

Reactivity of (3-aminopropyl)trimethoxysilane with cellulose

MAGDALENA WOŹNIAK, IZABELA RATAJCZAK

Poznań University of Life Sciences, Department of Chemistry

Abstract: *Reactivity of (3-aminopropyl)trimethoxysilane with cellulose.* The paper presents the results of tests for the reactivity of (3-aminopropyl)trimethoxysilane (APT MOS) with cellulose. The cellulose was treated with aqueous ethanolic solution of silane in two concentration: 5% and 20%. The reactivity of APT MOS with cellulose was analysed using instrumental methods: attenuated total reflectance Fourier transform infrared spectroscopy, atomic absorption spectrometry and elemental analysis. In the FTIR spectra of silane-treated cellulose, the bands of Si-O, Si-C and N-H bonds were detected. The analysis of silicon and nitrogen concentration in treated cellulose confirmed the presence of silane in cellulose structure. The presented results indicate that APT MOS forms chemical bonds with cellulose.

Keywords: cellulose, (3-aminopropyl)trimethoxysilane, infrared spectroscopy, elemental analysis, atomic absorption spectrometry

INTRODUCTION

Silicon compounds are a group of chemical compounds with the general formula Si_nH_{2n+2} , where hydrogen atoms may be substituted by organic or inorganic groups, such as chloride, alkyl or alkoxy groups (Donath et al. 2006). Silanes are known for their hydrophobic properties, thus they are applied in plastic, paper and textile industries (Donath et al. 2004; Panov and Terziev 2009). They are also used to impregnate and protect wood (Hill et al. 2004; Mai and Militz 2004). Many wood properties, including hydrophobicity, dimensional stability, fire and biological resistance and mechanical properties are improved thanks to the application of silicon compounds (Kartal et al. 2009; Mai and Militz 2004; Reinprecht and Grznanik 2015; Sebe et al. 2004).

The reactivity of wood and its main components (cellulose and lignin) with silicon compounds depends on many factors, including concentration and chemical structure of silane, a solvent applied, pH of reaction solution and also wood moisture content (Xie et al. 2011). According to the data found in the literature, even small water content in wood may cause hydrolysis of alkoxy groups from silanes, thus increasing the reactivity between silicon compounds and cellulose (Castellano et al. 2004).

The aim of this research was to determine the reactivity of cellulose with (3-aminopropyl)trimethoxysilane (APT MOS). The attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to determine the character of the bond between cellulose and silane. Atomic absorption spectroscopy (AAS) and elemental analyzer (EA) were used to analyse the silicon and nitrogen content in silane-treated cellulose.

MATERIALS AND METHODS

Reaction of cellulose with aminosilane

Cellulose *fibres* medium (Merck, Germany) was mixed with (3-aminopropyl)trimethoxysilane (APT MOS) (Merck, Germany) in two different concentrations: 5% and 20%. Ethanol: water in a ratio of 80:20 was used as a solvent. Cellulose was added to the tested solutions (1/25 w/v) 30 minutes after their preparation. The reactions were run for 3 h at room temperature, with simultaneous stirring using a magnetic bar stirrer (ChemLand, Poland). Next, the cellulose samples were filtered and dried in an air flow at a room temperature.

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

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

Atomic absorption spectrometry (AAS)

Silane-treated cellulose samples (0.5 g) were mineralized with 8 ml of nitric acid (Merck, Germany) in a microwave mineralization system (CEM Corporation, USA), 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, USA).

Elemental analysis

The analysis of nitrogen concentration in cellulose samples after being treated with APTMOS was carried out using a Thermo Scientific Flash 2000 CHNS/O Analyzer (Thermo Scientific, USA). Instrument calibration was performed with the BBOT (2,5-bis-(5-tert-butyl-benzoxazol-2-yl)thiophene) standard (Thermo Scientific) and certified reference material – Alfalfa (Elemental Microanalysis, UK).

