

Interactions of silicon compounds and mixture of linseed and tung oils with cellulose

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Abstract: Reactivity of cellulose with a formulation containing organosilanes and natural oil was analysed in order to determine the practical influence of the treatment on biological properties of wood. Structural analysis of cellulose after the reaction with organosilanes and after extraction was performed using FTIR spectroscopy. In FTIR spectra the analyzed bands included 800 cm⁻¹ responsible for vibrations of SiC and/or SiO groups. These bands are characteristic of silicon bonds with atoms of carbon and oxygen originating from the methoxy groups found in organosilanes. The presence of these bands in the spectra proves the occurrence of a reaction between cellulose and organosilanes.

Keywords: silicon compounds, MTMOS, NOTES, FTIR spectroscopy

INTRODUCTION

Treatment with coatings based on natural oil modified with silicon compounds considerably diminishes water uptake of wood. Structural analysis of bonds between wood basic chemical compounds and silicon compounds can determine developed structures, explain chemical reactions, thus proving the effectiveness of silicon compounds as agents enhancing wood properties. Donath et al. [2007] treated wood with alkoxy silanes and other organofunctional silanes. The method relies on hydrolysis of alkoxy silanes and a subsequent condensation of silanol groups formed within the porous wood surface. It was shown to be an effective method to reduce water uptake of wood after cyclic water immersion and drying exposure. The enhanced dimensional stability observed after these treatments is due to the replacement of hydrophilic hydroxyl groups with hydrophobic substances.

In this study we used cellulose fibers as the organic component. Cellulose is an extraordinary renewable polysaccharide with unique properties. Because of its abundance, biodegradability, and remarkable properties, it has been widely exploited as a source of materials, either close to its native form or after appropriate chemical modifications [Cunha et al. 2010]. The preparation of organic-inorganic hybrid materials combining polysaccharides, such as cellulose with silicon compounds, has only been reported within the last decade [Tanaka and Kozuka 2004, Maeda et al. 2006, Sequeira et al. 2007]. In the present article we have stated that it would be more effective, in comparison with the above approaches, to use film-forming polymersilane hybrid coatings specifically formulated to provide enhanced adhesion to cellulose and wood structural constituents and moisture barrier properties. The key advantage of using a combination of resin and silane rather than silane alone is that silane films are known to exhibit relatively poor moisture barrier properties and tend to be very thin, and therefore not very durable unless topcoated.

MATERIAL AND METHODS

The reaction of organosilane preparation solutions (methyltrimethoxysilane (MTMOS, CH₃Si(OCH₃)₃); N-Octyltriethoxysilane (NOTES, C₁₄H₃₂O₃Si) with a mixture of linseed and tung oils in an organic solvent was run at room temperature at different volumetric ratios. Reactions of cellulose of Merck with silane preparations (1/25 w/v) were run at room

temperature at the simultaneous stirring with a magnetic bar stirrer for 2 h. Samples were left at room temperature for 2 h and next filtered. They were left to dry at room temperature. The obtained materials were eluted using continuous extraction with deionized water at a constant ratio (1/100 w/v) for 2 h.

Infrared Spectroscopy

Cellulose samples were mixed with KBr 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.

RESULTS AND DISCUSSION

Figure 1 presents FTIR spectra of cellulose following a reaction with organosilane solutions (MTMOS/NOTES) and a mixture of linseed and tung oils, while fig. 2 – those of cellulose after the reaction and elution (after water extraction).

We need to stress here the fact that after the reaction a new band of 1750 cm^{-1} was found in all cellulose spectra, responsible for stretching vibrations of the C=O group. The presence of this band indicates the conversion of cellulose with natural oil and in the system with organosilanes (fig. 1). This band is visible also on IR spectra after extraction (fig. 2), which indicates a permanent bond of natural oil with cellulose.

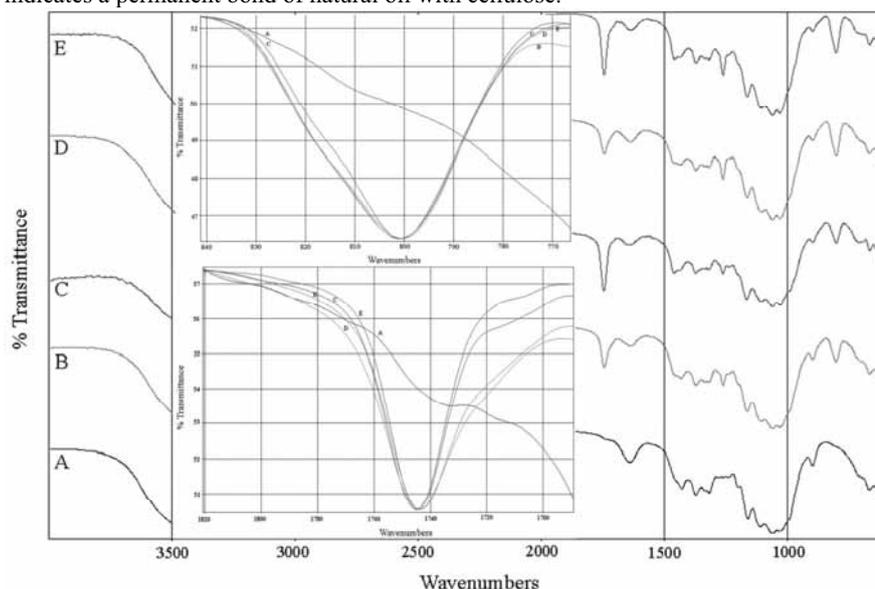


Fig. 1. IR spectra of cellulose (A), cellulose after reaction with mixture of linseed and tung oils (VEOPOL) 10% and MTMOS/NOTES (2.5%) (B), VEOPOL 20% and MTMOS/NOTES (2.5%) (C), VEOPOL 10% and MTMOS/NOTES (5%) (D), VEOPOL 20% and MTMOS/NOTES (5%) (E)

In spectra (fig. 1) of cellulose following the reaction with preparations of a mixture of linseed and tung oils/organosilanes a band of 800 cm^{-1} characteristic of Si-C and/or Si-O bonds was recorded. This band is found also in cellulose spectra after extraction (fig. 2). They are bands characteristic of a silicon bond with carbon and oxygen atoms originating from the methoxy group present in organosilanes [Ghosh et al. 2009; Tingaut et al. 2005, 2006; Tjeerdsma, Millitz 2005].

