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A reaction of [3-(2-aminoethylamino)propyl]trimethoxysilane with wood and cellulose – chemical analyses

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Abstract: *A reaction of [3-(2-aminoethylamino)propyl]trimethoxysilane with wood and cellulose – chemical analyses.* The paper presents tests results for [3-(2-aminoethylamino)propyl]trimethoxysilane (AATMOS) reactivity with cellulose and Scots pine wood. The tested material was treated with ethanolic solution of aminosilane and analyzed using instrumental methods, including elemental analysis, atomic absorption spectrometry and infrared spectroscopy. The results of the chemical analysis indicated that [3-(2-aminoethylamino)propyl]trimethoxysilane exhibited reactivity with both cellulose and pine wood. In addition, AATMOS-treated cellulose showed a higher content of silicon and nitrogen and more significant changes in FTIR spectra than the treated wood, suggesting that AATMOS showed a higher reactivity to cellulose than to wood.

Keywords: Scots pine, cellulose, [3-(2-aminoethylamino)propyl]trimethoxysilane, infrared spectroscopy, elemental analysis, atomic absorption spectrometry

INTRODUCTION

Wood is a natural lignocellulosic material containing a large number of hydroxyl group, whose high affinity for water is responsible for the hydrophilic nature of wood (Rowell 2005). The hydrophilic nature of wood has many drawbacks, including biodegradation by microorganisms, dimensional instability or weathering (Sebe et al. 2004). This decreases the service life of wood and limits it use mainly in outdoor application. For hydrophobisation of many materials applied in chemical, building or textile industries are used silicon compounds (Donath et al. 2006). Silanes have been also used in order to improve hydrophobicity of wood surface (Meada et al. 2006, Panov and Terziev 2009). Silicon compounds exhibit hydrophobic properties causes by the presence of organic groups (Sebe et al. 2004, Tingaut et al. 2016). The application of silanes in wood impregnation leads also to improved dimensional stability, fire and weather resistance and better mechanical properties (Hill et al. 2004, Mai and Militz 2004, Reinprecht and Grznarik 2015). Moreover, the aminosilanes improve the fungal resistance of treated wood (Donath et al. 2004, Reinprecht and Grznarik 2015).

The presence of amino group in silicon compounds may enhance reactivity in the reaction of hydrolysis. The reaction rate for silanes containing amino groups is influenced by different factors, such as pH of the solution, solvent, or the chemical structure and concentration of silane (Paquet et al. 2012, Xie et al. 2011). In order to determine the reactivity of silicon compounds with wood, and also its main components, numerous analytical methods were used, including infrared spectroscopy and nuclear magnetic spectroscopy (He et al. 2005, Ratajczak et al. 2020).

The aim of this research was to determine the reactivity of Scots pine wood and cellulose with [3-(2-aminoethylamino)propyl]trimethoxysilane (AATMOS). The reactivity of AATMOS with lignocellulosic material was determined using attenuated total reflectance Fourier transform infrared spectroscopy, elemental analysis and atomic absorption spectroscopy.

MATERIALS AND METHODS

Reaction of Scots pine wood and cellulose with aminosilane

Scots pine wood (*Pinus sylvestris* L.) in the form of powder and cellulose *fibers* medium (Merck, Germany) were mixed with [3-(2-aminoethylamino)propyl]trimethoxysilane (AATMOS) at a concentration of 20%. The solution of silane was prepared using 80% ethanol as a solvent. The lignocellulosic material was added to the tested solution (1/25 w/v) after 30 minutes since the solution was prepared. The reaction was run for 3 h at room temperature at the simultaneous stirring with a magnetic bar stirrer (ChemLand, Poland). After filtration, the samples of wood and cellulose were dried in air flow at 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 Scientific (Thermo Fisher Scientific, USA) equipment with deuterium triglycinesulfate detector. The spectrum of each sample was determined in the wave number range 4000–400 cm^{-1}, at a resolution of 4 cm^{-1}, registering 32 scans in the transmittance mode.

Atomic absorption spectrometry (AAS)

The lignocellulosic materials (0.5 g) were mineralized with 8 ml of nitric acid (Merck, Germany) in a microwave mineralization system (CEM Corporation, USA). Next, the solutions were filtered and diluted to 50.0 ml with deionised water. The content of silicon in the cellulose samples was determined by flame atomic absorption spectrometry, using an AA280FS spectrometer (Agilent Technologies, USA).

Elemental analysis

The analysis of nitrogen concentration in wood and cellulose samples was determined by the 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 the certified reference material – Alfalfa (Elemental Microanalysis, UK).