RESULTS AND DISCUSSION

Figure 1 presents FTIR cellulose spectra after the reaction with (3-aminopropyl)-trimethoxysilane (APTMOS).

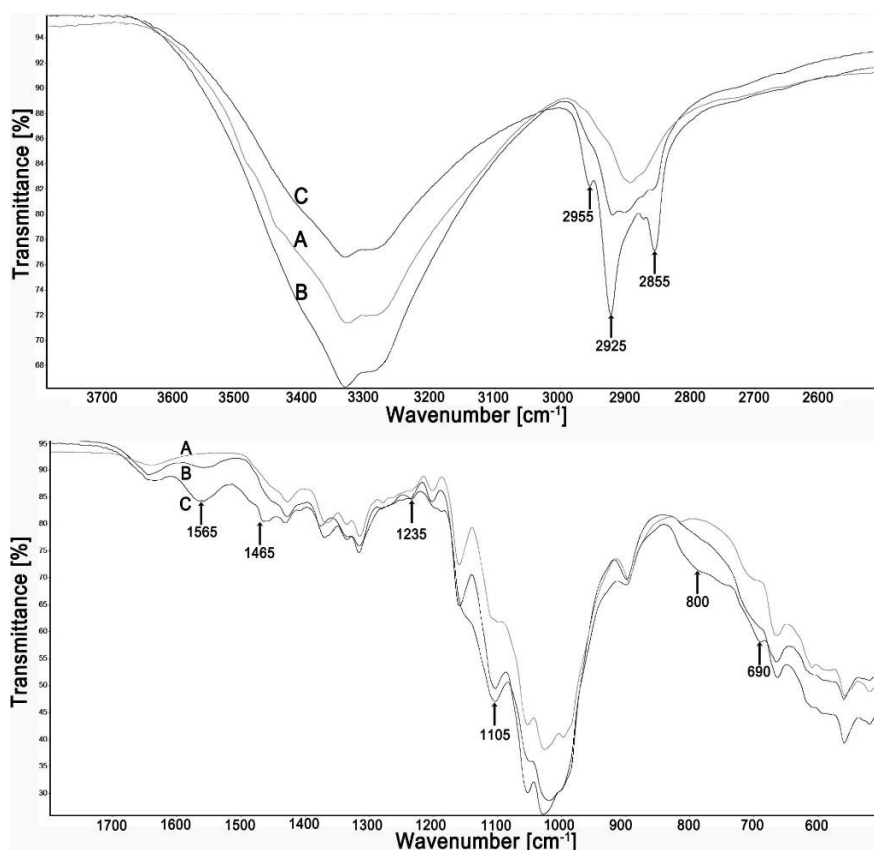


Figure 1 Spectra of cellulose (A), cellulose after reaction with 5% APTMOS (B), cellulose after reaction with 20% APTMOS (C).

The presented spectra showed changes in the structure of cellulose after reaction with aminosilane, compared with unmodified cellulose. In spectra of treated cellulose, there are bands at 2955 , 2925 and 2855 cm^{-1} , which were assigned to C-H stretching vibrations of –

CH₃ groups in APTMOS (Sebe et al. 2004). In treated cellulose spectra, visible deformations were recorded in the vibrations of the N-H group at 1565, 1465 cm⁻¹, which come from amino group of (3-aminopropyl)trimethoxysilane. In the spectra of APTMOS-treated cellulose bands were also observed at 1235, 800 and 690 cm⁻¹, which indicated the presence of stretching vibrations of the Si-O and Si-C bonds (Ratajczak et al. 2010; Sebe et al. 2004). The peaks near 1105 cm⁻¹ are related to residual unhydrolysed Si-OCH₃ groups and their small intensity, suggested that most of the silane under reaction had been hydrolysed (Abdelmouleh et al. 2004).

The contents of silicon and nitrogen in silane-treated cellulose are presented in Figure 2 and 3, respectively.

