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## **THE EFFECT OF ALKYD RESIN ON THE STABILITY OF BINDING (3-AMINOPROPYL) TRIETHOXYSILANE WITH CELLULOSE AND WOOD**

*Experiments were conducted using (3-aminopropyl) triethoxysilane (APTES) and alkyd resin in order to improve the reactivity of wood protective preparations with wood. The results presented concern a structural analysis (FTIR, AAS) of modified cellulose and wood, both after chemical reactions with silanes and after water extraction.*

*The FTIR spectrum of pine wood powder was presented after a reaction with organosilane preparations and with the addition of alkyd resin, and then after water extraction. The FTIR analysis detected vibrations of Si-C, Si-O and N-H groups, indicating permanent bonding with the organosilane preparation. The presence of bands at  $710\text{ cm}^{-1}$  (characteristic of vibrations of the silicon bond with an atom of carbon and oxygen) and at  $1600\text{-}1580\text{ cm}^{-1}$  (characteristic of deformation vibrations of N-H coming from the amine group) confirmed the reactivity of these preparations with the wood. The results of atomic absorption spectrometry confirmed the stability of the organosilane bonds with the cellulose and the wood.*

**Keywords:** (3-aminopropyl) triethoxysilane, alkyd resin, cellulose, wood, FTIR spectroscopy, atomic absorption spectrometry (AAS)

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## Introduction

Research has been conducted for several years on the application of organosilane preparations to improve wood properties such as hydrophobicity, resistance to high temperatures and biological corrosion (Hill et al., 2004). The hydrophobic properties of silanes mainly result from the presence of methoxy or ethoxy groups bound with a silicon atom. An additional advantage of the compound used in this study, (3-aminopropyl) triethoxysilane containing ethoxy groups, is its non-toxicity in relation to the environment. Advances in wood protection methods are closely related to the knowledge and understanding of the mechanisms of chemical reactions between wood components and organosilanes, as well as other additives. To date, two main wood treatment methods have been developed using silicon compounds, i.e. a system of surface wood protection (Hochmańska et al. 2007, 2014) and micro-emulsion primarily containing silane and siloxane mixtures. The other wood treatment method using silicon compounds is complete wood impregnation, such as the hydrolysis of monomer silanes initiated by the presence of water bound in the wood (Sèbe, Brook 2001; Mai, Millitz 2004; Muromachi et al. 2006; Tshabalala et al. 2003). In this case the sol-gel process occurs in the cell walls (Mai, Militz 2004), resulting in a considerable reduction in wood swelling and limited extraction to water (Hochmańska et al. 2007).

Analyses were conducted using (3-aminopropyl) triethoxysilane (APTES) and alkyd resin in order to improve the reactivity of the protective preparations with the wood.

## Materials and methods

### Chemical treatment

The reaction of an organic solution system containing (3-aminopropyl) triethoxysilane (APTES) (Sigma-Aldrich, Steinheim, Germany) (fig. 1) and alkyd resin (Ftalak S 6120) (PPG Polifarb, Cieszyn, Poland) was run at room temperature at different volumetric ratios (1, 2.5, 5% APTES, 20% alkyd resin, white spirit).

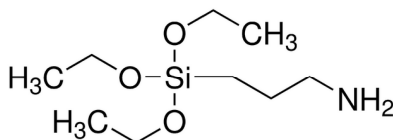


Fig. 1. Chemical structure of (3-aminopropyl) triethoxysilane

The homogenous material of cellulose and wood – Scots pine sapwood (*Pinus sylvestris* L.) in the form of powder – was treated with APTES (1/25 w/v) at room temperature with simultaneous stirring using a magnetic bar stirrer for 2 h. The cellulose (Sigma-Aldrich, Steinheim, Germany) and wood samples were left in working solutions at room temperature for the next 2 h, then filtered and dried in air flow at room temperature. The materials obtained were leached using continuous extraction with deionized water at a constant ratio (1/100 w/v) for 2 h.

### **Infrared Spectroscopy**

The samples of cellulose and wood were mixed with KBr (Sigma\_Aldrich, Steinheim, Germany) at a ratio of 1/200 mg. The spectra were registered using an Infinity spectrophotometer by ATI Mattson (Madison, USA) with Fourier transform at a range of 500–4000  $\text{cm}^{-1}$  at a resolution of  $2\text{cm}^{-1}$ , registering 64 scans.

