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Surface modified silica nanoparticles as emulsifier

Master of Science Thesis in the Master Degree Programme Materials and Nanotechnology

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This work has been performed at Eka Chemicals in cooperation with Chalmers
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ABSTRACT

Resent research work at Eka Chemicals and Chalmers University of Technology has involved methods for surface modification of silica particles. The surface modification comprises chemical modification of the silica surface with silanes. The silanes are covalently attached via condensation reaction and introduce hydrophilic and/or hydrophobic groups to the silica surface. These particles have been shown to be effective as emulsifier in model oil/water system.

In this study, the hydrophilic silane was synthesized by reacting a hydrophilic poly (ethylenglycol) methylether (MPEG) with a coupling agent, (3-Glycidyloxypropyl) triethoxysilane (GPTES). The hydrophilic MPEG-GPTES and hydrophobic isobutyl (trimethoxy) silane were hydrolyzed and grafted to the silica particles under alkaline conditions to avoid physisorption of the MPEG chain to the surface and favor the condensation reaction. Different ratios of the silanes were grafted to the particles to alter the surface coverage and thus the hydrophilic and hydrophobic character.

The amount of covalently bond hydrophilic silane to the silica surface was evaluated by NMR diffusometry. The most efficient grafting of the hydrophilic silane corresponded to a surface coverage of covalently bond MPEG-GPTES of 0.105 $\mu mol/m^2$. Isobutyl silane was grafted corresponding to a surface coverage of 0.5 to 3 $\mu mol/m^2$ with yields around 96 % measured by HPLC.

Surface and interfacial tension of the sols was measured at pH 2, 4, 7 and 10 to study effects of pH and evaluate the character of the particles with focus on emulsions. The most surface active particles were the ones grafted with 0.105 $\mu mol/m^2$ MPEG-GPTES and 1 $\mu mol/m^2$ isobutyl silane. These particles showed the lowest surface tension values and also the lowest interfacial tension value between paraffin oil and water.

Finally the modified silica particles were evaluated as emulsifier in the model oil-water systems of squalane, n-heptane and paraffin oil. Emulsification parameters were studied and the emulsion droplet sizes were evaluated by laser light diffraction and optical microscopy. Emulsification tests showed that the paraffin oil/water (70/30) system emulsified with 2 wt% modified silica particles of the oil mass at an operating speed of 24000 rpm for 5 min gave the best emulsions.

Keywords: Silica, Surface activity, Emulsion, Pickering emulsion, GPTES, MPEG2000

Acknowledgements

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1. Introduction

Silica is one of the main components of the crust of the earth. It has played an important role for the development for many plants and animals. Our civilization has been using silica in different forms for a long period of time e.g. as flint for tools and weapons. In present technology the great variety of application areas ranges from e.g. catalyst in oil refinery to microcircuits and fiber optics [1].

Since the 1940's stable dispersions of discrete particles of amorphous silica has been commercially available [2]. This product type named colloidal silica has been developed through optimization of the shape, size and stability. The industrial uses of colloidal silica are wide-ranging and examples could be as components in paint, flocculation agents and as a retention aid in paper industry.

Recent research work at Eka Chemicals in collaboration with Chalmers University of Technology has involved methods for surface modifications of colloidal silica particles. The modifications include chemical modification of the silica surface with silanes. The silanes introduce hydrophilic and/or hydrophobic groups to the silica surface. The surface modified particles have been shown to be effective as emulsifier in model oil/water system.

1.1 Aim of the project

As new input to the research, the relationship between surface activity and surface modification of particles is studied. The particles are tested as emulsifiers to increase knowledge of the systems studied and to be of assistance towards new applications of surface modified silica.

The aim of the diploma work is to prepare surface active silica as colloidal suspension and evaluate their properties with focus on emulsions. Relationships between surface activity and the modification of the surface are studied by measurements of the surface and interfacial tension. The particles with varying hydrophobic/hydrophilic character are tested as emulsifiers in model oil-water systems.

2. Background

In this section background to colloidal silica, emulsions and modification of the silica surface including the synthesis of the hydrophilic silane used in this study are presented followed by an introduction to the characterization techniques.

2.1 Chemistry of colloidal silica

Colloidal silica is a concentrated dispersion of discrete amorphous silica particles in a liquid. If the liquid is organic it is called an organosol but the most commonly used is water and then it is referred to as an aquasol or hydrosol [1]. The particle size is small enough to be unaffected by gravitational forces yet large enough to disassociate from a true solution. This gives a span of particle diameter between 1 and 1000 nm but the characteristic range of commercial silica sols is between 5 to 100 nm [1].

The particles of amorphous silica are built up by a random packing of $[SiO_4]^{4-}$ forming a nonperiodic structure with the general molecular formula SiO_2 [1]. The bulk structure terminates at the surface in two different ways; oxygen on the surface through siloxane groups ($\equiv$Si-O-Si$\equiv$) or silanol groups ($\equiv$Si-OH). Three different forms of silanol are illustrated in figure 1 [3]. The concentration of silanol groups on a maximum-hydroxylated silica surface is approximately 8 μmol/m^2 [4, 5].

Commercially available silica sols are usually produced from sodium silicate solutions neutralized by an acid. The synthesis starts by formation of a sol of silica nuclei via removal of the sodium ion trough ion-exchange. After heating the sol to form nuclei of desired size, dilute solution of sodium silicate is added. The pH is kept at about 8 by adding dilute sulfuric acid. The silicic acid formed under these conditions is deposited upon the silica nuclei. Very good agitation is needed to prevent that any part of the solution is exposed to low pH where aggregation can occur. The alkaline condition prevents the sol from flocculation or gelling by keeping the surfaces negatively charged [2].

Another process used to prepare colloidal silica is the Stöber method [6], which provides controlled growth of well defined silica spheres with narrow size distribution. These properties are fundamental when studying the surface properties of silica particles. In the Stöber method the silica particles are produced by base-catalysed hydrolysis and condensation of tetra alkyl orthosilic acid in an aqueous mixture of an alcohol and ammonia.
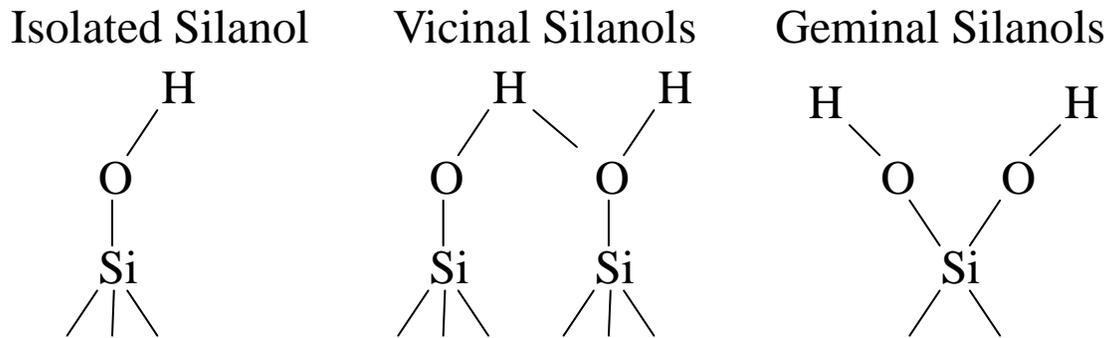
Figure 1. Different forms of silanol groups at the silica surface [2, 3].

Regardless if the silica sol is synthesized or formed by nature, it often has a very low silica concentration. Concentration of the silica sol is usually performed by evaporation of water or ultrafiltration. The latter method has the advantage of low energy requirement and works by removing water, small ions and solutes using a filter which only retains the silica particles [2].

2.1.1 Stability of colloidal silica

Small particles dispersed in solution will take long time to settle if only the gravity and viscous drag force are considered. But the Brownian motion, caused by natural kinetic energy, will cause the particles to move randomly in the solution. This lead to collisions and depending on the forces between the particles they either attract or repel each other [7].

The repulsive forces between two particles in a colloidal suspension need to be larger than the attractive forces to keep the particles from aggregating. The stability of a colloidal silica sol is dependent of attractive Van der Waals forces and the opposite repulsive electrostatic forces. There are also effects such as pH and ionic strength contributing from the medium in which the silica particles are dispersed [8].

A silica sol contradicts from the famous DLVO theory (Derjaguin, Landau, Verwey and Overbeek) which is useful to describe the stability by the ionic double layer for spherical particles. This theory is valid only in the presence of alkali and for larger silica particles. At pH 2 the silica particles has no charge and should according to the DLVO theory therefore be in the least stable region. This is not the case and could be because of steric stabilization from a monolayer of water molecules bonded to the hydroxyl groups on the surface by hydrogen bonding [1, 2, 9].

A silica sol is said to be stable if the particles do not settle or aggregate at a significant rate. The different forms of aggregation are gelation, coagulation, flocculation and coacervation [1].

Gelation of a sol is when a three-dimensional network is formed. The particles link together in branches resulting in increased viscosity and later on forming a solidified network which retains the liquid. The silica concentration of such a system is constant for all macroscopic regions. In the case of coagulation the particles come together in close packed clumps and when flocculation occurs they link together by bridges. For both these cases a precipitate is formed [1, 2].

Coacervation is a result of the particles forming a concentrated liquid phase which is immiscible in the aqueous phase. This is because of the particles becoming less hydrophilic when another material is adsorbed on the surface [2].

2.1.2 PEG-Silica interaction

The silica surface interacts with Poly Ethylene Glycol (PEG) through hydrogen bonding between silanol groups of the silica and ether oxygens in the PEG chain. The silanol groups act as proton donors and in the work by Rubio and Kitchener [10] the isolated silanols were proposed as the principal adsorption sites. The authors reported that the silica with both hydrophobic groups (either methyl or siloxane) and hydrophilic isolated silanol groups showed the most distinct adsorption and flocculation. The implied mechanism of adsorption was said to be a combination of hydrogen bonding and hydrophobic interaction. They also proposed an explanation of the pH effect on the affinity between PEG and silica to be caused by a competition between water and ether units for silanol sites on the surface. As pH increases the ionization of silica reduces its affinity for nonionic compounds as PEG.

The interaction between PEG and silica could either increase the stability of the suspension by providing steric stabilization or destabilize the suspension by causing bridge flocculation. This is possible irrespectively if the silica surface modified or not [11].

The interaction between silica and a nonionic surfactant of octylphenol polyoxyethylenic TX100 was studied by F. Giordano-Palmino et al. [12]. They suggested that the nonionic surfactant form micelle-like aggregates on the silica surface which help to create flocculation by bridging between the particles. The optimum flocculation for the suspension stability was found to be at half surface coverage.

2.2 Emulsions

A dispersion of two immiscible liquids is called an emulsion. It often consists of an aqueous phase and an organic phase, where the aqueous phase commonly refers to the water and organic phase to oil. However examples of emulsions with two aqueous phases and non-aqueous emulsions exist. The dispersed phase refers to the droplets in the emulsion and the continuous phase is the liquid surrounding the droplets. Oil-in-water (o/w) and water-in-oil (w/o) emulsions are the two most common types [13, 14].

The various fields of application for emulsions come from the strength of being able to solubilize and transport hydrophobic substances in a water phase. Hence organic solvents could be avoided in different surface treatments including painting, paper coating and road surfacing. Additionally they are also used in cosmetic and food industry because of their diversity in terms of rheology and for drug delivery in pharmaceutical applications [15].

