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Organofunctional alkoxysilanes in dilute aqueous solution: new accounts on the dynamic structural mutability

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Abstract

The condensation of alkyltrialkoxysilanes was studied using time-dependent ^{1}H- and ^{29}Si-NMR spectroscopy. The main goal was to correlate the results of these investigations with standard conditions in technical applications of the most commonly used commercial silane adhesion promoters. Thus, experiments with 3-aminopropyltriethoxysilane (DYNASYLAN® AMEO), 3-glycidyloxypropyltrimethoxysilane (DYNASYLAN® GLYMO) and 3-methacryloxypropyltrimethoxysilane (DYNASYLAN® MEMO) were carried out in aqueous solutions at a selected range of concentrations. This investigation reflects a convenient way to determine the total concentration of reactive silanol groups during the course of the reaction. Moreover, the activity of the solution in adhesion promoting processes can be monitored and measured. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Alkoxysilanes; Hydrolysis; Reaction rates; Condensation; Siloxanes

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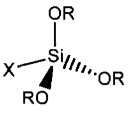
1. Introduction

Organofunctional silanes, such as 3-glycidyloxypropyltrimethoxysilane (DYNASYLAN® GLYMO; **1**), 3-methacryloxypropyltrimethoxysilane (DYNASYLAN® MEMO; **2**) or 3-aminopropyltriethoxysilane (DYNASYLAN® AMEO; **3**) [1–4], are used on an industrial scale as adhesion promoters, for surface modification, as crosslinking agents and for mechanical reinforcement of ceramic surfaces (Table 1; Fig. 1).



R = $-CH_2CH_3$, $-CH_3$
X = funct. org. substituent, -OR

Fig. 1. Structure of the silanes.

The wide range of applications is based on the bifunctionality of organofunctional silanes. These contain a structurally inherent silicon-alkoxy function and a functional organic substituent bonded via a C3-alkyl group. In practice, on the one hand, chemical binding to a generally inorganic material can be established by exchange of the alkoxy groups during use. On the other hand, the organic functionality permits an interaction with organic polymers. In this simple model, a permanent bond between inorganic substrate and organic matrix is produced by means of stable chemical bonds (Fig. 2).

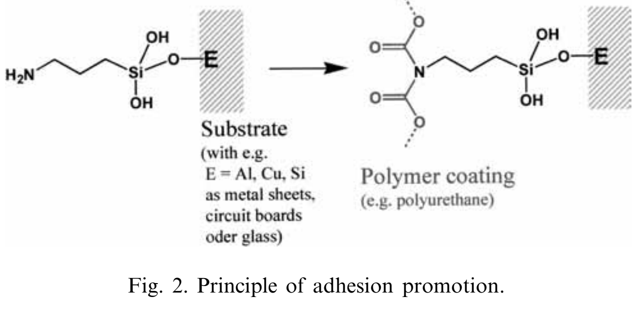


Fig. 2. Principle of adhesion promotion.

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Table 1
Structure, name and designation of the alkyltrialkoxysilane investigated

No.	Name	X	Ref.
1	3-Glycidyloxypropyltrimethoxysilane	$-(CH_2)_3-O-CH_2-CH(O)CH_2$	[4]
2	3-Methacryloxypropyltrimethoxysilane	$-(CH_2)_3-O-C(O)-C(CH_3)=CH_2$	[1]
3	3-Aminopropyltriethoxysilane	$-(CH_2)_3-NH_2$	[2,3]
4	3-(Triethoxysilylpropyl)ammonium acetate	$-(CH_2)_3-NH_3^+$	

Owing to their efficiency as adhesion promoters, functional organosilanes are now an integral part of high-performance composites and ‘intelligent’ coating systems.

2. Reactivity of organofunctional silanes

In practice, organofunctional silanes are usually applied in a concentration of 0.2–2% by weight as additives as such or from aqueous or water–alcohol solutions as a primer. As a result of the reaction with water or moisture, the methoxy groups of **1** and **2** are eliminated as methanol or the ethoxy groups of **3** as ethanol and are replaced by hydroxyl units (silanols) [4–7]. Below, the term ‘silanols’ is used as a simplified description of the monomeric compounds bearing at least one Si–OH function, i.e. monosilanol, silanediol and silanetriol in the case of trialkoxysilanes.

These Si–OH functions prove to be very reactive in establishing the bond between material and organofunctional silanes. In addition to a fast hydrolysis of the ethoxy- or methoxy-silicon bond, the availability of the reactive hydroxyl units on the central silicon atom significantly influences the reactivity of the organofunctional silane. In this context, it has long been postulated that exclusively silanetriols, i.e. the completely hydrolysed, monomeric silanes, are responsible for the activity of the adhesion promoter and these monomeric units are stable for a few hours to a few days in aqueous solutions [5–7]. Subsequently, the activity of the aqueous mixtures of silane hydrolysis products decreases as a result of crosslinking to give insoluble, polymeric siloxanes (gel structures), which is evident from a substantial decrease in the adhesion-promoting effect in the composite. Knowledge of the silanol concentration and of the degree of oligomerization is therefore of decisive importance for the practical use of the silane formulation. Detailed investigations into the type and concentration of the structures present in the mixture and their changes as a function of time are not available to date.

