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Function of Silane Type on its Reactivity for Surface and In-Depth Applications to Different Substrates

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Abstract

A study of the reactivity of silicon based model compounds was carried out on different substrates. Previous studies with similar compounds showed that the polymerization is mainly influenced by the type of substrate while reaction conditions are not as critical.
The present paper focuses on the influence of the type of bonding group as well as hydrophobic group of silanes on their performance when applied to limestone, sandstone and brick. Due to the complex nature of commercial products and the presence of crosslinking agents, model compounds were selected to allow a quantitative evaluation of the performance of the polymerizing mixture.
The results showed that chemical reactivity with the substrate is mainly obtained in the case of brick and limestone with methoxy functionalized silanes rather than ethoxy ones. Higher alkyl groups decrease the vapour pressure of alkoxy functionalized silanes resulting in an increased mass return which is characterized by a lower reactivity of the bonding groups and an increased amount of silanes intermolecularly polymerized, i.e., polymerization to siloxanes.

Keywords: silicon model compounds, reactivity, limestone, sandstone, brick

1 Introduction

Reactive silicon compounds are widely used to protect porous building materials against water uptake and damage caused by constant exposure to moisture. In situ investigations have shown that a successful water repellent performance is possible even after 35 years [1]. Studies of water repellent products usually focus on the effectiveness of the treatment in relation to the type of substrate, the nature of the polymer, the concentration of the active compounds, etc. [2-7].

A study on the type of interaction of ethoxy functionalized silicon compounds with brick and stone revealed an active participation of the substrate in the polymerization reaction [8,9]. Moreover, it was concluded that the polymerization of volatile compounds is mainly governed by evaporation conditions and appears to be strongly influenced by the characteristics of the substrate [10,11]. Furthermore, applications at lower temperatures did not necessarily result in poorly performing treatments.

Recently, a study was carried out on the chemical reactivity with cement based materials of triethoxy functionalized silanes having different hydrophobic groups [12]. It was concluded that lower alkyl groups favour the polymerization and stimulate intermolecular reaction while higher alkyl groups tend to lower polymerization favouring a reaction with CSH-gel. However, the crosslinked and hence insoluble properties of these polymerized silanes hinder a quantitative evaluation of the polymerization mixture.

This paper describes the results of a further study regarding the influences of both the type of hydrophobic and alkoxy groups of silicon based model compounds on their reactivity with limestone, sandstone or brick. The model compounds were selected so as to enable a quantitative evaluation of the polymerization mixture.

2 Experimental part

2.1 Silicon model compounds

The silicon model compounds and their properties are presented in Table 1. To the model compounds, 2 w% of dibutyltindilaurate (DBTDL) was added as a polymerization catalyst. Polymerization results in the formation of a linear, and hence soluble, polysiloxane.

2.2 Substrates

The properties of the selected substrates are presented in Table 2.

Table 1: Properties of the silicon model compounds

Name of model compound	Molecular weight	Boiling point (a) (°C)/mm (mp)
dimethyldimethoxysilane	120	82
isobutylmethyldimethoxysilane	162	131
n-octylmethyldimethoxsilane	218	-
dimethyldiethoxysilane	148	114
n-octylmethyldiethoxysilane	246	80 /2

(a) Data from [13]

Table 2: Properties of the substrates

Substrate	Type	Real density ($kg.m^{-3}$)	Porosity accessible to water (vol %)
Savonnières	Limestone	1670	38
Grès à Meule	Sandstone	2020	23
Red brick	Brick	1853	21

The Grès à Meule is a feldspatic sandstone with an argillaceous and ferruginous cement.

2.3 Preparation, treatment and conditioning

2.3.1 Surface application

Samples of 1 x 1 x 1 cm^3 were cut from the three materials and dried at 60 °C to constant weight. The application was carried out by capillary absorption of the catalysed model compounds until the upper face had been reached. Although not representative for applications in practice, this procedure was used because the amount of product absorbed (1 to 2 10^3 g.m^{-2}) reduced the weighing errors in the experimental procedure.

