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The application of instrumental methods for estimation of bonding between cellulose and aminosilanes

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

Abstract: *The application of instrumental methods for estimation of bonding between cellulose and aminosilanes*. The paper presents the results of reactivity of N-(2-aminoethyl)-3-(trimethoxysilyl) propylamine (AATMOS) and (3-aminopropyl)trimethoxysilane (APTMOS) with cellulose. The FTIR spectra showed changes in the structure of cellulose after reaction with both silanes, in comparison to unmodified material. Unfortunately, these changes were not observe in spectra of cellulose after reaction with aminosilanes and water extraction, which suggests that silanes were leached from structure of cellulose. Concentration of silicon and nitrogen analyzed in modified cellulose before and after water extraction confirmed that silicon compounds were leached from cellulose. Moreover, the presented results confirmed that instrumental analyses, including FTIR, AAS and elemental analysis can in simply and fast way assess the stable character of bonding between lignocellulosic material and silicon compounds or other agents used to its modification.

Keywords: (3-aminopropyl)trimethoxysilane, N-(2-aminoethyl)-3-(trimethoxysilyl)propylamine, infrared spectroscopy, elemental analysis, atomic absorption spectrometry

INTRODUCTION

Silicon compounds have been applied to hydrophobisation of many materials used in chemical, building, textile and other industries. Silanes have been also used in chemical modification of cellulose and impregnation of wood (Maeda et al. 2006, Mai and Militz 2004, Thakur et al. 2014). Treatment with silanes improves wood properties, including fire and weather resistance, hydrophobicity, dimensional stability and mechanical properties (Donath et al. 2004, Mai and Militz 2004, Panov and Terziev 2009). Moreover, aminosilanes can reduce wood susceptibility to fungal attack (Donath et al. 2006, Reinprecht and Grznarik 2015).

In order to evaluation the reactivity of wood with impregnating agents, numerous analytical methods are used, including Fourier transform infrared spectroscopy, X-ray diffraction and nuclear magnetic resonance (He et al. 2005, Sebe et al. 2004). Moreover, in chemical analyses besides wood also its components, mainly cellulose are used (Ratajczak et al. 2010, 2012).

The aim of this research was to determine the reactivity of cellulose with two aminosilanes: N-(2-aminoethyl)-3-(trimethoxysilyl)propylamine (AATMOS) and (3-amino propyl)trimethoxysilane (APTMOS) using three instrumental methods. Infrared spectroscopy was used to control bonding of the silicon compounds with cellulose. Whereas, atomic absorption spectrometry and elemental analysis were applied to determine concentrations of silicon and nitrogen in silane-modified cellulose, respectively.

MATERIALS AND METHODS

Reaction of cellulose with aminosilanes

Cellulose *fibers* medium (Sigma-Aldrich) was mixed with solutions containing aminosilanes at a 5% concentration and white spirit (Avantor Performance Materials) as a solvent. The silanes used in the study were N-(2-aminoethyl)-3-(trimethoxysilyl)propylamine (AATMOS) and (3-aminopropyl)trimethoxysilane (APTMOS), purchased from Sigma-Aldrich. The cellulose was added to the tested solutions (1/25 w/v) directly after their

preparation. The reactions were run for 3 h at room temperature at the simultaneous stirring with a magnetic bar stirrer. Next, cellulose samples were filtered and dried in air flow at room temperature. In order to confirm the stable character of chemical bonds between cellulose and silanes, the part of modified cellulose was subjected to extraction with deionized water at a constant ratio (1/100 w/v) for 3 h at room temperature at the simultaneous stirring with a magnetic bar stirrer. Finally, cellulose after filtration was dried in air flow at room temperature.

Fouriertransform infrared spectroscopy (FTIR)

Cellulose samples were mixed with KBr (Sigma-Aldrich) at a 1/200 mg ratio. Spectra were registered using an Infinity spectrophotometer by Mattson with Fourier transform at a range of 500-4000 cm^{-1} at a resolution of 2 cm^{-1}, registering 64 scans.

Atomic absorption spectrometry (AAS)

Cellulose (0.5000 g) was mineralized with nitric acid (Sigma-Aldrich) in the microwave mineralization system (CEM Corporation) and after cooling down the solutions were filtered and diluted to 50.0 ml with deionized water. The content of silicon in wood samples was determined using flame atomic absorption spectrometry – AA280FS spectrometer (Agilent Technologies).

Elemental analysis

The analysis of nitrogen concentration was determined by the Thermo Scientific Flash 2000 CHNS/O Analyzer (Thermo Scientific). 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).

RESULTS AND DISCUSSION

Figure 1 presents FTIR spectra of cellulose after the reaction with N-(2-aminoethyl)-3-(trimethoxysilyl)propylamine (AATMOS) and Figure 2 shows spectra of cellulose after reaction with (3-aminopropyl)trimethoxysilane (APTMOS).

