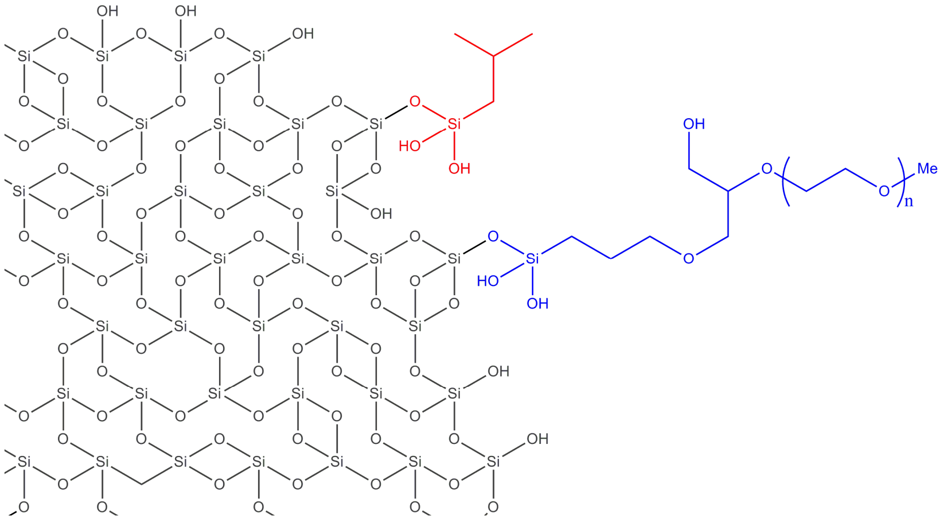

Amphiphilic surface modification of colloidal silica sols

Master of Science Thesis in the Master Degree Programme Chemistry and Bioscience

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Abstract

This study concerns a new route to surface modify silica sols. A simple method to produce a huge variety of silane compounds is investigated and also the grafting of these silanes to the surface of silica particles. The possible application as emulsifier for alkenyl succinic anhydride (ASA), for these silica sols is also studied.

The synthesis of the silanes was performed by a reaction between glycidoxy propyl trimethoxy silane (3GTO) and an ethoxylate, alcohol or amine with properties desirable to introduce to the silica surface. In this study the desired properties were obtained by using mono methyl poly ethylene glycol (MPEG). This silane, obtained from the reaction between 3GTO and MPEG, adds surface activity and steric stabilization to silica sols upon condensation to the silica surface. The yield of this condensation of silane to the silica surface was investigated at both alkaline and acidic conditions for isobutyl silane and the reaction product of MPEG and 3GTO.

A synthetic route exhibiting almost complete conversion between the 3GTO and the ethoxylate, alcohol or amine was found. Mild reaction conditions for the condensation of silanes to silica sols still avoiding gelling were also found.

The silica sols modified by MPEG containing silanes were able to decrease the surface tension of the resulting silica sol and displayed good stability towards electrolytes. These modified silica sols were also able to emulsify ASA in a manner suitable for sizing of paper.

Due to the mild reaction conditions and the simple synthetic route for production of silanes, it is possible to produce silanes with a vast variety of properties. These different functional silanes can further be condensed to the surface of silica sols, thus varying the surface modification of the sols to fit a huge range of different applications.

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Introduction

Colloidal silica sols have been commercially available since the 1940s when stable silica sols of SiO_2 contents higher than 10 wt% could be industrially produced. Since then, the shape, size and stability of the silica sols have been optimized so that a large variety of stable silica sols of different particle sizes are now available. The fields where silica sols are presently used include a vast field of industrial applications. Some of the applications of silica sols are as additives in concrete, flocculation agents, components in paint, as a retention aid in paper industry and as starting material for production of chromatographic materials.

Colloidal silica particles functionalized with both hydrophilic and lipophilic moieties have a great potential for a variety of applications since their surface activity and surface chemistry can be varied a lot. The same method for the synthesis of silanes, able to derivatize the silica surface, can be used both for introducing hydrophilic and lipophilic groups to the surface of the silica sol.

In this study the hydrophilic starting materials have been mono methyl poly ethylene glycol and the lipophilic starting materials have been fatty alcohols and amines. In addition the hydrophobic isobutyl trimethoxy silane has also been used.

The aim of this study is to develop a synthetic pathway to modify the surface of silica sols. This pathway should comprise covalent bonding of a wide variety of different functional groups to the surface of the silica particles. Further the derivatization of the silica surface introduces organic groups which induce both surface activity and steric stabilization to the colloidal silica particles. The increased surface activity of the silica particles enables them to act as emulsifiers. The introduction of steric stabilization to the silica sol, in addition to the already existing electrostatic stabilization, can increase its stability towards electrolytes. An increase in stability towards electrolytes expands the fields were silica sols can be used to areas with higher salt concentrations.

One of the potential applications for surface active silica sols is related to sizing in pulp and paper industry, especially concerning alkenyl succinic anhydride (ASA), which is a common sizing agent. ASA does hydrolyze rapidly when exposed to water, a process in which ASA loses its sizing abilities. To contribute to the sizing of paper ASA must be transferred to the cellulose in the aqueous phase. Since ASA is insoluble in water this is performed by emulsifying ASA. [1] However conventional ASA emulsifiers have one large disadvantage in the fact that they are ineffective emulsifiers at higher salt concentrations. Colloidal silica equipped with steric stabilization is a candidate to increase the salt stability of ASA emulsions.

Theory

First the characteristics of silica sols are described and then how silica sol can be surface modified. The surface modifications in this study are then described and how these may affect the silica sols, finally an example of a potential application for surface active silica sols as emulsifiers.

Colloidal silica sols

A silica sol is an aqueous suspension of colloidal silica particles. The particles are amorphous and have the general molecular formula SiO_2, but the surface of the particles consists of silanol groups which are hydroxyl groups attached to a silicon atom. The fully hydroxylated silica surface contains approximately 8 μmol silanol groups/m^2. [2] The diameter of the silica particles typically range from 5 to 100 nm in commercial silica sols.

Most industrially silica sols are produced from a dilute water glass, aqueous sodium silicate, which is ion exchanged to a pH of 8 – 9. Then the silicate solution is heated to produce small silica nuclei, followed by simultaneous addition of sodium silicate and sulphuric acid to keep the pH at about 9. This method is able to produce silica sols of a few wt% SiO_2 concentrations, why it is followed by evaporation of water or ultrafiltration to produce silica sols of higher concentrations. [3] The silica particles can also be produced by polymerization of orthosilicic acid, for example by addition of tetra alkyl orthosilicic acid to a mixture of water and an alcohol, the reaction can be catalyzed by either an acid [4] or a base [5], this reaction is illustrated in figure 1.

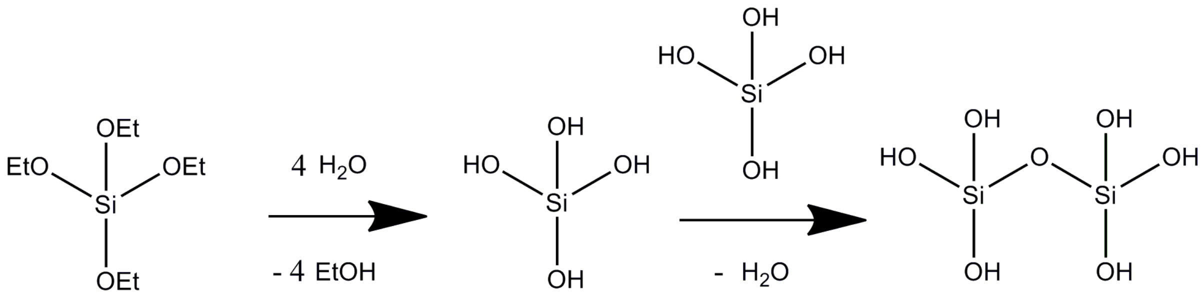


Figure 1. Hydrolysis of tetra ethyl orthosilicate, TEOS, to orthosilicic acid followed by polymerization to a silica particle via a condensation reaction. [4]

Colloidal stability of silica sols

At pH above 2.0 the silica surface will be negatively charged [6] due to deprotonation of the silanol groups with cations acting as counterions. Due to the increased surface charge of the silica particles at increased pH the silica sol has a high stability towards gelling at high pH due to repellation between the particles. [7] The silica sol also has a fairly high stability towards gelling at low pH due to the large possibilities to form hydrogen bonds between the silanol groups and the water, which is possible since very few or no protons are exchanged for cations. [8] The formation of hydrogen bonds between the water and the silica surface reduce the flocculation rate since a layer of water is physically adsorbed to the silica surface This layer of water has a higher viscosity than the rest of the water due to the viscoelectric effect which reduces the colliding velocity of the particles, which in turn reduces the flocculation. The net flocculation rate is also decreased when the size of the particles is reduced due to deflocculation. This is due to the shallow depth of the primary minimum of flocculation potential which enables smaller particles to deflocculate easier than larger particles. [9] Further, the stability of silica sols is decreased by an increase in salt concentration, stability is further decreased when charge is increased and size is decreased of the cations of the salt. [10]

The DLVO theory (Derjaguin, Landau, Verwey and Overbeek) [11] [12] suggests an increased stability of colloidal suspensions as the surface charge of the particles is increased and the salt concentration is decreased. This theory is, as described, not applicable to silica particles as they are stable at low pH, where the surface charge is close to zero, in addition to the high stability at high pH, where the surface is highly charged. Instead silica sols suffer from a stability minimum at intermediate pH. This disagreement with the DLVO theory is more pronounced as the particle size is in the nanometer scale, while silica particles with a size of hundred nanometers has a behaviour more closely resembling the DLVO theory.[7]

Modification of silica sols

The surface of the silica sol can be modified by substitution of the silanol groups for different organofunctional groups. This can be achieved by direct substitution of the silanol groups for organic groups, these organic groups are however quickly hydrolyzed in both acidic and alkaline water solutions [13], limiting their use to completely water free applications. Surface modification can also be achieved via condensation of organofunctional alkoxysilanes to the surface of the silica sol [14], which is much more stable towards hydrolysis due to the organic group being attached by a carbon-silicon bond.

