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Bonding of Silanes on CSH-Gel

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Abstract

Silanes (e.g. iso-Octyltriethoxysilan, n-Propyltriethoxysilan) represent a group of silicon organic compounds, which are used as water repellent agents for the surface protection of cement based materials. After application the silanes are transported into the covercrete by capillary suction. During the transport chemical reactions take place which lead to the formation of a water-repellent film on the inner surface of the pores. To raise the durability of cement based materials through a water-repellent film, it is necessary to understand how this silicon resin is linked to the CSH-Gel and how this film is formed on the surface. For that three mechanisms are responsible, chemical bonding, adsorption through van-der-Waals forces and hydrogen bonds. Information about these mechanisms lead to a better understanding of alteration processes of the silicon resin and therefor, the basics for the development of new silans based products. The soxhlet extraction of treated concrete with different solvents is investigated to get informations about types and strength of the bonding between silicon resin and cement-based material. Furthermore the behaviour of silanes is analysed in varying concentrations on Si-Wafer as a model substrate by atomic force microscopy to verify the development of silicon resin films and its bonding on the surface.

1 Introduction

The application field of silanes as a special group of silicon organic compound in civil engineering is growing. These silanes are used as water-repellent system for surface protection of cement-based materials and natural stones. They are also used as chemical compound between cement-based materials and composite materials for example for adhesives or sealants [1-4]. The structures of silanes are wide spread and so different possible functional molecules are conceivable. Therefore, the coupled process of transport and chemical reaction is crucial for the evaluation of existing systems and the development of new systems [5-8]. To optimize the performance of the silanes, it is necessary to find the ideal chemical structure for each possible application. This improvement leads to higher durability of the protected construction and helps to reduce the costs of maintenance and restoration.

To optimize the chemical structure of the silicon organic compounds, it is important to know how they are connected to the surface of the CSH-Gel. Three types of bonding between silane/siloxane and the surface are conceivable: chemical bonding, adsorption by van-der-Waals forces and hydrogen bonds [9].

The silane reacts in two steps; the hydrolysis, which leads to a meta stable silanol, and the poly-condensation of the silanol to the silicon resin [5,6,7]. Now the film building reaction on the surface is forming first monomers, oligomers and at last polymers depending on the number of functional groups in the silane molecule. To observe the surface morphology and roughness, an atomic force microscope (AFM) is used in this study, because it is a typical method to analyse structure and reactions on similar surfaces [10,11]. Similar experiments are done in our institute to observe behaviour of LDH on muscovite [12,13]. As a first step a Si-Wafer is used as model substrate to investigate the bond on the surface of silane [14]. The advantage of a Si-Wafer is his absolutely flat surface and his ability to form hydroxide groups, after an activation by UV radiation, which are necessary for the reaction with the silanes. In further experiments the Si-Wafer will be replaced by natural and synthetic tobermorite. The crystal structure of tobermorite is relatively similar to the structure of CSH-Gel, but the material is better for the use in AFM studies. Finally fresh made CSH-Gel should be prepared measured using an AFM, if possible.

In preliminary experiments it was shown that ether, hexane, heptane and octane can dissolve the polymers of n-propyltriethoxysilane, iso-butyltriethoxy-silane and iso-octyltriethoxysilane nearly completely at room temperature in only a few hours. The alteration of the silicon resin has to be observed and understood, because the protection of cement based materials, treated with silanes, often failed 3 to 12 years after the first application of a water-repellent system. To improve the durability of cement based material, it is important to understand the process of alteration and the identification of decomposition products. One way of simulating a long term test by simultaneous extraction of silicon resin is the use of a soxhlet extraction derive. In this study the extraction is done by using diethylether, hexane, heptane and octane as solvent, which are in contact with cubes of 2 cm edge length made of pure cement and treated with one of the three different silanes.

