(Ann. WULS-SGGW, For. and Wood Technol. 110, 2020)

Organosilanes in wood protection – chemical analysis of wood and cellulose treated with MTMOS

MARTA BABICKA, MAGDALENA WOŹNIAK, IZABELA RATAJCZAK
Poznań University of Life Sciences, Department of Chemistry, Wojska Polskiego 75, PL-60625 Poznan, Poland

Abstract: *Organosilanes in wood protection – chemical analysis of wood and cellulose treated with MTMOS.* The paper presents the results of methyltrimethoxysilane (MTMOS) reactivity with Scots pine wood and cellulose. The lignocellulosic material after treatment with ethanolic solution of MTMOS was analysed using instrumental methods – atomic absorption spectrometry (AAS) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). The analysis of silicon concentration in treated material indicated the presence of silane in structure of wood and cellulose. The bands characteristic of vibrations of the silicon-carbon and silicon-oxygen originating from MTMOS molecule were observed in the spectra of modified materials, which confirmed the reactivity of silane with wood and cellulose. Moreover, the chemical analysis indicated that MTMOS exhibited higher reactivity to cellulose than to pine wood.

Keywords: Scots pine, cellulose, methyltrimethoxysilane, infrared spectroscopy, atomic absorption spectrometry

INTRODUCTION

At present, there is great emphasis put on environmental protection in all areas, including wood protection and modification. It is important that the methods used are environmentally safe but also effective.

Organosilicon compounds have long been used for application on wood to improve its properties, such as fire resistance, dimensional stability and durability (Brebner and Schneider 1985; Hager 1995; Miyafuji and Saka 2001; Mai and Militz 2004a). Moreover, wood modification by silane can improve its decay resistance, hydrophilicity, dimensional and weather stability. It has also been proven that MTMOS can effectively increase wood creep resistance (Hung and Wu 2018).Various types of the functional groups within silane molecule can improve specific properties of wood (Mai and Militz 2004 b; Donath et al. 2006; Giudice et al. 2013). This work uses methyltrimethoxysilane (MTMOS), which is an optically transparent, self-cleaning, antibacterial, substrate penetration, as well as a water repellent compound, which makes it a promising agent for wood modification (Ismail et al. 2012; Tshabalala et al. 2009).

The aim of this research was to determine the reactivity of MTMOS with Scots pine wood and cellulose. The reactivity between the silicon compound and the lignocellulosic materials was determined using attenuated total reflectance infrared Fourier transform spectroscopy (ATR-FTIR). The silicon concentration in the samples was determined by atomic absorption spectroscopy (AAS).

MATERIALS AND METHODS

Reaction of Scots pine wood and cellulose with MTMOS

Scots pine wood (*Pinus sylvestris* L.) in the form of powder and cellulose purchased from Merck were used in this study. The tested silicon compound was methyltrimethoxysilane (MTMOS) from Merck, used in two concentrations – 5% and 20%. The silane was dissolved in 80% ethanol and after 30 minutes wood and cellulose solutions in ratio 1/25 w/v were added to silane. The reactions were run for 3 h at a room temperature, being simultaneously

stirred (ChemLand). Next, wood and cellulose samples were filtered and dried in air flow at a room temperature.

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR)

The ATR-FTIR spectra of wood and cellulose samples were recorded using a Nicolet iS5 spectrometer by Thermo Scintific (Thermo Fisher Scientific, USA) equipment with a deuterium triglycinesulfate detector and attached ATR units. The spectra were determined in the range of 4000–400 cm^{-1}, at a resolution of 4 cm^{-1}, registering 32 scans in the transmittance mode.

Atomic absorption spectrometry (AAS)

Wood and cellulose samples treated with MTMOS (0.5 g) were mineralised with 8 ml of nitric acid (Merck) in a microwave mineralization system (CEM Corporation) and after cooling down the solutions were filtered and diluted to 50.0 ml with deionised water. The content of silicon in cellulose samples was determined with flame atomic absorption spectrometry using a AA280FS spectrometer (Agilent Technologies).