To condense an alkoxysilane to the silica surface the alkoxy groups of the silane first must be hydrolyzed to produce silanol groups. This is a fast reaction and the reaction rate is significantly increased when the temperature [15] or the pH [16] is increased. The second step is the condensation of a silanol group of the silane to a silanol group of the silica surface. This reaction can be seen in figure 2. The condensation reaction is, within the pH range 1 – 10, significantly faster at high pH than low pH [17] and occurs before the silanes are completely hydrolyzed. [15] As a side reaction condensation also occurs between silane molecules which produce silane polymers. The condensation of silanes to the silica surface at alkaline conditions causes an increase in pH due to a hydroxide ion being released during the condensation reaction. [18]

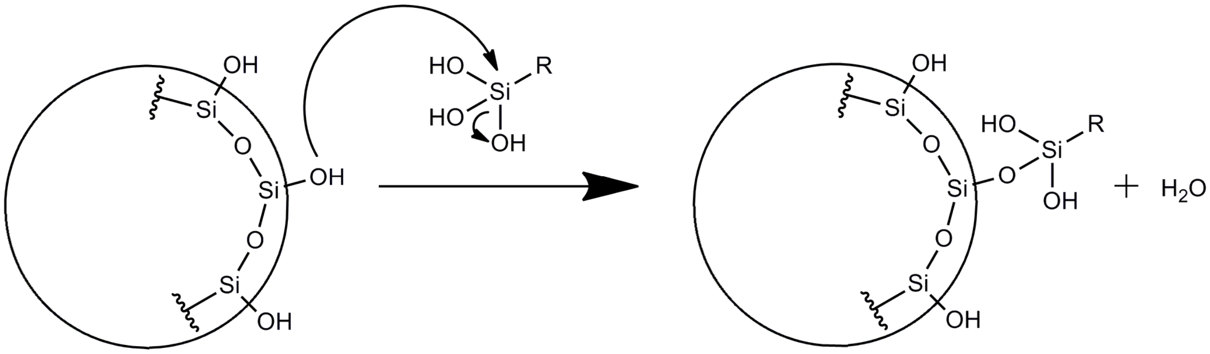


Figure 2. Condensation of a hydrolyzed trialkoxysilane to the silica surface at low pH

Synthesis of poly ethylene glycol containing silane

The silica sols in this study are derivatized by silanes produced via a reaction between glycidoxy propyl trimethoxy silane (3GTO) and different nucleophiles, mostly mono methyl poly ethylene glycol (MPEG) has been used as nucleophile. This MPEG containing silane is synthesized via a nucleophilic attack on the epoxide group in 3GTO. The reaction can be catalyzed by a Lewis or Brønstedt acid. In this study either a Brønstedt or a Lewis acid has been used for the epoxide alcoholysis and aminolysis.

The mechanism of the epoxide opening of the 3-GTO via an alcoholysis catalyzed by trifluoro acetic acid (TFA) is shown in figure 3. The reaction is initiated by a protonation of the epoxide oxygen creating an intermediate cation followed by a nucleophilic attack of an adjacent carbon atom. The regioselectivity of the nucleophilic attack is in favour of the most substituted carbon being attacked at acidic conditions, but the selectivity can be changed if an additional catalyst is used. [19] When a Lewis acid is used as catalyst the Lewis acid coordinates to the epoxide oxygen thus activating the epoxide through the formation of a trivalent oxygen in a manner similar to the Brønstedt acid. The mechanism of the aminolysis is basically the same but since an amine is used as nucleophile a nitrogen instead of an oxygen performs the nucleophilic attack.

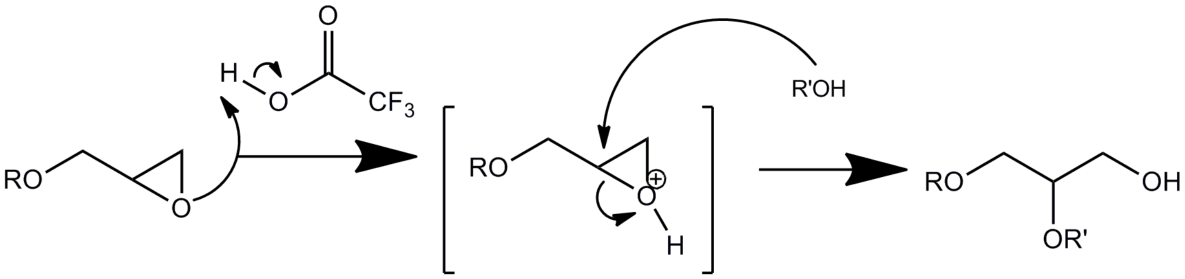


Figure 3. Detailed mechanism for the alcoholysis of 3-GTO (R=propyl trimethoxy silane) catalyzed by TFA [20]

The synthesis of the functional silanes is performed by a nucleophilic attack by the hydroxyl group of MPEG on the most hindered carbon of the epoxide in 3GTO catalyzed by TFA, producing a silane containing an MPEG chain. The reaction of 3GTO and MPEG can be seen in figure 4.

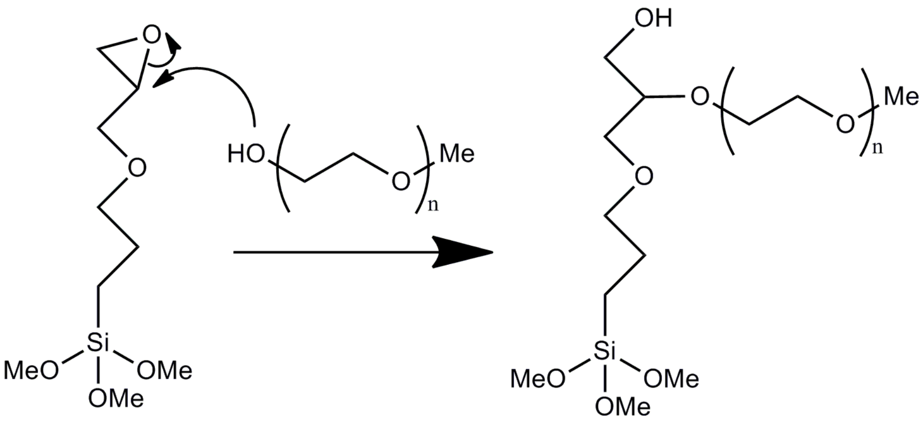


Figure 4. Simplified reaction mechanism of the nucleophilic attack of 3GTO by MPEG

The two main reasons to functionalize silica sols with MPEG are to increase the surface activity of the silica sol and, in addition to the stabilizing electrostatic interactions, introduce steric stabilization to the silica particles. The reason MPEG is used as nucleophile instead of poly ethylene glycol (PEG) in this study is to prevent the possibility for the PEG to react with two 3GTO molecules via alcoholysis by both of its hydroxyl groups acting as nucleophiles. This could lead to formation of covalent bridges between the silica particles if the silanol groups at each end would be condensed to two different silica particles, thus causing flocculation or gelling of the silica sol.

Possible unwanted side reactions in the synthesis of this MPEG containing silane include exchange of the methoxy groups on the silicon atom for MPEG groups. If this reaction occurs the MPEG will not give any contribution to the functionality of the silica sol since these alkoxy groups rapidly are hydrolyzed to silanol groups when in contact with water [16] [21]. Further this reaction yields methanol as a by-product which can act as a nucleophile to open the epoxide of 3GTO and thus compete with the MPEG. However the exchange of alkoxy groups should not occur unless water is present. [22] Other side reactions induced by water are nucleophilic attack of the epoxide, which gives a diol as a by-product. The water can also hydrolyze the methoxy groups of the silicon to silanol groups, which may cause polymerization of the silanes. [21] Due to these unwanted side reactions, the reaction vessel and the reactants should be protected from water contamination.

The condensation of the MPEG containing silanes produces MPEG modified silica particles, which can be seen in figure 5. When silica particles are functionalized with MPEG containing silanes the size and shape of the silica core of the particles are preserved. However the size of the functionalized particles is larger than the non modified particles, this is due to the formation of a MPEG layer located around the particles. [27]

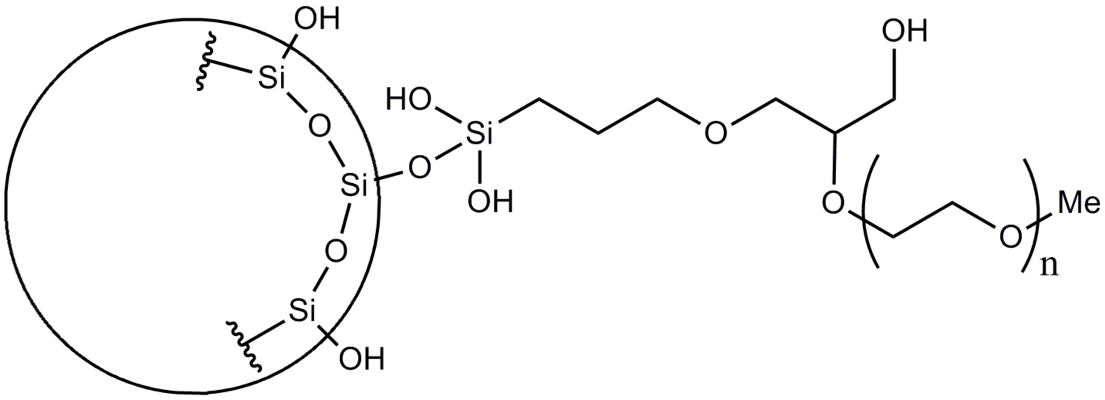


Figure 5. Principal appearance of a silica particle condensed with an MPEG containing silane

The size of the MPEG chain affects the maximum amount of MPEG containing silane that can be bonded to the silica surface due to sterical hindrance caused by the MPEG chains. The affinity to the silica surface causes the MPEG to physically adsorb to the silica surface and thus blocking unreacted silanol groups. When the molecular weight of MPEG increases, the maximum amount that can be bonded to the surface is decreased. [24]

Interactions between poly ethylene glycol and silica sols

Since PEG has an affinity to the silica surface, both non modified and hydrophobically modified silica, the MPEG containing silanes will be physically adsorbed to the silica surface independently of if the MPEG containing silane is chemically bonded to the silanol groups of the surface or not. The physical adsorption of PEG to the silica surface is caused by hydrogen bonding between the silanol groups of the silica surface and the ether oxygens of the PEG chain. As pH is increased the deprotonation of silanol groups is increased thus decreasing the possibilities of hydrogen bonding between PEG and the silica surface, hence the adsorption of PEG to the silica surface is decreased as pH is increased. [25]

The stability of the silica sol can be increased upon the adsorption of PEG to the silica surface. This is due to steric stabilization introduced by the PEG, this stabilization can be observed both for non modified and hydrophobically modified silica sols. [13] The PEG can also destabilize the silica sol by inducing bridge flocculation when added to a silica sol. At constant silica/PEG ratio the bridge flocculation increases with increasing molecular weight of PEG and increasing concentration of silica particles due to increased possibility for the PEG to reach two or more particles due to longer PEG chains and shorter distances between the particles respectively. [26]

Pickering emulsions

An emulsion is a dispersion of two or more immiscible liquids. All emulsions are thermodynamically unstable and will therefore eventually phase separate. However the lifetime of an emulsion can be prolonged by addition of emulsion stabilizing agents, these can be amphiphilic molecules, polymers or solid particles. These emulsion stabilizing agents, emulsifiers, gather at the interface of the two phases and thereby decrease the coalescence rate of the emulsified phase, which eventually completely will separate the two phases. Emulsions stabilized by solid particles are referred to as Pickering emulsions after the man who first described the phenomena. [27] To produce a Pickering emulsion the size of the emulsion stabilizing particles must be much smaller than the droplets of the emulsion. The stabilizing particles gather in a close packed ordered monolayer at the interface of the emulsion droplets. Since it is thermodynamically favourable for the particles to remain at the interface, the repulsive forces between the particles make the coalescence of particle stabilized emulsions very slow. [28]

To produce relatively stable Pickering emulsions the emulsion stabilizing particles should be wet by both phases [29] why both hydrophilic and lipophilic moieties are wanted for the silica surface of silica sols intended for use as emulsifiers.

Bridge flocculation caused by the MPEG may be an advantage if silica particles functionalized by MPEG chains are used as emulsion stabilizers. This is because the bridging between particles at an interface decreases the probability for the particles to leave the interface, thus stabilizing the emulsion.