Emulsions are thermodynamically unstable, which means that they break down with time. The specific interfacial area of emulsions tends to decrease as a result from the driving force to lower the interfacial Gibbs energy [14]. The different breakdown mechanisms, see figure 2, include creaming or sedimentation, flocculation, coalescence and Ostwald ripening. Where reversible processes are creaming or sedimentation caused by gravitational forces and flocculation because of e.g. attractive van der Waals forces. The irreversible processes of coalescence and Ostwald ripening are described as merging of two drops due to thin film rupture and material diffusion from small to larger drops respectively. The different processes for destabilization of an emulsion can occur simultaneously [13].
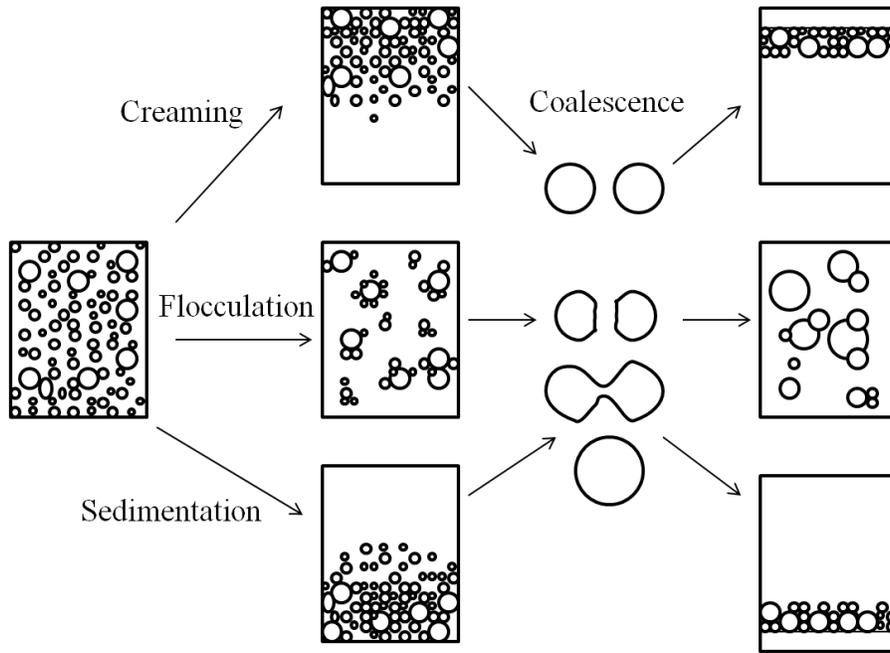
Figure 2. Different breakdown mechanisms of emulsions [13].
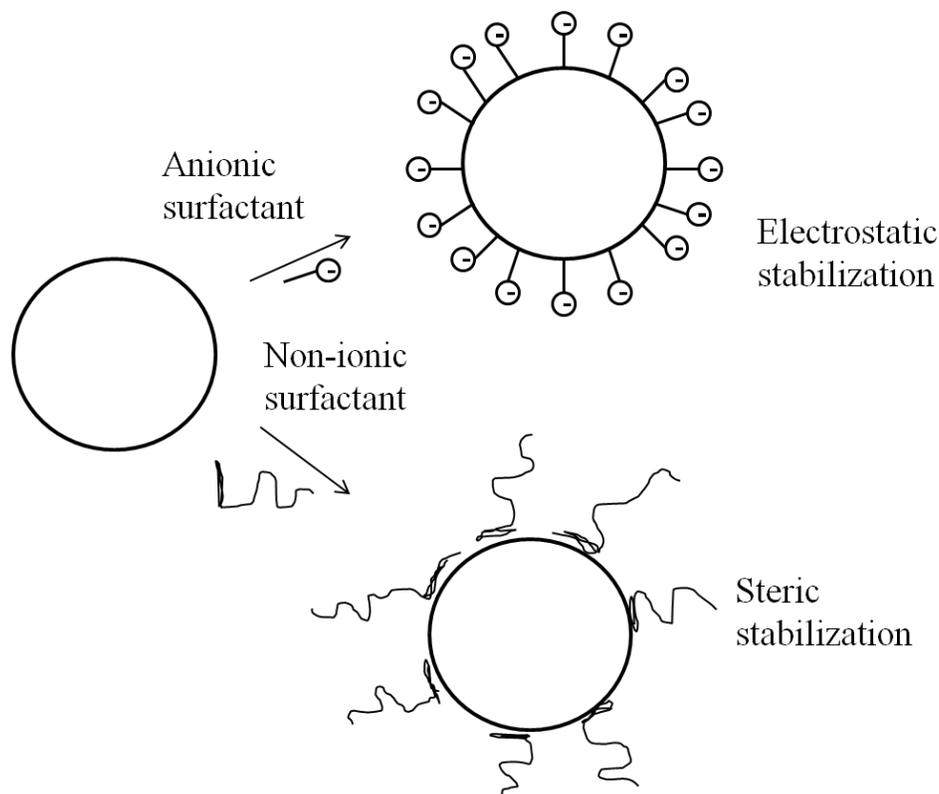
Figure 3. Types of stabilization of an emulsion *[13].*

An emulsifier is in most cases needed to reduce the oil-water interfacial tension for proper dispersion of the dispersed phase. It can be a surface active molecule, polymer or solid particle which lowers the interfacial tension by adsorption to the interface between oil and water [11]. What kind of emulsifier needed depends on the system studied. Figure 3 displays the stabilizing effects provided by an emulsifier which could be either steric or electrostatic stabilization or both [13]. Long term stability is however not usually provided by the emulsifier. In such cases a stabilizer is often added to prolong the shelf-life of the emulsion. The stabilizer usually consists of a water soluble polymer which is slowly diffused to the phase boundaries to stabilize the oil-water interface [11, 13].

The Bancroft's rule [16] stated in early 20th century say that the liquid in which the emulsifying agent is more soluble in will constitute the continuous phase. This was developed even further by Griffin [13, 17] in 1949 by introducing a hydrophilic-lipophilic balance (HLB) for non-ionic surfactants. This gave a powerful tool to screen surfactants for a specified application. Equation 1 is used for calculation of the HLB number of alcohol ethoxylates and alkyl ethoxylates.

$$HLB = \frac{wt\% \; ethylene \; oxide}{5} \qquad Eq.\,(1)$$

Surfactants with a HLB number of 3-6 is suitable for w/o emulsions while o/w emulsions required surfactants with HLB number in between 8-18 [13, 17]. A development of this method

by Davies [13, 17] was to calculate the HLB number using assigned contribution numbers to the constituent groups of the surfactant, see equation 2.

$$HLB = 7 + \sum (hydrophilic\ group\ numbers) + \sum (lipophilic\ group\ numbers) \quad Eq.\,(2)$$

The HLB method is as mentioned simply a screening tool for selection of appropriate surfactant and there are other factors dictating the quality of the emulsion. There could be impurities in the oil, electrolytes in the water and other additives or cosurfactants affecting the method [13]. The temperature sensitivity of non-ionic surfactants like polyoxyethylene also affects the type of emulsion along with the ratio between oil and water [13].

2.2.1 Pickering emulsions

Pickering emulsions are described as emulsions stabilized by fine solid particles and the name comes from the scientist who started to study them in the beginning of 20th century [18]. The solid particles adsorbs at the interface as a monolayer film and hinders droplets from coalesce trough steric hindrance. The criteria needed to be fulfilled are said to be that the particle size have to be smaller than the droplet size and the surface of the particle need to be wetted by the two phases [19, 20]. Particles which form a 90° contact angle (measured through the water phase) with the emulsion droplets gives the best stabilizing effect, see figure 4. The liquid which wet the particles the most will constitute the continuous phase of the emulsion. Thus, hydrophilic particles creating a contact angle below 90° will be at the interface stabilizing oil-in-water emulsion while hydrophobic particles with a contact angle above 90° will stabilize water-in-oil emulsions. Particles which are completely wetted by one of the phases will not stabilize the emulsion and instead of being drawn to the interface it will be dispersed in that phase [21]. There is however examples where the type of emulsion formed are not solely dictated by the contact angle formed by the particles. Phase inversion from could be induced by increasing the fraction of the dispersed phase of an emulsion stabilized by particles [22, 23].
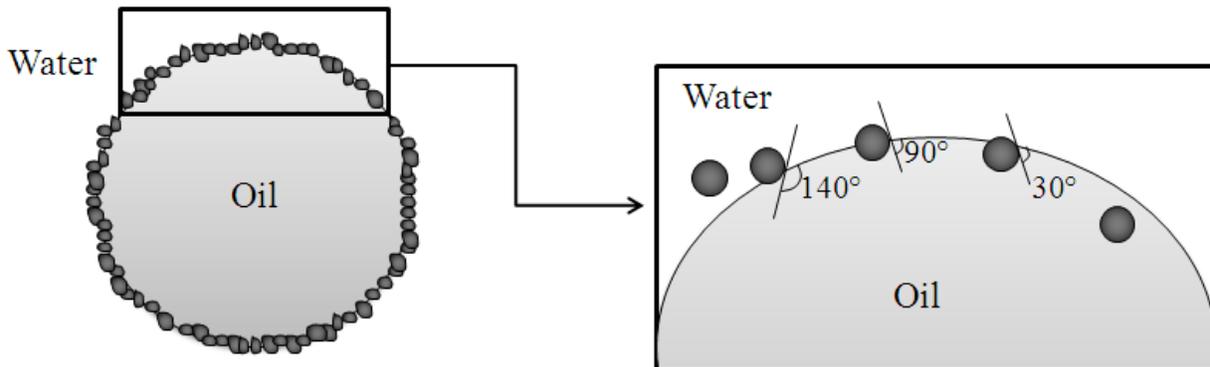

Figure 4.Particle stabilization of an emulsion [13].

The group of B.P Binks [22] studied how the wettability of silica particles stabilizing an emulsion is determined by the hydrophilic-lipophilic balance of the particles. In the case of very hydrophilic or hydrophobic particles the emulsion droplets exceeded 100 μm and were unstable to coalescence. The silica particles with intermediate hydrophobicity resulted in emulsions indefinitely stable towards coalescence and with submicrometer droplets. They also noticed a phase inversion from w/o- to o/w-emulsion when increasing the volume fraction of water, leading to decreased stability of the emulsions [22, 23]. For water-in-toluene emulsion they registered how an increase in particle concentration increased the viscosity of the continuous oil phase leading to enhanced stability to sedimentation [23].

2.2.2 Pickering emulsions with co surfactant

A co surfactant is often used to control the contact angle to help creating the emulsion. The co surfactant could additionally decrease the stability of the emsulsion after it is formed. The following review of research deals with Pickering emulsions when a co surfactant is present.

In a research by B.P. Binks and S.O. Lumsdon [24] the stability of oil in water emulsions stabilized by silica particles was studied. The dependence of the extent of particle flocculation and surface charge were investigated by varying the pH and salt concentration. Their results indicates that salt was needed for stabilizing emulsions from creaming and coalescence and the stability effects were dependent of type of salt. A significant increase in emulsion stability was shown at conditions were the silica particles were weakly flocculated. Complete flocculation resulted in destabilization of emulsions.

In a paper by Midmore [25] the stability of oil in water emulsions stabilized by non-ionic polyoxyethylene surfactant and silica was investigated and a synergy between the two was demonstrated. Neither the silica nor the surfactant solely produced a stable emulsion but in combination and the most stable emulsion was formed when using longer polyoxyethylene chains. By the use of freeze fracture TEM photomicrographs it was deduced that the silica arranged primarily as close-packed monolayers and preflocculation to a great extent was not essential for the adsorption.

Another study by Midmore [26] presents preparation of stable oil in water emulsions using a homopolymer of hydroxypropyl cellulose (HPC) to stabilize the emulsions trough flocculation of the silica particles. It was concluded that there was no need of complete coverage of silica particles on the oil droplets since an equivalent coverage of 29 % of close-packed silica achieved sufficient stabilization. The effects of pH were studied both for the silica-HPC interaction alone and the emulsion stabilizing effects. For the pure silica-HPC solution they reported a cloudiness starting at pH 8.0 increasing to complete flocculation at pH 2.5 with a phase separation with sedimenting flocs and supernatant water. The reducing droplet size of the emulsion with decreasing pH was proposed to be caused by increased flocculation of the silica particles. At high pH the stabilizing mechanism is said to be from the polymer costabilizer while at low pH the stabilizing effect comes from flocculated silica at the o/w interface.