3. ^{1}H- and ^{29}Si-NMR spectroscopy of the hydrolysates products

The hydrolysis of organofunctional alkyltrialkoxysilane was studied by means of ^{1}H-NMR spectroscopy [4,8,9]. Monitoring of the alkoxy groups bonded to the central silicon atom permits an unambiguous differentiation of the different hydrolysis intermediates -monosilanol and silanediol- and, owing to the fast measuring procedures, observation of even rapid hydrolysis reactions. However, nothing can be said about the completely hydrolysed silanetriols and possible secondary oligomerization products since the decisive information is not present in the ^{1}H-NMR spectra.

In the ^{29}Si-NMR spectra, all monomeric units are detectable in the initial stage of a hydrolysis reaction (see Fig. 3).

However, silanols are metastable units which undergo condensation to thermodynamically more stable siloxane units by elimination of water.

The formation of the silanols and of the oligomeric structures formed by condensation is influenced both by the functional group in the organic substituent and by the general conditions of the hydrolysis reaction (pH, temperature, concentration or catalyst) [4]. The present studies show that the partially hydrolysed silanols undergo condensation and hence oligomerization products are formed as early as in the hydrolysis step, as shown schematically in Fig. 4. Individual oligomer structures can be identified without problems in dilute aqueous solutions resembling those in practice, by means of ^{29}Si-NMR spectroscopy (Fig. 5). In the experiments, the addition of chromium(III) acetylacetonate proved useful, accelerating the relaxation of the excited silicon nuclei. Consequently, it

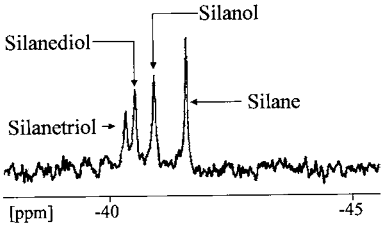

Fig. 3. ^{29}Si-NMR spectrum at beginning of hydrolysis of **1**.

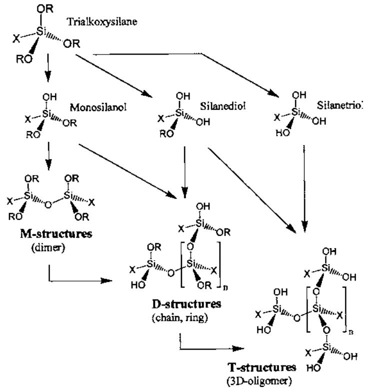

Fig. 4. Course of hydrolysis and condensation.

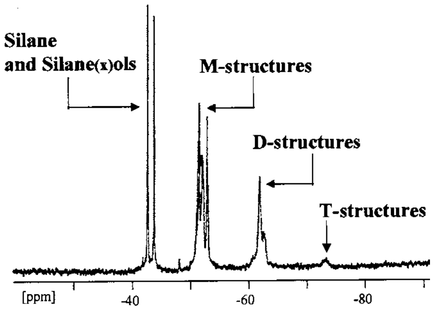

Fig. 5. Oligomers of **3** (analytically monitored in the ^{29}Si-NMR spectrum).

was possible on the one hand to obtain spectra with optimum sensitivity for reliable, quantitative ^{29}Si-NMR evaluation and, on the other hand, to achieve the short measuring times required for detecting the reaction kinetics. Due to the considerably longer measuring times compared with ^{1}H-NMR experiments, a determination of the initial intermediate hydrolysis steps is possible only to a limited extent. The hydrolysis products were monitored spectroscopically over a period of up to 3 months.

With the aid of ^{29}Si-NMR spectroscopy, it is possible to obtain information about the structure and amount of oligomers found [10–15]. For the characterization of the oligomer structures, the term M-structures is used for monocrosslinked units, D-structures for dicrosslinked units and T-structures for tricrosslinked units in general (see Figs. 4 and 5). For the case of a tetraalkoxysilane (e.g. tetramethoxysilane), additional signals for the siloxane units in which all four silanol units are oligomerized additionally occur (Q-structure) [11,16].

The chemical shift which initially characterize the fundamental environment of the silicon atom, i.e. the amount of siloxane bridges, is determined by a large number of different resonance lines. These signal lines indicate structural units of different environments. In the region of the uncrosslinked silane, a maximum of four resonance signals occur, these signals corresponding to the unhydrolysed silane and to the monosilanol, silanediol and silanetriol fraction (Fig. 3). Depending on the degree of hydrolysis at the individual silicon atoms, a large number of different environments, which are detectable as broad signal peaks in the ^{29}Si-NMR spectrum, result in the region of the M-, D- and in particular T-structures.

