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Characterization of Degradation of Silicon-based Water Repellents by MALDI-TOF/MS

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Abstract

Alkyl-trialkoxysilanes represent a group of silicon-based water repellents which are used for the surface protection of cement based materials. To optimize the structure of silanes and their application for long term durability it is important to understand the chemical reactions. These take place between silanes and the cement based matrix and also between the silicon-based coating and deterioration factors e.g. environmental conditions. Therefore characterization of reaction products and metabolites of Alkyl-Trialkoxysilanes is necessary. In this context an analytical method with high selectivity is used. This study used time-of-flight mass spectrometry combined with matrix assisted laser desorption ionisation (MALDI-TOF/MS) to characterize silicon based oligomeric and polymeric compounds. It is shown that acid and alkaline deterioration processes influence the degree of hydrolysis, condensation and crosslinking of the formed silsesquioxanes. MALDI-TOF/MS provides a useful tool for analysing both condensation products alkyl-trialkoxysilanes compounds and their degradation products.

Keywords: MALDI-TOF/MS, alkyltriethoxysilane, silsesquioxanes, degradation

1 Introduction

Buildings and structures made of concrete are exposed to various environmental conditions which may deteriorate the construction. Mainly the capillary uptake of chloride-containing aqueous solutions, e.g., de-icing salts or sea water, can lead to corrosion of the reinforcement. For the prevention of this and other damaging processes silicon-based water repellents e.g. alkyl-trialkoxysilanes are used for the surface protection of concrete. These compounds react by hydrolysis, condensation and crosslinking to silsesquioxanes. The performance and durability of the water repellent treatment depends on the properties of these silsesquioxanes. However, the fundamental chemical processes which determine the reaction of silsesquioxanes as well as their potential degradation have been hardly studied so far. This degradation may occur through a variety of chemical or physical processes.

For the qualitative and quantitative analysis of chemical compounds the use of Fourier-Transformation Infrared Spectroscopy (FTIR) is established [1]. This method serves to determine the penetration profiles of silanes applied on concrete in order to check the quality of the coating. However, this method is not suitable for the characterisation of unknown degradation products.

We use MALDI-TOF/MS, which allows determining the chemical structure and changes in the structure with high sensitivity. For separation of analytes time-of-flight mass spectrometry (TOF/MS) that allows the characterization with high selectivity and resolution. For the necessary ionization of the analyzed sample matrix assisted laser desorption ionization (MALDI) is used. Compared to conventional ionization methods by which large organic molecules are fragmented, this method is soft and thus allows the analysis of high molecular weight molecules and polymers.

Previous experiments have indicated that the characterization of the silsesquioxane structure is possible by MALDI/TOF-MS [2,3]. The objective of the present investigation is the adaption of this method for the analyses of degradation products of silsesquioxanes. This is necessary for the identification of the possible mechanismen of deterioration and degradation phenomena of silicon-based water repellents.

The degradation processes we analyzed were chemical attack by acids and bases and physical attack by repeated cycles of freezing and thawing and sulphate attack.

2 Experimental

2.1 Model system and specimen

Iso-octyltriethoxysilane (IUPAC: Triethoxy(2,2,4-trimethylpentyl)silane) was choosen as silane compound (Wacker Chemie). It was used as a pure chemical without dilution with any solvent.

Sodium hydroxide was used as a model compound to simulate the alkaline reaction of iso-octyltriethoxysilane on the surface of cement-based materials. For the synthesis of silsesquioxanes 100 µL of silane was mixed with 300 µl tetrahydrofurane and 28 µl of aqueous NaOH solution (c = 0,2 mol/L). The mixture was stirred by a magnetic stirrer in a closed tube at room temperature.

Specimen of hardened cement paste were made of CEM I 42,5 R with a w/c-ratio of 0,5 and stored under defined conditions (≥ 28 d, 20°C, 80 % r.h.). They were coated with iso-octyltriethoxysilane by complete impregnation and stored again under the same defined conditions.