RESULTS AND DISCUSSION

The concentrations of silicon in Scots pine wood and cellulose treated with MTMOS are shown in Figure 1 and Figure 2, respectively.

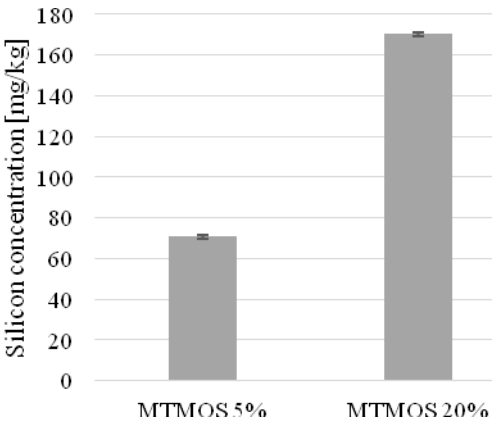

Fig. 1 Content of silicon in MTMOS-treated wood

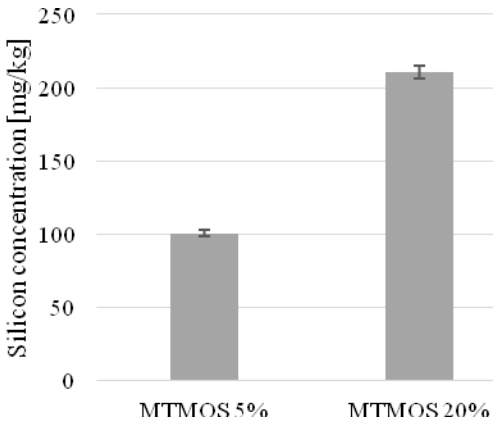

Fig. 2 Content of silicon in MTMOS-treated cellulose

The concentration of silicon coming from $–Si(CH_3)_3$ group in MTMOS molecule in treated cellulose was higher than in wood, suggesting that silane exhibited higher reactivity to cellulose than to pine wood. Higher reactivity of MTMOS with cellulose is probably connected with more amount of hydroxyl groups in raw cellulose than in wood. The reactivity of MTMOS with cellulose was confirmed in works by Ratajczak and Mazela (2009). Moreover, the results of AAS analysis indicated that fourfold increase in concentration of silane caused only around twofold increase of silicon concentration in treated materials. The results of tests for silicon concentration in cellulose treated with methyltrimethoxysilane at different concentration described by Ratajczak et al. (2010) also show that an increase of MTMOS concentration in the impregnation solution does not cause a proportional increase of the silicon content in treated material.

Figure 3 presents FTIR-ATR spectra of cellulose and wood treated with methyltrimethoxysilane. In the spectra of treated cellulose there are bands at 1270 and 1105 cm^{-1}, which can be attributed to the Si-O group which is part of the MTMOS molecule. In the spectra of MTMOS treated cellulose, bands at 925 and 780 cm^{-1} were also observed, which indicated the presence of Si-O and Si-C bonds from silane. In the spectra of wood treated with silane, a band at 1270 cm^{-1} of Si-O was present. In addition, in the treated wood spectra there

are observed bands at 915 and 775 cm^{-1} coming from Si-O and Si-C bonds present in MTMOS molecule.

