Silicon compounds as additives improving coating performance: fixation of silicon compounds with cellulose

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Abstract: In this study the reactivity of cellulose with new solvent born preparations containing organosilanes, alkyd resin and natural oil was analysed. Structural analysis of cellulose after reaction with organosilanes and after extraction was performed using Fourier-transform infrared spectroscopy (FTIR). In IR spectra the analyzed bands included 1250 cm^{-1} responsible for vibrations of the SiC group and 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. The concentration of silicon was determined by AAS in cellulose after reaction with preparations and after extraction.

1 Introduction

In the past, several researchers investigated the applicability of silanes and their organic and inorganic derivatives for timber hydrophobisation. One approach for applying such a protective coating to timber is to use cold plasma with hexamethyldisiloxane (HMDSO) (Denes et al. 1999). Donath et al. (2006) treated wood with alkoxysilanes and other organofunctional silanes. The method relies on the hydrolysis of alkoxysilanes and a subsequent condensation of the silanol groups formed within the porous wood surface. It was shown to be an effective method to reduce water uptake of wood by over 80% 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 the present article, it is 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 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.
Treatment with coatings based on alkyd resin 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 and explain chemical reactions, thus proving the effectiveness of silicon compounds as agents enhancing wood properties. Investigations on cellulose / silicon compounds reactions and their effects on silicon concentration in cellulose were confirmed by Infrared Spectroscopy and Atomic Absorption Spectrometry analyses.

2 Materials and methods

2.1 Chemicals

The reaction of organosilane preparation solutions (methyltrimethoxysilane (MTMOS, $CH_3Si(OCH_3)_3$); N-Octyltriethoxysilane (NOTES, $C_{14}H_{32}O_3Si$) with alkyd resin in an organic solvent was run at room temperature at different volumetric ratios. Organic solutions of organosilanes (MTMOS, NOTES and MTMOS/NOTES: 1%, 2.5% and 5% w/v solution) were mixed with alkyd resin (10% and 30% w/v solution). Alkyd resin (made by Sigma Coatings) was 55% solution in 40 D Exsol and methylopropanol. Reactions of cellulose with silane preparations (1/25 w/v) were run at room temperature by simultaneous stirring with a magnetic bar stirrer for 2 h. Cellulose of Merck was investigated. Samples were left at room temperature for 2 h and then 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.

2.2 Infrared Spectroscopy

Cellulose samples were mixed with KBr at a 2/200 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 $2cm^{-1}$, registering 64 scans.

2.3 Atomic Absorption Spectrometry

The material was collected twice: after the reaction and after extraction in a way ensuring homogeneity and the representative character of the samples. The collected material was dried at room temperature. From such a prepared material a representative sample of 0.5 g powder was collected. Samples were mineralized in a Marsexpress CEM International semi-closed microwave mineralization system.
Solutions prepared after mineralization of cellulose samples and control samples (before reactions) were subjected to analyses of silicon contents by flame atomic absorption spectrometry (FAAS) using a Spectra 200 AA spectrometer by Varian. The deuteron background correction was applied to minimize interference during measurements. The final results were median values of three simultaneous measurements. Results repeated three times were characterized by very good compatibility. Before each assay analytical curves were prepared on the basis of a series of freshly prepared standard obtained from a standard solution of silicon at a concentration of 1000 mg/dm^3.

3 Results and discussion

Figure 1 presents FTIR spectra of cellulose and cellulose following a reaction with organosilane solutions (MTMOS, NOTES, MTMOS/NOTES) and alkyd resin.
It must be emphasised here 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 alkyd resin and in the system with organosilanes (Fig. 1)..
In spectra of cellulose following the reaction with the preparations of alkyd resin/organosilanes a band of 800 cm^{-1} characteristic of Si-C and/or Si-O bonds was recorded.. They are bands characteristic of a silicon bond with carbon and oxygen atoms originating from the methoxy group present in organosilanes. The highest intensity in this

respect was found for the spectrum of cellulose after the reaction with 30% alkyd resin as well as 5% and 2.5% mixture of silanes, i.e., MTMOS/NOTES. High reactivity of these two preparations in relation to cellulose was also confirmed in the analyses of silicon concentration by AAS (Table 1).

Fig. 1. IR spectra of cellulose (A), cellulose after reaction with alkyd 30% (B), alkyd 10% and NOTES/MTMOS (2.5%) (C), alkyd 30% and NOTES/MTMOS (1%) (D), alkyd 30% and NOTES/MTMOS (2.5%) (E), alkyd 30% and NOTES/MTMOS (5%) (F)

Abb. 1 (A) IR-Spektren der Cellulose, Cellulose nach Reaktion mit (B) Alkyd (30%), (C) Alkyd 10 % und NOTES/MTMOS (2,5%), (D) Alkyd 30% und NOTES/MTMOS (1%), (E) Alkyd 30 % und NOTES/MTMOS (2,5%), (F) Alkyd 30 % und NOTES/MTMOS (5%),

Moreover, bands with a similar intensity of 1250 cm^{-1}, responsible for vibrations of the Si-C group, were observed in all spectra. The presence of these bands in spectra of cellulose after the reaction (Fig. 1) shows the occurrence of a reaction between cellulose and organosilanes, as well as a permanent character of the formed bond (Tingaut et al. 2005, 2006; Sèbe et al. 2004; Tjeerdsma and Militz 2005).

