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TOF/MS for Characterization of Silicone Based Water Repellents

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Abstract

Alkoxysilanes represent a group of silicon organic compounds which are used as water repellent agents 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 which take place between the silicon organic compounds and the matrix. Therefore characterization of alkoxysilanes and their condensation products and metabolites is necessary. In this contribution an analytical method with high selectivity is presented. The study used time-of-flight mass spectrometry (TOF/MS) combined with two ionization techniques, ESI (electrospray ionization) and MALDI (matrix assisted laser desorption ionization) to characterize trialkoxysilanes with different alkyl-groups by the detection of the corresponding [M+H$^+$]-species. It is shown that MALDI is suitable for analyzing reaction products of alkoxysilanes in an alkaline environment. Therefore, oligomeric and polymeric compounds, e.g. siloxanes and silsesquioxanes with high degree of condensation, could be detected through their [M+Na$^+$]-species. TOF/MS provides a useful tool for analysing both monomeric trialkoxysilanes compounds as well as their condensation products.

Keywords: MALDI-TOF-MS, alkyltriethoxysilane, alkaline environment

1 Introduction

Concrete in buildings and structures is exposed to various environmental factors that lead to its deterioration. In particular, the capillary uptake of chloride-containing aqueous solutions, e.g., de-icing salts or sea water, can lead to a fast corrosion of the reinforcement. For the prevention of this and other damaging processes silicon organic compounds, e.g., organo-functional alkoxysilanes, are used as water repellents for the surface protection of cement based materials. These products are sprayed on the concrete surface and during the capillary transport into the concrete, the silane reacts chemically with the formation of a very thin water repellent polymer film that attaches to the inner surfaces of the pores. The performance and durability of the water repellent treatment depends on the properties of these polysiloxanes. In turn, the formation of the polysiloxanes depends on several factors such as the type and amount of silane, composition and pH-value of the treated concrete.

However, the fundamental chemical processes which determine the properties of polysiloxanes as well as the silicone polymer degradation have been hardly studied so far. The present investigation focuses on the characterization of the alkoxysilanes and their reaction products during polymerization in alkaline medium using highly-sophisticated analytical methods. So far there is no suitable method for the characterization of the chemical structure of polysiloxanes formed in the presence of hardened cement paste.

For the qualitative and quantitative analysis of chemical compounds Fourier-Transformation Infrared Spectroscopy (FTIR) based on solid transmission is used [1]. This method serves to determine the penetration profiles of silanes applied on concrete in order to check the quality of the treatment. However, this method is not suitable for the characterization of complex polymer structures.

Another analytical method useful in the characterization of superplasticizer, polymer based additives and other organic binders in the field of building materials, is mass spectrometry (MS) [2]. With this technique the chemical structure and changes in the structure can be determined accurately and with high sensitivity. A variation of this method is the time-of-flight mass spectrometry (TOF/MS) that allows the characterization of polymers with high selectivity and resolution. For the necessary ionization of the analyzed sample, two new techniques are available: electrospray ionization (ESI) and matrix assisted laser desorption ionization (MALDI). Compared to conventional ionization methods by which large organic molecules are fragmented, these methods are not as aggressive and thus allow the analysis of high molecular weight organic molecules and polymers. ESI is suitable for the characterization of low molecular weight compounds and oligomers, while MALDI can be used for polymeric compounds of high molecular weight. In case of MALDI the component is added to a matrix to protect the molecules to be analysed. By means of laser the matrix molecules are ionized followed by a charge transfer to the so called sample molecules. The ionized species are analysed by TOF/MS. Fundamentals of these techniques are presented elsewhere [4]. Previous experiments with these methods have indicated that the characterization of the polysiloxane structure should be possible. But so far the requirements for the analyses of products formed in cement based materials have not been met.

The objective of the present research is the development of an analytical method for the analyses of silanes and polysiloxanes by means of MALDI-TOF/MS. This is necessary for the identification of the basic polycondensation properties of silanes in the presence of cement based materials as well as the degradation phenomena of polysiloxanes.

2 Experimental methods and materials

2.1 Chemicals

Triethoxysilanes with different alkyl groups, of high purity were used and supplied by Wacker Chemie (methyl-, n-propyl, iso-butyl-) and Evonik (n-octyl). High purity sodium hydroxide was used to prepare the solutions required for the hydrolysis and condensation of the triethoxysilanes.

2.2 Instruments

The ESI-TOF/MS unit („Mariner“ Applied Biosystems/Sciex) was used to analyse low molecular weight compounds, such as alkyltriethoxysilanes. The mass spectra were obtained after infusing the silane solution (c =10-100 ppm) into the ESI ion source [5]. Different organic solvents and cationizing agents, such as ammonium acetate were tested. The MS-parameter “nozzle potential” varied between 50 and 300V. Polyethyleneglycols (PEG) were used for mass calibration.