After treatment, the samples were conditioned at 20°C and 55 % relative humidity (R.H.). Their weight was monitored at different time intervals. Once the weight had stabilized, the samples were extracted with chloroform (see 2.4). The extract was analyzed by Fourier Transformation Infrared Spectroscopy (FT-IR, Nicolet, KBr-method, solid transmission). Also, the samples, after washing with chloroform, were analyzed by FT-IR after drying at 60°C for 2 hours.

2.3.2 In-depth application

The 1 x 1 x 1 cm^3 samples were dried at 60°C to constant weight. For each type of substrate, 3 samples were treated by capillary absorption of the catalyzed model compounds until the upper face had been reached. Then the 3 treated samples were placed above each other and all the sides of the resulting prismatic form, except the upper face, were covered with aluminium foil to avoid evaporation during conditioning for 1 week at 20°C and 55 % R.H.. This set up simulates in-depth applications of silanes as in the case of creams and gels.

After removal of the aluminium foil, the upper (T, top), middle (M) and lower (B, bottom) samples were weighed followed by an extraction (see 2.4). Then, all samples were washed with chloroform and dried at 60°C for 2 hours. FT-IR analyses was carried out both on the extract and the dried samples.

2.4 Extraction procedure

The composition of the reaction mixture of the model compounds was evaluated in terms of both the polycondensated fraction chemically linked to the substrate and the one resulting from intermolecular polycondensation extracted with chloroform (20 °C).

For the extraction, the samples were put in a glass vessel containing an amount of chloroform equivalent to tenfold the weight of the introduced silicon compounds. The closed vessel was then kept at 20 °C for 30 minutes. After that, the samples were removed and washed two times with 5 ml of chloroform followed by drying at 60 °C for 2 hours. The extracted fraction represents the non reacted and intermolecularly polymerized silane content. The weight increase of the treated samples after extraction is representative of the amount of siloxanes chemically linked to the substrate.

2.5 Analysis of the extracted samples and extract

The reactivity of the bonding groups of the silane fraction extracted as well as that chemically linked to the substrate was determined from the ratio of the integrated peak attributed to the ethoxy groups (960 cm^{-1}) or the methoxy groups (2845 cm^{-1}) to the peak area of the methyl group attached to silicon (1262 cm^{-1}) this being the most characteristic peak for CH_3 deformation mode of methylsilicon compounds in the FT-IR spectrum.

3 Results and discussion

3.1 Reactivity on an inert substrate

It is important to understand the influence of the hydrophobic and reactive groups on some of the basic properties of the compound. One important property of a water repellent product is its volatility. Too high a vapour pressure, i.e. too low a boiling point, leads to excessive evaporation of the water repellent material. However, other properties, such as steric effects, come into play in the balancing act of alkoxysilane reactivity. Steric effects, or steric hindrance, consist in the blocking of the central silicon atom by larger or geometrically more complex alkyl or alkoxy groups. The blocking will reduce the rate of hydrolysis and condensation [14]. Following this logic, methyl and methoxy functionalized silanes hydrolyse more rapidly than higher alkyl and ethoxy functionalized ones. Some sense of the combined influence of volatility and steric hindrance can be gained by exposing several alkoxysilanes to the same reaction conditions. Table 3 indicates the theoretical and experimental mass return, or dry weight, and reactivity of the catalyzed model compounds on an inert substrate reflecting the balance between evaporation and steric hindrance of the tested model compounds.

The theoretical mass return, or dry weight, is calculated assuming complete hydrolysis and condensation with no evaporation of the alkoxysilane. For example, if the dimethyldiethoxysilane polymerizes completely, then the mass return is (74/148)x100 % = 50 %.

The experimental mass return is determined by adding 0.5 g of the model compound, with 2 w % of DBTDL, in an aluminium cup. This is conditioned at 20 °C and 55 % RH to constant weight.