In the work by Hassander [27] silica particles was used with different costabilizers to create o/w emulsions with excellent stability towards coalescence. They suggested a two step stabilization mechanism initiated by agglomeration of silica particles followed by adsorption of these at the oil/water interface.

The stability and formation of a Pickering emulsion are dependent of each other and a lot of factors contribute to the droplet size and stability of the emulsion. The particle size, shape, wettability, inter-particle interactions and concentration affect the result as well as the intensity of agitation. The idea of modifying the silica surface is to tailor make the contact angle of silica particles for the right application without the need of an added surfactant [14].

2.3 Chemical modification of silica surface

Chemical modification of the silica surface makes it possible to combine the mechanical and structural properties of the pure silica particles with the ability of specific chemical and physical interaction. This creates a broad field of both industrial and analytical applications. The stationary phase in different chromatographic techniques often consists of modified silica and other areas such as support material in heterogeneous catalysis and as reinforcement agents in composite materials are only to mention a few examples [3].

Organofunctional silanes are commonly used to modify the surface of silica [3]. They have been developed since 1950's and holds their ability to act as a coupling agent due to one organofunctional group, R, and three hydrolysable groups, X, displayed in figure 5 [28, 29].

Exemples of organofunctional silanes are: chloro-, amino- and alkoxysilanes. The most common are the trialkoxysilanes which hydrolyses in water forming reactive silanetriols, see figure 6. The reactive silanetriols condenses to the silica surface via siloxanebonds ($\equiv$Si-O-Si$\equiv$). Both the hydrolysation and condensation reaction rate are at a minimum at intermediate pH. The condensation reaction is slower (hours) than the hydrolysation reaction (minutes) [28, 29].

Silylation of the surface of an aqueous silica sol requires silanes which are sufficiently soluble in water for the hydrolysis to be possible and that the hydrolysed silanes do not self-condensate. Since the chloro- and aminosilanes releases hydrochloric acid and alkali repectively, which increases the reaction rate of the condensation reaction, they are not appropriate for aqueous silylation. Neither are silanes with a too hydrophobic functional group [28, 29].
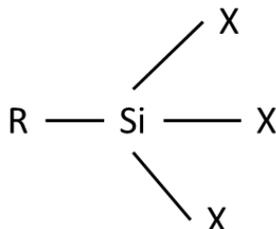
Figure 5.Structure of an organofunctional silane [28, 29].

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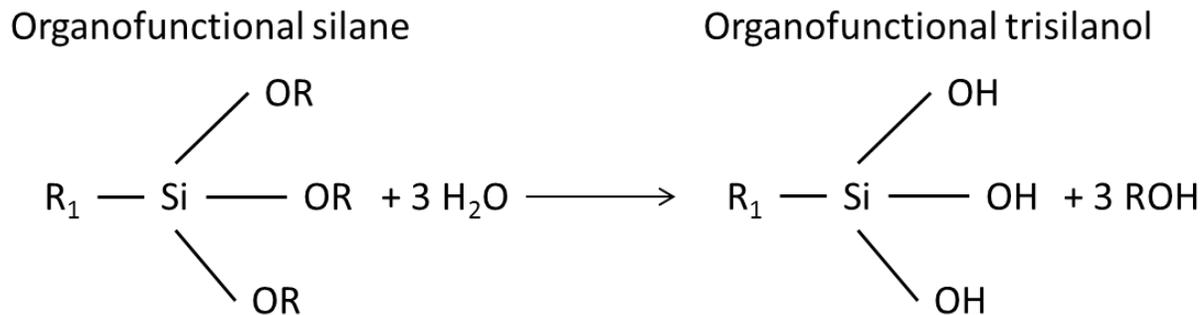
Figure 6.Hydrolysis of an organofunctional silane [28, 29].
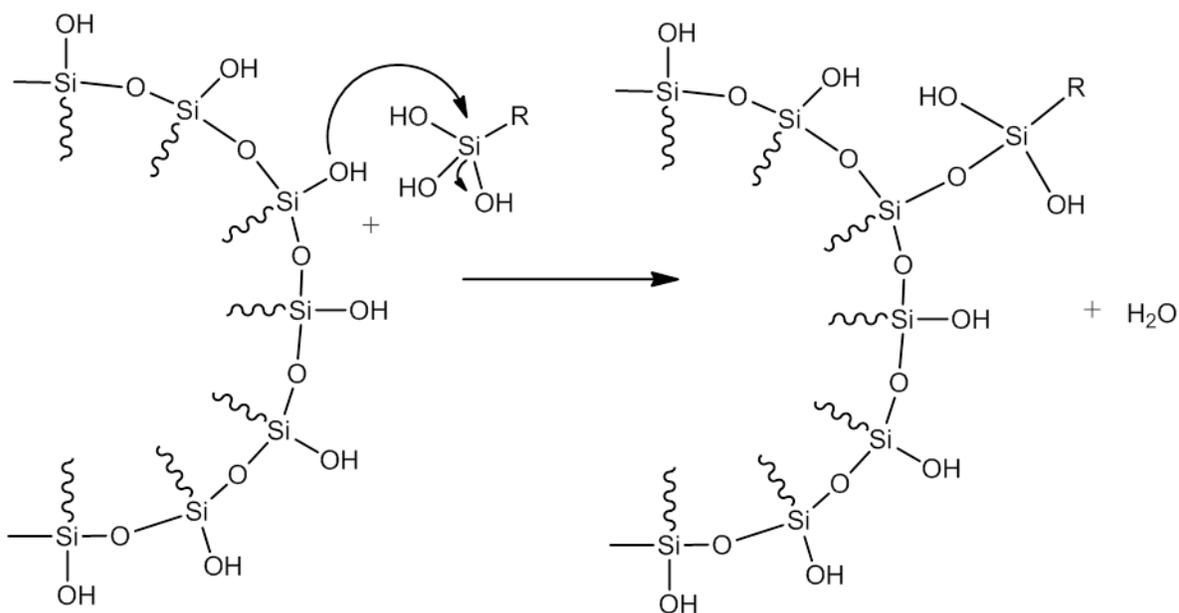
Figure 7.Condensation of an organofunctional trisilanol to a silica surface.

A principle reaction scheme of a condensation reaction of an organofunctional trisilanol to a silica surface is illustrated in figure 7. This modification of the silica surface offers the possibility of introducing hydrophobic and/or hydrophilic groups to the surface.

2.3.1 Synthesis of the hydrophilic silane

The hydrophilic silane in this work was synthesized by reacting a hydrophilic poly (ethyleneglycol) methylether (MPEG) with a coupling agent, (3-Glycidyloxypropyl) triethoxysilane (GPTES).
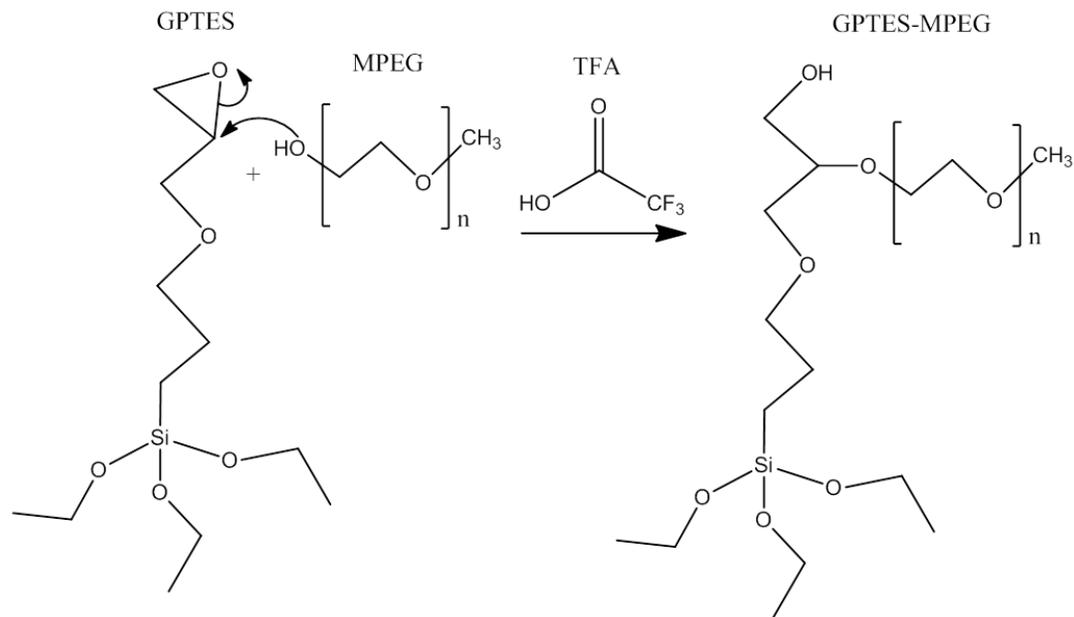
Figure 8.Reaction mechanism of the synthesis of the MPEG containing silane.

Figure 8 shows the mechanism of the epoxide ring-opening reaction catalysed by trifluoro acetic acid (TFA). The use of a PEG ending with a methyl group prevents the formation of a PEG product with a GPTES group at each end. Such product could lead to connection of the silica particles through covalent bridges resulting in poor stability of the silica sol. In order to avoid any unwanted side reactions the synthesis is performed in a water free environment. The water may cause polymerization of the silanes by hydrolysis of the ethoxy groups to silanol groups [30] or perform a nucleophilic attack of the epoxide resulting in a diol.

2.4 Characterization techniques

Here follows a brief description of the characterization techniques that was used in this study.

2.4.1 High Performance Liquid Chromatography (HPLC)

HPLC is a chromatographic technique used to identify and quantify compounds in analytical chemistry [31]. The sample is injected into a solvent which carry the sample through a stationary phase column. Depending on differences in the physical and chemical interactions between the components in the sample and the stationary phase, different components elute from the column at different time. A detector quantifies the eluted compounds and the retention time gives information of the compound characteristics. The preferred HPLC detector is an ultraviolet detector since it has a low detection limit and many solutes absorb ultraviolet light. An alternative among many is the refractive index detector. Even though the detection limit is poor and it is sensitive to temperature and pressure changes, it responds to almost every solute even those with insufficient ultraviolet light absorption.

There are many different techniques in HPLC to separate the components and optimizing the efficiency for the system studied. The most common is the reversed-phase chromatography with a nonpolar stationary phase and a polar solvent. The column is packed with particles with diameters typically of 1.5-5 µm. The efficiency of the column increase with smaller particle sizes. The increased efficiency result in an increased pressure acquired to pump the liquid through the column. Most common is microporous silica particles covered by a covalently bonded liquid phase e.g. octadecyl groups ($-C_{18}H_{37}$).

2.4.2 NMR Diffusometry

A widely used technique to measure random translational motion (diffusion) of molecules or ions is Nuclear magnetic resonance (NMR) diffusometry [32, 33]. This is a noninvasive technique and thus very suitable for studies of molecular dynamics in chemical and biological systems. The atomic nuclei of the probe molecules are exposed to well define radiofrequency magnetic gradient pulses in a static magnetic field. The translational motions of the spins get out of phase due to interactions with the specific gradient pulses. This leads to attenuation of the spin-echo signal which is recorded and used to determine the self-diffusion coefficient.

The self-diffusion coefficient of the particle measured is related to the size according to the Stoke-Einstein relation [34], see equation 3, where k_B is the Boltzmann constant, T is the absolute temperature, µ is the dynamic viscosity of the solvent and d_p is the particle diameter..

$$D = \frac{k_B T}{3\pi\mu d_p} \quad Eq.\,(3)$$

Because of differences between the self-diffusion coefficients of free silane in solution and silica particles with covalently attached silane, it is possible to determine the amount of covalently attached silane to the surface.