Emulsification of alkenyl succinic anhydride

Alkenyl succinic anhydride (ASA) is a commonly used sizing agent in paper production to make the paper more hydrophobic. ASA consists of a cyclic anhydride of succinic acid with an alkenyl chain attached to one of the carbon atoms α to the carbonyl carbons, see figure 6. The sizing of the paper is performed via an alcoholysis of the anhydride by a hydroxyl group of the cellulose, which creates an ester bond between the ASA and the cellulose [1], see figure 7. When the ASA comes in contact with water the anhydride is rapidly hydrolyzed to a dicarboxylic acid. The dicarboxylic acids formed do not contribute to the sizing of the paper why ASA and water must be kept separated from each other. Since ASA is insoluble in water, the separation of the ASA from the water is commonly performed by the creation of an emulsion with water as the continuous phase and ASA as the dispersed phase. The emulsification of ASA is often performed by creation of emulsions using cationic starch as emulsion stabilizer. However these emulsions are not stable when hard water is used since insoluble succinate salts of for example calcium and magnesium are formed. [1]

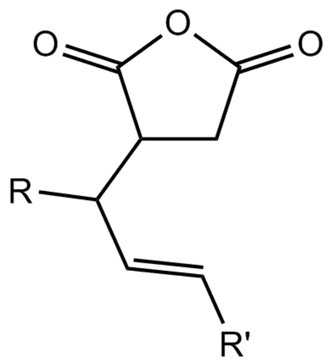


Figure 6. The structure of ASA (Alkenyl Succinc Anhydride), R and R' are either hydrogen atoms or linear alkyl groups. Typical lengths of the alkenyl group are around 18 carbon atoms.

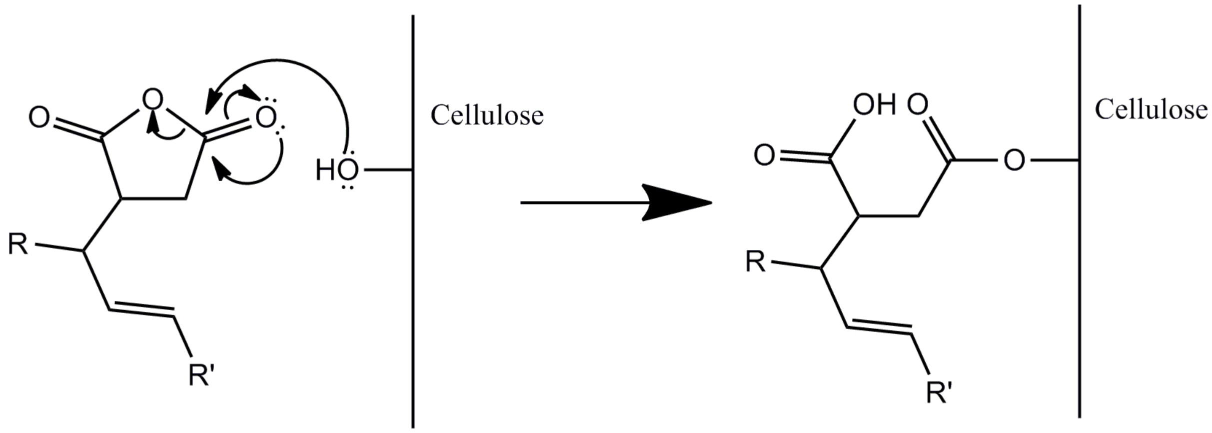


Figure 7. The creation of an ester bond between ASA and cellulose via an alcoholysis of the anhydride [19]

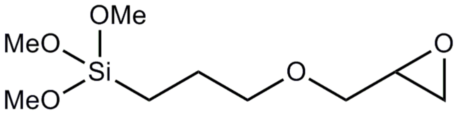
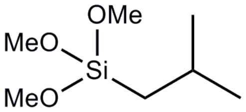
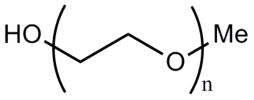
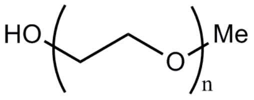
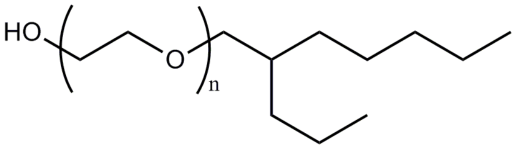
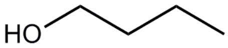
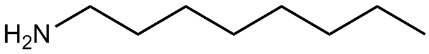
Materials and methods

First the chemicals used in this study are described followed by a description of the different synthetic routes used to achieve a high yielding synthesis of both the silanes and the condensation of the silanes to the silica surface. Then the different methods used to characterize the silica sols are described followed by salt stability of the surface modified silica sols and ASA emulsification tests.

Chemicals

During the syntheses of functional silanes five different nucleophiles were used as ring openers of the epoxide in 3GTO. These nucleophiles together with 3GTO and the isobutyl silane, which was also used in the derivatizations of silica sols, are listed in Table 1.

Table 1. Silanes and starting materials for syntheses of functional silanes

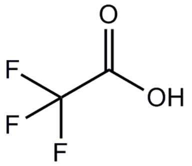
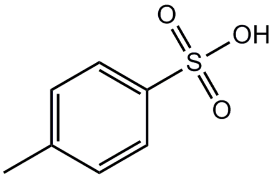
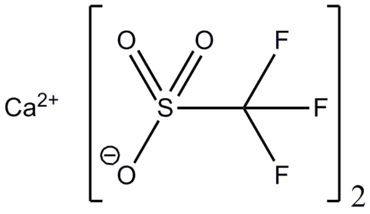
Abbreviation used in the thesis	IUPAC name	Structure	Supplier
3GTO	Glycidoxy propyl trimethoxy silane		Momentive Performance Materials
Isobutyl silane and iBuSi	iso-butyl trimethoxysilane		ABCR
MPEG 550	poly (ethylene glycol) mono methyl ether n≈12		Sigma-Aldrich
MPEG 2000	poly (ethylene glycol) mono methyl ether n≈45		Sigma-Aldrich
Ethylan 1005	poly (ethylene glycol) mono 2-propyl heptyl ether n≈5		Akzo Nobel surface chemistry
n-BuOH	1-Butanol		Acros
Octylamine	1-octylamine		Sigma-Aldrich

The syntheses of functional silanes were performed in either toluene (Fisher) or acetonitrile, MeCN (Fisher).

The inorganic salts used for salt stability test were $CaCl_2{\cdot}2H_2O$ (Scharlau) and $MgCl_2{\cdot}6H_2O$ (Scharlau)

The different catalysts used are displayed in Table 2. TFA and TsOH are Brønstedt acids while $Ca(OTf)_2$ is a Lewis acid. [30]

Table 2. The different catalysts used in the syntheses of functional silanes.

Abbreviation used in the thesis	IUPAC name	Structure	Supplier
TFA	Trifluoro acetic acid		Fisher
TsOH	para-toluene sulfonic acid mono hydrate		Fisher
$Ca(OTf)_2$	Calcium trifluoromethane sulfonate		Fisher

Two different silica sols have been used in this study, Bindzil® 40/130 with a pH of 9.07, a SiO_2 concentration of 40 wt% and a specific surface area of 130 m^2/g SiO_2. The second silica sol was Bindzil® 30/130 with a pH of 1.9, a SiO_2 concentration of 32 wt% and a specific surface area of 130 m^2/g SiO_2.

Syntheses of functional silanes

The synthesis of functional silanes was investigated by varying several reaction parameters. One of the three different catalysts TFA, TsOH and $Ca(OTf)_2$ were used in the syntheses. The amount of catalyst was also varied, from 5 mol% up to 200 mol% for TFA, the amount of $Ca(OTf)_2$ was varied from 5 mol% to 50 mol% while TsOH only was tested at 10 mol%. Further the reaction temperature was kept at 60˚C when toluene was used as solvent and at the boiling point of MeCN, 82˚C, when MeCN was used as solvent.

The amount toluene used was 100 ml when MPEG2000 was used as nucleophile and 50 ml when Ethylan 1005, MPEG550 or octylamine were used as nucleophiles. In these syntheses 8.5 mmol of both 3GTO and the nucleophile were used. When MeCN was used as solvent 12.5 mmol 3GTO and nucleophile were allowed to react in 150 ml MeCN.

Experimental procedure

3GTO was dissolved in the solvent prior to the addition of the nucleophile. After addition of the nucleophile the catalyst was added under stirring at room temperature. The reaction vessel was equipped with reflux cooling before the reaction vessel was heated to the reaction temperature.

The removal of the solvent was in the case of MeCN performed by evaporation at atmospheric pressure. The evaporation of the toluene was performed at 50˚C and a pressure of 10 kPa which was successively lowered to 5 kPa, which is well below 12 kPa, the vapour pressure of toluene at 50˚C. The vapour pressure of toluene at 50˚C was calculated using the Antoine equation (equation 1)

$$\ln P_{vap}(kPa) = A - \frac{B}{(T(K) + C)} \qquad \text{Eq. 1}$$

Where A=14.27; B=3290.24; C=-43.03 for toluene. [31]

The products were characterized by ^{1}H-NMR and ^{13}C-NMR.

Derivatization of silica sol

The condensation reaction of the different silanes to the surface of silica sols was also investigated at different reaction conditions. The reactions were all performed at 90°C but at different SiO_2 concentrations and with silica sols of different pH. The silica sols derived from the acidic Bindzil® 30/130 were not diluted but derivatized at the original concentration of 32 wt% SiO_2. The silica sols derived from the alkaline Bindzil® 40/130 were allowed to react at SiO_2 concentrations ranging from the original 40 wt% to 22 wt%. The dilutions were performed by addition of deionized water to the silica sols at room temperature.

Experimental procedure

The derivatizations were performed by heating the silica sol to 90°C, the silane was then added dropwise to the silica sol. In cases where two different silanes were used the addition procedure was performed in different manners. The silanes were either mixed before they were added to the silica sol, or added one at the time, either by adding the second directly after the first or one hour after the first. When the two silanes were added one at the time the isobutyl silane was added first.

To investigate if more silane could be grafted to the silica sol a prehydrolysis of the isobutyl silane was performed by mixing isobutyl silane and 2 equivalents of water, with respect to the methoxy groups, two hours before they were added to the silica sol. This time should be enough to achieve a low degree of polymerization of the silanes. [15] Bindzil® 40/130 diluted to 22.2 wt% SiO_2 and the prehydrolyzed silanes were then mixed at room temperature and the mixture heated to 90˚C and allowed to react for two hours at 90˚C.

To remove unreacted silanes 40 ml of the derivatized silica sol was diluted to four times its original volume and then ultrafiltered until the original volume was obtained. This procedure was performed four times. The ultrafiltration was performed in an Amicon 8400 stirred ultrafiltration cell equipped with a filter with a cutoff of 100 kDa supplied by Millipore. The operating pressure of the ultrafiltration cell was 5.3 bar.

Size measurements

The size measurements were performed by diluting the silica sols to approximately 0.5 wt% SiO_2 with deionized water. A few size measurements were also performed by diluting the silica sols with 20 mM aqueous NaCl instead of deionized water. The temperature of the cuvette was adjusted to 20°C before the measurements. The measurements were performed by dynamic light scattering on a Malvern Zeta Sizer Nano ZS, scanning each sample ten times, each scan lasting twenty seconds.

Surface tension measurements

The surface tension measurements were performed by diluting the ultrafiltered silica sols with deionized water to a SiO_2 concentration of 5 wt%. The measurements were performed by the du Noüy ring method on a Krüss Tensiometer K-6.