In soxhlet-extractions it is shown what happens to the water-repellent system when the silicon resin is affected by the chemicals. During the 24 hour extraction with the solvents, no reduction of the efficiency of the protection system was found. In that study the voluntary absorption and the voluntary loss of water in a cement cube of 2 cm edge length treated with different silanes and extracted with different solvents is compared.

2 Experimental methods and materials

2.1 Chemicals

The used chemicals were of high purity and supplied by Wacker Chemie GmbH (iso-Octyltriethoxysilane (SILAN IO-TRIETHOXY), n-Propyltriethoxysilane, iso-Butyltriethoxysilane, Silres®BS 290) and Merck KGaA (n-Heptan, n-Hexane, iso-Octane, Diethylether, Ethanol). The eluent was self made saturated $Ca(OH)_2$ solution with pure calcium hydroxide ($Ca(OH)_2$) from Merck KGaA. The Si-Wafer is supplied by Wacker Chemie GmbH.

2.2 Instruments

The devious used for soxhlet-extraction experiments is a Behrotest TRS 200 (Fa. behr Labor Technik). The surface observation was done with a MultiMode Atomic Force Microscope with a Nanoscope IIIa controller. The used cantilevers (NSC36/noAl/50; NSC36/Si3N4/noAl/50) were supplied by Fa. MikroMasch.

2.3 Experimental conditions

2.3.1 Extration experiments

In a preliminary experiment solutions were made each with one of four organic solvents (hexane, heptane, octane and diethylether) and with a self made siloxane in a concentration of 100 mmol/l. After that the solutions were mixed for three weeks with a magnetic stir bar. This experiment was done to show type of solvents that are suitable for our soxhlet extraction.

For this soxhlet extraction experiment of pure cement were made with an edge length of 2 cm. Then all cubes were treated similar to analyse the water content and the uptake by water absorption without water-repellent treatment and with one of our silanes. Therefore the cubes were dried in an oven at 60 °C up to weight stability. In a next step the cubes were stored in pure water for 24 hours and weighed. Then they were weighed every hour to verify the uptake of water. In a next step these cubes were dried again at 60 °C up to weight stability. After that treatment the cubes were divided into four groups. One group as a reference group and three groups each for one used silane. The cubes of the three silane groups were treated with the silane in full contact for one minute. After this conditioning the silanes were stored for three weeks. When the reaction was finished, the cubes were dried again and stored in pure water to analyse the capillary water uptake according to the silane treatment. To see, if the silanes react to a siloxane, a reference cube was mortared and measured by FTIR, to analyse the amount of silicon resin. In a last step the cubes were extracted in a soxhlet-system with hexane, heptane, octane and diethylether for 24 hours and again treated like before to analyse the AFM-investigation adsorption and the loss of water.

The sample preparation for the surface observation with the Atomic Force Microscope (AFM) starts with the activation of a Si-Wafer by UV radiation for two hours. In the first step Si-Wafers were used as model substrate. Then, the Wafer was cut into pieces of 1×1 cm^2 in size, cleaned with ethanol, and in a first experimental setting, stored in pure iso-octylsilane or n-propylsilane for 3 minutes. After this treatment the Si-Wafers were stored in a nearly saturated $Ca(OH)_2$ solution. The use of saturated $Ca(OH)_2$ creates small calcite crystals on the surface, which disturb the observation by AFM. In a second experiment a cleaned Si-Wafer was stored in a glass box with two cups, one filled with pure silane and the other filled with HCl (0,1M). With this setup the silane gets in contact with the Si-Wafer surface over the gas phase and reacts to a silicon resin.

The measurements were performed both in tapping mode and in contact mode using a JV-scanner. In tapping mode the tip of the cantilever is stimulated near its resonant frequency and the sample is moved by a piezo crystal under this tip. In the vicinity of the surface, the tip interacts with the sample and changes its frequency. This change possesses an information of the surface and is transformed into an image. During contact mode, the tip of the cantilever is moved over the sample while in direct contact to the surface. The difference in the elevation on the surface is measured by a laser and a photodiode and then transformed into an image. The force of the tip can move particles, which are not chemical bonded, on the surface. So it is possible to decide if the silicon resin linked to the surface by a strong chemical bonding or not.