A “7400 Proteomics Analyzer” MALDI-TOF/MS (Applied Biosystems/Sciex) equipped with a Nd-YAG-laser (wavelength of 355 nm) was used for analyzing oligomeric and polymeric compounds. Usually 1000 spectra in the positive mode were accumulated. Different matrixes, such as DHB (2,5-dihydroxybenzoic acid), dithranol (1,8,9-trihydroxyanthracen) and trans-3-indolacrylic acid were used. Sodium iodide was added as a cationizing agent. Angiotensine was used for mass calibration.

2.3 Experimental conditions

Sodium hydroxide was used as a model system to simulate the alkaline reaction of trialkoxysilanes on the surface of cement based materials. For synthesizing the hydrolyzis and condensation products of alkoxysilanes, 1ml of alkoxysilane was mixed with 3ml tetrahydrofuran and 250µl of 4 M

NaOH solution [6],[7]. The mixture was stirred at room temperature. After 24 h a sample (5 µL) was taken and added to 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.

3 Results and discussion

3.1 Identification of silanes

Figure 1 shows the overlaid mass spectra of triethoxysilanes with different alkyl groups, such as methyl, n-propyl, iso-butyl and n-octyl. They are selectively identified by their [M+H$^+$]-species, e.g. their molecular mass plus 1 Da. Best results with regards to the intensity in mass spectra were obtained with ethanol as solvent, so that the concentration of the triethoxy functionalized silane was of 100 ppm, and using NH_4OAc as cationizing agent (10 mmol/L). Optimized nozzle potential was 150 V.

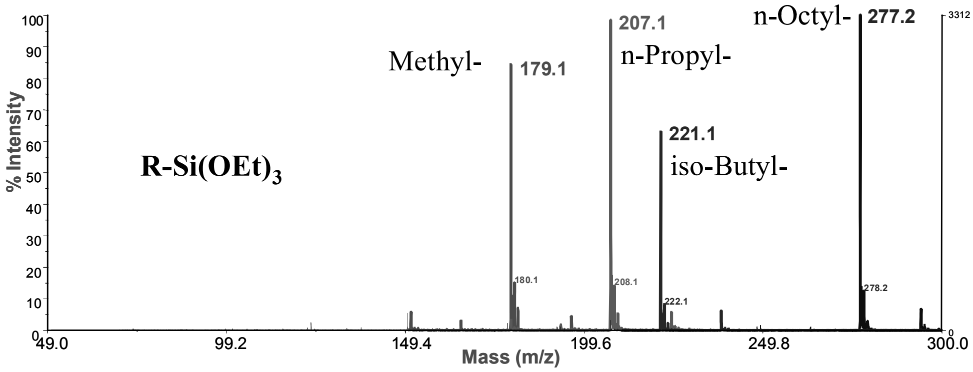

Figure 1: ESI-TOF mass spectra of triethoxysilanes with different alkyl groups (overlaid view, [M+ H$^+$]-species, solvent: ethanol/10 mmol/L NH_4OAc)

The results show clearly that ESI-TOF/MS is applicable for the chemical identification of different trialkoxysilanes, using suitable solvents and cationizing agents. Since the determination is based on their molecular mass, it is possible to distinguish the different silanes used for water repellent treatment with a very good selectivity.

3.2 Identification of polymerized silanes in an alkaline medium

Figure 2 shows the MALDI-TOF/MS mass spectrum of n-octyltriethoxysilane submitted to an alkaline environment simulated by

NaOH using DHB as matrix. For qualitative identification of the reaction products the sample was taken after 24 h.

The isotopic distribution in the inset of Figure 2 shows an equidistance of m/z = 1 between the peaks. So only single charged species appear which can be assigned to $[M+Na^+]$-species by means of data analysis software.

Considering the three reactive alkoxy groups, the mass of the different condensed silane structures can be calculated. These siloxane compounds can have a linear or a cyclic structure. The calculated masses are compared with those obtained from MS enabling the assignment of the peaks to the corresponding siloxanes (Table 1). The data reveals that during condensation no linear siloxanes are formed but rather cyclic products, generally called silsesquioxanes. These species are characterized by the formula [8],[9]:

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

Species with seven Si atoms corresponding to a m/z = 1200, are the most frequently formed as shown by the high peaks in the spectrum.

The results have shown that after 24 hours in an alkaline environment all ethoxy groups have hydrolyzed to silanol with release of ethanol. Under real conditions, the chemical processes take place in the pore structure of cement based materials. A previous study had shown that under these conditions only 60 % of the theoretical amount of ethanol is released after 4 days [10]. The difference in the rate of hydrolyzis implies that the hardened cement paste has an influence on the chemical process. Therefore, it can be assumed that in the latter case the polymerized silanes will differ from those obtained in a pure alkaline solution. Nonetheless, the analyses of the reaction products will be helpful in identifying the decisive chemical mechanisms and will serve to characterize the chemical behaviour of the hardened cement paste.