Salt stability

The derivatized silica sols were diluted to 1.0 wt%, followed by addition of salt to the diluted silica sols. Salt additions were performed by addition of a 1.0 wt% stock solution prepared from each salt to the silica sols. The vials were then thoroughly shaken to distribute the salt homogeneously throughout the sample. The samples were then stored at room temperature.

Emulsification of ASA

To emulsify ASA 0.58 g silica (dry weight) was diluted by tap water to 190 g followed by addition of 10 g ASA. This mixture was mixed for 60 seconds at the ice crush high mode of an Osterizer 16 speed blender.

The size distribution of the emulsion droplets was measured by laser diffraction on a Malvern Mastersizer microplus. This was performed by addition of a few drops of the emulsion to 1 liter of deionized water.

Results and discussion

The results of this study are divided into one part covering the syntheses of silanes and silica sols and one part containing the properties of the surface modified silica sols. The part covering the syntheses consists of both the syntheses of functional silanes and the grafting of the different silanes to the silica surface. The properties of surface modified silica sols include pH, surface activity, salt stability and ability to emulsify ASA.

Syntheses of functionalized silanes

The reaction yield of the syntheses of the functional silanes was determined by ^{1}H-NMR by comparing the relative peak area of the epoxide in 3GTO and the peak area of the methylene group adjacent to the silicon atom after the synthesis. The ^{1}H-NMR spectrum of 3GTO can be seen in figure 8. The peaks corresponding to the epoxide are located at 2.52; 2.69 and 3.05 ppm while the peak corresponding to the methylene adjacent to the silicon is located at 0.63 ppm.

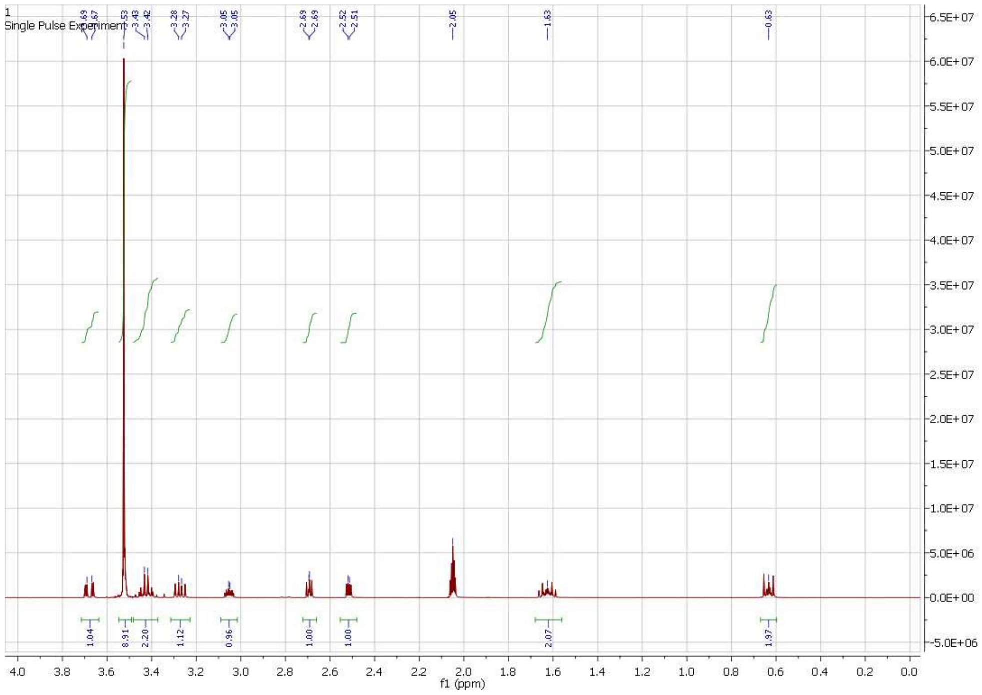


Figure 8. ^{1}H-NMR spectra of 3-GTO, the peak at 2.05 ppm corresponds to the solvent, acetone-d6 [32]

The functional silanes were produced by a few different synthetic routes, see table 3. The syntheses performed for two hours with 5-10 mol% catalyst did not yield a high opening of the epoxide. Due to this, the reaction time and the amount of catalyst were increased to 100 or 200 mol% catalyst and five hours reaction time respectively. This synthetic route proved to yield complete or almost complete opening of the epoxide. Of the two syntheses with octylamine as nucleophile one was performed according to a similar reaction found in the literature, using 50 mol% $Ca(OTf)_2$ as catalyst, [33] and one with the same amount of TFA as catalyst to investigate how amines react in these syntheses. Both of these reaction conditions appear to yield an effective opening of the epoxide.

Table 3. Overview of synthesized functional silanes listed according to the nucleophile used in the synthesis. Amount catalyst and epoxide opening displayed as mol%.

Abbreviation	Nucleophile	Solvent	Catalyst	Reaction time	Epoxide opening	Appearance
MP1	MPEG2000	MeCN	10% TFA	2 h	20%	Yellow solid
MP2	MPEG2000	MeCN	10% TsOH	2 h	20%	Slightly yellow mix of solid and liquid
MP3	MPEG2000	MeCN	10% $Ca(OTf)_2$	2 h	0%	Non coloured liquid
MP9	MPEG2000	Toluene	100% TFA	5 h	90%	Yellow solid
MP12	MPEG2000	Toluene	100% TFA	5 h	100%	Yellow solid
MP14	MPEG2000	Toluene	100% TFA	5 h	100%	Yellow solid
MP4	MPEG550	MeCN	5% TFA	2 h	0%	Orange-brown liquid
MP5	MPEG550	MeCN	5% $Ca(OTf)_2$	1 h without cat. 3 h with cat.	0%	Non coloured liquid
MP8	MPEG 550	Toluene	200% TFA	5 h	100%	Non coloured liquid
MP13	Ethylan1005	Toluene	100% TFA	5 h	80%	Non coloured liquid
MP6	n-BuOH	MeCN	10% TFA	2 h	10%	Yellow-orange liquid
MP7	n-BuOH	MeCN	10% $Ca(OTf)_2$	2 h	5%	Yellow liquid
MP10	Octylamine	MeCN	50% $Ca(OTf)_2$	5 h	100%	Yellow liquid
MP11	Octylamine	Toluene	50% TFA	5 h	100%	Slightly yellow liquid

As can be observed in table 3 the majority of the synthesized functional silanes turned out to be more or less yellow in colour. Since both high and low yielding syntheses display this colour to approximately the same extent the reason for the yellow colour cannot be the product.

During the synthesis of MP5 when the $Ca(OTf)_2$ was added to the boiling mixture of MeCN, 3GTO and n-BuOH the mixture overflowed the reactor due to extensive foaming. This implies that the catalyst should be added to the reaction mixture at low temperature to avoid such unpleasant events.

During the synthesis of MP11 when the TFA was added to the room temperate mixture of toluene, 3GTO and octylamine, a white gas appeared in the reactor. The gas did not fill the reactor, instead it remained close to the liquid phase indicating a density higher than air. After 10 minutes the white gas had completely disappeared.

It can also be noted that the functional silanes synthesized with MPEG2000 as nucleophile with only two exceptions, MP2 and MP3, are solids at room temperature suggesting the liquid products is due to incomplete evaporation of the solvent. This is also confirmed by ^{1}H-NMR, quite much MeCN does still exist in these products. When nucleophiles smaller than MPEG2000 were used the functional silanes all turned out to be liquids.

The reason for the low reaction yields when 5-10 mol% catalyst were used is probably due to that these reactions were allowed to react for only two hours since none of the three catalysts were able to induce a high reaction rate. This might be due to the low amount of catalyst was unable to induce a sufficiently high reaction rate. The low reaction rate of syntheses catalyzed by TFA performed in reflux boiling MeCN is probably also due to the boiling point of TFA, 72°C, causing most of it to be evaporated during the reaction.

The TsOH was abandoned as a catalyst due to the fact that it contained water of crystallization, which, as mentioned earlier, can induce several unwanted side reactions.

To elucidate if any TFA remained in the functional silanes ^{13}C-NMR was run. If TFA remained, the splitting of one of the signals by the three fluorine atoms would give a very distinct quartet in a ^{13}C-NMR spectrum. As can be seen in figure 9 no quartet can be observed. This means that all of the TFA is evaporated from the functional silane and that the TFA itself does not form any side-products with the reagents. From this ^{13}C-NMR spectrum it can also be noted that there is no peak corresponding to the formation of a diol of the epoxide, which would be located at around 63 ppm. [18]

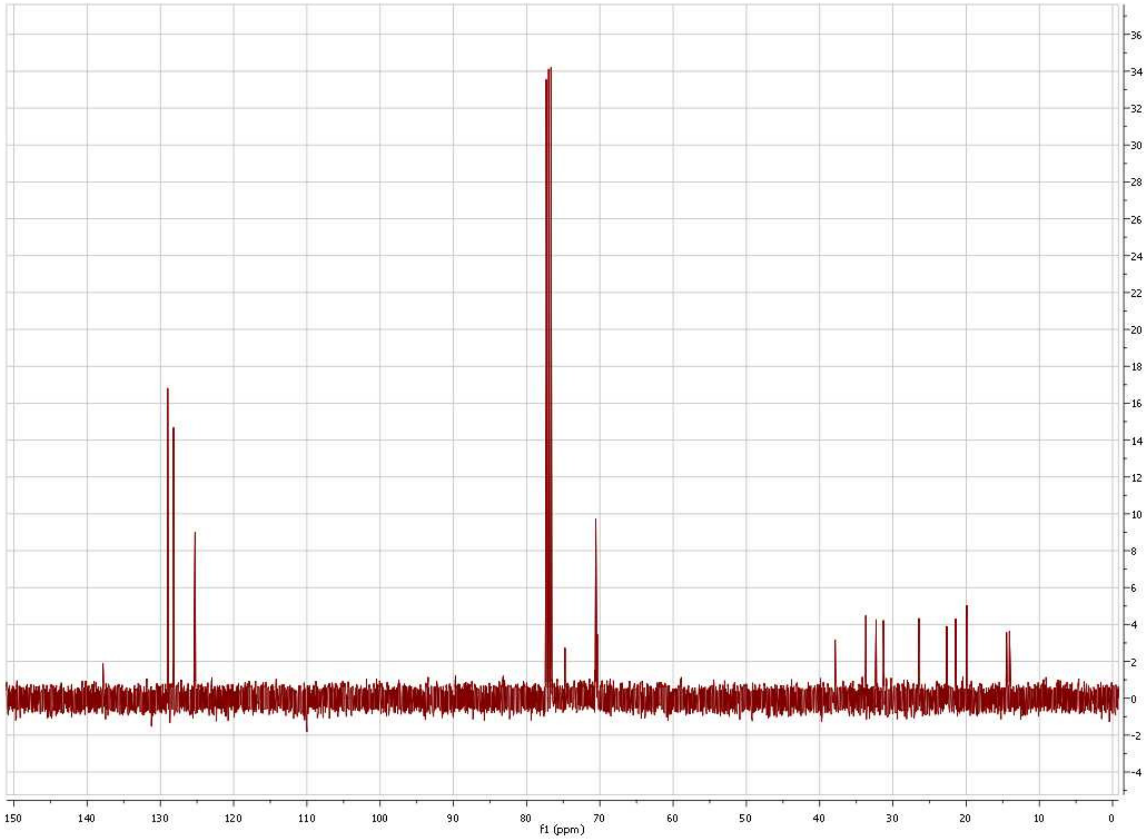


Figure 9. ^{13}C-NMR spectrum of MP13. The peaks at 21, 125, 128,129 and 137 ppm corresponds to remaining toluene in the product. [32]

In addition to the almost complete disappearance of the epoxide peaks in the ^{1}H-NMR spectrums of functional silanes with 100% TFA catalyzing the reaction, and the absence of TFA in the ^{13}C-NMR spectrums indicates that the desired product has been formed. The only remaining possible products from the reagents are nucleophilic attack by the amine group of octylamine or the hydroxyl group of MPEG, Ethylan 1005 or n-BuOH respectively at one of the epoxide carbons of 3GTO. Which carbon being attacked is of less importance since the small structural difference between the two possible products will be negligible compared to the size of the MPEG chain.