2.4.3 Surface tension - Du Noüy ring method

An easy method to measure the suface tension is the du Noüy ring method where the required force to pull a ring of platinum submerged in the liquid through the surface is recorded. Other possibilities are to use a platinum sheet or plate [13].

2.4.4 Interfacial tension – Pendant drop method

The pendant drop method uses optics to measure the surface tension of a liquid or the interfacial tension between two insoluble liquids [13]. A camera records images of a droplet formed from the tip of a needle. The surface and interfacial tension could be calculated from the shape of the drop which depends on the surrounding medium.

2.4.5 Dynamic Light Scattering (DLS)

Dynamic light scattering is a technique to measure the particle size. A laser illuminates the particles and the intensity fluctuations in the scattered light are analyzed and correlated to the

particle size. The intensity fluctuations are due to Brownian motion of the particles. The Brownian motion is caused by the random collisions of particles with the surrounding liquid molecules. The size of the particles are related to its speed and defined by the Stokes-Einstein equation. The smaller particles move more quickly than the large particles. So the measured intensity fluctuations of the scattered light are used to calculate the particle size. Smaller particles move more quickly and thus the intensity of the scattered light is fluctuating more quickly [35].

2.4.6 Laser Light Diffraction

Laser light diffraction is a technique used to measure droplet size and droplet size distribution. The technique uses laser light which passes through a measuring chamber. By the use of an optical model, in modern instruments often the Mie theory [36], the scattering pattern of the measured light is calculated. The diffraction pattern caused by the droplets is characteristic for the size and shape. Because of the scattered rays superimposes additively, the light intensity distribution is used to calculate the volumetric size distribution of the sample droplets by the help of a mathematical deconvolution procedure [37, 38].

2.4.7 Optical Microscopy

Optical microscopy is a technique to view magnified images of small samples. The four basic elements of a microscope are an illumination source, mechanical stage for samples, optical system and detector. The illumination source of visual light interacts with the sample and the optical system with lenses collects and focuses the light into the eye and/or camera [39].

3. Materials

In this section the chemicals used for synthesis of the hydrophilic silane together with the hydrophobic silane are presented. Then the solvent, silica sol and different oils for emulsion study are described.

3.1 Chemicals

The reactants for synthesis of the hydrophilic silane includes coupling agent (GPTES), catalyst (TFA) and hydrophilic nucleophile (MPEG) and are all listed in table 1 together with the hydrophilic silane (iBu). The hydrophilic silane is also reffered to as MPEG-GPTES in this study.

Table 1. Chemicals used for surface modification of silica and synthesis of hydrophilic silane.

Abbreviation	IUPAC name	Structure	Supplier
iBu, iBu-silane or isobutyl silane	Isobutyl (trimethoxy) silane		ABCR
GPTES	(3-Glycidyloxypropyl) triethoxysilane		Momentive Performace Materials
MPEG 2000	Poly (ethylene glycol) mono methyl ether n≈45		Sigma-Aldrich
TFA	Trifluoro acetic acid		Sigma-Aldrich
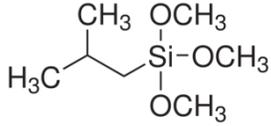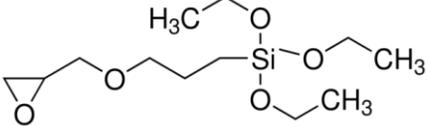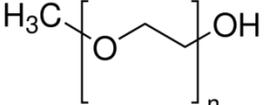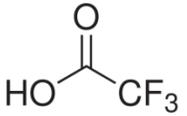
The synthesis of the hydrophilic silane was performed in toluene (Fisher).

The silica sol used in this study was Bindzil® 40/130 with a SiO_2 concentration of 40 wt%, a specific surface area of 130 m^2/g SiO_2 and a pH of 9.07.

The different oils used for emulsion are displayed in table 2.

Table 2. The different oils used for emulsion study.

Name	Cas nr	Supplier	Required HLB	Density (g/cm³)
Paraffin oil	8012-95-1	Riedel-de Haën, Sigma-Aldrich GmbH	10 [13]	0.8585
n-Heptane	142-82-5	Fisher Scientific	10.5-11[*] [40]	0.6795
Squalane	111-01-3	Aldrich	12-12.9[41]	0.810

*Value of hexane

4. Methods

In this section the experimental work is described. First the synthesis of the hydrophilic silane is described followed by the modification of the silica surface and the characterization of the silica sols. The last part of the section presents the emulsification procedure and characterization of the emulsions.

4.1 Synthesis of hydrophilic silane

The synthesis of the hydrophilic silane was performed by the following procedures. The synthesized hydrophilic silanes are referred to as MP (Middle Product).

4.1.1 MP3

MPEG2000 was dried at 60 °C in an oven during night to remove any traces of water. After drying, the MPEG2000 was dissolved in 2.27 ml toluene per gram and the catalyst (TFA) was added after the reaction vessel was equipped with reflux cooling and heated to the reaction temperature 60 °C under agitation. When the reaction temperature was obtained GPTES was added during 2 hours using a syringe pump and the total reaction time was 5 hours. The ratio between MPEG2000, GPTES and TFA was 4:2:1 mole equivalents respectively. The tube between the syringe and the reaction vessel was filled with GPTES to eliminate the dead volume. Toluene and TFA was removed by evaporation under reduced pressure at 50 °C.

4.1.2 MP4 and MP5

For synthesis of MP4 and MP5 a 3Å zeolite as drying agent was employed to reduce any traces of water present. The reaction conditions were the same as for MP3 regarding temperature, agitation and solvent. The addition time of GPTES was extended to 12 hours and the total reaction time to 24 hours. For MP4 the same ratio between MPEG2000, GPTES and TFA was employed as for MP3. MP5 was synthesized with a ratio of MPEG2000, GPTES and TFA of 2:1:1 mole equivalents. The drying agent was filtered off before removal of the solvent and catalyst.

To remove any unreacted starting materials, the product was dialyzed for 24 hours using a Spectra/Por 6 membrane of regenerated cellulose with a 3.5 kDa cut-off value in water adjusted to pH 9.6. Before the dialysis the product was dissolved in water and pH adjusted to 9.6 using NaOH 0.1 M under agitation. The dialyzed product was concentrated through evaporation under reduced pressure at 50 °C before the grafting step.

4.2 Surface modification of silica nanoparticles

The silanes were prehydrolysed for easier condensation to the silica surface. The silica sols were diluted from 40 to 5 wt% SiO_2 using a solution of NaOH with pH 9.6. High pH and dilute sols are preferred for homogeneous and rapid condensation of the silane to the silica surface.

4.2.1 Hydrophobic modification – Isobutyl silane (SS1, SS2, SS3, SS5, SS9 and SS10)
Prehydrolysis of the isobutyl silane was performed by mixing the silane and 30 mole equivalents of water adjusted to pH 9.6 by NaOH 0.1 M. The mixture was put under stirring over the night and the grafting of the isobutyl silane was done the following day.

The surface modifications of silica with isobutyl silane were performed by adding prehydrolysed isobutyl silane drop wise for two hours using a syringe pump. The silica sols contained 5 wt% SiO_2 and were kept at 90 °C in an oil bath during agitation. The total reaction time was 4 hours.

4.2.2. Hydrophilic modification – MPEG-GPTES (SS11 and SS14)
In the case of modification with hydrophilic silane, the prehydrolysed, dialyzed and concentrated silane was added manually using a syringe and the total reaction time was 24 hours. The addition time of the silane was approximately 10 minutes. The reaction conditions were the same as for modification with isobutyl silane regarding temperature, agitation, concentration of the silica sol and pH.

4.2.3 Amphiphilic modification – MPEG-GPTES and Isobutyl silane
When both the hydrophilic and hydrophobic silane was grafted to the silica surface, the order of which the silanes were grafted was varied.

4.2.3.1 SS16, SS17 and SS18
Isobutyl silane was grafted to MPEG-GPTES modified silica particles by the same procedure as when grafted to bare silica particles. Before grafting with isobutyl silane the MPEG-GPTES modified sol was purified by ultrafiltration to remove any unreacted silanes or MPEG molecules.

4.2.3.2 SS15
MPEG-GPTES was grafted to isobutyl modified silica particles by two procedures. The first procedure was performed by addition of a dialyzed, prehydrolyzed and concentrated solution of the hydrophilic silane to the isobutyl modified sol using the same method as when grafting to bare silica particles. The second procedure (SS15) was performed by adding the isobutyl modified sol of 5 wt% SiO_2 drop wise using a syringe pump during 12 hours to a dilute solution

of dialyzed and prehydrolyzed MPEG-GPTES. The low concentration and slow addition time of the second procedure hinders flocculation of the silica particles.

4.2.4 Ultrafiltration of silica sols
The silica sols grafted with hydrophobic silane were purified by ultrafiltration to remove any unreacted silanes using a Millipore Ultrafiltration Cell. The pressure of 2 bar using compressed air was applied under stirring. The membrane was made of regenerated cellulose with a cut-off value of 100 kDa. The purification was performed by diluting the sol four times with distilled water adjusted to pH 9.6 and filtrating the sol back to the original volume. This procedure was repeated four times. For the MPEG-GPTES modified sols the same purification procedure was employed except for the dilution that was repeated six times instead of four.

4.3 Characterization of the silica sols
The procedure to characterize the silica sols are presented in this section.

4.3.1 HPLC
The yield for both the grafting of the iBu-silane to the silica surface and the synthesis of the hydrophilic silane was determined by measuring the unreacted amount of free silane in solution using HPLC. The measurements were performed by the analytical laboratory at Eka Chemicals in Bohus by Robert Butler. The specifications of the equipment and method are displayed in table 3.

Table 3. Specifications of the HPLC.

Column	25 cm reversed phase "C2" experimental column
Detector	RI, La Chrome L-7490
Eluent	H_2O
Standard	Isobutyl (trimethoxy) silane or (3-Glycidyloxypropyl) triethoxysilane
Pump	La Chrome L-7100
Membrane degasser	MERCK solvent degasser L-7612
Control box	Shimadzu SCL-10A VP
Auto sampler	Kontron HPLC 360 or 560
Injector	Loop 100 µl
Loop	7 µl
Flow	0.5 ml/min

4.3.2 NMR Diffusometry

An estimation of the amount of the MPEG containing silane that is covalently attached to the silica surface was determined by ^{1}H NMR Diffusometry on a Bruker DRX600 spectrometer, using a Bruker diffusion probe with a maximum gradient strength of 1200 G/cm. All the measurements were performed using 50 ms diffusion time, 1 ms gradient pulse length and a ramped gradient strength linearly from 15 to 1000 G/cm in the stimulated-echo sequence. Free MPEG in water was used as reference. The measurements were performed by assistant professor Lars Nordstierna at the Division of Applied Surface Chemistry, Chalmers University of Technology.

4.3.3 Du Noüy ring method

The surface tension measurements were performed by the du Noüy ring method on a Krüss Tensiometer K-6. In between each measurement the ring was cleaned using ethanol, water and flame. Each sample was evaluated until at least five measurements in series with less than 1.0 mN/m in deviation. All solutions were evaluated at pH: 2, 4, 7 and 10, by addition of HCl (1 M) and NaOH (0.1 M).

4.3.4 Pendant drop method

The interfacial tension was measured by the pendant drop method on a Theta optical tensiometer from Attension (Biolin Scientific). Samples of modified silica sol, silica sol with added free MPEG2000 and distilled water were evaluated in surrounding media of different oils; squalane, paraffin and n-heptane. Interfacial tensions were measured with the denser liquid in the syringe.