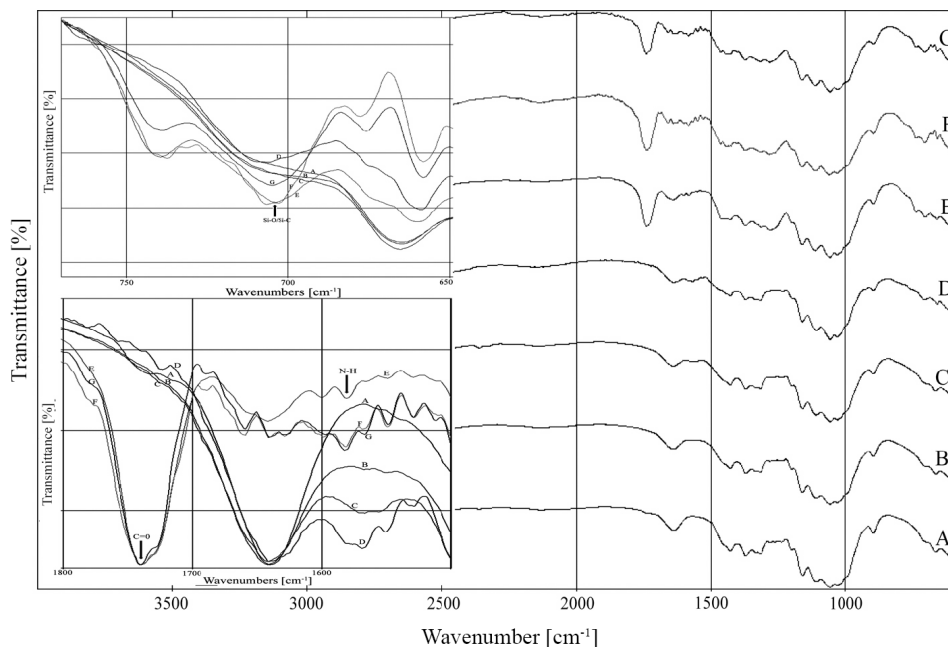
### **Atomic Absorption Spectrometry**

Representative samples of cellulose and wood powder measuring 0.5 g were collected from the prepared material. The samples were mineralized in a semi-closed microwave mineralization system (Marsexpress, CEM, Matthews, USA). After each step of treatment, the samples were submitted for AAS analysis of silicon content using a Spectra 280 AA spectrometer by Agilent Technologies (Santa Clara, USA). The final results were the median values of three simultaneous measurements.

## **Results and discussion**

The figures below present the IR spectra of the cellulose following the reaction with the organosilane preparations and with the organosilane preparations containing alkyd resin in an organic solvent. The spectra of the cellulose after reactions with these preparations and then after water extraction are also given. The bands in the analysed spectra indicate changes occurring in the cellulose systems after the reactions with the organosilane preparations and following the subsequent water extraction process. These results were also confirmed in a study by Ratajczak (2010).

The IR spectrum (1800–1500  $\text{cm}^{-1}$ ) (fig. 2) analysis of the experimental material was the main tool used to estimate the effect of the alkyd resin on the binding of the aminosilane with the wood. The band at 1745  $\text{cm}^{-1}$  proved to be characteristic for the vibrations of the carbonyl group  $\text{C}=\text{O}$  originating from the alkyd resin. This band was also found in the spectra of the modified cellulose following extraction with water (fig. 3).



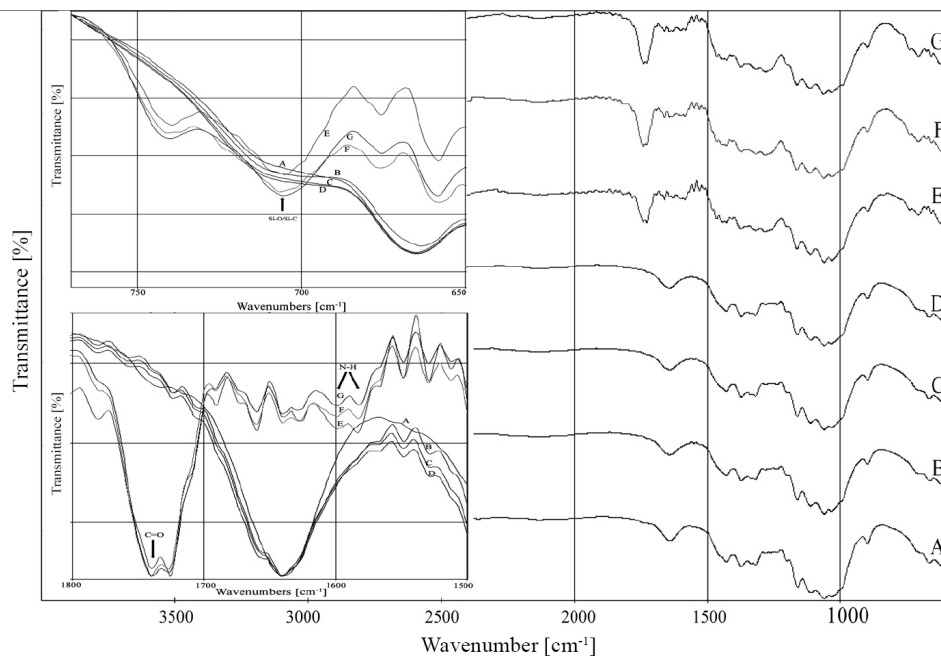
**Fig. 2. Spectra of cellulose (A), cellulose after reaction with: 1% APTES (B), 2.5% APTES (C), 5% APTES (D) 1% APTES + 20% alkyd resin (E), 2.5% APTES + 20% alkyd resin (F), 5% APTES + 20% alkyd resin (G)**