RESULTS AND DISCUSSION

The concentrations of silicon and nitrogen in Scots pine wood and cellulose treated with [3-(2-aminoethylamino)propyl]trimethoxysilane are presented in Figure 1 and Figure 2.

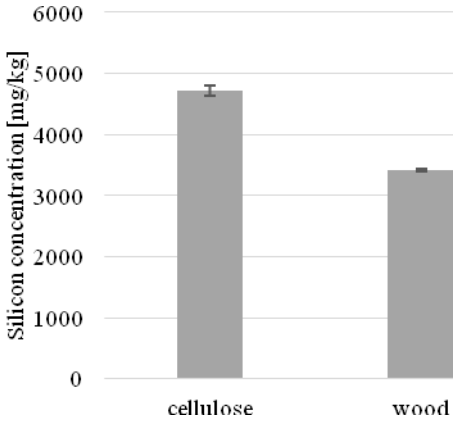

Fig. 1 Silicon content in cellulose and wood treated with AATMOS

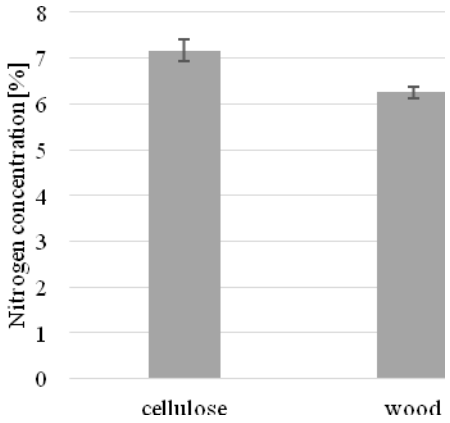

Fig.2 Nitrogen content in cellulose and wood treated with AATMOS

The analysis of silicon (coming from -Si-$(OCH_3)_3$ group in AATMOS) and nitrogen (coming from -NH- and -NH_2 group from AATMOS molecule) concentration in wood and cellulose structure allows to determine AATMOS presence in the structure of lignocellulosic materials. The silicon and nitrogen content in the treated cellulose was higher than in wood after treatment with AATMOS, which suggests that [3-(2-aminoethylamino) propyl]trimethoxysilane exhibits higher reactivity to cellulose than pine wood.

The reactivity of AATMOS with wood and cellulose was also analysed by determining changes in the structure of wood and cellulose treated with aminosilane. The spectra of Scots pine wood and cellulose treated with AATMOS are presented at Figure 3 and Figure 4.

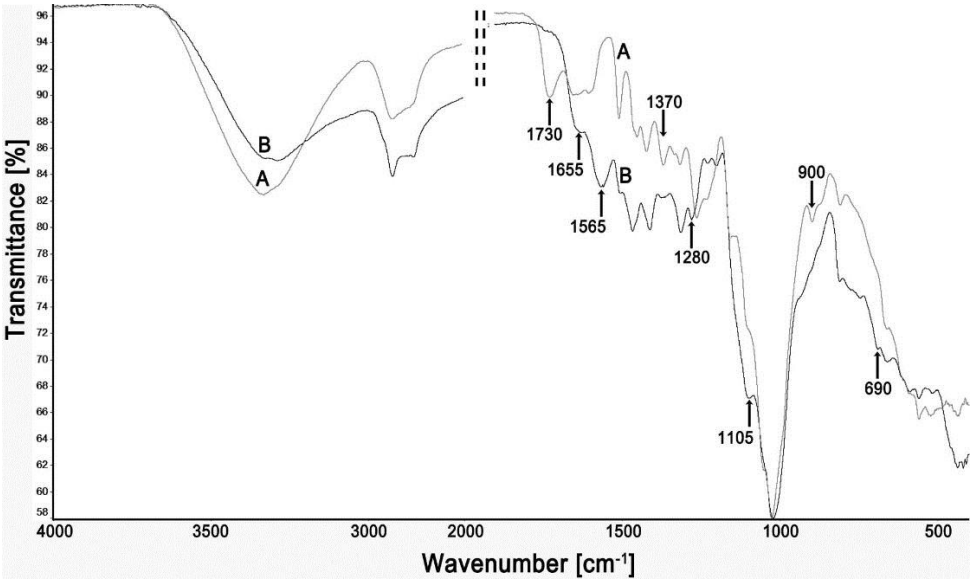

Figure 3 Spectra of wood (A), wood after reaction with AATMOS (B)