4.3.5 Dynamic Light Scattering

The particles were evaluated by dynamic light scattering (DLS) to compare the particle size of modified silica particles with the bare Bindzil® particles. The measurements were performed on a Zetasizer Nano ZS from Malvern Instruments Ltd. The silica sols were diluted in approximately 2 ml background electrolyte of 20 mM NaCl to a silica concentration of 0.5 wt%.

4.4 Emulsification

Emulsions of 20 g were prepared by adding the oil and the silica sol to a graduated cylinder. The mixture was emulsified using an Ultra-Turrax® T25 basic disperser from IKA®-WERKE with a 17 mm head operating at 11000 or 24000 rpm for 5 min. The emulsions were transferred into glass vials.

4.5 Characterization of the emulsions

The emulsions were characterized by monitoring the destabilization process visually and the emulsions drop size distributions were determined using a Malvern Mastersizer Microplus light diffractometer and an Olympus CX41 microscope. Some of the samples were diluted in distilled water for easier characterization in the microscope.

5. Results and discussion

The first parts of this section present the results from the synthesis of the hydrophilic silane and the grafting of the silanes to the surface of silica. Then the evaluations of the modified sols are presented which include the stability, appearance and surface and interfacial tension at different pH. Finally the results from the emulsion study are discussed with focus on stability and droplet size.

The synthesized hydrophilic silanes are referred to as MP (Middle Product). SS and UFSS are shortenings of silica sol and ultrafiltrated silica sol respectively.

5.1 Synthesis of the hydrophilic silane

The efficiency of the synthesis of the hydrophilic silane was deduced from the measured amount of unreacted GPTES by HPLC. The results from the HPLC measurements are displayed in table 4 along with the reaction specifications. The most efficient synthesized hydrophilic silane was MP3 where 32.2 % of the GPTES remained after reaction.

To investigate if any unwanted side reactions with water could be avoided, a drying agent was used for MP4 and MP5. The drying agent consisted of a zeolite with molecular sieve of 3 Å. The use of a drying agent seems to increase the amount of unreacted GPTES. This could imply that possible side reactions with water are avoided to a greater extend.

Epoxide was detected for MP4 which mean that the epoxide opening of the GPTES was incomplete. This however could be a result of the drying agent reducing the amount of water to open the epoxide. When the amount of catalyst was increased for MP5 no epoxide was detected.

Table 4. HPLC results and reaction specifications of the synthesis of hydrophilic silane.

Abbreviation	Ratio of MPEG2000: GPTES:TFA (moles)	Time of adding GPTES (hours)	Total reaction time (hours)	Zeolite 3Å	Unreacted GPTES (%)	Epoxide detected
MP3	4:2:1	2	5	None	32.2	No
MP4	4:2:1	12	24	2 g/50 ml toluene	49.2	Yes
MP5	2:1:1	12	24	1.659 g/50 ml toluene	43	No

There is a great uncertainty of the formed products and it is not possible to know exactly what has been formed by using only HPLC. The only information gained from the HPLC measurements is the amount of GPTES which has reacted and formed something else plus if any epoxide remains. In addition to HPLC the synthesized hydrophilic silanes were also evaluated by ^{1}H-NMR. The strong signals related to the PEG in the ^{1}H-NMR spectrum did however overlap

with several signals from the epoxide which complicated the analysis. The ^{1}H-NMR analysis only confirmed the results from the HPLC measurements and could unfortunately not be used to identify the desired product.

The calculations necessary for the proceeded work with grafting of the hydrophilic silanes to the surface of silica particles are based on the assumption that the all the reacted GPTES forms the desired product of MPEG-GPTES.

The synthesized hydrophilic silanes were dialyzed to remove any unreacted starting materials which could interfere with the grafting of the product to the surface of silica. The result displayed in table 5 shows a significant decrease in amount of unreacted GPTES.

Table 5. HPLC results of the dialyzed hydrophilic silane.

Abbreviation	Unreacted GPTES (wt %) BEFORE dialysis	Unreacted GPTES (wt %) AFTER dialysis
MP3-1	2.1	0.29
MP4-1	3.2	0.22
MP5-1	2.8	0.34

5.2 Surface modification of silica nanoparticles

This section deals with the surface modification of the silica particles by hydrophobic and/or hydrophilic silane. The grafting with hydrophobic isobutyl silane was evaluated by HPLC at Eka Chemicals. Since no suitable method to study the grafting with hydrophilic MPEG-GPTES was available at Eka Chemicals this was evaluated by assistant professor Lars Nordstierna (Division of Applied Surface Chemistry, Chalmers University of Technology) using NMR diffusometry.

Furthermore, the size of the silica particles was measured by DLS before and after the grafting to see how it is affected. Effects from the heat treatment during grafting were studied by measurement of the surface area before and after treatment of bare silica particles.

5.2.1 Hydrophobic modification – Isobutyl silane

From the HPLC results of the silica particles grafted with isobutyl silane shown in table 6 the reaction yield was calculated to see the efficiency of the synthesis. Grafting of the hydrophobic silane to Bindzil® 40/130 silica particles was efficient with yields around 96 %. The result from the ultra filtrated samples, UFSS1 and UFSS2, show that the sols are indeed purified from free isobutyl silane but since it is equilibrium between free and grafted silane it should be hard to accomplish a 100 % yield. Due to the already high yields when grafting the isobutyl silane, the subsequent isobutyl grafted sols were not ultrafiltrated.

The decrease in yield for the grafting of isobutyl silane to the sols SS16-SS18 could be related to the amount of MPEG-GPTES grafted on the surface. The large silanes of MPEG-GPTES could hinder the isobutyl silane sterically. Since the surface silanol groups of the surface are not fully

occupied with MPEG-GPTES silanes there are still room for the isobutyl silane to covalently bond to the surface. The alkaline conditions when grafting helps to keep the MPEG chain from physically adsorbing to the surface silanol groups which would hinder the grafting of the hydrophobic silane.

Table 6. HPLC results of silica grafted with isobutyl silane.

Abbreviation	Target surface coverage (μmol/m^2)	Added amount of isobutyl silane (g/kg sol)	Type of particles	Free isobutyl silane detected (mg/kg sol)	Yield (%)
SS1	1	1.14	Bindzil® 40/130	50	96
UFSS1	1	1.14	Bindzil® 40/130	30	97
SS2	0.5	0.57	Bindzil® 40/130	20	97
UFSS2	0.5	0.57	Bindzil® 40/130	10	98
SS3	1.5	1.71	Bindzil® 40/130	60	97
SS5	2	2.28	Bindzil® 40/130	110	95
SS9	1	1.14	Bindzil® 40/130	40	97
SS10	3	3.40	Bindzil® 40/130	130	96
SS16 (UFSS14)	1	1.10	UFSS14 (>0.06 μmol/m^2)	60	95
SS17 (UFSS14)	3	3.27	UFSS14 (>0.06 μmol/m^2)	190	94
SS18 (UFSS11)	1	1.14	UFSS11 (0.105 μmol/m^2)	90	92

5.2.2 Hydrophilic modification – MPEG-GPTES

The results from the NMR diffusometry are displayed in figure 9. The percentage of MPEG covalently bond to the silica surface and MPEG free in solution is calculated from the ratio of the slope of the curve at low x-values and at higher x-values.
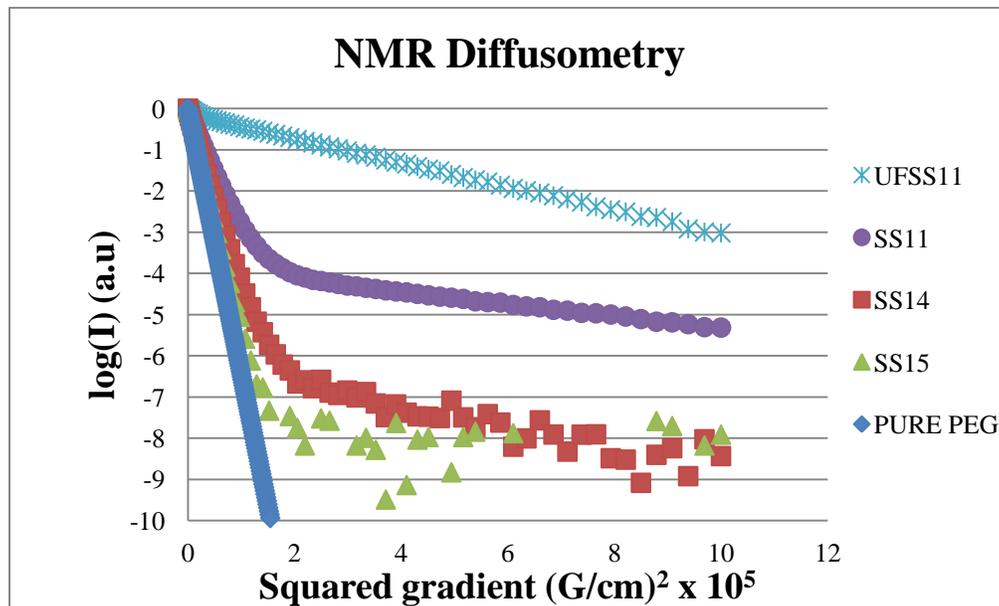

Figure 9. Results from the NMR diffusometry. Free MPEG is used as reference sample.

Table 7. Calculated results and specifications of silica grafted with hydrophilic silane.

Abbreviation	Target surface coverage (μmol/m^2)	Used silane	Type of particles	Percent of hydrophilic silane grafted (%)	Surface coverage (μmol/m^2)
SS11	3.5	MP3-1	Bindzil$^®$ 40/130	3	0.105
SS14	2	MP5-1	Bindzil$^®$ 40/130	>3	>0.06
SS15	2	MP4-2	SS9 (1 μmol/m2 iBu)	>3	>0.06

The calculated results from the NMR diffusometry are presented in table 7. Modification of the silica particles with the hydrophilic silane was performed with a large excess of the silane since previous work has shown inefficient grafting. The highest surface coverage of covalently bond MPEG-GPTES obtained was 0.105 μmol/m^2 for SS11.

When the hydrophilic silane was grafted to isobutyl grafted particles by the first procedure described in 4.2.3.2, the sol turned white in the reactor only a few hours after addition of the

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MPEG-GPTES. The change in appearance of the sol from transparent to white indicates flocculation of the sol and the sol was therefore not further evaluated.

The isobutyl modified sol grafted by the second procedure, SS15, showed no signs of flocculation. The NMR measurement showed that less than 3 % of the silane was grafted to the surface and comparison of the slope of the curves in figure 9 indicates that the amount grafted for SS15 is less than for SS14.

The very low values of $\geq$ 3 % silane grafted demonstrate the suspected inefficiency of the synthesis of MPEG grafted silica. But more precise explanation to why the hydrophilic silane is difficult to attach to the silica surface is hard to deduce. It could be related to the synthesis of the hydrophilic silane or to the grafting of the silane to the silica surface. Surface modification of silica particles using a purchased and well-defined MPEG-silane has been carried out at Eka Chemicals with significantly improved yields. This indicates that the low yields obtained in this work are related to the synthesis of the silane. The low reaction yields of the synthesis of the hydrophilic silane, see table 4, show that the reaction conditions are not optimal.

The hydrophilic modified sols were purified by ultrafiltration to decrease the amount of free MPEG-GPTES as much as possible prior to further modification with isobutyl silane, measurements and emulsification. Measurements with NMR diffusometry of the ultrafiltrated sol, UFSS11, showed that the amount of free MPEG-GPTES in the sample was decreased from 97 to 11 % of. UFSS11 was purified even further and the other sols SS14 and SS15 were purified to the same extent. The amount o free MPEG-GPTES in the samples was decreased to around 1-2 %.