There was a band in the IR spectra at  $710\text{ cm}^{-1}$  which was characteristic for the cellulose after the reaction of the (3-aminopropyl) triethoxysilane with the alkyd resin (fig. 2). This band is was typical for bonds between silicon and carbon (Si-O-C-R3). The presence of this band indicated a reaction between the cellulose and organosilane. The results of the analyses confirmed the mechanism of this reaction discussed in studies by Tingaut et al. (2006), Sèbe et al. (2004) and Ratajczak et al. (2010). Moreover, an increase in the intensity of the vibrations of Si-C and Si-O groups was observed at  $700\text{ cm}^{-1}$ . This band is was characteristic of the experimental material modified with the silane containing alkyd resin. The highest intensity was recorded for the preparations with 1% and 2.5% APTES and 20% alkyd resin.

There were also deformation vibrations of N-H groups found at  $1580\text{ cm}^{-1}$  of the IR spectra. These vibrations originated from the I amine group of the (3-aminopropyl) triethoxysilane.

The IR spectrum ( $1800\text{--}1500\text{ cm}^{-1}$ ) (fig. 3) analysis of the experimental material was the main tool used to estimate the alkyd resin effect on the binding of the aminosilane with the cellulose. The band at  $1750\text{ cm}^{-1}$  proved to be characteristic for the vibrations of the carbonyl group C = O originating from the

alkyd resin. The presence of this band indicated bonding of the silane preparations containing alkyd resin with the cellulose.



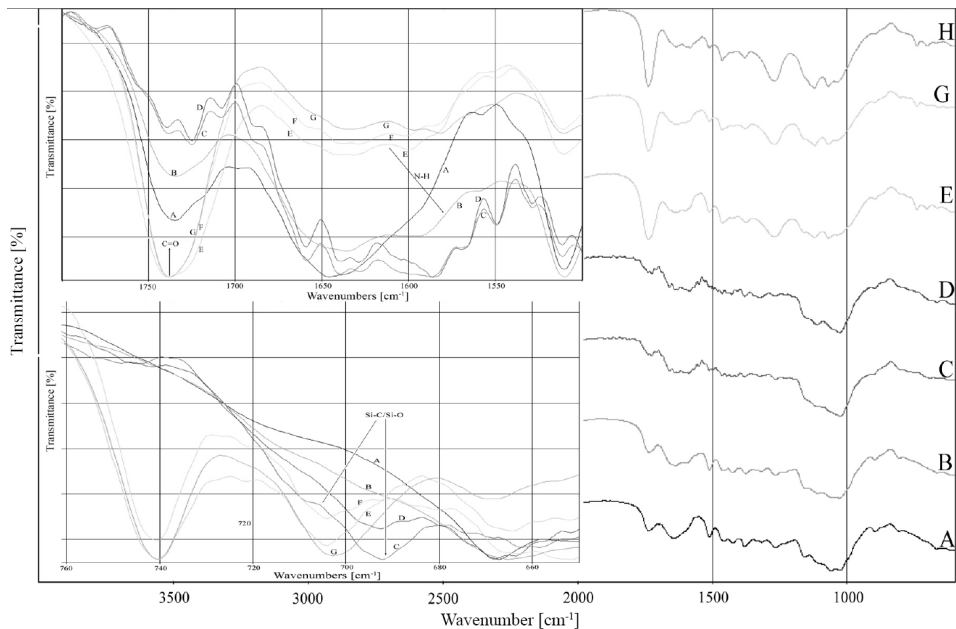
**Fig. 3. Spectra of cellulose after extraction with water (A), cellulose with: 1% APTES (B), 2.5% APTES (C), 5% APTES (D) 1% APTES + 20% alkyd resin (E), 2.5% APTES + 20% alkyd resin (F), 5% APTES + 20% alkyd resin (G)**