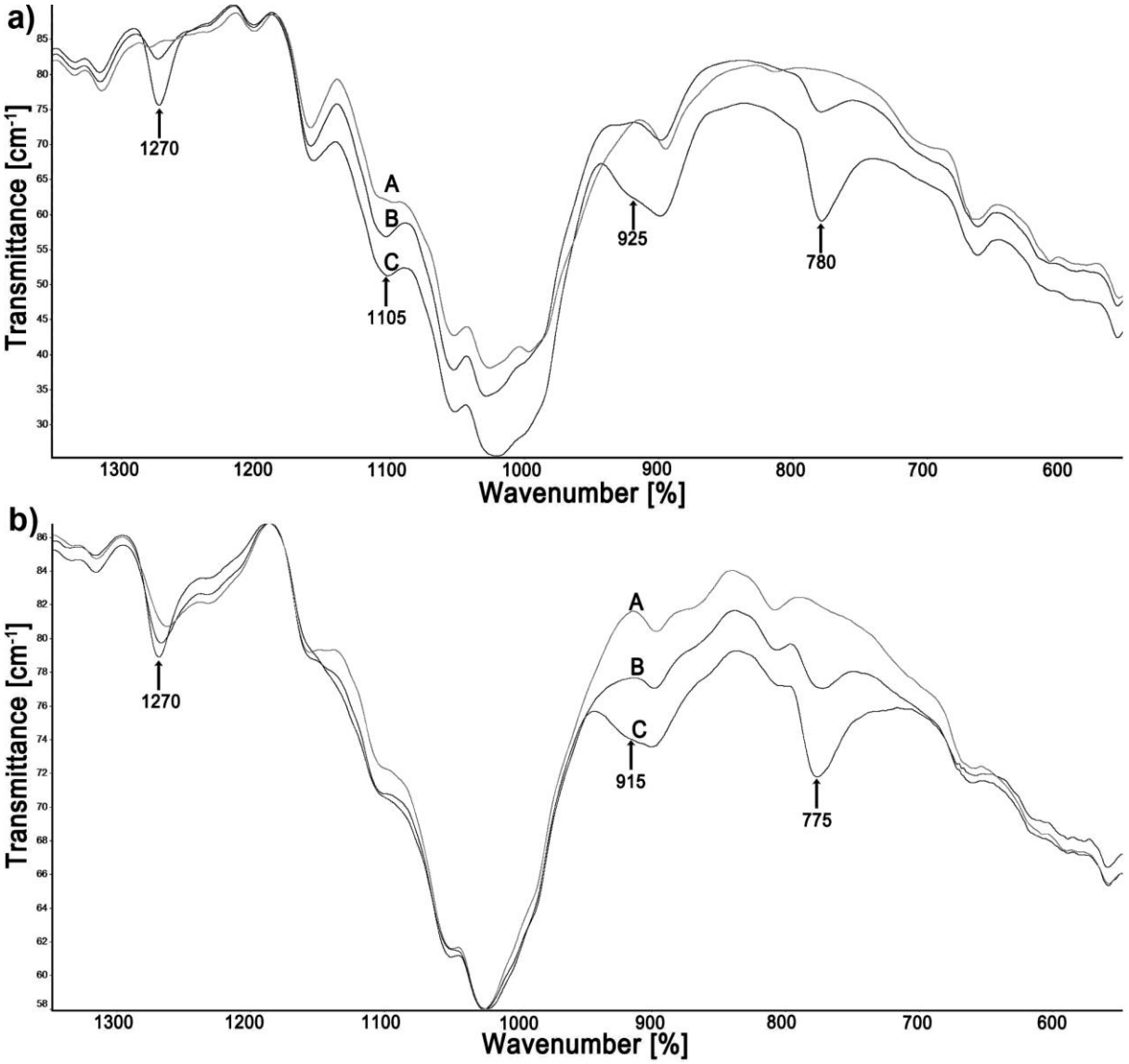

Fig. 3 a) Spectra of cellulose (A), cellulose treated with 5% MTMOS (B), cellulose treated with 20% MTMOS (C); b) Spectra of wood (A), wood treated with 5% MTMOS (B), wood treated with 20% MTMOS (C)

The presence of these changes in the wood spectra and cellulose treated with MTMOS confirms an interaction between the tested materials and organosilane.

CONCLUSIONS

The test results for silicon concentration in Scots pine wood and cellulose treated with methyltrimethoxysilane indicated that the structure of the tested lignocellulosic materials contained silicon coming from silane molecule. The reactivity of MTMOS with wood and cellulose has also been confirmed by changes in FTIR spectra of the treated materials. The bands characteristic of the vibrations of the silicon-carbon and silicon-oxygen originating from MTMOS molecule were observed in the spectra of the modified materials.