The large amount of TFA needed to achieve a high yield can be used industrially in a sustainable way if the TFA is recycled together with the toluene. This should be possible since the vapour pressure of toluene and TFA allows them to be evaporated from the reaction mixture thus leaving a crude product free from solvent and catalyst, but possibly together with unreacted material and side products. As mentioned previously the TFA can be quantitatively evaporated at reduced pressure together with the toluene. It is also important to completely remove the TFA from the functional silane before the addition to the silica sol to prevent changes in pH, caused by the TFA. If remains of TFA change the pH to the region 4-7.5 the sol will rapidly form a gel. [3]

The $Ca(OTf)_2$ also has the capability to yield a complete opening of the epoxide with an amine as nucleophile already at 50 mol%, but since it is non volatile it cannot be recycled together with the toluene, but has to be separated from the synthesized silane via extraction with water. [33] This means that the functional silane must be poorly soluble in water to achieve a good separation from the $Ca(OTf)_2$. Due to the destabilizing effect on silica sols caused by Ca^{2+} ions the $Ca(OTf)_2$ must be quantitatively removed from the functional silane before addition to the silica sol. [10] This limits the use of $Ca(OTf)_2$ as catalyst for this reaction.

The catalyst that seems to be the most promising is TFA. The catalysis by $Ca(OTf)_2$ does require that the resulting product is hydrophobic to achieve a good separation of the functional silane from the Ca^{2+} ions.

The most convenient synthetic route able to yield complete opening of the epoxide was to react equal amounts of 3GTO and nucleophile in toluene at 60°C for five hours with a stoichiometric amount of TFA catalyzing the reaction. After the reaction, the toluene and TFA were evaporated at reduced pressure. The amount of toluene was 100 ml when MPEG2000 was used as nucleophile and 50 ml when Ethylan 1005 or MPEG550 were used as nucleophile.

Appearance of derivatized silica sols

It is important that the silica sols after derivatization remain stable sols to be useful in emulsification applications, since extensively flocculated particles are less effective emulsion stabilizers and also are less stable suspensions. From an industrial perspective it is important that no gelling of the silica sols occurs during the reaction to avoid time consuming maintenance work. Further it is important that the silica sols are stable enough to be stored or transported longer distances without any changes in the properties of the silica sol.

Upon the addition of MPEG containing silanes to the silica sols, initially all the sols turned whiter and more turbid. In the syntheses producing silica sols of the same appearance as the original sol the sol slowly became less white and less turbid during the reaction. This is due to local excess of MPEG containing silanes inducing flocculation of the silica particles, but as the mixture of silica sol and MPEG containing silanes is stirred the MPEG containing silanes becomes more evenly distributed throughout the sol, thus decreasing the initial flocculation. [3] The turbidity might also occur due to poor solubility of the silanes prior to hydrolysis of the methoxy groups, followed by a higher solubility after the hydrolysis due to increased hydrophilicity as well as release of methanol to the water. During the addition of isobutyl silane to the silica sol no changes in appearance could be observed.

The initial derivatizations of silica sols were performed with the acidic Bindzil® 30/130 to eliminate the destabilizing effect remaining acid would induce to an alkaline silica sol. The appearance and intended surface modification of some of the silica sols produced from Bindzil® 30/130 can be seen in table 4, the complete table of derivatized silica sols can be seen in Appendix I.

The silica sols derivatized with only isobutyl silane with an intended surface coverage above 1.33 µmol/m^2, SS6 and SS8, both gelled already in the reactor. The silica sol derivatized with 1 µmol isobutyl silane/m^2, SS7 was stable for a month. The silica sol SS9, derivatized with 1.33 µmol isobutyl silane/m^2, gelled after two weeks. This indicates that the maximum surface coverage by isobutyl silane of Bindzil® 30/130 is around 1.33 µmol/m^2, and if it is exceeded the silica sol is quickly gelled, possibly the gelling can be avoided by addition of an alcohol to the sol.

The silica sols produced by derivatization of Bindzil® 30/130 by addition of only isobutyl silane did not show any long time stability but gelled already during the reaction time or within a month unless they were ultrafiltered. This implies that unreacted isobutyl silane causes the silica sol to gel. This is further substantiated since an increase in added isobutyl silane causes the silica sol to gel faster. The ultrafiltered silica sols derivatized with isobutyl silane were stable for at least a few months.

Further, it can be seen that SS5 did not show any long time stability either as it settled within a few hours. Since it contains MPEG2000, from a synthesis exhibiting low yield in the epoxide opening of 3GTO by MPEG2000, in amounts corresponding to 1 µmol/m^2, bridge flocculation caused by the MPEG may have contributed to the settling. Another reason for the settling may be that too much silane has been added to the silica sol. [18]

Table 4. Some of the derivatized silica sols with Bindzil® 30/130 as the original sol

Abbreviation	SiO_2 concentration	Used silanes	Appearance	Appearance after ultrafiltration
SS2	32 wt%	MP1 (2 µmol/m^2)	Slightly whiter than 30/130	Gelled
SS4	32 wt%	MP3 (2 µmol/m^2)	Whiter than 30/130	Much whiter and more viscous than 30/130
SS5	32 wt%	iBuSi (2 µmol/m^2) MP1 (1 µmol/m^2)	Settled within a few hours	
SS6	32 wt%	iBuSi (2 µmol/m^2)	Gelled in the reactor	
SS7	32 wt%	iBuSi (1 µmol/m^2)	Gelled within a month	As before ultrafiltration
SS8	32 wt%	iBuSi (1,67 µmol/m^2)	Gelled in the reactor	
SS9	32 wt%	iBuSi (1,33 µmol/m^2)	Gelled within 2 weeks	As before ultrafiltration

Since no remaining TFA could be found in the functional silanes, no decrease in pH was expected. Therefore later derivatizations of silica sols were performed with the alkaline Bindzil® 40/130 to take advantage of the faster condensation at alkaline pH. [17] The appearance and intended surface modification of some of the silica sols produced from Bindzil® 40/130 can be seen in table 5, for the complete table of derivatized silica sols see Appendix I.

As can be seen from the silica sols produced from Bindzil® 40/130, the SiO_2 concentration is an important factor regarding the appearance of the derivatized silica sols. The best examples of this are SS17 and SS18 compared to SS20 and SS21 respectively, since they are modified in the same way but at different SiO_2 concentrations. At a SiO_2 concentration of 33 wt% the silica sols gelled already in the reactor, SS17 and SS18, but at a SiO_2 concentration of 22 wt% the silica sols remained a stable sol for at least a month of storage, SS20 and SS21. These observations suggest that gelling appears when the solid weight reaches a certain threshold concentration. To overcome this problem the following derivatizations were performed at the lower SiO_2 concentration.

Since it is important to avoid gelling of the silica sol in industrial production the derivatizations of silica sols should be carried out at low SiO_2 concentrations, possibly followed by a concentration step after the reaction by evaporation or ultrafiltration, to remove water and methanol formed from the hydrolysis of the methoxy groups.

Since the gelled silica sols could be redispersed when diluted with water followed by shaking, no network of covalent bonds existed throughout the gel. This indicates instead a network of intermolecular forces which were reduced as the distance between the particles increased upon dilution thus enabling a redispersion. However several of the redispersed silica sols, but not all, started to settle within a week indicating that the produced silica sols still were unstable even at lower SiO_2 concentrations. The cause of the settling may also be that the particles were flocculated to larger aggregates during the gelling and thus were less stable. The whiter colour and higher turbidity of redispersed silica sols compared to silica sols remaining suspensions indicate the presence of larger aggregates in the redispersed silica sols. This observation implies that aggregation of the particles that occurred during the flocculation were not completely reversible. Since the silica sols remaining suspensions after derivatization not displayed more than a slight increase in turbidity no extensive formation of aggregates seems to have occurred in these sols.

The prehydrolysis of isobutyl silane prior to the derivatization of SS25 was performed by mixing isobutyl silane with 2 equivalents of water, based on the methoxy groups, two hours before the addition to the Bindzil® 40/130. Since they were immiscible the prehydrolysis route was not successful. A high degree of hydrolysis would have yielded significant amount of methanol which would have improved the solubility of isobutyl silane in water thus further increased the hydrolysis of methoxy groups. The prehydrolysis might be more successful if the silane is mixed with water for a longer time or at a higher temperature than two hours at room temperature, the hydrolysis might also be increased if effective stirring is applied to the mixture, or the silane being added to a mixture of water and an alcohol thus increasing the solubility of the isobutyl silane.

The silica sols SS24 and SS27, derivatized with the Ethylan 1005 containing MP13, both started to settle already in the reactor indicating that too much silane had been added to the silica sol. These silica sols are derivatized with the lowest amount of silane of all settled silica sols in this study. This indicates that the Ethylan 1005 containing MP13 destabilizes the silica sol already at relatively low coverage of the silica surface. This might be due to the cloud point of Ethylan 1005, which is 50°C, is exceeded during the reaction, which was performed at 90°C.

Table 5. Some of the derivatized silica sols with Bindzil® 40/130 as original sol

Abbreviation	SiO_2 concentration	Used silanes	Appearance	Appearance after ultrafiltration
SS17	33 wt%	iBuSi (1 µmol/m^2) MP9 (0,75 µmol/m^2)	Gelled in the reactor. Very turbid and white efter redispersion	
SS18	33 wt%	iBuSi (1 µmol/m^2) MP9 (0,5 µmol/m^2)	Gelled in the reactor. Very turbid and white efter redispersion	
SS20	22 wt%	iBuSi (1 µmol/m^2) MP12 (0,75 µmol/m^2)	Slightly whiter than 40/130	As before ultrafiltration
SS21	22 wt%	iBuSi (1 µmol/m^2) MP12 (0,5 µmol/m^2)	Slightly whiter than 40/130	Slightly whiter than SS21
SS23	22 wt%	iBuSi (1 µmol/m^2) MP12 (0,25 µmol/m^2)	Slightly whiter than 40/130	As before ultrafiltration
SS24	22 wt%	MP13 (1 µmol/m^2)	Whiter than 40/130. Some precipitate formed in the reactor	
SS25	22 wt%	iBuSi (1 µmol/m^2) “prehydrolyzed”	As 40/130	As before ultrafiltration
SS26	22 wt%	iBuSi (1 µmol/m^2)	As 40/130	As before ultrafiltration
SS27	22 wt%	MP13 (0,75 µmol/m^2)	Whiter than 40/130. Some precipitate formed in the reactor	
SS28	22 wt%	MP14 (1 µmol/m^2)	Whiter than 40/130	Slightly whiter than SS28

The silica sols remaining suspensions which were about as clear as the original sol, Bindzil® 40/130, did not suffer from the disadvantage of formation of a filter cake during ultrafiltration. The silica sols turning very turbid and white during either the derivatization or the ultrafiltration formed a significant filter cake. The formation of a filter cake during ultrafiltration of the turbid silica sols is most likely due to flocculation of the particles. These aggregates are irreversibly caught as a gel at the filter membrane due to their slower diffusion rate. [3]

The derivatization of silica sols can conveniently be carried out by diluting the alkaline Bindzil® 40/130 to 22 wt% SiO_2 by deionized water followed by heating, in a reaction vessel equipped with stirring and reflux cooling, to 90°C. When 90°C is reached the first silane is added dropwise and then allowed to react for one hour when the second silane is added. The mixture is then allowed to react for two hours. The MPEG containing silane should be added last to avoid the MPEG chain to block the silanol groups thus sterically hinder the second silane to bind to the silica surface. If only one silane is to be added the mixture should be allowed to react for two hours. To avoid gelling during storage of the silica sols ungrafted silanes should be removed by ultrafiltration.

pH of derivatized silica sols

According to the results of the pH measurements, displayed in table 6, the addition of silane to the silica sol increased the pH, which is in accordance with earlier studies. [18] One exception to this is displayed by SS28 where pH decreased. The pH is also shifted towards pH 7 after the ultrafiltration which was expected since the dilution during the ultrafiltration is performed by deionized water.