In the spectra of the modified cellulose after extraction with the (3-aminopropyl) triethoxysilane and alkyd resin, there was also a band at  $710\text{ cm}^{-1}$ , characteristic of vibrations of Si–C and Si–O groups (fig. 3). Moreover, the IR spectra contained bands at  $1550\text{ cm}^{-1}$ , characteristic of deformation vibrations of N–H coming from the amine group in the silane. The presence of these bands in the IR spectra of the modified cellulose following extraction also confirmed the stable bonding of the silane preparations and alkyd resin with the cellulose.

Figure 4 presents the IR spectrum of the pine wood powder after the reaction with the organosilane preparations and with the addition of alkyd resin in the organic solvent. It also shows the spectrum of the wood powder after the reaction with these preparations, and then after water extraction.

When analysing the bands in the IR spectrum at  $1800\text{--}1500\text{ cm}^{-1}$  (fig. 4), a band at  $1740\text{ cm}^{-1}$  could be seen which was characteristic of stretching vibrations of the carbonyl group C = O coming from the alkyd resin. This band

in the IR spectrum may have originated from vibrations occurring in the wood. This band was also seen in the spectra of the pine wood after extraction (fig 5).

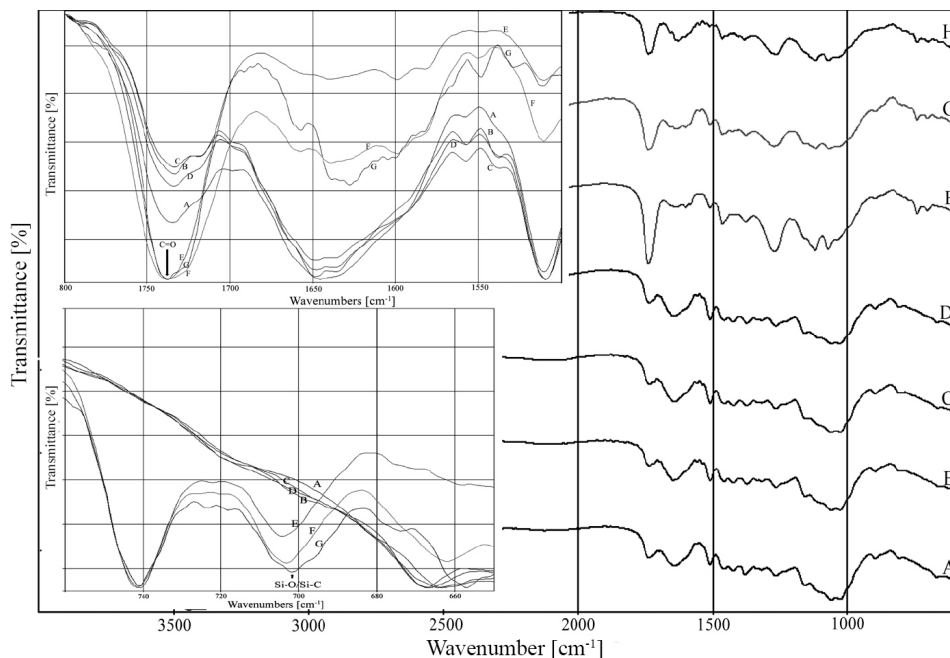


**Fig. 4. Spectra of wood (A), wood after reaction with: 1% APTES (B), 2.5% APTES (C), 5% APTES (D) 1% APTES + 20% alkyd resin (E), 2.5% APTES + 20% alkyd resin (F), 5% APTES + 20% alkyd resin (G)**