Reactivity is defined as the percentage of the experimental mass return over the theoretical mass return.

Table 3: Theoretical and experimental mass return and reactivity of the catalyzed model compounds.

Name of model compound	Theoretical mass return (%)	Experimental mass return (%)	Reactivity (%)
Dimethyldimethoxysilane	61,7	1,4	2,3
isobutylmethyldimethoxysilane	71,6	2,8	3,9
n-octylmethyldimethoxsilane	78,9	17,1	21,7
Dimethyldiethoxysilane	50,0	1,7	3,4
n-octylmethyldiethoxysilane	70,0	3,7	5,3

In the series of similar alkoxy functionalized model compounds, the volatility decreases with decreasing molecular weight. In the balance between steric hindrance and evaporation, the latter prevails since within each series reactivity increases.

In the series of dimethylsilanes, replacing methoxy by ethoxy results in a slightly increased mass return, indicating that evaporation conditions also prevail. The opposite effect is obtained for higher alkyl groups: replacing methoxy by ethoxy in n-octylmethylsilane results in a remarkably lower mass return, indicating that steric hindrance prevails in the balance between evaporation and steric hindrance.

3.2 Reactivity for surface application

Figure 1 presents the experimental percent mass return of DBTDL catalyzed model compounds applied on limestone. The mass return and reactivity obtained when constant weight is reached are listed in Table 4.

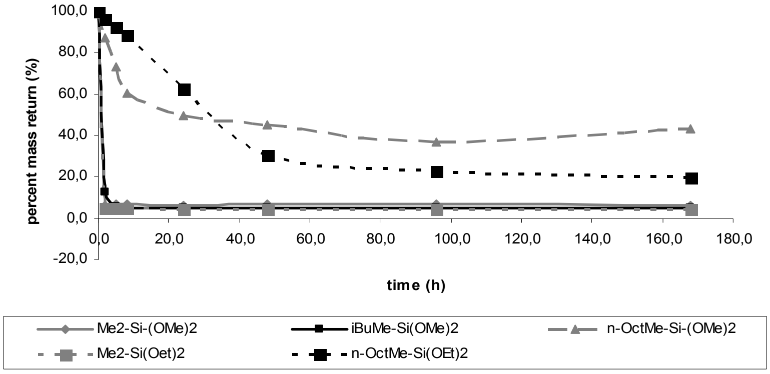

Figure 1: Experimental percent mass return of DBTDL catalyzed model compounds applied on limestone over time.

Table 4: Experimental mass return and reactivity of DBTDL catalyzed silanes applied on limestone.

Model compound	Experimental mass return (%)	Reactivity (%)
Dimethyldimethoxysilane	6,2	10,0
Isobutylmethyldimethoxysilane	4,9	6,8
n-octylmethyldimethoxsilane	37,1	47,0
Dimethyldiethoxysilane	4,2	8,4
n-octylmethyldiethoxysilane	19,6	28,0

From Figure 1 it can be concluded that in case of surface application, polymerization of silanes is completed after at least 96 hours of conditioning. Dimethyldimethoxysilane, dimethyldiethoxysilane and iso-butylmethyldimethoxysilane react as well as evaporate very fast. It takes less than 2, 5 and 8 hours respectively, for these compounds to have over 95 % of their alkoxy groups polymerized.

In the series of similar functionalized silanes, replacing a methyl by an octyl group is reflected by an increased mass return, indicating that evaporation conditions prevail. However, replacing a methyl by an isobutyl, although characterized by a lower vapour pressure, results in a lower mass return which is also the case for replacing methoxy by ethoxy. These results indicate that, compared to applications on an inert substrate, the polymerization is less governed by evaporation effects and hence in the balance between evaporation and steric hindrance, the last takes on greater importance.