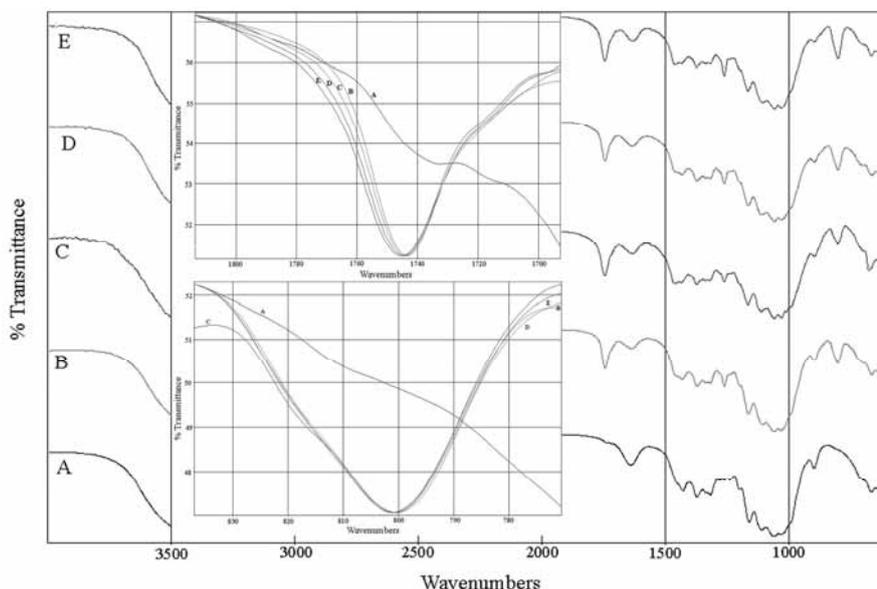


Fig. 2. IR spectra of cellulose after extraction: cellulose (A), cellulose after reaction with mixture of linseed and tung oils (VEOPOL) 10% and MTMOS/NOTES (2.5%) (B), VEOPOL 20% and MTMOS/NOTES (2.5%) (C), VEOPOL 10% and MTMOS/NOTES (5%) (D), VEOPOL 20% and MTMOS/NOTES (5%) (E)

A confirmation for the reactivity of organosilanes with cellulose comes from the results of atomic absorption spectrometry. The highest values of silicon concentration in cellulose, amounting to 1235 mg/kg, were recorded after a reaction with a 20% natural oil solution and a 5% mixture of MTMOS/NOTES.

A marked difference was also observed in the degree of reactivity of cellulose with MTMOS and NOTES (at all analyzed concentrations) in comparison to a MTMOS/NOTES organosilane mixture, to the advantage of the latter system. We need to particularly stress the fact that the level at which silicon concentration was determined in cellulose after water extraction, in comparison to the level of silicon concentration in cellulose after the reaction with all organosilanes, was only slightly lower.

CONCLUSIONS

In FTIR spectra the presence of bands characteristic of vibrations of the silicon-carbon and silicon-oxygen bonds, coming from the SiC and SiO groups at 800 cm^{-1} , from organosilane solutions shows that a chemical reaction has occurred between cellulose and organosilanes (particularly a MTMOS/NOTES mixture). The presence of bands responsible for vibrations of the SiOCH₃ group on IR spectra of cellulose after reaction and extraction proves a permanent character of the formed bond between the hydroxyl and methoxy groups of organosilanes. The silanol groups formed after hydrolysis of the alkoxy groups of the silanes can react with hydroxyl groups of cell wall polymers. However, these Si-O-C bonds are susceptible to hydrolysis. The high concentration of silicon determined in cellulose and in wood powder after extraction in comparison to the high silicon concentration in cellulose and wood powder after a reaction with organosilanes (particularly in case of the application of a MTMOS/NOTES organosilane mixture) confirms the permanent character of the bond between cellulose or wood powder and the analyzed preparations.

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Streszczenie: *Wzajemne oddziaływanie związków krzemoorganicznych, mieszaniny olejów lnianego i tungowego z celulozą.* Praca miała na celu zbadanie reaktywności celulozy z nowymi preparatami krzemoorganicznymi z udziałem oleju lnianego i tungowego. Analizę strukturalną celulozy po reakcji z organosilanami oraz po ekstrakcji wykonano metodą spektroskopii w podczerwieni (FTIR). Przedstawione wyniki analizy strukturalnej modyfikowanej celulozy organosilanami wskazują na ich wysoką reaktywność z celulozą. Zarejestrowane pasma absorpcji w widmach IR modyfikowanej celulozy organosilanami jak i po ekstrakcji w zakresie 1235 cm^{-1} są odpowiedzialne za drgania grupy SiC oraz 800 cm^{-1} są odpowiedzialne za drgania grup SiC i/lub SiO. Pasma te zarejestrowane w widmach IR modyfikowanej celulozy organosilanami są charakterystyczne dla wiązania krzemu z atomem węgla i tlenu pochodzącym od grupy metoksylowej obecnej w organosilanach. Obecność tych pasm w widmie świadczy o zajściu reakcji między celulozą a organosilanami.

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