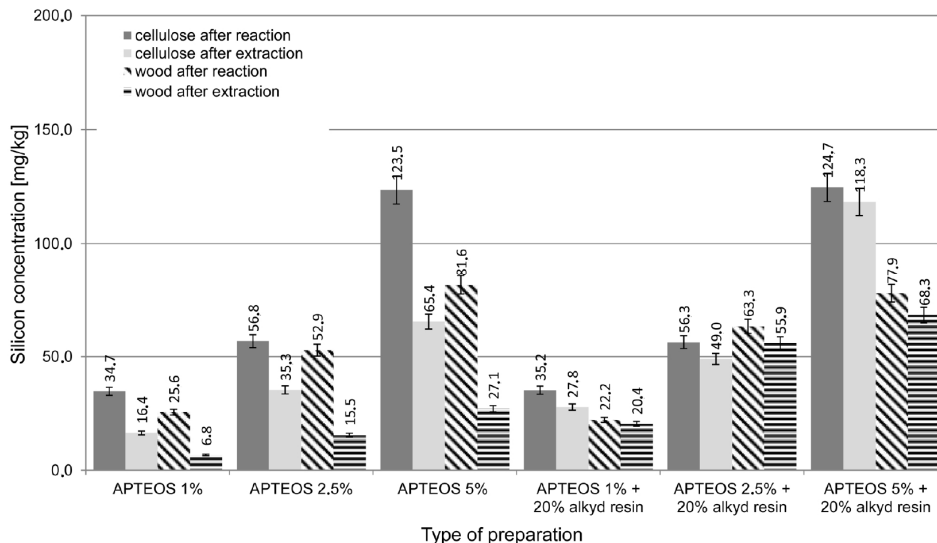
The spectra of the pine wood after reaction with the (3-aminopropyl) triethoxysilane and alkyd resin contained a band at  $710\text{ cm}^{-1}$ , characteristic of vibrations of the silicon bond with an atom of carbon and oxygen coming from the ethoxy group in the organosilane. This confirmed that a reaction had occurred between the cellulose and organosilane, as discussed earlier. Moreover, at  $700\text{ cm}^{-1}$ , characteristic of the bonds of Si–C and Si–O, an increased intensity was observed in the case of the modification with the silane preparations containing resin.

In addition, the IR spectra contained bands at  $1600\text{--}1580\text{ cm}^{-1}$ , characteristic of deformation vibrations of N–H coming from the I amine group in the (3-aminopropyl) triethoxysilane (fig. 5).

The effectiveness of the organosilane bonding with the cellulose was confirmed by the results of the atomic absorption spectrometry, presented in figure 6.



**Fig. 5. Spectra of wood after extraction with water (A), wood with: 1% APTES (B), 2.5% APTES (C), 5% APTES (D) 1% APTES + 20% alkyd resin (E), 2.5% APTES + 20% alkyd resin (F), 5% APTES + 20% alkyd resin (G)**



**Fig. 6. Silicon concentrations in cellulose and wood after reaction and after extraction**

The highest silicon concentration was assayed in the cellulose modified with a preparation containing 5% APTES, both with no alkyd resin added and with a 20% resin content (fig. 6). In each sample of APTES-modified cellulose with no alkyd resin added, the silicon concentration decreased after water extraction. In the modified cellulose preparation (5% APTES + 20% alkyd resin), the silicon concentration was 124.7 mg/kg, while in the same sample after water extraction it was 118.3 mg/kg.

The concentration of the silicon decreased in each sample of modified wood powder after water extraction. In the pine wood modified with the 2.5% APTES + 20% alkyd resin preparation, the silicon concentration was 63.33 mg/kg, while in the same sample after water extraction it was 55.90 mg/kg. A similar leaching rate was observed when using the 5% APTES + 20% alkyd resin preparation. The silicon concentration was recorded at 77.90 mg/kg, whereas in the same sample after water extraction it was 68.30 mg/kg. In this case, one beneficial effect of the alkyl resin was observed, manifested in the retention of the active substance in the cellulose and the wood.

## Conclusions

The analysis performed using infrared spectroscopy (FTIR) and atomic absorption spectrometry (AAS) confirmed the hydrophobation capacity of the APTES and 20% alkyd resin solution applied on the pine wood and cellulose. For the cellulose and pine wood after the reaction with the APTES – alkyd resin preparations and after extraction, a band was visible at  $1750\text{ cm}^{-1}$ , characteristic of vibrations of the carbonyl group  $\text{C}=\text{O}$  in the alkyd resin. The presence of this band indicated the bonding of the silane preparations containing alkyl resin with the cellulose and wood. The presence of bands at  $710\text{ cm}^{-1}$  (characteristic of vibrations of the silicon bond with an atom of carbon and oxygen) and at  $1600\text{--}1580\text{ cm}^{-1}$  (characteristic of deformation vibrations of  $\text{N-H}$  coming from the amine group) confirmed the reactivity of these preparations with the wood. The results of the atomic absorption spectrometry confirmed the stability of the organosilane bonds with the cellulose and the wood.

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## Acknowledgements

Part of the study was funded by the research project: “Superior bio-friendly systems for enhanced wood durability” (No. Pol-Nor/203119/32, DURAWOOD) – supported by Norway Grants and the Polish National Centre for Research and Development (NCRD) as part of the Polish-Norwegian Research Programme.