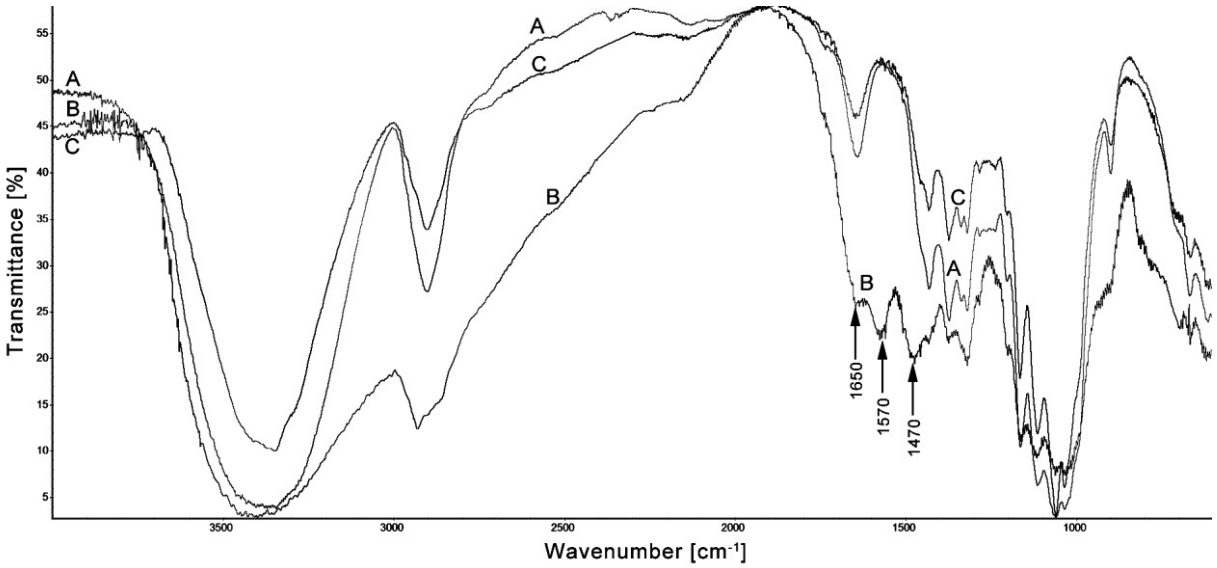

Figure 1. Spectra of cellulose (A), cellulose after reaction with AATMOS (B), cellulose after reaction with AATMOS and water extraction

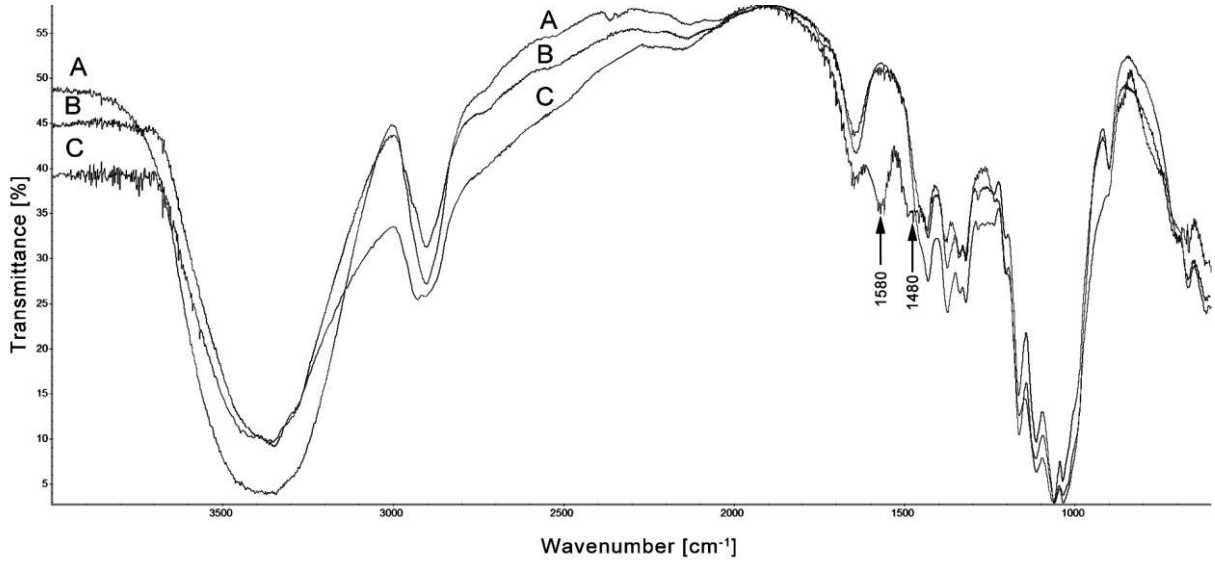

Figure 2. Spectra of cellulose (A), cellulose after reaction with APTMOS (B), cellulose after reaction with APTMOS and water extraction

The presented spectra showed changes in the structure of cellulose after reaction with aminosilanes in comparison to unmodified cellulose. The main changes in spectra of modified cellulose were observed in bands at 1650, 1570 and 1470 cm^{-1} for reaction with AATMOS and in bands at 1580 and 1480 cm^{-1} for reaction with APTMOS, respectively. In the spectra of modified cellulose after water extraction mentioned changes were not observe, which suggests that silanes were leached from structure of cellulose.