Estimation of how many MPEG-GPTES silanes that were grafted to the surface of each particle for the SS11 are carried out to evaluate if the maximum coverage of the silane is obtained.

Calculations on the amount of available sites per particle were carried out to increase the knowledge of the surface coverage of the silica particles. The surface area per silica particle was calculated according to equation 4. The particle diameter of Bindzil® 40/130 was measured by DLS to 33 nm and estimation based on the surface area per gram and density gives a diameter of 21 nm. But since the estimation assumes a smooth surface and the measurement probably includes a layer of physisorbed water on the silica surface, the particle diameter was approximated to 25 nm.

$$S.A_{particle} = \pi d^2 = \pi \cdot (25 \cdot 10^{-9})^2 \ m^2 = 1.96349541 \cdot 10^{-15} \ m^2 \ \ Eq. (4)$$

An approximation of the number of available sites per silica particle was calculated by equation 5.

$$Nr\ of\ available\ sites\ per\ particle = silanol\ groups\ per\ m^2 \cdot S.A_{particle} \cdot N_A$$

$$= 8 \cdot 10^{-6} \frac{mol}{m^2} \cdot 1.96349541 \cdot 10^{-15} m^2 \cdot 6.022 \cdot 10^{23} \frac{nr\ of\ sites}{mol}$$

$$= 9459 \quad Eq.(5)$$

The surface coverage of 0.105 µmol/m^2 corresponds to 124 silanes per particle, see equation 6.

$$Nr\ of\ hydrophilic\ silanes\ per\ particle = Surface\ coverage\ \cdot S.A_{particle} \cdot N_A$$

$$= 0.105 \cdot 10^{-6} \frac{mol}{m^2} \cdot 1.96349541 \cdot 10^{-15} m^2 \cdot 6.022 \cdot 10^{23} \frac{nr\ of\ silanes}{mol}$$

$$= 124 \quad Eq.(6)$$

MPEG2000 molecule has approximately 45 ether units available for hydrogen bonding to the silanol groups on the silica surface. The 124 hydrophilic silanes grafted to one particle could thus interact with a total of 5580 silanol groups on the silica surface. This would mean a surface coverage of 60 % calculated on available sites per particle.

These calculations are only to get a better idea of the maximum surface coverage possible if all the conditions are right. Of course there are a lot more factors influencing such as pH of the sol and the affinity of water. Disregarding the uncertainties and approximations in the calculations, the surface coverage of the hydrophilic silanes are strongly affected by the pH and configuration of the PEG molecule.

The hydrophilic silanes can be imagined as grafted with an equal distance between each other, forming a grid with one silane in each corner. The calculations above indicate a distance of approximately 4 nm inbetween the hydrophilic silanes. The fully extended MPEG2000 chain in water was estimated by Chern et al. [42] to a length between 8.9 and 16.9 nm. This indicates that a surface coverage of 0.1 µmol/m^2 can be relatively close to the maximum due to steric hindrance of the MPEG-chain.

5.2.3 Particle size measurement (DLS)
The particle size of unmodified Bindzil® 40/130, GPTES-MPEG2000 modified and isobutyl modified particles are listed in table 8. The measured value of 33 nm in diameter is probably a result from a layer of physisorbed water on the silica surface.

Table 8. Particle size of particles with different modifications.

Sample	Particle size Z-average, diameter (nm)	Polydispersity index
Bindzil® 40/130	33	0.042
UFSS11, pH≈9	43	0.102
UFSS11, pH≈2	43	0.132
SS9 (iBu 1 µmol/m^2)	36	0.225

The increase in particle size was measured to be approximately 3 nm in diameter when isobutyl is grafted to the surface and 10 nm when GPTES-MPEG2000 is grafted. This corresponds to a silane length of 1.5 nm for isobutyl silane and 5 nm for GPTES-MPEG2000. Chern et al. [42] estimated the fully extended MPEG2000 chain in water to a length between 8.9 and 16.9 nm. The length of 5 nm indicates that the MPEG chains are not fully extended in the surrounding media and probably is a bit coiled. At low pH the affinity of the PEG chain to the silica surface should be increased due to more hydroxyl groups are available for hydrogen bonding. The measured decrease in particle size are however negligible at low pH and no effect of increased affinity is detected.

The increase in polydispersity index could imply an inhomogeneous grafting among the particles. This seems more prominent when isobutyl is grafted to the silica surface.

5.2.4 Effect of heat treatment on surface area
To study any effects of the heat treatment when grafting the silanes to the surface of the silica particles, the surface area of Bindzil® 40/130 was measured before and after heat treatment. A 5 wt% silica sol of Bindzil® 40/130 at pH 9.6 was kept at 90 °C for 24 hours under agitation and reflux cooling.

The measurements of surface area were performed on a Ω Metrohm 702 SM Titrino. The sample was titrated with 0.1 M NaOH and the surface adsorbed hydroxyl ions. The volume of base needed to increase the pH from 4 to 9 was measured and related to the surface area of the silica.

According to the surface area measurements, the heat treatment did not have any effect on the surface area.

5.3 Stability of the silica sols at different pH
The pH-values of the sols were adjusted to values of 2, 4, 7 and 10 during the surface tension measurements. The adjustments were performed by addition of HCl (1 M) and NaOH (0.1 M). Visual observation of the appearance and stability of the sols were carried out during the measurements to study the pH-dependency of the sols.

In the case of silica sol of bare particles, there were not any visual differences at any pH-value. When the particles were grafted with isobutyl silane, a decrease in stability when the pH was dropped was observed. The appearance of the sols turned white and turbid, see figure 10, when pH was dropped down to 7 or below. This phenomenon was amplified when the surface coverage of isobutyl silane increased. The flocculation or agglomeration was probably due to hydrophobic interaction between the isobutyl regions on the particles along with decreased surface charge. The higher the surface coverage the stronger are the hydrophobic interactions between the particles. This was visible when increasing the surface coverage from 0.5 to 1 μmol/m^2 (SS1 and SS2) leading to a more prominent turbidity and finally sedimentation at pH 2 when as much as 3 μmol/m^2 (SS10) was covered by isobutyl silane.
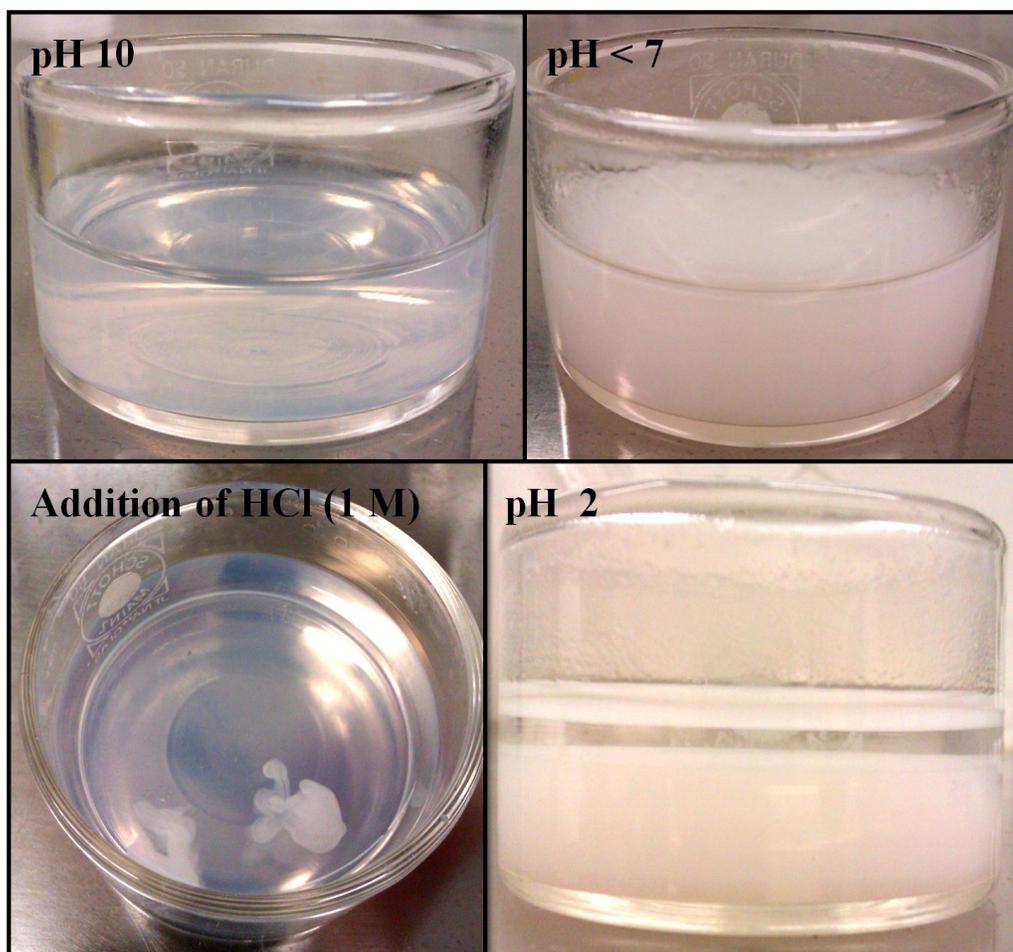
Figure 10. Examples of the appearance of silica sol with a concentration of 5 wt% modified with iBu.

In all the cases where free MPEG is added, both to silica sol of bare particles as well as isobutyl modified silica particles, a flocculation and sedimentation with supernatant water were visible when pH was decreased. This is possibly because of the decrease in ionization of the silica surface attracts the MPEG. The ether units of the MPEG molecule is attracted by the exposed hydroxyl groups of the silica surface which makes is possible to cause bridge flocculation. This is possible also if the surface is modified. But if the surface is completely covered by silanes, no hydroxyl groups are available.

When MPEG was covalently attached to the silica surface, UFSS11 (0.105 μmol/m^2), the adjustment of the pH from 10 to 2 did not affect the appearance at all. The UFSS11 sol did not get turbid and the appearance was more similar to that of sol of bare silica particles. A possible explanation to the appearance of the UFSS11 could be steric stabilization from the MPEG-chains grafted on the surface of the particles. Even if the surface is not completely covered (in terms of available hydroxyl groups), the relatively long MPEG chains grafted to the silica particles provides stability to the sol. This supports the fact that 0.105 μmol/m^2 is relatively close to maximum coverage for MPEG2000. The other silica sol with less MPEG covalently attached to

the surface, UFSS14 (>0.06 µmol/m^2), did not show the same appearance and stability as UFSS11. The sol got white aggregates when adjusting the pH with HCl and lost the transparency at pH 2 indicating an insufficient surface coverage of MPEG-GPTES for providing stability to the sol.

In the case with both hydrophobic and hydrophilic silane covalently attached to the silica surface there were difference in appearance dependent of the order in which the silanes were grafted. The silica sol SS18, isobutyl modified UFSS11, showed no sign of aggregation or loss in transparency in conformity with UFSS11. The two isobutyl modified UFSS14 sols, SS17 and SS16, turned white at pH below 7 and 4 respectively. MPEG-GPTES grafted to isobutyl modified SS15 turned white at pH 4. Sediment was formed for both the SS17 and SS15.

5.4 Surface tension of the modified silica sols

The surface tension was measured at four different pH; 2, 4, 7 and 10, using the Du Noüy ring technique. The sols were measured at a silica concentration of 5 wt% and the pH was adjusted by HCL (1 M) and NaOH (0.1 M).