4. Results and discussion

The literature [15,17] reports on reactions of organofunctional alkyltrialkoxysilanes with equimolar amounts of water. On the basis of the work on the hydrolysis of organofunctional trialkoxysilanes [4], the present work focuses on a very close relationship with industrial use in which the organofunctional trialkoxysilanes are generally reacted at low concentrations (0.2–2%) with water. The inorganic surface to be modified is then brought into contact with the dilute silane solution, and a chemical bond can rapidly form between silane and workpiece. In general, the solvent water and the alcohol fractions liberated during the hydrolysis reaction are then removed. The result is an increase in the concentration of the dissolved silicon compound and the condensation of present silanol groups. In this way, a covalently bonded, crosslinked polysiloxane layer forms on the material surface. A decisive factor in practice is that this process takes place as completely as possible, since only very extensive coverage of the material surface guarantees optimum properties (adhesion promotion, surface modification). For this reason, fairly dilute aqueous systems were used in the present work (silane concentrations 4–10%), in order to be able to investigate the oligomerization during the hydrolysis reaction in a manner closely resembling that in practice. The experiments at higher concentrations (50% of silane) serve as

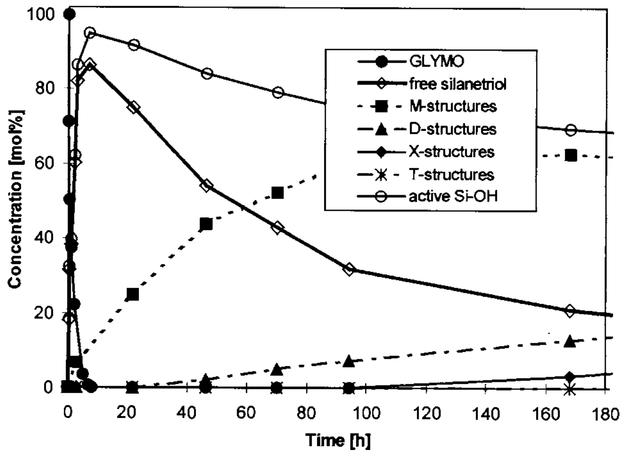

Fig. 6. Course of hydrolysis/oligomerization of **1** in a 10% aqueous solution (pH 6).

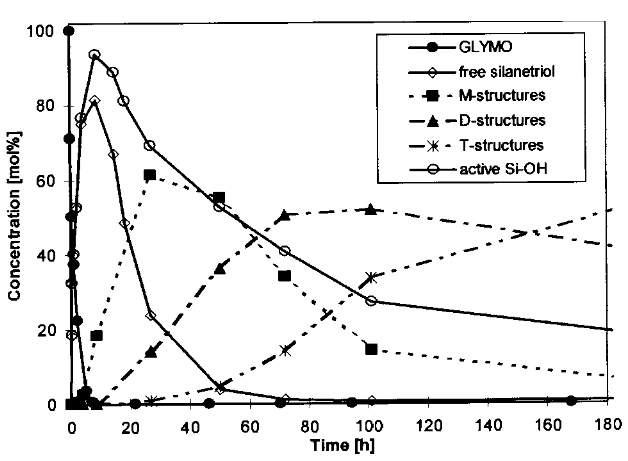

Fig. 7. Course of hydrolysis/oligomerization of **1** in a 50% aqueous solution (pH 6).

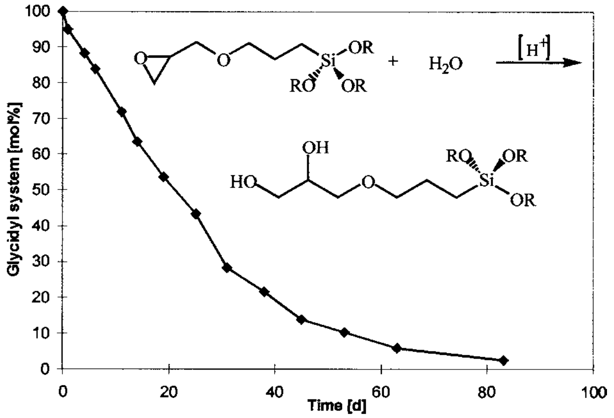

Fig. 8. Ring opening of **1** in a 10% aqueous solution (pH 6).

a model for describing reactions in the concentration phase during drying on the material surface.

4.1. 3-Glycidyloxypropyltrimethoxysilane (*1*)

In demineralized water (pH 6), hydrolysis to the corresponding silanols and consecutive oligomerization take place, as expected, relatively slowly, since the rate of the reaction is decisively influenced by the H^+ concentration [4].

At the same time, the opening of the terminal oxirane to give the diol (Fig. 8) can be observed, although much more slowly [18,19].

Surprisingly, a so far unknown reaction product of diol and 3-glycidyloxypropylsilanols or OH-functional oligomers is detected after only 1 h ('X component'), the concentration of which increases to > 25% during the period of observation (1600 h) [20,21] (Fig. 9).

The proportion of free, monomeric silanetriol decreases in the course of the hydrolysis from initially about 75% (15 h) to < 10% (1600 h).

From the available data the absolute concentration of remaining reactive Si–OH functions can be determined as a function of the reaction time. This concentration being decisive with regard to the reactivity with a substrate, in particular in the case of pretreatment with dilute aqueous silane solutions (primer applications). It is to be expected that even proportionately oligomerized trialkoxysilanes having free Si–OH functions are capable of binding to inorganic surfaces. In principle, a more uniform coating can be expected when a material surface is coated with, for example, short-chain, doubly bridged oligomers (D-structures). A homogeneous coverage of the material surfaces has many advantages even for industrial manufacture, since shorter coating times can be achieved.