Despite the pH shift towards pH 7 for the derivatized silica sols only UFSS2, which was gelled, showed a significant decrease in stability upon dilution with deionized water. Since the stability of silica sols decreases as pH approaches pH 7 [3], the derivatization of the silica particles seems to have decreased the pH sensitivity of the silica sols by adding steric stabilization to the sols.

Table 6. pH measurements of derivatized silica sols

Silica sol	pH prior to derivatization	pH prior to ultrafiltration	pH after ultrafiltration
SS2	1.9	2.55	
SS4	1.9	2.93	3.46
SS7	1.9	2.40	2.89
SS9	1.9	2.45	2.77
SS17	9.1	9.54	
SS18	9.1	9.76	
SS20	9.1	9.27	7.37
SS21	9.1	9.53	7.93
SS23	9.1	9.68	8.05
SS25	9.1	9.53	8.28
SS26	9.1	9.56	8.45
SS28	9.1	8.61	7.25

The shift of pH towards 7 after ultrafiltration is more significant for the silica sols modified by MPEG2000 containing silanes. The shift towards pH 7 is also less significant when the amount of isobutyl silane is increased. When both MPEG2000 containing silanes and isobutyl silane were used to derivatize the silica sol the silica sols with the highest ratio of MPEG containing silane compared to isobutyl silane shifted the most towards pH 7.

The surface charge of silica is not affected by the grafting of hydrocarbon chains to the silica surface [6] why the silica sols derivatized with only isobutyl silane should behave very similar to non modified silica sols upon ultrafiltration. Due to the surface charge of the silica sol counterions are located close to the silica surface. Outside of this layer an additional layer with higher concentration of anions than the bulk are located. Due to these ionic layers around the particles ions might be hard to remove by ultrafiltration [3]. The longer MPEG2000 chains grafted to the silica surface may however be able to disturb this type of layers formed around the silica particles. This might be the reason for the relatively low change in pH for the silica sols derivatized with high amounts of isobutyl silane compared to silanes containing MPEG2000.

Carbon content of derivatized silica sols

Some of the derivatized silica sols were analyzed for SiO_2 and carbon content after ultrafiltration, by X-ray fluorescence (XRF) and total organic carbon (TOC) respectively. The results from these analyzes can be seen in table 7.

Assumptions and approximations done for the calculations of theoretic maximal ratio and thereof derived yield are

- No SiO_2 is lost during the ultrafiltration of the silica sol

- All methoxy groups of the silanes are hydrolyzed and the formed methanol is washed away during the ultrafiltration
- The MPEG containing silane is free from solvent, unreacted starting materials and side products
- The increase in SiO_2 content through the addition of the silanes is negligible
- All the remaining carbon in the silica sol is covalently bond to the silica sol
- All MPEG2000 polymers consists of 45 monomers

Table 7. SiO_2 and carbon content of derivatized and ultrafiltered silica sols

Silica sol	SiO_2 content (%)	Carbon content (ppm)	Ratio carbon:SiO_2	Theoretic maximal ratio	Yield (%)
UFSS4	13.7	2900	0.0212	0.316	6.71
UFSS7	23.7	920	0.00388	0.00556	69.8
UFSS9	20.5	1100	0.00537	0.00787	68.2
UFSS20	9.2	2400	0.026	0.12	21.7
UFSS21	20.0	4600	0.0230	0.0867	26.5
UFSS23	21.1	640	0.00303	0.0481	6.30
UFSS25	14.6	810	0.00548	0.00613	89.4
UFSS26	20.4	1200	0.00588	0.00615	95.6
UFSS28	12.0	3300	0.0275	0.146	18.8

The yield of the silane condensation to the silica surface is significantly higher at alkaline pH, which can be observed when the yield of the grafting of isobutyl silane to the silica surface is highlighted. This modification was done with UFSS7 (1 $\mu mol/m^2$), UFSS9 (1,33 $\mu mol/m^2$) and UFSS26 (1 $\mu mol/m^2$), where UFSS26 was prepared at alkaline pH while UFSS7 and UFSS9 were prepared at acidic pH, otherwise the reaction conditions were identical except a more diluted silica sol was used for production of UFSS26. Since the yield for UFSS26 is 95.6% compared to 69.8 and 68.2% for UFSS7 and UFSS9 respectively this supports earlier studies where the condensation is found out to be faster at alkaline pH than acidic pH. [17] The grafting of the MPEG2000 containing silanes to the silica surface is also improved at alkaline conditions, but the higher yield is probably to a major extent due to the higher yield in the synthesis of the MPEG2000 containing silanes used in the derivatizations of silica sols at alkaline pH.

If the condensation yield of isobutyl silane is assumed to be 100% for the silica sols UFSS20 and UFSS21 the yield of the grafting of MPEG containing silane is 17.8% and 20.1% respectively indicating that slightly below 20% of the MPEG containing silane is covalently bond to the silica surface after two hours at 90°C. This corresponds well to the 18.8% yield in the grafting of only MPEG2000 containing silane to UFSS28. The results from UFSS20, UFSS21 and UFSS28 suggests that slightly below 20% of the MPEG2000 containing silane are covalently bond to the silica surface after two hours at 90°C.

The carbon content of UFSS23 corresponds to approximately half of the added isobutyl silane have been covalently bound to the silica particles. The differing carbon content displayed by this silica sol is probably due to some kind of error during either the synthesis or the measurement.

The yield of grafting MPEG2000 containing silane to the silica surface is slightly below 20% independent of the added amount and the added amount of isobutyl silane. This implies that the lower grafting of MPEG2000 containing silane than isobutyl silane to the silica is due to a slower reaction for MPEG2000 containing silane, probably in combination with steric hindrance from the MPEG2000 chain.

Since the grafting of isobutyl silane to the silica surface is almost quantitative after two hours reaction at 90˚C this synthetic route seems to be very efficient. To improve the yield of the MPEG2000 containing silane condensation to the silica surface, a longer reaction time might be necessary since it is a much larger molecule than the isobutyl silane and thus the reaction speed is decreased. Another reason that might contribute to the slower condensating of MPEG2000 containing silane is that the MPEG chain of the silane adsorbs to the silica surface and thus sterically blocks a large share of the silanol groups, thus disabling them from condensation with the silane. To decrease this phenomena a more effective stirring might be successful. A prolonged addition time might eliminate local excess of MPEG containing silanes thus enabling them to be more evenly distributed throughout the silica sol thereby minimizing the risk of locally high steric hindrance of the silica surfaces.

Of the two alkaline silica sols surface modified with 1 µmol isobutyl silane / m^2, UFSS26 displays a higher carbon:SiO_2 ratio than UFSS25. This result indicates that the prehydrolysis of isobutyl silane not resulted in an increased grafting of isobutyl silane to the silica. Instead simple addition of the isobutyl silane to the silica appears to be the most convenient synthetic route to hydrophobically modify silica sols.

The significant decrease in SiO_2 content of UFSS4, UFSS20, UFSS25 and UFSS28 is probably due to losses during the filtration. During the ultrafiltration of UFSS4 a filter cake had formed, which probably contained most of the lost silica. During the ultrafiltration of UFSS20, UFSS25 and UFSS28 the filtrate was somewhat turbid at the beginning of the ultrafiltration indicating minor damages or leaks in the filter eventually plugged by precipitated particles.

Particle size of derivatized silica sols

The size of the silica particles of both the derivatized silica sols and the original silica sol was measured by dynamic light scattering. The results from the size measurements of silica sols prepared from Bindzil® 40/130 can be seen in table 8, for a complete list of particle diameters see Appendix II.

Since PEG forms a layer around silica particles thus increasing their size, the size measurements are able to imply if the MPEG containing silanes are present at the surface of the silica particles. If the particle diameter of the surface modified silica sols is slightly higher than for the nonmodified silica sols after the ultrafiltration, the silanes are most likely bound to the surface since unreacted silanes are most likely removed. The size measurements can also indicate if flocculation of the silica particles has occurred since particles much larger than the original silica particles then are present.

Table 8. Results from size measurements performed by dynamic light scattering. Silica sols abbreviated SS and UFSS corresponds to before and after ultrafiltration respectively. [†]could not be filtered through a 0.2 µm filter before measurement

Silica sol	Z average (nm)	Polydispersity
40/130	28.00	0.119
40/130 in NaCl solution	33.86	0.032
SS17[†]	163.2	0.210
SS18[†]	159.3	0.211
SS20	35.38	0.124
UFSS20	32.08	0.207
SS21	32.63	0.136
UFSS21	26.38	0.246
SS23	27.99	0.104
UFSS23	21.69	0.294
SS25	25.03	0.128
UFSS25	22.65	0.215
UFSS25 in NaCl solution	35.75	0.049
SS26	25.01	0.108
UFSS26	22.00	0.261
UFSS26 in NaCl solution	36.34	0.058
SS28	31.19	0.085
UFSS28	20.63	0.265
UFSS28 in NaCl solution	38.56	0.046

From these results it can be observed that the particle size of the derivatized silica sols generally is larger than the size of the original silica sol. Before the ultrafiltration this is true for all but three. SS25 and SS26 have particle diameters slightly below Bindzil® 40/130, and UFSS23 of the same size as Bindzil® 40/130, which could be due to a thinner layer of water molecules adsorbed to the surface due to its hydrophobic nature or due to changed light scattering properties due to the surface modification.

The ultrafiltrated silica sols produced from Bindzil® 40/130, with one exception, display particle diameters smaller than the original sol. The reason for these smaller particle diameters is not known. But the size measurements were repeated by dissolving the silica sols in 20mM NaCl instead of deionized water. This caused instant flocculation of UFSS20 and UFSS21, while a fairly fast flocculation was induced to UFSS23.

The silica sols UFSS25, UFSS26 and UFSS28 did however display particle diameters slightly larger than Bindzil® 40/130 in NaCl solution. The larger size of UFSS28 compared to UFSS25 and UFSS26 is most likely due to the much larger size of the MPEG2000 containing silane compared to the isobutyl silane.