Extraction of the treated limestone samples with chloroform resulted in nearly regaining their original weight for the case of dimethyldimethoxysilane, dimethyldiethoxysilane and isobutylmethyldimethoxysilane indicating a low chemical bonding with the substrate. Bonding to the substrate was preferentially obtained for the tested n-octylsilanes. This result is in agreement with previous studies [12] showing that sterically hindered silanes have a slower hydrolysis and therefore a rather low content of hydrolysed silanes in the reaction mixture. Higher reactive silanes are characterized by a high content of silanols. Hence, the probability that two silanols interact to condensate is higher resulting in a preferential intermolecular reaction.

3.3 Reactivity for in-depth application

Samples of the different materials which had been treated with an in-depth application of the catalyzed silane model compounds were subjected to analysis after 1 week conditioning. The results of the performed analyses are presented in Table 5 for the methoxysilanes, and, in Table 6 for the ethoxysilanes. The reaction mixture is described in terms of non reacted silane or monomer content as well as polymerized content, more specifically, the amount intermolecularly polymerized and chemically bonded to the substrate.

In the case of in-depth impregnations, evaporation of the monomer is hindered and influenced by migration properties. In the similar alkoxy functionalized silane series, migration to the surface decreases with increasing molecular size. The highest material loss resulting from surface evaporation, including migration from lower parts towards the surface, is obtained in case of dimethyldiethoxysilane followed by dimethyldimethoxysilane, although the latter has a higher vapour pressure. This shows that steric hindrance controls the polymerization rate. The lowest material loss is obtained for n-octylsilanes characterized by their low migration properties.

After one week of conditioning, the silicon model compounds were almost completely polymerized, except for the n-octylmethylsilanes. For the latter, a much lower reactivity of the ethoxy functionalized compound was observed as compared to the methoxy functionalized one, although both have a similar mass return. The mass return of the bottom sample treated with n-octylmethyldiethoxysilane is at least 81 %. This is mainly non reacted monomer highlighting the importance of steric hindrance on the polymerization reaction.

For limestone and brick, in the series of methoxy functionalized model compounds, the content of siloxanes chemically bonded to the substrate is quite comparable although more pronounced for limestone. The reactive dimethyldimethoxysilane reacts preferentially with the substrate. The increased mass return obtained for higher alkylgroups reflects an increased amount of silanes intermolecularly polymerized. Although more sterically hindered, the ethoxy functionalized silanes show a lesser extent of chemical bonding to the substrate than the methoxy functionalized silanes.

The lowest reactivity was obtained for the feldspatic sandstone. Although silicate minerals as well as quartz and feldspars, with their abundant OH-groups, offer receptive surfaces for alkoxysilanes [13], very low bonding to the substrate was observed for the dimethyldimethoxysilane. N-octylmethyldiethoxysilane hardly reacts when applied on the feldspatic, ferruginous clay bound sandstone. Previous studies showed that ferruginous sandstones can be successfully treated with tetraethoxysilane [15] or with a water repellent [1]. Data about the influence of clay minerals on the reactivity of sandstones is rather contradictory and hence a definitive conclusion about the influence of clay minerals on the reactivity of alkoxysilanes can not be drawn. For the tested sandstone, it seems that the clay minerals decrease the performance of a water repellent treatment with alkoxysilanes.

Figures 2 and 3 illustrate the FT-IR spectrum of brick and sandstone, respectively, treated with isobutylmethyldimethoxysilane after one week conditioning and extraction with chloroform. For brick, typical absorption bands around 2900 cm^{-1} and 1450 – 1480 cm^{-1}, indicative for C-H bonds, as well as 1262 cm^{-1} being the absorption peak typical for methyl groups attached to silicon, can be observed (Figure 2). In case of sandstone however, none of these absorption bands are present in the FT-IR spectrum (Figure 3).