The contents of silicon and nitrogen in silane-modified cellulose before and after water extraction are presented in Figure 3 and 4, respectively.

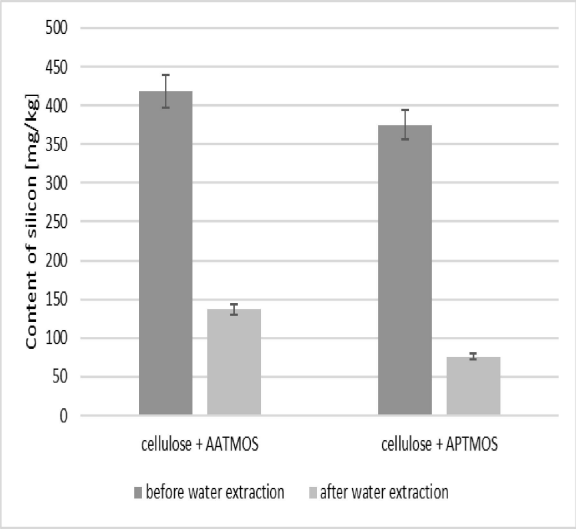

Figure 3. Content of silicon in silane-modified cellulose before and after water extraction

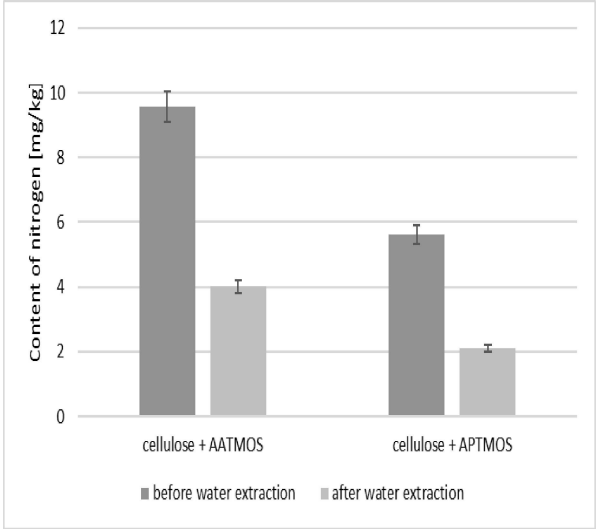

Figure 4. Content of nitrogen in silane-modified cellulose before and after water extraction

Silicon content in cellulose samples determined by flame atomic absorption spectrometry indicated that Si (coming from $Si(OCH_3)_3$ groups) was leached from modified cellulose. The degree of Si leaching from cellulose modified with AATMOS and APTMOS was 67.2% and 79.8%, respectively. The concentration of nitrogen (coming from NH and NH_2 groups) according to elemental analysis of silane-modified cellulose indicated that the degree of N leaching from this material was 58.1% for cellulose after reaction with AATMOS and 62.7% for APTMOS-modified cellulose. The results of silicon and nitrogen content in

cellulose samples indicate that both of silanes used to modification of cellulose were leached from its structure.

CONCLUSIONS

The results of FTIR analyses indicate that modification of cellulose with AATMOS and APTMOS caused changes in IR spectra. The bands observed in spectra of modified cellulose there were not present in spectra of silane-modification material after water extraction, which suggests that the bonds between cellulose and silanes do not have stable character. This fact was confirmed also the results of silicon and nitrogen content in silane-modification cellulose, which indicates that silicon compounds were leached from structure of cellulose.

The results present in this study confirm that instrumental analyses, including FTIR, AAS and elemental analysis can in simply and fast way assess the stable character of bonding between lignocellulosic material and silicon compounds or other agents used to its treatment or modification.

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Streszczenie: *Zastosowanie metod instrumentalnych do oceny wiązania celulozy z aminosilanami*. W pracy przedstawiono wyniki badań reaktywności [3-(2-aminoetylo-amino)propylo]trimetoksysilanu (AATMOS) i 3-(aminopropylo)trimetoksysilanu (APTMOS) z celulozą. W widmach FTIR celulozy po reakcji z silanami widoczne są pasma wskazujące na zmiany w strukturze celulozy. Pasma te zanikają w widmach celulozy po reakcji z aminosilanami i ekstrakcji wodą, co sugeruje, że silany uległy wymyciu ze struktury celulozy. Wymycie silanów z celulozy potwierdzają również wyniki stężenia krzemu i azotu oznaczone w modyfikowanej celulozie przed i po wodnej ekstrakcji. Przedstawione wyniki wskazują, że metody instrumentalne, m.in. FTIR, AAS i analiza elementarna mogą w prosty i szybki sposób określić trwały charakter wiązania występującego pomiędzy materiałem ligninocelulozowym, a związkami krzemoorganicznymi czy innymi substancjami stosowanymi do jego modyfikacji.

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