A confirmation for the reactivity of organosilanes with cellulose comes from the results of atomic absorption spectrometry (Table 1).The highest values of silicon concentration in cellulose amounting to 4083 mg/kg were recorded after a reaction with a 10% alkyd resin solution and a 2.5% mixture of MTMOS/NOTES (Table 1).
Table 1 Concentration of silicon in cellulose treated with silanes/alkyd resin formulations

Tabelle 1 Siliconkonzentration in Cellulose, die mit verschiedenen Silan/Alkydharzmischungen behandelt wurde

A clear difference is also observed in the degree of reactivity of cellulose with MTMOS and NOTES (at all analyzed concentrations) in comparison to a mixture of organosilanes MTMOS/NOTES, being to the advantage of the latter system. It must be particularly stressed 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 (Table 1) is only slightly lower.

A very low percentage of silicon elution from cellulose amounting to 33%, at its simultaneous high reactivity, is particularly evident in case of the system of 30% alkyd resin/ 2.5% MTMOS/NOTES. This shows a permanent chemical bond between organosilane and cellulose, which was not broken in the hydrolysis process.

4 Conclusion

In FTIR spectra the presence of bands characteristic of vibrations of the silicon-carbon and silicon-oxygen bonds, coming from the SiC group at 800 and 1250 cm^{-1}, from organosilane

solutions show that a chemical reaction has occurred between cellulose and organosilanes (particularly a MTMOS/NOTES mixture). The presence of bands responsible for vibrations of the $SiOCH_3$ group on IR spectra of cellulose after reaction proves the permanent character of the formed bond between the hydroxyl and methoxy groups of organosilanes.
The high concentration of silicon determined in cellulose after extraction in comparison to the high silicon concentration in cellulose 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 and analyzed preparations.

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Table 1 Concentration of silicon in cellulose treated with silanes/alkyd resin formulations
Tabelle 1 Siliconkonzentration in Cellulose, die mit verschiedenen Silan/Alkydharzmischungen behandelt wurde

Formulations content		Concentration of silicon in cellulose [mg/kg]	
Concentration of silanes	Concentration of alkyd resin	after reaction	after leaching
MTMOS 2.5%	10%	234 ± 33	163 ± 2
NOTES 2.5%		823 ± 33	228 ± 16
MTMOS/NOTES 2.5%		4084 ± 42	1122 ± 19
MTMOS 1%	30%	314 ± 6	208 ± 7
NOTES 1%		216 ± 11	207 ± 8
MTMOS/NOTES 1%		497 ± 11	260 ± 13
MTMOS 2.5%		533 ± 13	241 ± 23
NOTES 2.5%		624 ± 3	236 ± 11
MTMOS/NOTES 2.5%		2553 ± 29	1718 ± 14
MTMOS 5%		306 ± 8	286 ± 10
NOTES 5%		380 ± 17	354 ± 15
MTMOS/NOTES 5%		729 ± 24	538 ± 31

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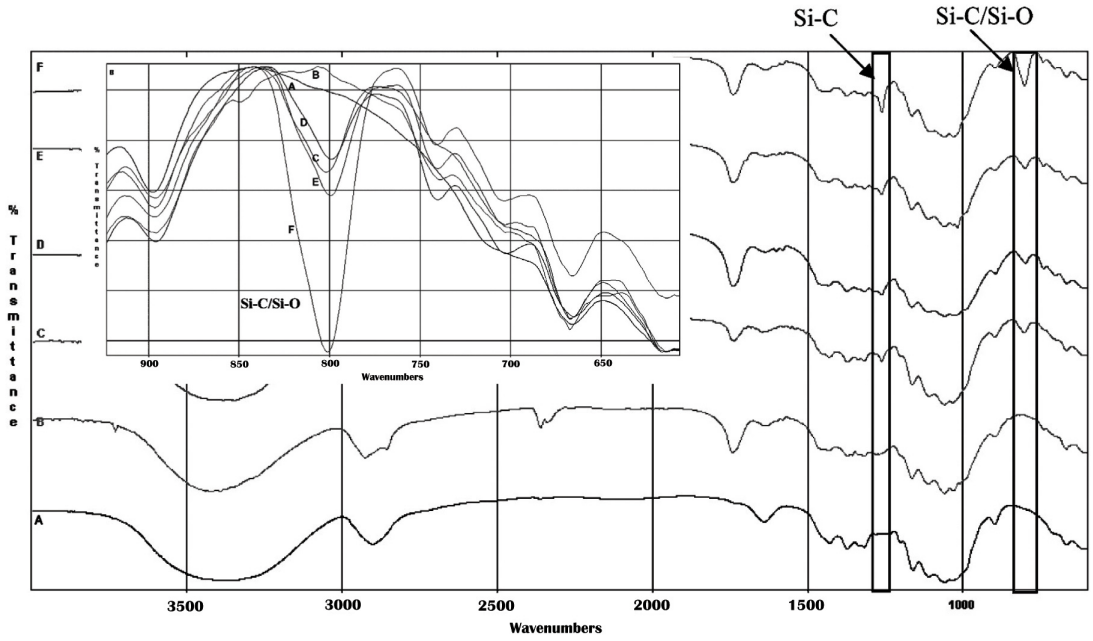

IR spectra of cellulose (A), cellulose after reaction with alkyd 30% (B), alkyd 10% and NOTES/MTMOS (2.5%) (C), alkyd 30% and NOTES/MTMOS (1%) (D), alkyd 30% and NOTES/MTMOS (2.5%) (E), alkyd 30% and NOTES/MTMOS (5%) (F) 480x277mm (100 x 100 DPI)