2.2 Degradation experiments

For simulating the attack of acid compounds like SO_3 and NO_x the acids of H_2SO_4 and HNO_3 in different concentration were used. The deterioration of basic environment was examined by using aqueous NaOH in high concentration. Sulphate attack was studied by using aqueous Na_2SO_4 (3%) [4]. Repeated cycles of freezing and thawing were simulated with and without aqueous NaCl (c= 3%).

The deterioration solutions were added to batch mixtures of the model systems by stirring continuously. The mixture ratio was 1:15 (volume/volume).

The coated specimen were placed into the deterioration solutions. The liquid-to-solid ratio was 10:1 (volume/mass). At the end of the treatment the specimen were leached in static tank tests using tetrahydrofurane (THF) as an organic solvent. The liquid-to-solid ratio was 5:1 (volume/mass).

Samples (5 µL) of batch mixture and tank tests were taken and mixed with the matrix (50 µL, c = 25 mg/mL in THF) and cationizing agent (2,5 µL, c = 20 mmol/L in THF). 1 µl of this mixture was spotted on a MALDI plate and measured by TOF/MS.

2.3 Instruments

A 4800 MALDI TOF/TOF-Analyzer (AB Sciex) equipped with a Nd-YAG-laser (wavelength of 355 nm) was used for analyzing oligomeric and polymeric compounds. Usually 1000 spectra were accumulated in the positive mode. DHB (2,5-dihydroxybenzoic acid) was used as matrix.

Sodium iodide was added as a cationizing agent. Polypropyleneglycols (PPG) were used for mass calibration. The assignment of the peaks were done by comparison with a especially created data base where possible reaction products of alkyl-alkoxysilanes, e.g. silsesquioxanes with different number of Si-atoms, rings and hydroxyl-groups are listed. Semi-quantitative analysis was made by the height of the peaks.

3 Results and discussion

3.1 Identification of silsesquioxanes

Figure 1 shows a MALDI-TOF/MS-spectra of silsesquioxanes formed in the model system iso-octyltriethoxysilane with NaOH. The peaks are mainly single charged Na-adducts, less single charged cations.

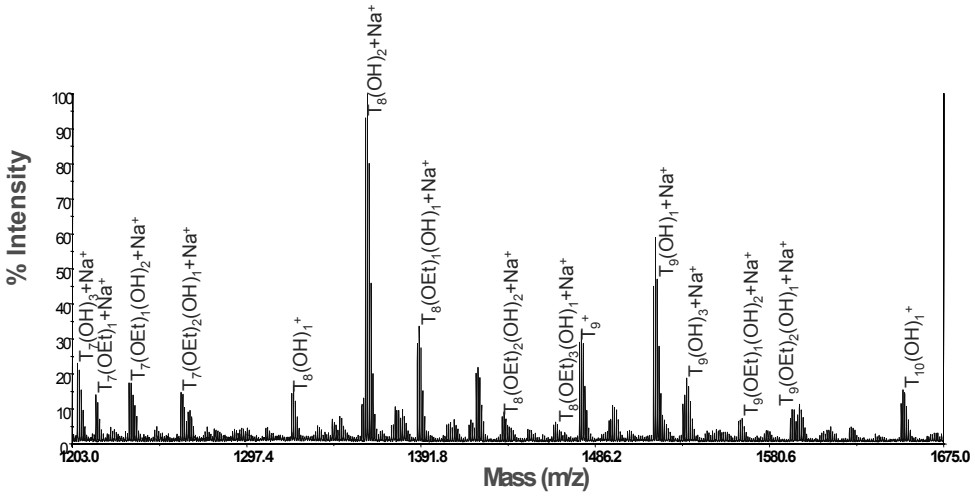

Figure 1: Mass spectra of silsesquioxanes formed by iso-octyltriethoxysilane with NaOH (identification of peaks see below)

These peaks could be assigned to silsesquioxanes with a variable degree of hydrolysis, condensation and crosslinking. They can be described by the formula [5,6]:

$$T_n(OC_2H_5)_x\,(OH)_y, \text{ with } T = RSiO_{1.5-m/2n} \text{ and } x + y = m$$

They mainly consist of Si-atomes between seven and ten, where the species $T_8(OH)_2$ and $T_9(OH)_1$ showed the highest intensity.