The following equation is used for determining the proportion of *active Si–OH functions*:

Active Si–OH functions (mol%)

$$= \frac{3 \cdot \mathrm{mol\%}_{\mathrm{Silanetriol}} + 2 \cdot \mathrm{mol\%}_{\mathrm{M}} + \mathrm{mol\%}_{\mathrm{D}}}{3}$$

In a 10% solution, starting from 85% (15 h), it is still > 70% after a standing time of 160 h (corresponding to about 2.1 hydroxyl units per silicon atom). In a 50% solution, a maximum hydroxyl group concentration is reached after only 8.5 h (> 93%) and decreases to < 15% (corresponding to about 0.4 hydroxyl unit per silicon atom) after a standing time of 550 h (Figs. 6–8).

4.2. 3-Methacryloxypropyltrimethoxysilane (*2*)

The time-dependent concentration curve of the resulting structures of monomers and oligomers (M-/D-/

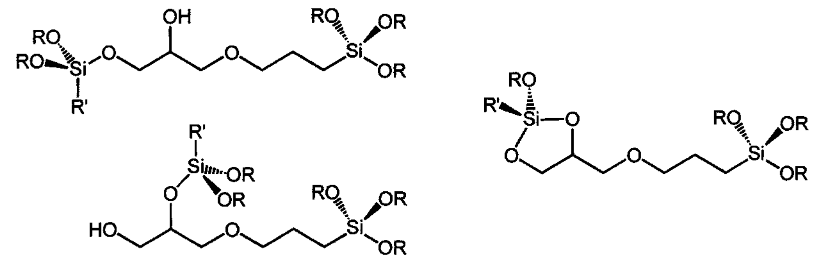

Fig. 9. Possible structural elements of the 'X component'.

T-structures; Fig. 5) during hydrolysis and condensation of **2** is essentially comparable with **1** at pH 6. In an earlier paper [4], it was possible to show that the rate of the reaction (kinetics: pseudo-first order) is influenced foremostly by the pH. By way of example, the course of the hydrolysis to the monomeric silanols is shown in Fig. 10, as the result of the ^{1}H-NMR analysis.

The corresponding free silanetriol cannot be detected but is clearly quantifiable by combination of ^{1}H-NMR and ^{29}Si-NMR data. The results of measurements on 10% solutions at pH 6 and pH 4 are compared in Figs. 11 and 12.

The experiments had to be terminated after 74 h (pH 4) and 188 h (pH 6) since the aqueous solution became cloudy and therefore complete detection of all secondary hydrolysis and condensation products could no longer be guaranteed (Figs. 11 and 12).

Nevertheless, the experimental data for **2** show a picture analogous to **1**, with high initial concentrations of silanetriol (after 1.5 h: 88% at pH 4 and after 2.5 h: 95% at pH 6), which decreased to below 15% (pH 4) and below 35% (pH 6). In contrast, an Si–OH concentration of more than 60% is maintained in both cases (i.e. on average about two hydroxyl functions per silicon atom), finally ensuring the reactivity of the formulations. In comparison, the hydrolysis of **2** takes place much more rapidly in acidic solution but the yield of active Si–OH functions is higher at neutral pH and the tendency to oligomerization is suppressed. This means that acid catalyses both the hydrolysis and the condensation of the silanols formed.

The supplementary hydrolysis experiments on 50% aqueous solutions (pH 6) of **2** underline the relationships presented (Fig. 13).

The loss of silanetriol and the higher proportion of T-structures impressively illustrate the crosslinking effects which occur on the material surface, for example in the drying step after application of the aqueous primer solution, owing to concentration of the organosilicon compounds present. The remaining Si–OH concentration of about 45% after the solution has been left to stand for 223 h (corresponding on average to 1.35 hydroxyl radicals per silicon atom) guarantees in part the activity of the primer formulation.

*4.3. 3-Aminopropyltriethoxysilane (**3**) and 3-(triethoxysilylpropyl)ammonium acetate (**4**)*

In contrast to most other organofunctional silanes, the hydrolysis and condensation of silanes having primary amino functions in aqueous solutions are autocatalysed. This is evident from the pronounced polarization of the molecule (electrostatic interaction of $NH_2 \leftrightarrow SiOR$) and from the strong interaction of the NH_2 group with the polar solvent itself. An aqueous solution of **3** exhibits a pH of 11 so that the hydrolysis, which is complete in a few minutes, is comparable with that in a strongly acidic medium. Another special feature is that the amino function causes both the unhydrolysed silane and its hydrolysis and condensation products to have excellent water solubility. The aqueous solutions of **3** are therefore stable for months.

The results of the ^{29}Si-NMR investigations on the aqueous solutions of **3** with different initial concentrations are illustrated in Figs. 14–17.