The effects on surface tension from the starting materials of the synthesis of the hydrophilic silane and isobutyl modified sols have been studied and are presented in appendix A. The result showed only a slight decrease in surface tension of GPTES in compared with pure water and the surface tension decreased as the amount of added MPEG2000 increased. Isobutyl modified sols showed no significant decrease in surface tension compared to pure water when no MPEG was added. There were no sign of pH dependency for any starting material or isobutyl modified sol.
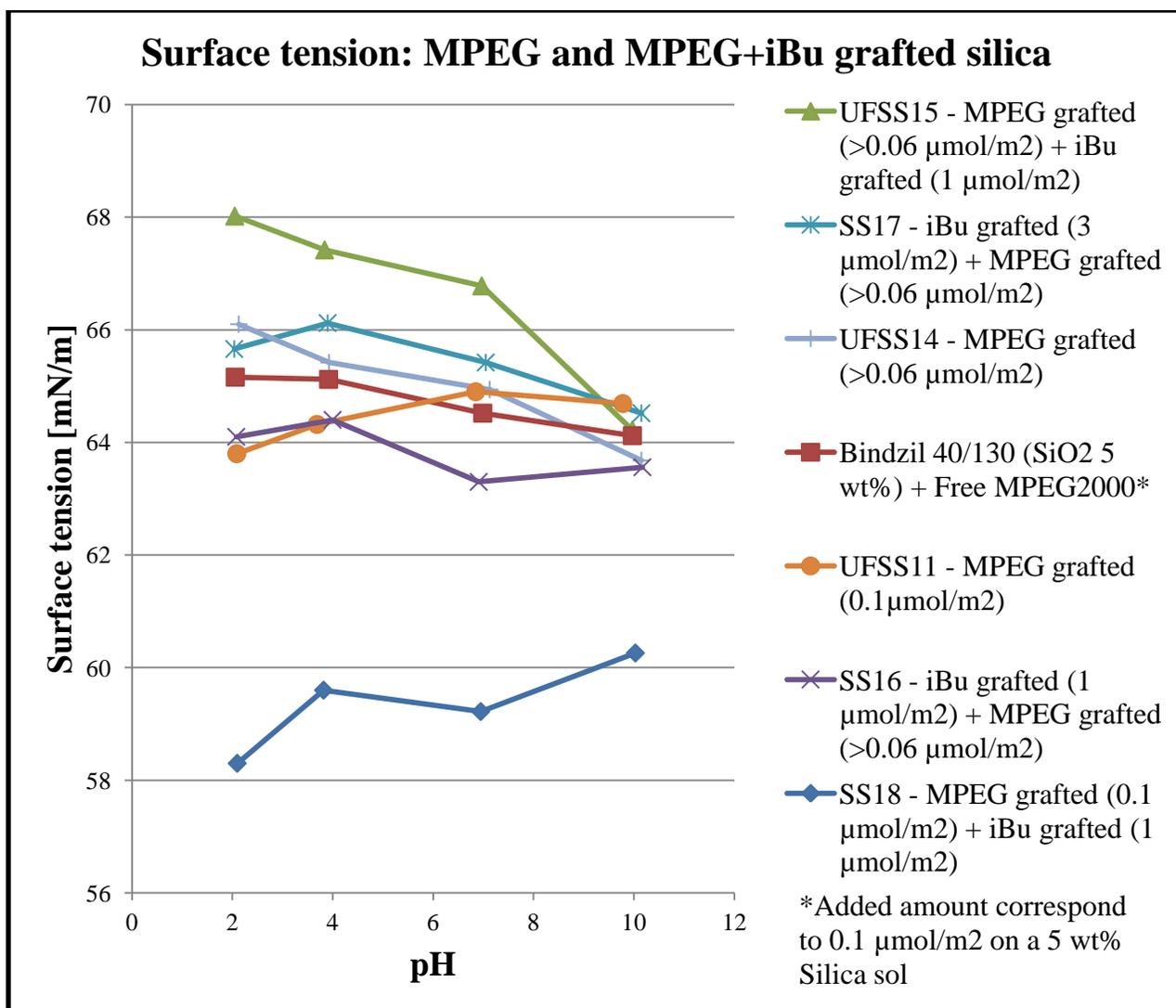
Figure 11. Surface tension values of sols with silica particles grafted with MPEG2000 and iBu silane at different pH. The lines are only added as visual help.

The surface tension values of sols with silica particles grafted with both silanes are presented in figure 11. Surface tension values of the MPEG grafted silica (UFSS11, yellow dots) are in the same order of magnitude as the value of the sol with free MPEG (red squares). This in combination with no visible flocculation occurring, when the pH is lowered, indicates a successful grafting of the hydrophilic silane.

The silica sols UFSS14, UFSS15, SS17 and SS16 show surface tension values in the same order of magnitude as the MPEG grafted UFSS11, which most probably is due to small amounts of free MPEG still left after ultrafiltration. The isobutyl grafted UFSS11, abbreviated SS18, show an increase in surface activity. The surface tension has dropped at pH 10 from 64.7 mN/m (UFSS11, yellow dots) to 60.3 mN/m (SS18, blue diamonds). This indicates that the optimal surface activity is obtained when the particles are modified with both hydrophilic and hydrophobic silanes.

5.5 Interfacial tension

The results from the pendant drop technique are presented in table 9. Three different oils were tested against water, unmodified silica particles and modified silica particles. The measurements were only performed at pH 9.6 since no significant effect in surface activity was detected when pH was altered in the surface tension measurements.

Table 9. Interfacial tension values of the different oils.

Squalane		n-Heptane		Paraffin oil	
Heavy phase liquid	**Interfacial tension (mN/m)**	**Heavy phase liquid**	**Interfacial tension (mN/m)**	**Heavy phase liquid**	**Interfacial tension (mN/m)**
Water	39.98	Water	49.88	Water	56.07
Bindzil® 40/130 + Free MPEG*	26.30	Bindzil® 40/130 + Free MPEG*	29.48	Bindzil® 40/130 + Free MPEG*	41.48
UFSS11	35.75	UFSS11	36.76	UFSS11	45.77
UFSS14	37.32	UFSS14	38.28	UFSS14	44.58
UFSS15	33.14	UFSS15	38.91	UFSS15	46.35
SS16	31.82	SS16	36.14	SS16	43.43
SS17	32.73	SS17	39.12	SS17	45.50
SS18	29.61	SS18	33.66	/SS18	40.22

* corresponds to 0.1 μmol/m^2

The interfacial tension value between paraffin oil (275 seconds viscosity) and water is 42.5 mN/m^2 according to an article by Johansen [44]. This differs quite much compared to the measured values of 56.07 mN/m^2. An explanation could be the purity of the oil used in the measurements. Any impurities in the oil would lead to an altered interfacial tension value. The interfacial tension value of the MPEG grafted sol (UFSS11) is a litte bit higher than when the same amount of MPEG is added free in solution. It seems as if the free MPEG chains have a higher tendency to adsorb at the oil/water interface compared to the silica particles grafted with MPEG chains. The silica sol grafted with both MPEG-GPTES and isobutyl silane (SS18) show the lowest interfacial tension value with paraffin oil.

Similar results as paraffin oil are seen in the case of squalane. The measured interfacial tension value of 39.98 mN/m^2 between squalane and water is low in comparison with 52.3 mN/m^2 according to an article by Fowkes et al. [45]. Comparing the silica particles grafted only with MPEG or both MPEG and isobutyl to the unmodified particles with free MPEG, there is an even larger difference in interfacial tension. The larger difference could be because of the more hydrophilic nature of the squalane is favoring the hydrophilic MPEG free in solution.

Interfacial tension value between n-heptane and water is 48.6 mN/m^2 according to an article by M. Alpaz, A. Bilgesü and O. Tutkun [46]. This corresponds quite well to the measured value of 49.88 mN/m^2. Even in this case of n-heptane the MPEG free in solution is the most efficient at lowering the interfacial tension.

The measurements of the interfacial tension illustrates the fact that the more hydrophobic nature of the oil the higher the interfacial tension with pure water. The free MPEG and unmodified particles lowers the interfacial tension more than the silane grafted particles for the more hydrophilic oils; squalane and n-heptane. The more hydrophobic paraffin oil show the lowest interfacial tension value with the particles modified with both MPEG and isobutyl grafted particles. For required HLB values see table 2.

5.6 Emulsions
The surface modified silica particles were studied as emulsifier by investigation of model oil-water systems. This section first presents the evaluation of three oils with different polarity as suited model system for the modified silica particles. The evaluation includes screening of the oils using the original bare silica particles, the isobutyl modified particles and particles with free MPEG added. This part also comprises evaluation of the emulsification condictions; particle concentration, energy input, added amount of MPEG and pH of the water phase.

5.6.1 Evaluation of model oil-water systems and emulsification conditions
Evaluation of model oil-water systems and emulsification conditions are presented in appendix B.

Suited model oil-water systems for the modified silica particles as emulsifier were studied by screening three oils with different polarity. Squalane (HBL 12-12.9 [40]), n-heptane (HBL 10.5-11 for hexane [39]) and paraffin oil (HBL 10 [13]). Silica particles of Bindzil® and isobutyl modified particles were tested as emulsifiers with or without addition of free MPEG. Particles modified with MPEG-GPTES were not synthesized at that time and are thus not included in the screening process. Those particles are instead included in the next section where iBu and MPEG-GPTES grafted silica particles are tested as emulsifiers.

The screening of the oils showed that only energy input, free MPEG or bare silica particles alone was insufficient to create an emulsion. The bare silica particles only created an emulsion in combination with free MPEG for squalane and n-heptane. Bare silica particles with or without free MPEG did not create a stable emulsion for paraffin oil. The isobutyl silane modified particles alone did however only create stable emulsion for paraffin oil and squalane, not for n-heptane.

Due to the differences in the results by using different particles with or without free MPEG, the three oils were used for further investigation of the silica particles grafted with both isobutyl and MPEG-GPTES silane.

Different emulsification conditions were varied to study correlations to texture and droplet size. The emulsion droplet size and size distribution were studied by laser light diffraction and optical microscopy. The increase of particle concentration, energy input and added amount of MPEG tends to decrease the mean droplet diameter of the emulsion created. The pH of the water phase used when emulsifying also seemed to have a decreasing effect of the mean droplet diameter.

The study was however only performed at two different pH-values and further investigation is needed to verify the result.

5.6.2 iBu and MPEG-GPTES grafted silica particles as emulsifier

Silica particles grafted with both hydrophilic and hydrophobic silanes were tested as emulsifiers using the three different oils. All emulsions were emulsified at an operation speed of 11000 rpm for 5 minutes.