The images were received in constant amplitude mode with a resolution of 256 × 256 pixels at a scanning rate of 1 Hz.

3 Results and discussion

3.1 Dissolving experiment

In the first preliminary experiment it was found, that the iso-octylsiloxane and the iso-butylsiloxane were completely dissolved by diethylether, hexane, heptan and octane after a few hours, while being mixed with a magnetic stir bar. Only the n-propylsiloxane needed more time to dissolve. This can be explained by the degree of polymerisation. The n-propyltriethoxysilane reacts nearly completely to a silicon resin. Because of sterical influences, iso-butyltriethoxysilane and even more the n-octyltriethoxysilane condensates with rests of not reacted functional groups, which are the point of contact for the solvents [5]. This experiment shows that these solvents are extraction agents for the following soxhlet-extraction experiment. Additionally extraction of n-propylsiloxane is not so efficient compared to iso-butyl- and iso-octylsiloxane because of its behaviour during this dissolving experiment.

3.2 Soxhlet extraction

In the soxhlet-extraction experiment an improvement of the water-repellent system after the extraction with diethylether, hexane, heptane and octane was found. As it is shown in figures 1-3, the results for the normalised water content of the extracted cubes are better than the water content of the pure silane treated cubes. For optical reasons in the figures the water content of untreated cement cubes was normalized to 100 % and is not displayed in the figures. The best improvement of the water-repellent system is to achieve after the octane extraction although in a preliminary experiment the siloxanes dissolve in the solvents especially in octane in the best and fastest way. Additionally it can be shown that the iso-octyltriethoxysilane treated sample could be improved better than the other samples.

These results disagree with the observations of Stoppek-Langern [9] on similar experiments with natural stones, where a reduction of the efficiency of the silicon resin was noticed.

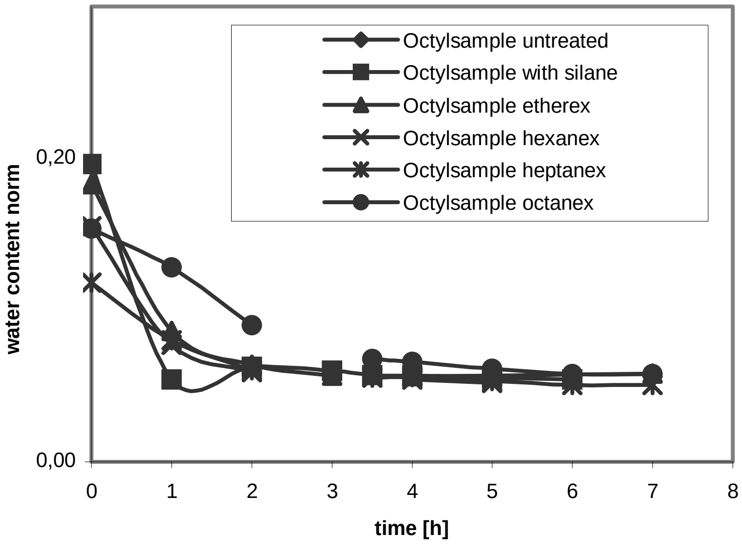

Figure 1: Normalised water contact of samples treated with iso-octyltriethoxy-silane