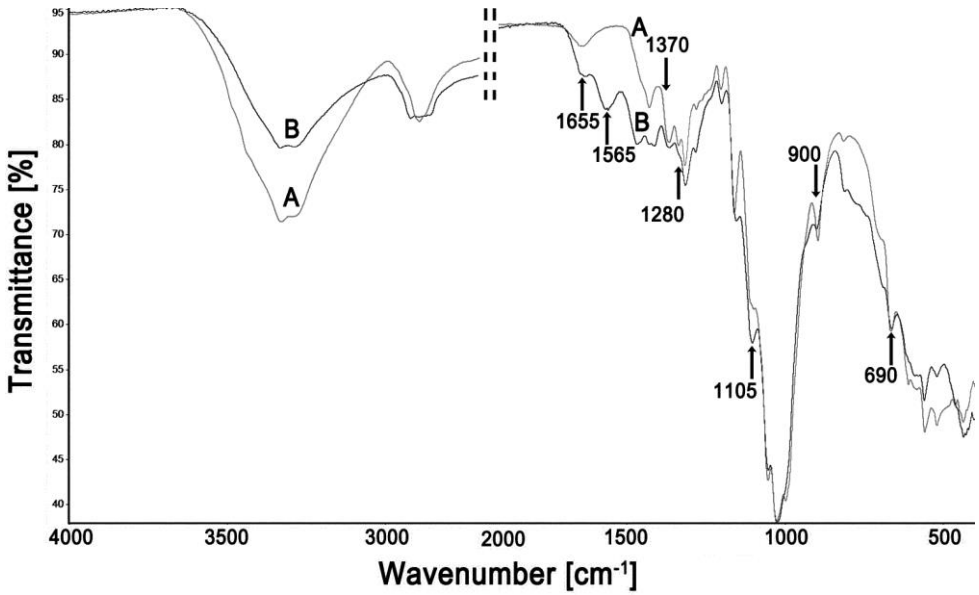

Figure 4 Spectra of cellulose (A), cellulose after reaction with AATMOS (B)

The presented spectra show changes in the structure of wood and cellulose after a reaction with [3-(2-aminoethylamino)propyl]trimethoxysilane, in comparison with unmodified materials. In the spectra of AATMOS-treated wood, the band at 1565 cm^{-1} characteristic of vibrations of N-H and the bands at 1280 and 1105 cm^{-1}, assigned to Si-O

or/and Si-C bonds, originating from AATMOS molecule were observed. In the spectra of AATMOS-treated cellulose, the bands were observed at 1565 and 1655 cm^{-1}, characteristic for N-H group and the bands at 1280, 1105 and 690 cm^{-1}, which indicated the presence of stretching vibrations of the Si-O and Si-C bonds, originating from AATMOS. In addition, in the spectra of treated wood and cellulose the intensity of bands at 1370 cm^{-1} (coming from CH_2 group in cellulose) and 900 cm^{-1} (originating from C-O-C in β-(1,4)-glycoside bond) decreased. The changes in the spectrum of cellulose treated with AATMOS are more significant than the changes in the spectrum of treated wood, suggesting that the reactivity of AATMOS with cellulose is higher than wood. Higher reactivity of AATMOS with cellulose was also confirmed by analyzing the silicon and nitrogen content of treated materials.

CONCLUSIONS

The results of chemical analyses, including attenuated total reflectance Fourier transform infrared spectroscopy, atomic absorption spectroscopy and elemental analysis, indicate that [3-(2-aminoethylamino)propyl]trimethoxysilane exhibits reactivity with cellulose and pine wood. The silicon and nitrogen content in the treated material shows that the silane molecule was present in the structure of wood and cellulose. The changes in the spectra of the treated material in comparison with the spectra of the untreated cellulose and wood indicated also the reactivity of AATMOS with these materials. Moreover, the presented results point out that the AATMOS reactivity with cellulose was higher than that with pine wood.

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Streszczenie: *Reakcja [3-(2-aminoetyloamino)propylo]trimetoksysilanu z drewnem i celulozą – analizy chemiczne.* W pracy przedstawiono wyniki reaktywności [3-(2-aminoetyloamino)-propylo]trimetoksysilanu (AATMOS) z celulozą i drewnem sosny zwyczajnej. Badany materiał traktowano etanolowym roztworem aminosilanu i analizowano z wykorzystaniem metod instrumentalnych, takich jak: analiza elementarna, atomowa spektrometria absorpcyjna i spektroskopia w podczerwieni. Uzyskane wyniki wskazują, na reaktywność [3-(2-aminoetyloamino)propylo]trimetoksysilanu zarówno z celulozą jak i drewnem sosny. Ponadto, celuloza traktowana AATMOS charakteryzowała się większą zawartością krzemu i azotu oraz intensywniejszymi zmianami w widmach FTIR w porównaniu do impregnowanego drewna, co sugeruje, że AATMOS wykazuje większą reaktywność do celulozy niż do drewna.

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