In all experiments, a rapid build-up of oligomers (D- and T-structures) is detectable. The percentage of the doubly and triply bridged units, and hence the rate of the condensation, increases with increasing initial concentration as expected. Overall, depending on the initial concentration of **3**, a virtually steady state is reached after a reaction time of about 15 h (50%), about 50 h (10%) and about 100 h (4%). In the further course of the reaction, no significant changes are observed in the reaction solutions. The mixtures then remain stable

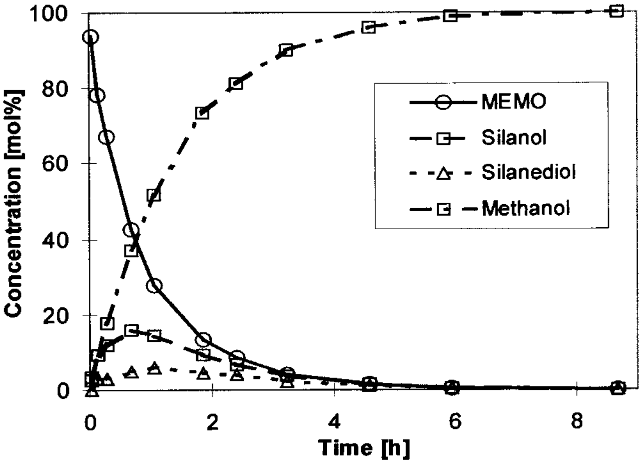

Fig. 10. Course of hydrolysis of **2** in a 2% aqueous solution (^{1}H-NMR; pH 6).

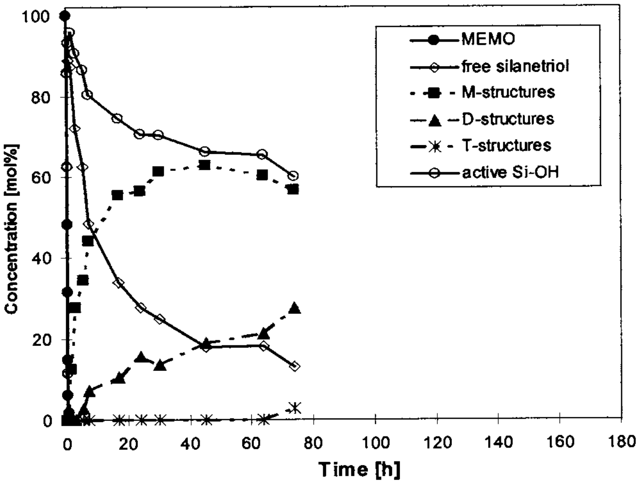

Fig. 11. Course of hydrolysis/oligomerization of **2** in a 10% aqueous solution (pH 4).

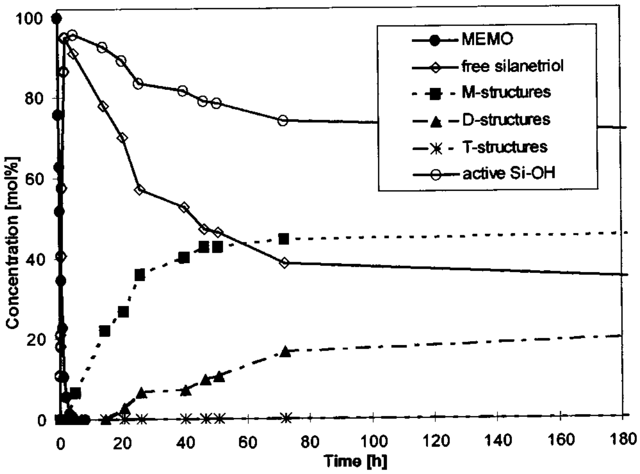

Fig. 12. Course of hydrolysis/oligomerization of **2** in a 10% aqueous solution (pH 6).

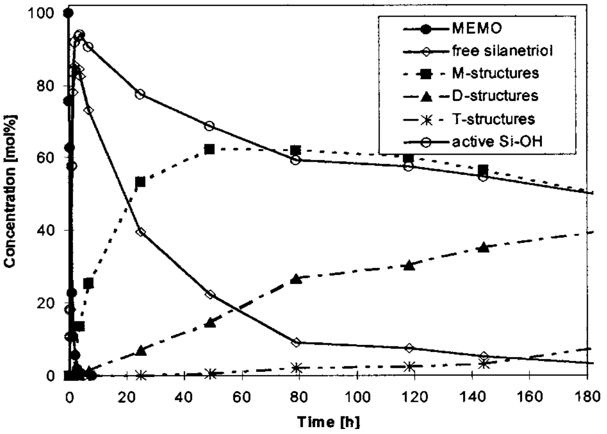

Fig. 13. Course of hydrolysis/oligomerization of **2** in a 50% aqueous solution (pH 6).

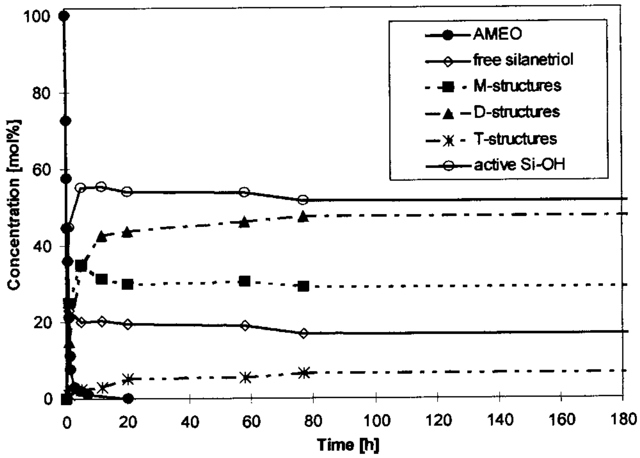

Fig. 14. Course of hydrolysis/oligomerization of **3** in a 4% aqueous solution (pH 11).

over several weeks to months, as it was possible to show by long-term experiments.