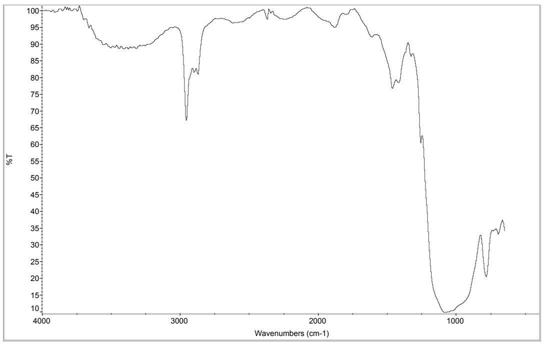

Figure 2: FT-IR spectrum of brick (bottom sample) treated with isobutylmethyldimethoxysilane after one week conditioning and extraction with chloroform

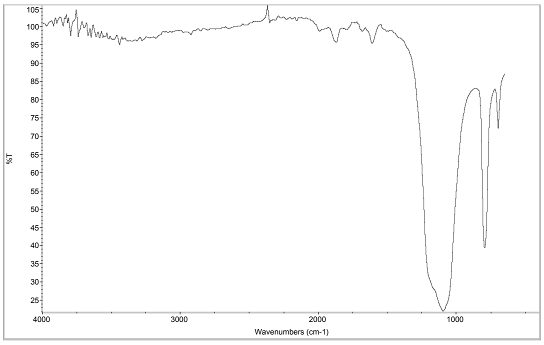

Figure 3: FT-IR spectrum of sandstone (bottom sample) treated with isobutylmethyldimethoxysilane after one week conditioning and extraction with chloroform

4 Conclusions

Understanding the influence of the hydrophobic and bonding groups on the reactivity of volatile silanes is relatively easy for inert substrates such as aluminium. Volatility decreases with molecular weight for similar alkoxy functionalized model compounds. Furthermore, evaporation prevails over steric hindrance of the polymerization as shown by the increased mass return in each series. Replacing methoxy by ethoxy results in a slight increased mass return for dimethylsilane, indicating that evaporation conditions also prevail, while the opposite effect is obtained for n-octylmethylsilane.

For surface applications on limestone, the polymerization is less governed by evaporation effects and hence in the balance between evaporation and steric hindrance, the latter prevails. This tendency is even more pronounced for in-depth applications.

From the quantitative evaluation of the polymerization properties of in-depth applications of ethoxy and methoxy functionalized silanes, it was found that the highest reactivity is generally obtained for limestone followed by brick. From previous studies dealing with ethoxy functionalized oligodimethylsilioxanes [8] and model compounds [11] it was concluded that in general a better performance on brick was obtained than for limestones. Concerning the latter type of stone, no systematic results were obtained indicating that polycondensation is highly influenced by the limestone properties such as pore structure.

The lowest reactivity was obtained for the tested clay containing feldspatic sandstone. It seems that the presence of clay minerals provokes a decreased performance of water repellent treatment with silanes.

In the series of methoxy functionalized model compounds, the content of silanes chemically bonded to the surface was similar for limestone and brick. The increased mass return obtained for higher alkylgroups is reflected in an increased amount of silanes intermolecularly polymerized, i.e., polymerization to siloxanes.

Highest material loss due to evaporation at the surface, including migration from lower parts towards the surface, was obtained for the dimethyldiethoxysilane; while the lowest material loss after one week of conditioning was obtained for the n-octyl containing silanes. For the latter, the diethoxy functionalized compounds show a much lower reactivity reflecting the importance of steric hindrance in the polymerization.

Overall, it can be concluded that the type of model compound that seems to show the best performance in terms of low migration properties and material loss due to evaporation combined with high chemical reactivity with the substrate is the n-octylmethyldimethoxysilane applied to brick and limestone. This is also the case for the tested sandstone, although a remarkable lower reactivity and almost no chemical bonding to the substrate was obtained.

The study has shown that the polymerization properties of silane compounds are highly influenced by the type of hydrophobic and bonding groups, as well as the substrate to which they are applied and even the application methodology.