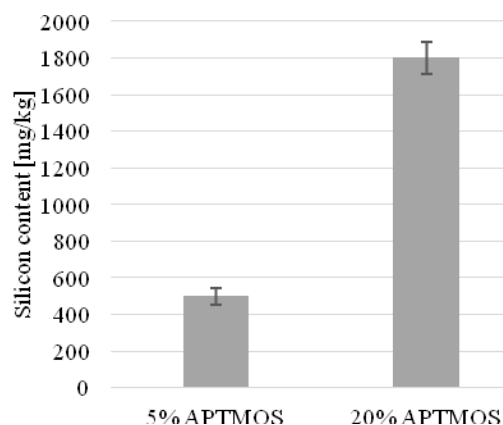


Figure 2 Content of silicon in silane-treated cellulose

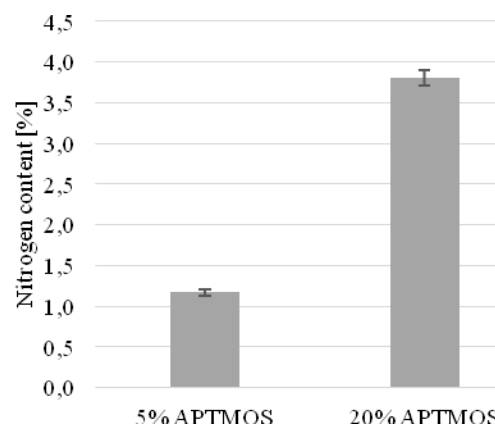


Figure 3 Content of nitrogen in silane-treated cellulose

The concentration of silicon coming from Si(OCH₃)₃ groups in APTMOS in silane-treated cellulose was determined by atomic absorption spectrometry. The results of AAS analysis indicated that silicon content in the cellulose treated with silane at a concentration of 20% was about 3 times higher than in the cellulose treated with APTMOS in a lower concentration. Moreover, the Si concentration in cellulose treated with 5% APTMOS was higher than in cellulose treated with this aminosilane presented in work by Babicka et al. (2018). These changes in silicon content in APTMOS-treated cellulose can be involve with different solvent used to prepare silane solution. In our research we used aqueous ethanolic solution, whereas Babicka et al. (2018) prepared the silane solution using a white spirit as a solvent. It seems that the use of an aqueous solution of ethanol as a silane solvent causes its greater reactivity, due to the presence of water necessary to initiate the silanols formation reaction (Castellano et al. 2004; Ratajczak et al. 2010). The concentration of nitrogen, coming from amine group presents in silane compound was analysed using elemental analyzer. The results showed that nitrogen content in cellulose treated with solution containing 20% silane was around 3 times higher than in cellulose treated with (3-aminopropyl)trimethoxysilane at 5% concentration. The results of silicon and nitrogen content in APTMOS-treated cellulose indicated that aminosilane was present in the cellulose structure. A fourfold increase of APTMOS concentration in the solution caused only a threefold increase of silicone and nitrogen concentration in the treated cellulose, which suggests that the increase of aminosilane concentration in the impregnating solution does not cause the same increase of aminosilane content, analysed in the form of Si and N concentration, in the treated cellulose.

CONCLUSIONS

The results of chemical analyses, including attenuated total reflectance Fourier transform infrared spectroscopy, atomic absorption spectroscopy and elemental analysis,

indicated that APTMOS formed chemical bonds with cellulose. In the FTIR spectra of silane-treated cellulose samples, the bands characteristic of vibration of the silicon-carbon, silicon-oxygen and nitrogen-hydrogen bonds coming from silicon compound were recorded. In addition, the analysis of silicon and nitrogen concentration in APTMOS-treated cellulose confirmed the presence of silane in the cellulose structure.