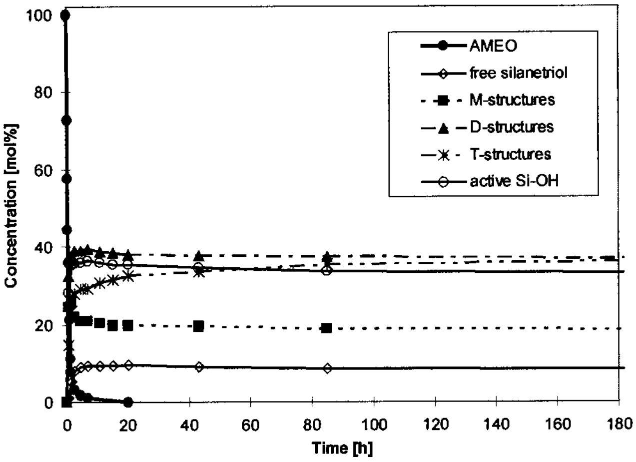

Fig. 15. Course of hydrolysis/oligomerization of **3** in a 10% aqueous solution (pH 11).

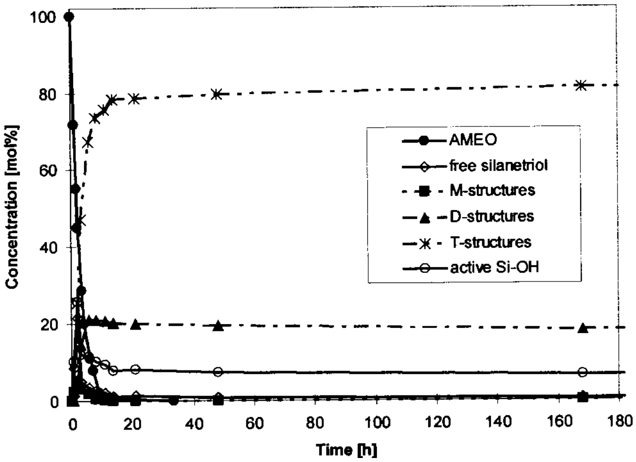

Fig. 16. Course of hydrolysis/oligomerization of **3** in a 50% aqueous solution (pH 11).

The absolute concentration of remaining reactive Si–OH functions is 48% in the case of a 4% solution after complete hydrolysis, increases to a maximum value of > 55% after 7 h and is still > 47% (about 1.4 hydroxyl units per silicon atom) after a standing time of 172 days. In contrast, following a brief rise to about 23%, the percentage of silanetriol in the 4% solution of **3** decreases to 19% after 3 days and only 12% after 172 days (Fig. 18).

In 10% and 50% solution of **3** this threshold cannot be reached even in the initial part. The maximum hydroxyl group concentration is about 37% (corresponding to about 1.1 hydroxyl units per silicon atom) for the 10% solution and < 26%, i.e. 0.8 hydroxyl unit per silicon atom, in the case of the 50% solution.

For the experiments with **4**, in comparison with **3**, an approximately 25% decrease in the crosslinked structures can be detected at both concentrations (10% and 50%) for the hydrolysis at neutral pH in the first 3–5 days. In the case of hydrolysis in water containing

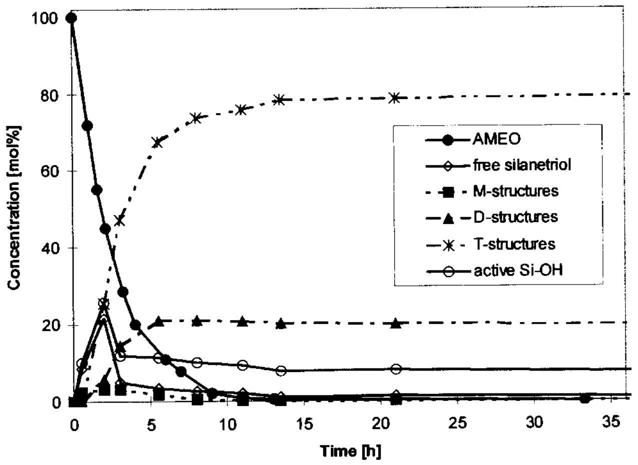

Fig. 17. Course of hydrolysis/oligomerization of **3** in a 50% aqueous solution (pH 11) in initial part.

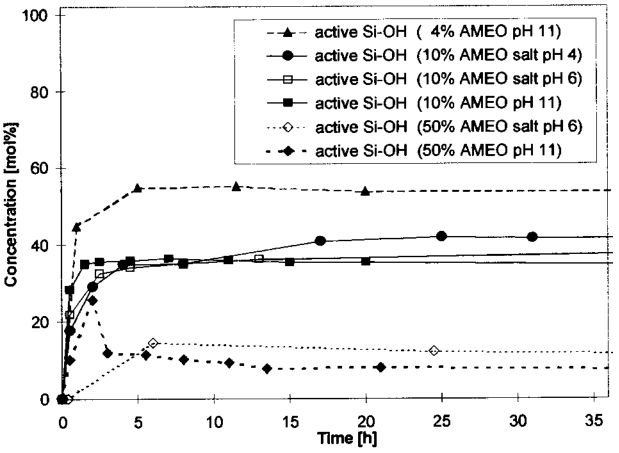

Fig. 18. Comparison of the active Si–OH functions of **3** and **4**.