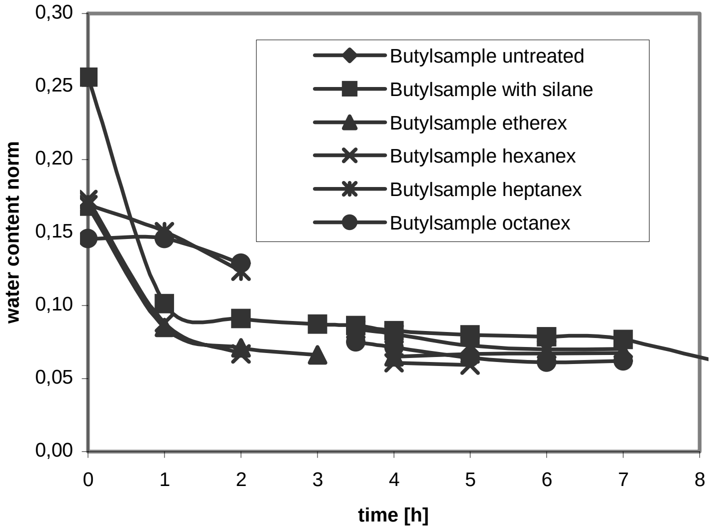

Figure 2: Normalised water contact of samples treated with iso-butyltriethoxy-silane

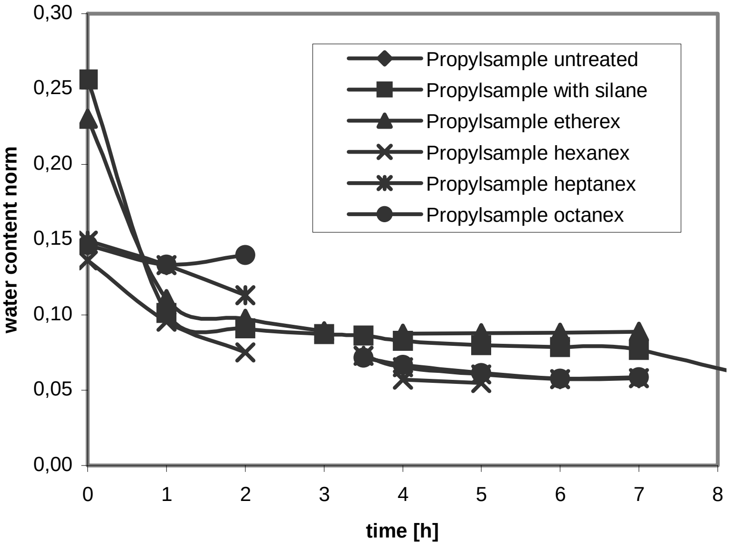

Figure 3: Normalised water contact of samples treated with propyl-triethoxysilane

3.3 AFM measurements

Pictures of the AFM measurements are shown in figure 4. In the first image (1) a Si-Wafer with a scratch is presented. This Wafer has a contact time with n-propylsilane and nearly saturated $Ca(OH)_2$ solution for five days. The silane reacts to a silicon resin by forming a network during the relatively long reaction time. This picture is not representative to verify the bonding but gives an information about the look of a fresh silicon resin on a model surface.

The next picture (2) is done in tapping mode. It shows a Si-Wafer with a statistical distribution of n-propylsilane dots after a reaction time of one day. This distribution can be explained by the static influences of the silanes on each other.

This island growth describes the first step in the formation of a silicon resin film on the surface and at the end of this film building process a network is established like in picture one. The small dots of silane had enough time to react to a silicon resin but they did not react with the surface. In picture three the same area is scanned in tapping mode. The smaller area in the middle was scanned before in contact mode. This scan window in contact mode is totally cleared from the siloxane dots by the cantilever during the measurement. The moved particles can be found on the edge of the scanned area.