REFERENCES

1. ABDELMOULEH M., BOUFI S., BELGACEM M.N., DUARTE A.P., BEN SALAH A., GANDINI A. 2004: Modification of cellulosic fibres with functionalised silanes: development of surface properties. *International Journal of Adhesion & Adhesives* 24: pp. 43–54.
2. BABICKA M., WOŹNIAK M., SZENTNER K., RISSMANN I., RATAJCZAK I. 2018: The application of instrumental methods for estimation of bonding between cellulose and aminosilanes. *Annals of Warsaw University of Life Sciences – SGGW, Forestry and Wood Technology* No 103: pp. 169-173.
3. CASTELLANO M., GANDINI A., FABBRI P., BELGACEM M.N. 2004: Modification of cellulose fibers with organosilanes: Under what conditions does coupling occur? *Journal of Colloid and Interface Science* 273: pp. 505–511.
4. DONATH S., MILITZ H., MAI C. 2004: Wood modification with alkoxy silanes. *Wood Science and Technology* 38: pp. 555–566.
5. DONATH S., MILITZ H., MAI C. 2006: Treatment of wood with aminofunctional silanes for protection against wood destroying fungi. *Holzforschung* 60: pp. 210–216.
6. HILL C.A.S., FARAHANI M.R.M., HALE M.D.C. 2004: The use of organo alkoxy silane coupling agents for wood preservation. *Holzforschung* 58: pp. 316–325.
7. KARTAL S.N., YOSHIMURA T., IMAMURA Y. 2009: Modification of wood with Si compounds to limit boron leaching from treated wood and to increase termite and decay resistance. *International Biodeterioration & Biodegradation* 63: pp. 187–190.
8. MAI C., MILITZ H. 2004: Modification of wood with silicon compounds. Treatment systems based on organic silicon compounds – a review. *Wood Science and Technology* 37: pp. 453–461.
9. PANOV D., TERZIEV N. 2009: Study on some alkoxy silanes used for hydrophobation and protection of wood against decay. *International Biodeterioration & Biodegradation* 63: pp. 456–461.
10. RATAJCZAK I., WICHLACZ-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.
11. REINPRECHT L., GRZNARIK T. 2015: Biological durability of Scots pine (*Pinus sylvestris* L.) sapwood modified with selected organo-silanes. *Wood Research* 60(5): pp. 687–696.
12. SEBE G., TINGAUT P., SAFOU-TCHIAMA R., GRELIER S., DE JESO B. 2004: Chemical reaction of maritime pine sapwood (*Pinus pinaster* Soland) with alkoxy silane molecules: A study of chemical pathways. *Holzforschung* 58: pp. 511–518.
13. XIE Y., HILL C. A. S., SUN D., JALALUDIN Z., WANG Q., MAI C. 2011: Effects of dynamic aging (hydrolysis and condensation) behavior of organofunctional silanes in the aqueous solution on their penetrability into the cell walls of wood. *BioResources* 6(3): pp. 2323–2339.

Streszczenie: *Reaktywność 3-(aminopropyl)trimetoksysilanu z celulozą. W pracy przedstawiono wyniki badań reaktywności 3-(aminopropyl)trimetoksysilanu (APTMOŚ)*

z celulozą. Celuloza była traktowana etanolem w dwóch stężeniach, wynoszących 5 i 20%. Reaktywność APTMOS z celulożą była analizowana z wykorzystaniem metod instrumentalnych, w tym spektroskopii osłabionego całkowitego odbicia w podczerwieni z transformacją Fouriera, atomowej spektroskopii absorpcyjnej oraz analizy elementarnej. W widmach FTIR celulozy poddanej działaniu silanu obserwowano pasma pochodzące od wiązań Si-O, Si-C i N-H. Analiza stężenia krzemu i azotu w modyfikowanej celulozie potwierdziła obecność silanu w strukturze celulozy. Przedstawione wyniki wskazują, że APTMOS tworzy wiązania chemiczne z celulożą.

Corresponding author:

Izabela Ratajczak
Poznań University of Life Sciences
Department of Chemistry
Wojska Polskiego 75
PL-60-625 Poznan, Poland
e-mail: izabela.ratajczak@up.poznan.pl