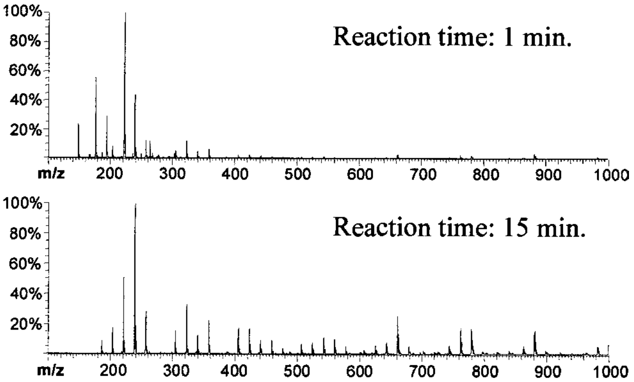

Fig. 19. Time-dependent mass spectra of an 1% aqueous solution of **3** (reaction time 1 and 15 min).

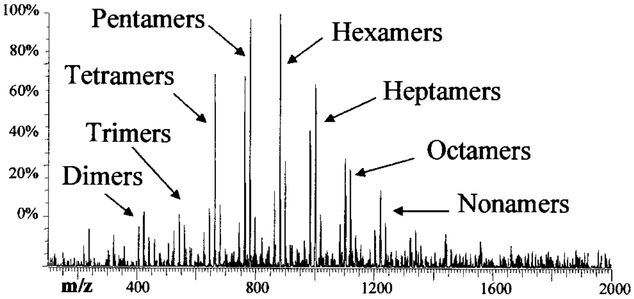

Fig. 20. Time-dependent mass spectra of an 10% aqueous solution of **3** (reaction time 21 min).

acetic acid, the reduction is even >30%. Associated with this is an increase in active Si–OH functions. However, this increase corresponds only to a fraction of the percentage to be observed in the crosslinked structures, since the crosslinking starts somewhat retarded. Accordingly, up to about 60 h in neutral and acidic media, the content of M- and D-structures is higher and the content of active Si–OH is only about 5% (pH 6) or 10% (pH 4) higher than in the investigations at pH 11.

The NMR results are backed up by LC-MS studies on aqueous solutions of **3**. The aim of the comparative measurements was to detect the low molecular weight silanols in the initial stage of the hydrolysis reaction and of the molecular weight build-up as a consequence of condensation reaction taking place in the solution (Figs. 19 and 20).

A modified LC-MS technique with direct injection was used in order on the one hand to rule out reaction of the reactive Si–OH functions with the column material of the LC separation and, on the other hand, to suppress fragmentation in the mass spectrometer by the use of a mild ionization procedure (APCI). The mass spectra can therefore be used only for the qualitative detection of silicon species and do not reflect the percentage distribution of the individual components. While the molecular peaks of silane (M + H: m/e 222), monosilanol (M + H: m/e 194), silanediol (M + H: m/e 166) and silanetriol (M + H: m/e 138) can be detected in the spectra of 1% solutions of **3** after a hydrolysis period of about 1 min, a substantial build-up of oligomers is observable even after only 15 min. The mass spectrum of a 10% solution of **3** recorded after hydrolysis for 21 min shows structural units which prominently indicate siloxanes with two to nine SiO units.

On the basis of the present investigations, and contrary to all postulates [5–7], initially no reduction in the reactivity of the aqueous silane solutions is associated with the oligomer build-up in aqueous solutions of organofunctional silanes. In contrast, through the proportionate crosslinking, material surfaces to be modified are offered with relatively large agglomerates which permit homogeneous, complete coverage.

In comparison with the hydrolysis of **3**, the two non-amine trialkoxysilanes **1** and **2** have a significantly lower tendency to crosslinking. Particularly in the first 1–3 days, substantially higher contents of silanetriol and active Si–OH functions are associated with the

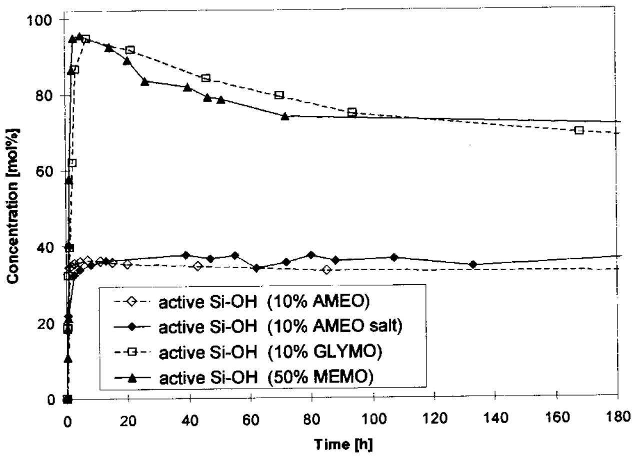

Fig. 21. Active Si–OH functions of **1**–**4** in comparison (10% aqueous solutions).

reduced crosslinking of the hydrolysis products of **1** and **2** (Fig. 21).