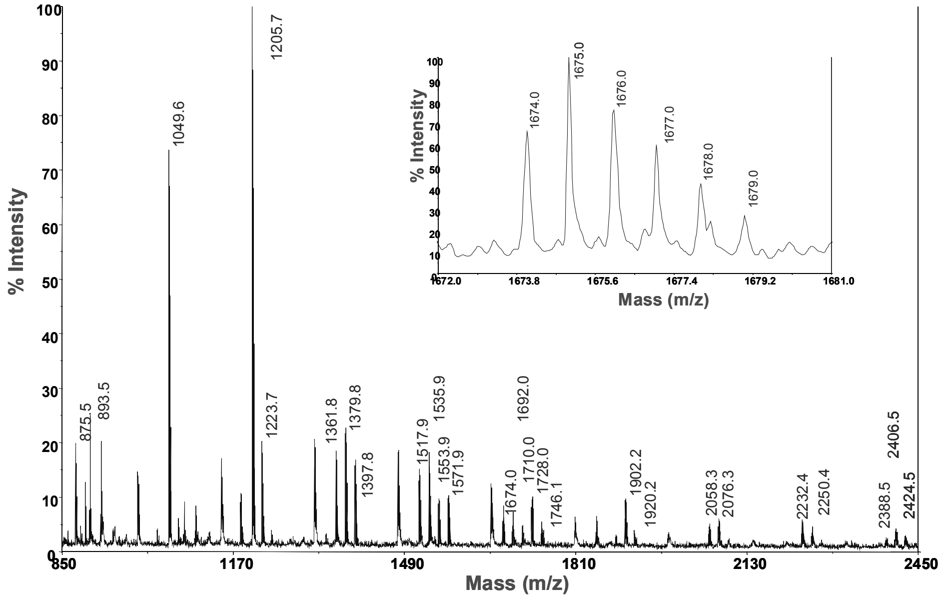

Figure 2: MALDI-TOF mass spectrum of alkaline treated n-octyltriethoxysilane (matrix: DHB, $[M+zNa^+]$ species with z=1)

4 Conclusions and outlook

The obtained results show that the MALDI-TOF/MS technique is a useful tool for the analysis of the chemical structure of polymerized silanes. Using suitable matrices and cationizing agents an optimum ionization is obtained that allows the identification of siloxane compounds by their masses. MALDI is therefore an optimal supplement to ESI. A further optimization of selectivity and sensitivity could be achieved by tandem mass spectrometry (TOFqTOF/MS). Coupling with HPLC will also upgrade the selectivity of TOF/MS [11].

From the results obtained for n-octyltriethoxysilane, the following conclusions can be drawn:

- In alkaline solutions no linear siloxanes are formed and polycondensation leads to cyclic products that are generally called silsesquioxanes.
- The main species formed by polycondensation are $T_7(OH)_3$ and $T_6(OH)_4$, consisting seven and six silicon atoms.

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.

On going experiments deal with the analysis of alkoxysilanes applied on cement based materials by TOF/MS after extraction by different solvents. The degradation phenomena of synthesized condensation products of alkoxysilanes are being studied by treating them with corrosive agents, such as SO_2, to identify potential metabolites.

Table 1: Assignment of MALDI-TOF/MS peaks ($[M+Na^+]$-species) of products of n-octyltriethoxysilane treated with NaOH; formula: $T_n(OH)_m$,with $T = RSiO_{1.5-m/2n}$

m/z	intensity (rel.) in %	assignment		m/z	intensity (rel.) in %	assignment
875,5	21	$T_5(OH)_3$		1692,0	4	$T_{10}(OH)_2$
893,5	13	$T_5(OH)_5$		1710,0	3	$T_{10}(OH)_4$
1049,6	75	$T_6(OH)_4$		1728,0	8	$T_{10}(OH)_6$
1205,7	100	$T_7(OH)_3$		1746,1	4	$T_{10}(OH)_8$
1223,7	21	$T_7(OH)_5$		1902,2	7	$T_{11}(OH)_7$
1361,8	19	$T_8(OH)_2$		1920,2	4	$T_{11}(OH)_9$
1379,8	22	$T_8(OH)_4$		2058,3	4	$T_{12}(OH)_6$
1397,8	17	$T_8(OH)_6$		2076,3	5	$T_{12}(OH)_8$
1517,9	13	$T_9(OH)_1$		2232,4	4	$T_{13}(OH)_7$
1535,9	17	$T_9(OH)_3$		2250,4	4	$T_{13}(OH)_9$
1553,9	9	$T_9(OH)_5$		2388,5	2	$T_{14}(OH)_6$
1571,9	11	$T_9(OH)_7$		2406,5	2	$T_{14}(OH)_8$
1674,0	6	T_{10}		2424,5	3	$T_{14}(OH)_{10}$

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