The redispersed silica sols SS17 and SS18, does in accordance with their white and turbid appearance display much larger particles sizes than SS20 and SS21. SS20 and SS21 were derivatized in the same manner as SS17 and SS18 respectively but at a lower SiO_2 concentration, which prevented them from gelling. This confirms the hypothesis that the particles had formed larger aggregates during the flocculation.

Stability of modified silica sols towards electrolytes

The stability towards electrolytes was examined for the silica sols at a concentration of 1 wt% SiO_2 in aqueous solution to which different amounts of calcium chloride and magnesium chloride were added.

Instantly after the addition of salt to the diluted silica sols all the vials containing UFSS20, UFSS21 and UFSS23 turned completely turbid. Three of the vials containing UFSS28 also instantly turned turbid, the vials containing 0.06 wt% $CaCl_2$, 0.10 wt% $CaCl_2$ and 0.05 wt% $MgCl_2$, while the rest remained clear. All the vials containing UFSS26 remained clear during the addition of salt.

The appearance of UFSS26 and UFSS28 one week after the salt addition can be seen in figure 10 and figure 11 respectively. At this time the samples appeared the same as they did one day after the salt addition. Almost no differences at all could be noticed, one is that UFSS26 with 0.10 wt% $CaCl_2$ added is a bit more transparent at the top than the rest of the vial suggesting an early stage of sedimentation. Another is that UFSS28 with 0.03 wt% $MgCl_2$ displays a slight turbidity. This suggests that UFSS26 is almost unaffected by salt concentrations of 0.02 wt% $CaCl_2$ respectively 0.03 wt% $MgCl_2$ since these suspensions did not show any signs of decrease in stability. Even when the salt concentration was raised to 0.10 wt% $CaCl_2$ and 0.05 wt% $MgCl_2$ UFSS26 proved to be stable towards sedimentation despite flocculation of the silica particles. UFSS28 is unaffected by a salt concentration of 0.01 wt% $MgCl_2$ and is stable towards sedimentation, but not flocculation at salt concentrations of 0.02 wt% $CaCl_2$ and 0.03 wt% $MgCl_2$. Higher salt concentrations caused settling of UFSS28.

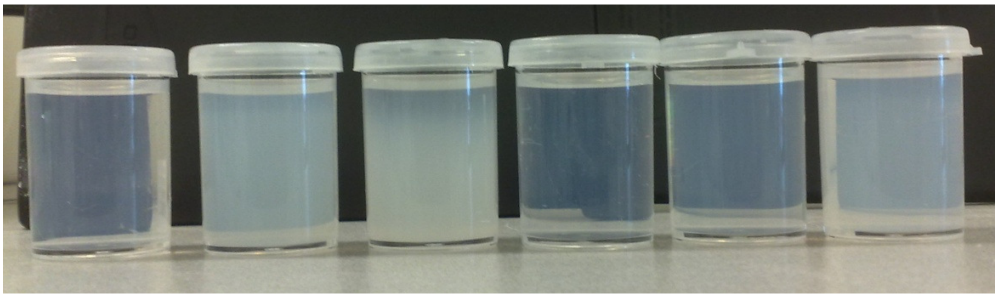


Figure 10. Appearance of salt stability samples of UFSS26 after one week. From left to right 0.02 wt% $CaCl_2$,0.06 wt% $CaCl_2$, 0.10 wt% $CaCl_2$, 0.01 wt% $MgCl_2$, 0.03 wt% $MgCl_2$ and 0.05 wt% $MgCl_2$.

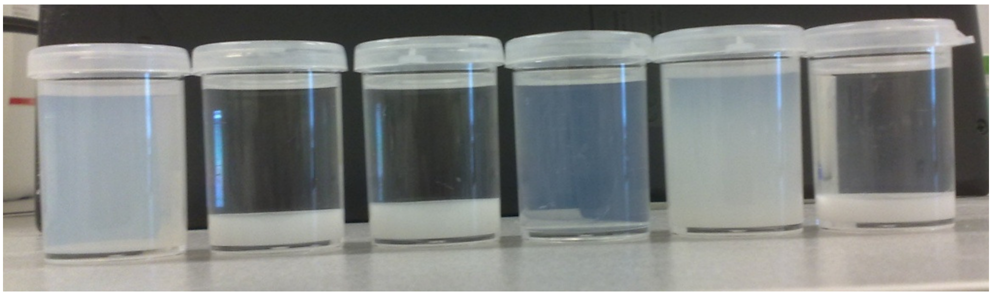


Figure 11. Appearance of salt stability samples of UFSS28 after one week. From left to right 0.02 wt% $CaCl_2$,0.06 wt% $CaCl_2$, 0.10 wt% $CaCl_2$, 0.01 wt% $MgCl_2$, 0.03 wt% $MgCl_2$ and 0.05 wt% $MgCl_2$.

The silica sols UFSS20, UFSS21 and UFSS23, which were derivatized by two different silanes, display a poor stability towards electrolytes. The reason for this might be a synergistic effect originating from the bridging caused by MPEG2000 and the hydrophobic effect introduced by the isobutyl silane. The increase of counterions enables the particles to come close to each other, an effect increased by the hydrophobic isobutyl groups introduced to the silica surface, then the MPEG2000 chains are able to form bridges between the particles thus causing flocculation of the particles. When only isobutyl silane exists on the silica surface no attracting forces exists between the particles except van der Waals interactions which are unable to overcome the repulsive electrostatic interactions of the silica surface. When only MPEG2000 containing groups exist on the silica surface the stabilizing effect is most likely due to electrostatic stabilization and possibly to a lesser degree the intended steric stabilization.

These observations indicate that the most effective stabilization of the silica sol is obtained when only one silane is bond to the silica surface. No conclusions can be made regarding the increase of stability related to the type of silica derivatization since the difference in surface coverage of UFSS26 and UFSS28 is that about four times more silane is grafted to UFSS26 compared to UFSS28. There might also be minor differences in pH between the different silica sols since they did not have the same pH prior to the dilution.

Surface tension of modified silica sols

The surface tension measurements of some of the silica sols produced from derivatization of Bindzil® 40/130 were measured at 5 wt% SiO_2 concentration in water. The results from these measurements can be seen in table 9.

Table 9. Surface tension of derivatized silica sols

Silica sol	First measurement surface tension (mN/m)	Second measurement surface tension (mN/m)
UFSS20	64.3	64.9
UFSS21	65.4	65.2
UFSS23	65.2	65.3
UFSS25	70.7	71.0
UFSS26	71.1	71.1
UFSS28	64.0	64.0

Silica sols modified with isobutyl silane only do not exhibit increased surface activity of the silica sol, as non modified silica sols has a surface tension of 71 mN/m at 5 wt% SiO_2. When MPEG2000 containing silanes are attached to the silica surface the surface tension is decreased implying that silica particles modified with MPEG2000 are surface active. The decrease in surface tension induced by the MPEG2000 is however not very significant and is almost the same independent of the amount of MPEG2000 relative to the isobutyl silane. The silica sols with higher amount of MPEG2000 display slightly lower surface tensions.

The surface tension of non-derivatized silica sols are approximately the same as of water even at relatively high concentrations of silica particles. But for Bindzil® CC30, which is functionalized by a surface coverage of approximately 2 µmol 3GTO/m^2, the surface tension is somewhat reduced when the concentration of silica particles is increased. [34] The reduction of the surface tension induced by Bindzil® CC30 is however less significant than the decrease induced by the addition of silica particles modified with MPEG2000 containing silanes, but still more than the nonexistent decrease by isobutyl modified silica sols. This is another indication that not only 3GTO is grafted to the silica surface since that would have resulted in a lesser degree of surface tension decrease than Bindzil CC30 induces, due to lower surface coverage of the modified silica sols in this study.

These results further indicate that already small amounts of MPEG2000 grafted to the silica surface significantly decrease the surface tension independently of the hydrophobic silica modification introduced by isobutyl. This is probably due to the size of the isobutyl group being too small or too few to introduce hydrophobic interactions able to counteract the electrostatic interactions of the charged silica particles thus making them hydrophobic enough to migrate towards the surfaces. The surface activity of MPEG2000 is however already at low surface coverage enough to decrease the surface tension significantly. This is probably due to the size of the MPEG2000, which enables it to already at very low surface coverage introduce enough surface activity to the silica sol to lower the surface tension. Even UFSS23, which displayed an extremely low yield in the condensation of the silanes, induces a significant decrease of the surface tension. This also indicates that MPEG2000 containing silanes are present at the surface of UFSS23.

Emulsification of ASA

Emulsification of ASA was tested using UFSS20, UFSS21, UFSS23, UFSS25, UFSS26 and UFSS28 as emulsion stabilizers. The size of the emulsion droplets can be seen in table 10. UFSS25 and UFSS26 are not included in this table due to the emulsions produced by these silica sols almost completely creamed after less than 30 seconds which makes them unsuitable as emulsifiers for ASA. The commercially available ASA emulsifier Eka SA 650, consisting of a mixture of silica sol, with particle diameters of 7-9 nm, and an amine, was used as a reference. The measurements of UFSS28a and UFSS28b originate from the same emulsion but UFSS28b was measured approximately 3 minutes later than UFSS28a.

As can be noticed in table 10, UFSS28 produces emulsion droplets of approximately the same size as Eka SA 650 and despite the larger size range it does show potential as an emulsifier for ASA. UFSS20, UFSS21 and UFSS23 produce too large droplets to yield an effective sizing of the paper by ASA.

Table 10. Emulsion droplet size from ASA emulsification experiments.

Silica sol	D(v, 0.1) (µm)	D(v, 0.5) (µm)	D(v, 0.9) (µm)	% droplets < 2 µm	Surface area (m^2/g)
Eka SA 650	0.14	0.44	1.4	96.1	20.14
UFSS20	0.23	2.59	12.98	43.9	9.09
UFSS21	0.64	7.22	14.42	11.8	3.12
UFSS23	10.58	22.70	45.70	0	0.3
UFSS28a	0.11	0.33	2.36	87.7	25.55
UFSS28b	0.16	0.70	2.94	82.0	16.10

The size distribution of the ASA emulsion droplet size produced by Eka SA 650 and UFSS28 are displayed in figure 12. Eka SA 650 displays a more narrow distribution than UFSS28, but the dominating peak of UFSS28a consists of droplets slightly smaller than Eka SA 650. When comparing UFSS28a and UFSS28b the dominating peak of UFSS28a has decreased while the second peak has increased to approximately the same size, indicating coalescence of the droplets. This might be due to poor stability of the formed emulsion but it cannot be concluded without further experiments.