The non-amine aqueous solutions of hydrolysis products of **1** and **2** have limited usability in terms of adhesion promotion not because of insufficient Si–OH concentration but as the result of the precipitation of the active ingredient from the aqueous solution after standing for a few days. The cause of the poor solubility of the oligomers of **1** and **2** is the loss of hydrophilic functions which occurs with increasing condensation. A minimum concentration of 50% of active Si–OH functions, i.e. on average 1.5 hydroxyl groups per silicon atom, proves to be a limit which can be used as a neutral evaluation criterion for the activity of a silane solution. Consequently, a period of 5–40 h can be recommended for optimum processing of **1** and **2** at pH 3–4 and of **3** at pH 4–11. The present investigations were carried out on trialkoxysilanes with very different functional groups and are therefore sufficient to reflect a broad cross section of possible functionalities. Further work on the evaluation of the reaction behavior of functional alkoxysilanes will be presented shortly.

5. Experimental

All experimental work was carried out in glass apparatuses and NMR tubes pretreated with hexamethyldisiloxane, in order to suppress a reaction with the glass surface. pH: Metrohm E 597/1; NMR: ^{1}H: Bruker AC 250 (250 MHz) and DPX 360 (360 MHz), internal standard TMS or TMS salt (hydrolysis experiments); ^{29}Si: Bruker AC 250 (49 MHz) and DPX 360 (71 MHz), relaxation accelerator chromium(III) acetylacetonate, internal standard TMS. ^{29}Si-NMR spectra were ^{1}H-broadband-decoupled; ^{1}H-NMR spectra of alkyltriethoxysilanes were recorded in selectively decoupled form [22]. A positive sign means a shift to low field and a negative sign means a shift to high field relative to the standard. To ensure an acceptable relaxation time, a relaxation accelerator in an organic solvent had to be added to the reaction mixture before the measurement.

5.1. Starting compounds

The organofunctional trialkoxysilanes (DYNASYLAN® GLYMO, DYNASYLAN® MEMO, DYNASYLAN® MTES, DYNASYLAN® AMEO) used in the hydrolysis experiments originate from the production of Degussa-Hüls AG, Rheinfelden Works. The purity was > 98% in each case.

5.2. Characterization of the secondary hydrolysis products

Two, 10 or 50% of the trialkoxysilane to be investigated were stirred with demineralized water in a glass beaker at 500 rev min^{-1}. At fixed time intervals, the stirrer was switched off and a 2 ml sample was taken from the reaction mixture. The ^{29}Si-NMR spectroscopic analysis was carried out after addition of 1 ml of acetone-d_6 with 3% of chromium(III) acetylacetonate as an internal lock substance and relaxation accelerator. At the same time, the homogeneity of the solution was checked by means of a turbidity measurement.

5.3. Synthesis of 3-(triethoxysilylpropyl)ammonium acetate

A total of 1000 g (4.52 mol) of 3-aminopropyltriethoxysilane was placed in a 2 l three-necked stirrer apparatus with a dropping funnel, KPG stirrer, reflux condenser and thermometer, ice water and nitrogen blanketing. The reactor was cooled in an ice-water bath. A total of 271.7 g (4.52 mol) of glacial acetic acid was added dropwise while stirring, at a rate such that a bottom temperature of about 50°C was not exceeded. After the end of the addition, stirring was continued for about a further 30 min at room temperature.

*5.4. Spectroscopic data of 3-(triethoxysilylpropyl)-ammoniumacetate (**4**)*

pH 7.2; ^{29}Si-NMR ($C_2D_2Cl_4$): $\delta = -46.8$; ^{13}C-NMR ($C_2D_2Cl_4$): $\delta = 178.7$ (1C, $CH_3\mathbf{C}OO^-$), 59.0 (3C, $Si(O\mathbf{C}H_2CH_3)_3$), 42.5 (1C, $^+NH_3\mathbf{C}H_2CH_2CH_2Si$), 25.1 (1C, $\mathbf{C}H_3COO^-$), 22.3 (1C, $^+NH_3CH_2\mathbf{C}H_2CH_2Si$), 19.1 (3C, $Si(OCH_2\mathbf{C}H_3)_3$), 8.6 (1C, $^+NH_3CH_2CH_2\mathbf{C}H_2Si$); ^{1}H-NMR ($C_2D_2Cl_4$): $\delta = 6.34$ (m, 3H, $^+\mathbf{NH_3}CH_2CH_2CH_2Si$), 3.74 (q, 6H, $J = 7.04$ Hz, $Si(O\mathbf{CH_2}CH_3)_3$), 2.75 (tq, 2H, $J = 8.3$ and 7.3 Hz, $^+NH_3\mathbf{CH_2}CH_2CH_2Si$), 1.84 (s, 3H, $\mathbf{CH_3}COO^-$), 1.67 (quin, 2H, $J = 8.3$ Hz, $^+NH_3CH_2\mathbf{CH_2}CH_2Si$), 1,15 (t, 9H, $J = 7.04$ Hz, $Si(OCH_2\mathbf{CH_3})_3$), 0.57 (t, 2H, $J = 8.3$

Hz, $^{+}NH_3CH_2CH_2C\mathbf{H}_2Si$); $C_{11}H_{27}O_5NSi$ (239.33): Ber.: C, 46.93; H, 9.69; N, 4.98; Gef.: C, 45.89; H, 9.55; N, 5.05%

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