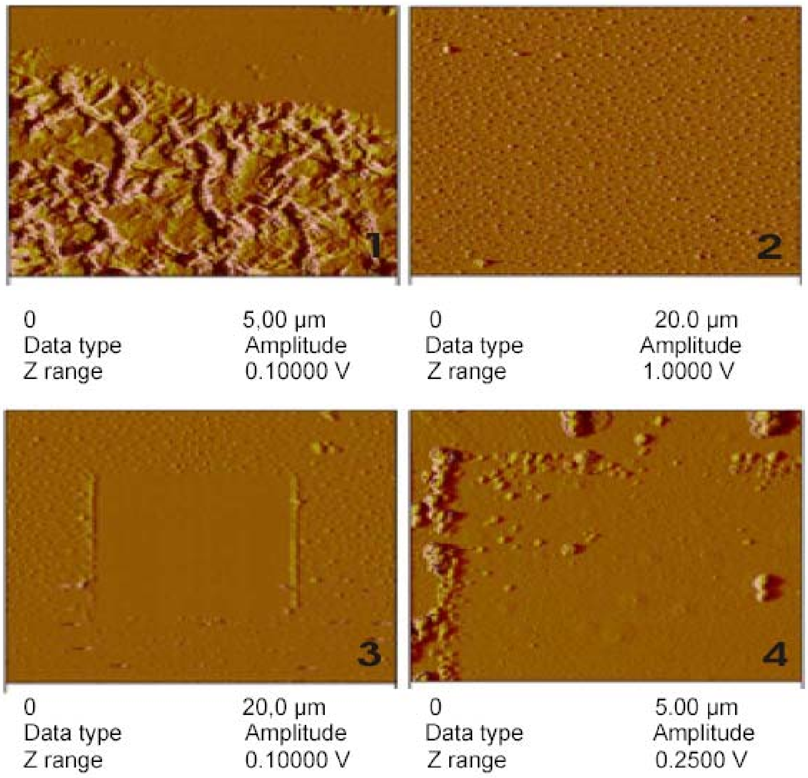

Figure 4: AFM images

The n-propyltriethoxysilane reacts to a silicon resin first with other silane molecules but not with the OH-groups on the surface of the Si-Wafer, so that no strong chemical bonding can be verified in this experimental setup.

In the last picture (4) the same measurements were done with iso-octyltriethoxysilane. The picture is done in tapping mode and shows an area at the edge of a scan size after measurements in contact mode. This image indicates that during contact mode observation not all the siloxanes could be moved over the surface of the Si-Wafer by the cantiliver. Compared to the measurements with n-propyl there are strong interactions between the iso-octyltriethoxysilane and the model substrate because the force of the cantilever during contact mode is not sufficient to move particles over the surface.

In a relatively short reaction time the behaviour of n-propylsilane and iso-octylsilane differs enormously. The octyltriethoxysilane is able to develop strongly, interacting to the model surface compared to the propylsilane. These results compared to the other experiments indicates that chemical bonding of silanes with mineralic surface are formed. But this must be verified in further experiments with AFM and CSH-Gel surfaces.

4 Conclusions and future prospects

It is shown that the reaction kinetics and the molecule structure of the silanes play an important role in the bonding behaviour. Until today it ist not possible to verify the bonding between the silicon resin and the CSH-Gel or a model substrate like a Si-Wafer. But it can be seen that the bearing of the silanes differ in the kind of use as protection system in natural stones and in cement and concrete. Further experiments will be needed in order to describe the discrepancies between the practical and theoretical behaviour. An improvement of the water-repellent system after extraction with all four solvents was found against the results of our preliminary experiment and against the results of Stoppek-Langern [9] made with natural stones. One explanation for that is the dissolving of the silicon resin and out from that the distribution in fine pores. The results from the AFM measurements support the observed varieties in the bonding performance of the silanes. These achievements must be verified in further experiments to understand the bonding and the growth of the siloxane film.

In further experiments the chemical bonding between the silicon resin and the CSH-Gel or model substances should be investigated by using XPS and NMR measurements. Additionally other spectroscopic analysis will be done, using photothermical deflection and Raman spectroscopy. In situ observations of the typical silane reactions in contact with CSH-Gel and other model substances using a fluid cell in AFM measurements are also planned.

5 References

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