Table 5: Results from the analysis of the in-depth applied dimethoxy functionalized catalysed model compounds on limestone (L), sandstone (S) and brick (B). (T : Top ; M : middle ; B : bottom) after one week conditioning.

Substrate	Location	Exper. mass return (%)	Extract (%)	Reactivity of functional groups (%) [a]	Polymerized monomer content		Unreacted monomer content in mass return	Evaporated/ migrated monomer content
					Intermolecularly polymerized	chemically linked to substrate		
dimethyldimethoxysilane								
L	T	33	5	>95	8	45	<5	47
	M	23	4	>95	6	31	<5	63
	B	22	3	>95	5	31	<5	64
S	T	3	2	>95	4	<1	<5	≤95
	M	8	4	>95	6	7	<5	≤86
	B	6	3	>95	4	6	<5	≤ 90
B	T	6	3	>95	4	6	<5	≤90
	M	14	2	>95	3	20	<5	≤77
	B	13	1	>95	2	19	<5	≤79
isobutylmethyldimethoxysilane								
L	T	42	16	>95	22	36	<5	≤41
	M	38	17	>95	24	29	<5	≤47
	B	34	14	>95	20	28	<5	≤52
S	T	11	11	>95	15	0	<5	≤ 85
	M	15	15	>95	21	0	<5	≤ 79
	B	10	10	>95	14	0	<5	≤ 86
B	T	12	6	>95	10	9	<5	≤ 81
	M	52	34	78	37	25	<5	≤38
	B	49	36	68	40	18	<5	≤42
n-octylmethyldimethoxysilane								
L	T	69	29	>95	36	45	<5	≤20
	M	81	39	90	44	46	<5	≤10
	B	84	40	76	39	48	<5	≤13
S	T	54	54	>95	68	0	<5	≤32
	M	86	86	67	>95	0	< 5	<5
	B	93	93	33	67	0	33	<1
B	T	67	31	>95	39	40	<5	20-25
	M	91	53	43	47	39	13	<5
	B	89	51	52	≤51	41	<5	<5

(a) : determined from quantitative integration of FT-IR spectra

Table 6: Results from the analysis of the in-depth applied diethoxy functionalized catalysed model compounds on limestone (L), sandstone (S) and brick (B). (T : Top ; M : middle ; B : bottom) after one week conditioning.

Substrate	Location	Exper. mass return (%)	Extract (%)	Reactivity of functional groups (%) (a)	Polymerized monomer content		Unreacted monomer content in mass return	Evaporated/ migrated monomer content
					Intermolecularly polymerized	chemically linked to substrate		
dimethyldiethoxysilane								
L	T	15	15	>95	30	0	<5	≤70
	M	12	12	>95	24	0	<5	≤76
	B	12	12	>95	24	0	<5	≤76
S	T	3	3	>95	5	0	<5	≤95
	M	3	3	>95	7	0	<5	≤93
	B	3	3	>95	7	0	<5	≤93
B	T	3	3	>95	6	0	<5	≤94
	M	6	4	>95	7	6	<5	≤87
	B	6	3	>95	7	6	<5	≤87
n-octylmethyldiethoxysilane								
L	T	86	64	24	35	25	34	3
	M	63	52	37	44	13	14	21
	B	92	64	<5	0	32	64	<5
S	T	74	74	<5	<5	0	≤ 74	≤26
	M	79	79	<5	<5	0	≤ 79	≤21
	B	81	81	<5	<5	0	≤ 81	≤19
B	T	81	56	19	25	29	35	10
	M	96	77	18	32	22	49	<1
	B	96	77	<5	<5	22	72-77	<1

(a): determined from quantitative integration of FT-IR spectra

Although the mass return of a water repellent product obtained on an inert substrate like aluminium [6] is useful as quality control of the product, this information is not directly transferable to active substrates since different reactivities will be obtained. Consequently, defining general consumption criteria for a reliable water repellent treatment with silanes [16] is hardly possible.

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