3.2 Characterization of metabolites of silsesquioxanes

The model systems of silsesquioxanes showed significant changes in the obtained MS-spectra after treatment with deterioration agents with acids like HNO_3 und H_2SO_4. After adding of acid the degree of hydrolysation increased, in contrast the degree of crosslinking and mainly the degree of condensation decreased tremendously. At high concentration of acid the compounds $T_4(OH)_4$ und $T_5(OH)_3$ showed the highest intensities of peaks. A significant change concerning the type of acid was not detected. Also the analogous treatment with acids of the coated specimen showed an influence on the structure of extractable silsesquioxane compounds. Deterioration agents like H_2SO_4 the degree of hydrolysis increased analogously with the results of the model systems.

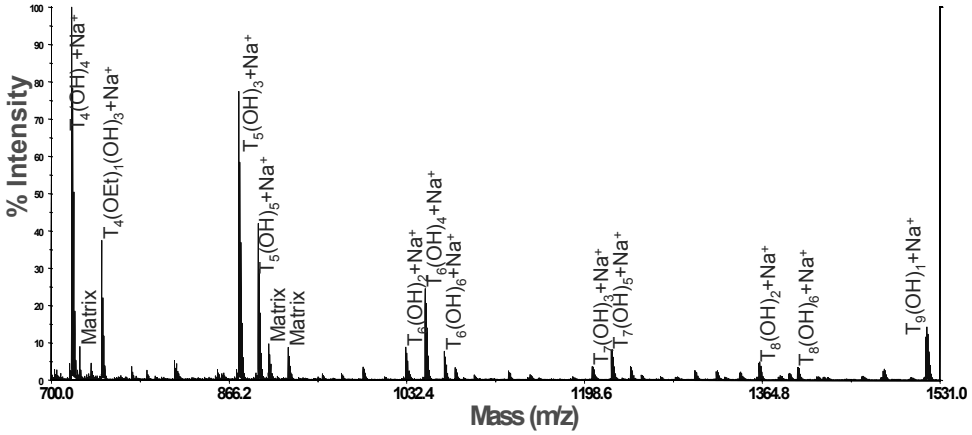

Figure 2: Mass spectra of degradation products of the model system of iso-octyltriethoxysilane after treatment with H_2SO_4

High alkaline agents like sodium hydroxide induced a decreasing of degree of condensation and crosslinking of silsesquioxanes. The specimen made of cement paste which were coated by silane and treated by repeated freeze-thaw-changes showed no significant change concerning extractable silsesquioxane compounds in MALDI-TOF spectra compared to the specimen without treatment. Also there was no difference if the specimen were stored in solution of NaCl or not. Furthermore no effect on the chemical structure of silsesquioxanes could be detected by treatment with sulphate attacking Na_2SO_4 solution.

4 Conclusions and outlook

The obtained results show that the MALDI-TOF/MS technique is a useful tool for the analysis of silicon-based water repellents. The chemical structure of silsesquioxanes formed by reaction of alkyl-triethoxysilanes under the environment of cement-based materials and their degradation products can be detected.

From the results the following conclusions can be drawn:

Silsesquioxanes are modified by treatment of acid and basic agents. The chemical structure of the compounds is changed, mainly the degree of hydrolysis, condensation and crosslinking by deterioration agents like sulfuric and nitric acid. The pH of the deterioration agents is the main force for this chemical degradation process. Other chemical damage of concrete like sulphate attack at neutral pH-value has no effect on the chemical structure of silsesquioxanes. Equally physical processes like freezing and thawing has no impact.

This data can be used to establish a relationship between chemical structure and chemical reactivity which is important for the development of new silane-based water repellents with a higher long-term durability.

Ongoing experiments are treating silsesquioxanes applied on cement based materials by UV-radiation and ozone for the investigation of oxidative degradation. Also a detailed quantification of certain silsesquioxane compounds by treatment of acids and bases as a function of the pH-value will be done.

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