REFERENCES

1. BREBNER K.I., SCHNEIDER M.H. 1985: Wood-polymer combinations: bonding of alkoxysilane coupling agents to wood. Wood Science Technology 19: pp. 75–81.

2. DONATH S., MILITZ H., MAI C. 2006: Treatment of wood with aminofunctional silanes for protection against wood destroying fungi. Holzforschung 60: pp. 210–216.
3. GIUDICE C.A., ALFIERI P.V., CANOSA G. 2013: Decay resistance and dimensional stability of *Araucaria angustifolia* using siloxanes synthesized by sol–gel process. International Biodeterioration & Biodegradation 83: pp. 166–170.
4. HAGER R. 1995: Waterborne silicones as wood preservatives. International Research Group on Wood Preservation (IRG/WP 95–30062) Stockholm.
5. HUNG K.C., WU J.H. 2018: Effect of SiO_2 content on the extended creep behaviour of SiO_2-based wood-inorganic composites derived via the sol-gel process using the stepped isostress method. Polymers 10 (409): pp. 1–12.
6. ISMAIL W.A., ALI Z.A., PUTEH R. 2012: Optical and physical properties of methyltrimethoxysilane transparent film incorporated with nanoparticles. Hindawi Publishing Corporation, Advances in Materials Science and Engineering, Article ID 124820.
7. MAI C., MILITZ H. 2004a: Modification of wood with silicon compounds. Inorganic silicon compounds and sol-gel systems: A review. Wood Science and Technology 37(5): pp. 339–348.
8. MAI C., MILITZ H. 2004b: Modification of wood with silicon compounds. Treatment systems based on organic silicon compounds – a review. Wood Science and Technology 37(6): pp. 453–461.
9. MIYAFUJI H., SAKA S. 2001: Na_2O-SiO_2 wood inorganic composites prepared by the sol-gel process and their fire resistant properties. Journal of Wood Science 47: 483-489.
10. RATAJCZAK I., MAZELA B. 2009: Chemical reaction of cellulose with alkoxysilane molecules. Part II. AAS analysis. Annals of Warsaw University of Life Sciences – SGGW Forestry and Wood Technology No 69: pp. 223–226.
11. RATAJCZAK I., WICHŁACZ-SZENTNER K., MAZELA B., HOCHMAŃSKA P., RISSMANN I. 2010: Silicon compounds as additives improving coating performance: fixation of silicon compounds with cellulose. European Journal of Wood and Wood Products 68: pp. 483–486.
12. TSHABALALA M.A., YANG V., LIBERT R. 2009: Surface modification of wood by alkoxysilane sol-gel deposition to create anti-mold and anti-fungal characteristics. Silanes and Other Coupling Agents 5: pp. 135–150.

Streszczenie: *Organosilany w ochronie drewna – analizy chemiczne drewna i celulozy traktowanej MTMOS*. W pracy przedstawiono wyniki badań reaktywności metylotrimetoksysilanu (MTMOS) z drewnem sosny zwyczajnej oraz celulozą. Materiał lignocelulozowy po działaniu etanolowego roztworu MTMOS był analizowany z wykorzystaniem metod instrumentalnych – AAS oraz ATR-FTIR. Analiza stężenia krzemu w impregnowanym materiale wskazuje na obecność silanu w strukturze drewna i celulozy. Charakterystyczne pasma dla drgań krzem-węgiel oraz krzem-tlen, pochodzące z cząsteczki MTMOS obserwowane w widmach modyfikowanych materiałów potwierdzają reaktywność silanu z drewnem oraz celulozą. Ponadto, analiza chemiczna wykazała, że MTMOS wykazywał wyższą reaktywność wobec celulozy niż drewna sosny.

Corresponding author:

Izabela Ratajczak
Poznań University of Life Sciences, Department of Chemistry
Wojska Polskiego 75, PL-60625 Poznan, Poland
e-mail: izabela.ratajczak@up.poznan.pl