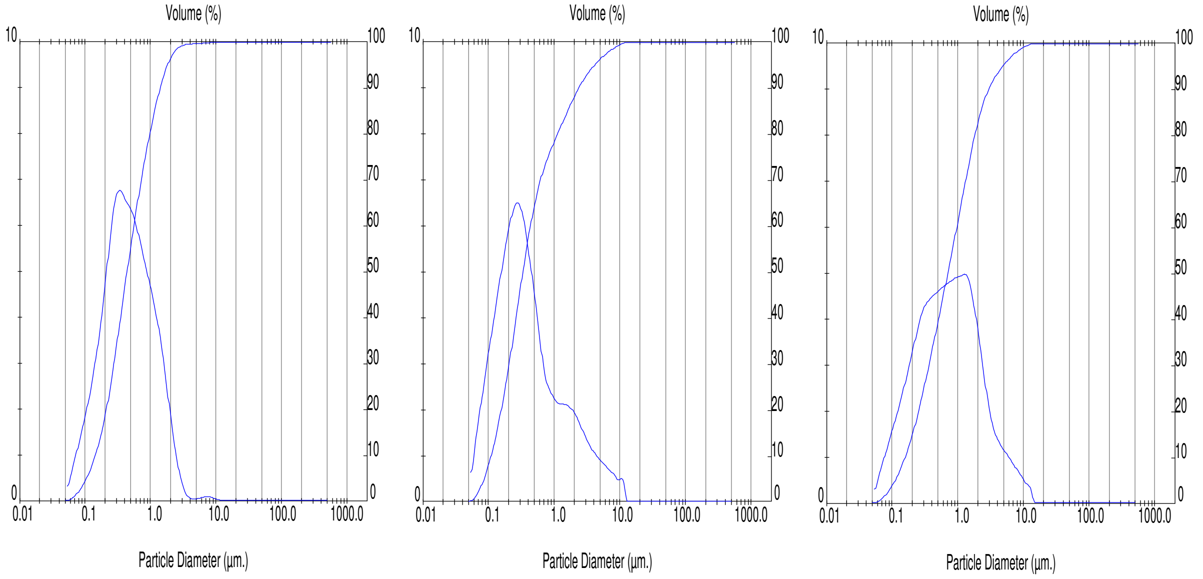


Figure 12. Size distribution of emulsion droplets from ASA emulsion tests. From the left Eka SA 650, UFSS28a and UFSS28b

Despite the fact that UFSS28 consists of larger, and thereby fewer, silica particles than Eka SA 650 they are able to produce ASA emulsion droplets of approximately the same size.

No apparent correlation can be observed between the emulsification properties of the silica sols and the reduction of the surface tension of water. A very small difference in surface tension reduction between two silica sols can be accompanied by a huge difference in emulsion droplet size, which can be clearly seen with UFSS20 compared to UFSS28, surface tensions of 64.6 and 64.0 mN/m respectively while the percent of emulsion droplets below 2.0 µm are 43.9% and 87.7% respectively. The only clear relationship between surface tension and ability to emulsify ASA is that if the silica sol is unable to reduce the surface tension of water it is also unable to form stable emulsions of ASA.

The higher stability towards electrolytes introduced by grafting of one type of silane to the silica surface compared to the lower electrolyte stability when two different silanes are grafted to the silica surface makes the silica sols containing two different silanes unsuitable as ASA emulsifiers since they hardly can increase the stability of ASA emulsions towards electrolytes. Since silica sols surface modified with only isobutyl silane are unable to form sufficiently stable emulsions of ASA the surface modified silica sols that might be suitable for further ASA emulsion experiments are silica sols modified by MPEG containing silanes.

Conclusions

This study has provided an effective synthetic route to react 3GTO with a variety of nucleophiles producing silanes with huge variety of chemical properties. Also the grafting of these silanes along with isobutyl silane to silica surfaces was determined. The salt stability and the ability to emulsify ASA of such silica sols was evaluated.

To obtain a high degree of opening of the epoxide of 3GTO by MPEG2000 a stoichiometric amount of TFA was needed. The low boiling point of TFA enables the TFA to be recycled together with the solvent providing a technically viable method to make use of this synthetic route on a large scale.

Two hours at 90°C yields a grafting of 90% of the added isobutyl silane to the silica surface, but for grafting of MPEG2000 containing silanes, the same reaction conditions only provides a yield of around 20%, probably due to its larger structure blocking parts of the silica surface and possibly its own silanol groups. The grafting of silane to the silica surface was confirmed to be significantly higher at alkaline pH than at acidic pH.

A grafting of up to around 2 µmol silane / m^2 to silica particles, with a diameter of 20 nm, can be conveniently carried out at 22 wt% SiO_2 without gelling of the silica sol. The isobutyl silane has proven to be more sensitive towards gelling than the MPEG containing silanes why syntheses where high amounts of isobutyl is wanted at the silica surface should be carried out at even lower SiO_2 concentrations. Silica sols surface modified with isobutyl silane must be ultrafiltered to remove remaining ungrafted silane to prevent gelling and thus provide storage stability.

The stability towards electrolytes was higher by the grafting of one silane to the silica surface compared to grafting of two silanes. If two different, one hydrophobic and one hydrophilic, silanes were grafted to the silica surface the stability towards electrolytes was severely decreased.

In emulsion tests with ASA the size of the emulsion droplets was decreased when the amount of MPEG2000 containing silane compared to amount of isobutyl silane increased. The smallest, and thereby most promising, emulsion droplets were obtained when the silica particles were surface modified with only MPEG2000 containing silane. No clear correlation can be observed between the decrease of surface tension of water induced by the particles and size of emulsion droplets. Silica particles modified with only isobutyl silane were unable to emulsify ASA as creaming occurred within 30 seconds. Since silica particles modified with both isobutyl silane and MPEG2000 containing silane display a significant decrease in stability towards electrolytes silica sols surface modified only by MPEG2000 containing silane have the highest potential to produce ASA emulsions with an increased stability towards electrolytes. These results indicate that ASA emulsions with improved stability towards electrolytes can be obtained by the developed method.

Future studies

More studies regarding different nucleophiles in the synthesis of functional silanes are interesting, especially different lengths of the MPEG chain, Berol type surfactants and different alcohols and amines.

Further studies also include achieving a higher yield of the condensation of MPEG containing silanes to the silica surface. Further studies of silica sols with these surface modifications include using silica particles of different sizes and also alternating the surface coverage by MPEG of the silica particles. Studies of the stability towards electrolytes related to the amount and type of surface modification are also interesting.

The emulsification of ASA should also be studied further, for example by optimizing the surface modification and particle sizes to achieve stable emulsion droplets of suitable size. Further the salt stability of these ASA emulsions should be studied.

Evaluation of other possible fields of applications should be done, since these silica sols may be useful for other purposes than surface sizing of paper.

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Appendix I

A complete list of the silica sols derivatized during this study can be seen in table I.

Table I. Derivatized silica sols. SS1 – SS14 were produced by derivatization of Bindzil® 30/130 (pH 1.9) while SS15 – SS29 were produced from Bindzil® 40/130 (pH 9.1)

Abbreviation	SiO_2 concentration	Used silanes	Appearance	Appearance after ultrafiltration
SS1	32 wt%	MP1 (1 µmol/m^2)	Sedimented within 48 hours	
SS2	32 wt%	MP1 (2 µmol/m^2)	Slightly whiter than 30/130	Gelled
SS3	32 wt%	MP2 (2 µmol/m^2)	Gelled within 12 hours	
SS4	32 wt%	MP3 (2 µmol/m^2)	Whiter than 30/130	Much whiter and viscous than 30/130
SS5	32 wt%	iBuSi (2 µmol/m^2) MP1 (1 µmol/m^2)	Settled after a few hours	
SS6	32 wt%	iBuSi (2 µmol/m^2)	Gelled in the reactor	
SS7	32 wt%	iBuSi (1 µmol/m^2)	Gelled within a month	As before ultrafiltration
SS8	32 wt%	iBuSi (1,67 µmol/m^2)	Gelled in the reactor	
SS9	32 wt%	iBuSi (1,33 µmol/m^2)	Gelled within 2 weeks	As before ultrafiltration
SS10	32 wt%	iBuSi (1,33 µmol/m^2)	Gelled within 16 hours	
SS11	32 wt%	iBuSi (1 µmol/m^2)	Gelled within six weeks	As before ultrafiltration
SS12	ca 32 wt%	MP8 (1 µmol/m^2)	Settled within 24 hours	Settled within 24 hours
SS13	ca 32 wt%	MP8 (1,5 µmol/m^2)	Settled within 48 hours	
SS14	32 wt%	iBuSi (1 µmol/m^2) MP8 (1,5 µmol/m^2)	Settled within 24 hours	
SS15	40 wt%	iBuSi (1 µmol/m^2) MP8 (1,5 µmol/m^2)	Gelled in the reactor. Settled within a week after redispersion	
SS16	40 wt%	iBuSi (1 µmol/m^2) MP8 (1 µmol/m^2)	Gelled in the reactor. Settled within a week after redispersion	

SS17	33 wt%	iBuSi (1 µmol/m^2) MP9 (0,75 µmol/m^2)	Gelled in the reactor. Very turbid and white efter redispersion	
SS18	33 wt%	iBuSi (1 µmol/m^2) MP9 (0,5 µmol/m^2)	Gelled in the reactor. Very turbid and white efter redispersion	
SS19	29 wt%	iBuSi (1,5 µmol/m^2) MP9 (0,75 µmol/m^2)	Gelled in the reactor. Settled within a week after redispersion	
SS20	22 wt%	iBuSi (1 µmol/m^2) MP12 (0,75 µmol/m^2)	Slightly whiter than 40/130	As before ultrafiltration
SS21	22 wt%	iBuSi (1 µmol/m^2) MP12 (0,5 µmol/m^2)	Slightly whiter than 40/130	Slightly whiter than SS21
SS22	22 wt%	iBuSi (1,5 µmol/m^2) MP12 (0,5 µmol/m^2)	Gelled in the reactor	
SS23	22 wt%	iBuSi (1 µmol/m^2) MP12 (0,25 µmol/m^2)	Slightly whiter than 40/130	As before ultrafiltration
SS24	22 wt%	MP13 (1 µmol/m^2)	Whiter than 40/130. Some precipitate formed in the reactor	
SS25	22 wt%	iBuSi (1 µmol/m^2) “prehydrolyzed”	As 40/130	As before ultrafiltration
SS26	22 wt%	iBuSi (1 µmol/m^2)	As 40/130	As before ultrafiltration
SS27	22 wt%	MP13 (0,75 µmol/m^2)	Whiter than 40/130. Some precipitate formed in the reactor	
SS28	22 wt%	MP14 (1 µmol/m^2)	Whiter than 40/130	Slightly whiter than SS28
SS29	22 wt%	iBuSi (1 µmol/m^2) MP14 (1 µmol/m^2)	Whiter than 40/130	

Appendix II

All performed particle size measurements can be seen in table II.

*Table II. Complete table of measured particle diameters. Silica sols abbreviated SS and UFSS corresponds to before and after ultrafiltration respectively. *does not meet the quality criteria of the software, †could not be filtered through a 0.2 µm filter before measurement*

Silica sol	Z average (nm)	Polydispersity
40/130	28,00	0.119
40/130 in NaCl solution	33,86	0.032
30/130	33,04	0.110
SS2	99,95	0.235
SS4*†	821,0	0.816
UFSS4*†	636,4	0.509
SS7	40,16	0.169
UFSS7	47,35	0.490
SS9	48,89	0.192
UFSS9	107,1	0.283
SS17†	163,2	0.210
SS18†	159,3	0.211
SS20	35,38	0.124
UFSS20	32,08	0.207
SS21	32,63	0.136
UFSS21	26,38	0.246
SS23	27,99	0.104
UFSS23	21,69	0.294
SS25	25,03	0.128
UFSS25	22,65	0.215
UFSS25 in NaCl solution	35,75	0.049
SS26	25,01	0.108
UFSS26	22,00	0.261
UFSS26 in NaCl solution	36,34	0.058
SS28	31,19	0.085
UFSS28	20,63	0.265
UFSS28 in NaCl solution	38,56	0.046
SS29	33,44	0.082