Emulsions with squalane are displayed in figure 12. Unmodified Bindzil® 40/130 with free MPEG corresponding to 0.1 µmol/m^2 created a stable oil-in-water emulsion. The particles of UFSS15 created an o/w emulsion with excess water. The emulsion created by SS16 had both excess water and oil. The particles of UFSS11, SS17 and SS18 did not create stable emulsions at all.
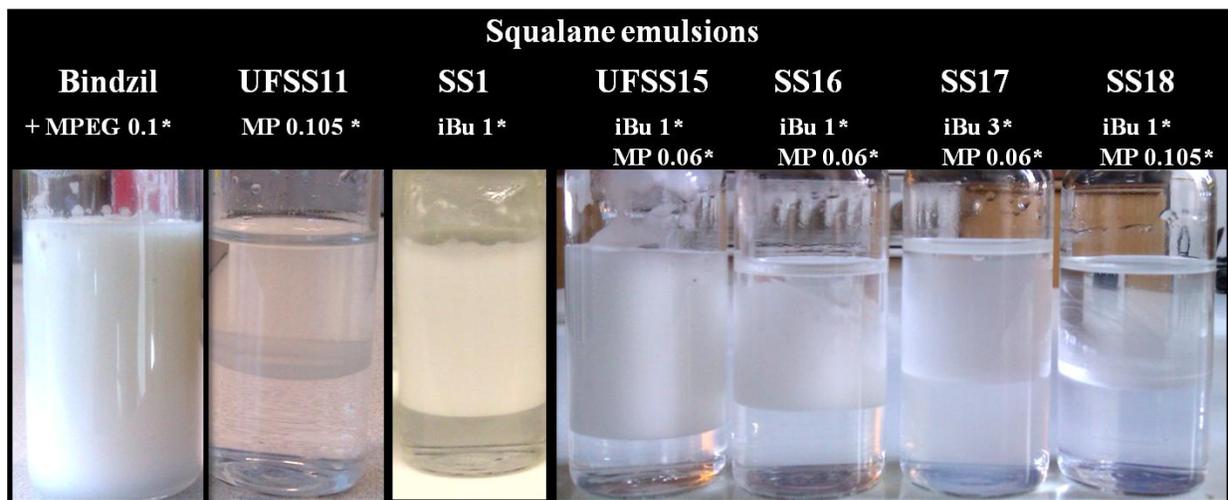

*Figure 12. Emulsions with 50 wt% squalane and 50 wt% water. The silica content is 0.5 wt% of the oil mass. * refers to the surface coverage in µmol/m^2 for more details see table 6 and 7. The emulsions are o/w. Picture taken three days after emulsification.*

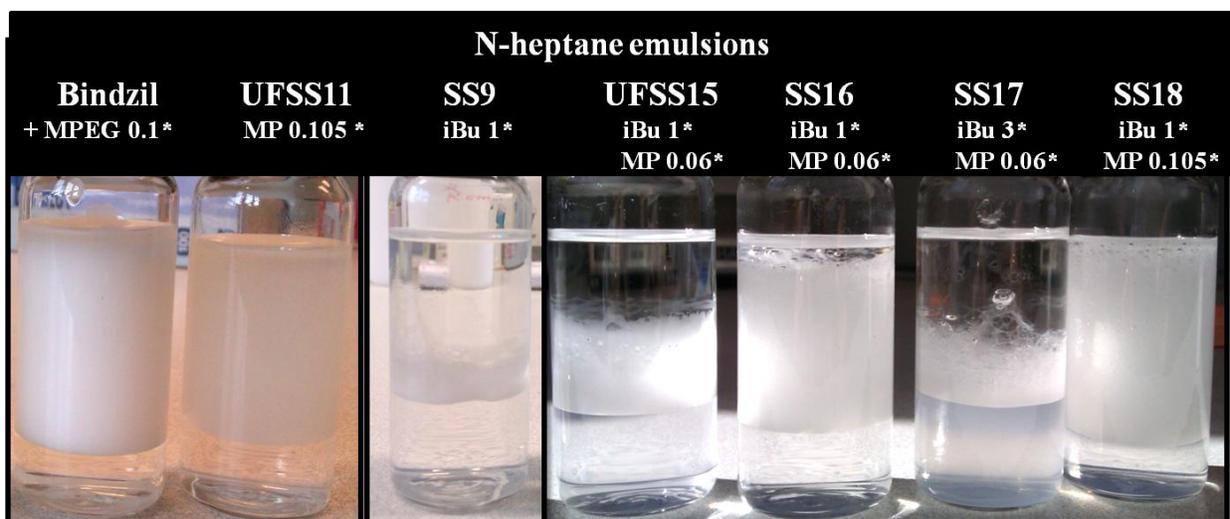| N-heptane emulsions						
Bindzil + MPEG 0.1*	UFSS11 MP 0.105 *	SS9 iBu 1*	UFSS15 iBu 1* MP 0.06*	SS16 iBu 1* MP 0.06*	SS17 iBu 3* MP 0.06*	SS18 iBu 1* MP 0.105*

*Figure 13. Emulsions with 50 wt% n-heptane and 50 wt% water. The silica content is 0.5 wt% of the oil mass. * refers to the surface coverage in µmol/m² for more details see table 6 and 7. The emulsions are o/w. Picture taken three days after emulsification.*

The emulsions with n-heptane displayed in figure 13 show in similarity to squalane how unmodified Bindzil® 40/130 with free MPEG corresponding to 0.1 µmol/m² created a stable oil-in-water emulsion. The other particles were not as efficient. UFSS11, SS16 and SS18 created emulsions with visual large droplets.
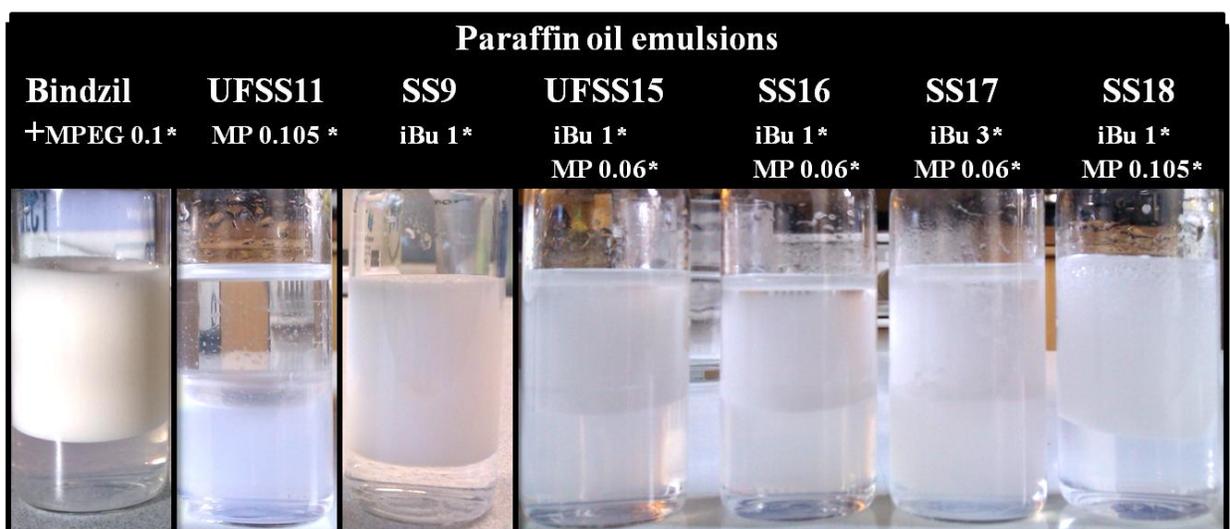

Paraffin oil emulsions						
Bindzil +MPEG 0.1*	UFSS11 MP 0.105 *	SS9 iBu 1*	UFSS15 iBu 1* MP 0.06*	SS16 iBu 1* MP 0.06*	SS17 iBu 3* MP 0.06*	SS18 iBu 1* MP 0.105*

*Figure 14. Emulsions with 50 wt% paraffin oil and 50 wt% water. The silica content is 0.5 wt% of the oil mass. * refers to the surface coverage in µmol/m² for more details see table 6 and 7. The emulsions are o/w. Picture taken three days after emulsification.*

Emulsions with paraffin oil and the modified silica sols are displayed in figure 14. The unmodified Bindzil® 40/130 with free MPEG corresponding to 0.1 µmol/m² created a stable oil-
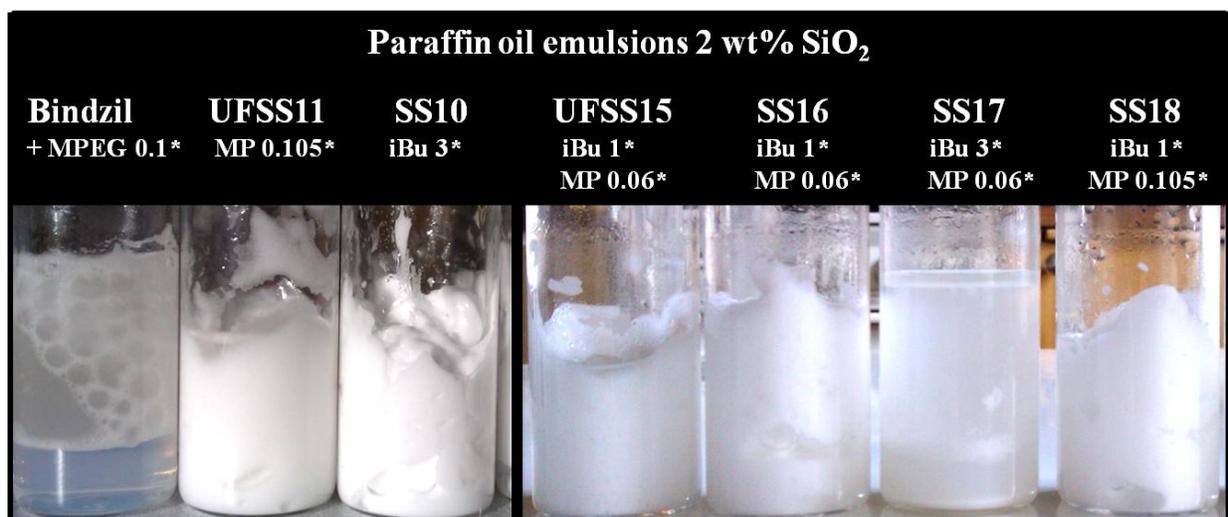
in-water emulsion with excess water. SS9 created a stable emulsion similar to the unmodified particles with free MPEG. SS18 created an emulsion with visual large droplets. The other particles created emulsions which destabilized within a week. UFSS11 did not create an emulsion at all.

Bindzil® 40/130 with free MPEG seems to work best for all the three oil-water systems at low particle concentration. The surface modified particles seem to work differently in the three model systems. It is difficult to find any correlation of their emulsifying properties to the surface and interfacial tensions. The surface and interfacial tension are however affected by the different modifications of the surface of the silica particles. Hence further studies of correlations between the emulsifying properties of the silica particles and the surface and interfacial tensions are needed.

The evaluation of emulsification conditions in appendix B showed that viscous oil-in-water emulsions with small droplets were formed when increasing the particle concentration of paraffin oil emulsions. Additional tests of increased particle concentration with the iBu and MPEG grafted particles as emulsifiers in paraffin oil-water system were therefore conducted.

When the o/w-ratio was set to 70/30 and the particle concentration increased to 2 wt%, see figure 15, the silica particles modified with isobutyl silane (SS10) alone created the best emulsion. The other surface modified particles also created stable viscous oil-in-water emulsions with a texture similar to a cream. The silica particles modified with a high amount of isobutyl silane in combination with MPEG-GPTES (SS17) formed gel-like sediment of high water content. The unmodified Bindzil® 40/130 with free MPEG corresponding to 0.1 μmol/m^2 did not create an emulsion.

An interesting result is that when increasing the particle concentration to 2 wt%, the unmodified particles with free MPEG did not form a stable emulsion. Instead the previously unsuccessful modified silica particles created stable emulsions and it seemed be an advantage of having the MPEG covalently attached to the particles.

Paraffin oil emulsions 2 wt% SiO₂						
Bindzil + MPEG 0.1*	**UFSS11** MP 0.105*	**SS10** iBu 3*	**UFSS15** iBu 1* MP 0.06*	**SS16** iBu 1* MP 0.06*	**SS17** iBu 3* MP 0.06*	**SS18** iBu 1* MP 0.105*

*Figure 15. Emulsions at 24000 rpm for 5min with 70 wt% paraffin oil and 30 wt% water. The silica content is 2 wt% of the oil mass. * refers to the surface coverage in μmol/m^2 for more details see table 6 and 7. The emulsions are o/w. Picture taken three days after emulsification.*

Table 10 presents the result from the droplet size measurement by laser light diffraction. The smallest droplets of 13.76 μm in diameter were measured with the particles modified isobutyl silane (3 mol/m^2), SS10. The emulsion droplet diameter measured for the emulsification with SS18 particles is in the same range. This could be a result of the low interfacial tension (40.22 mN/m) between paraffin oil and water obtained with the SS18 particles.

Table 10. Droplet size of emulsions with 70 wt% paraffin oil and 2 wt% SiO₂ at 24000 rpm for 5 min.

Silica sol	D (v, 0.5) (μm)	Surface area (m^2/g)
UFSS11	55.12	0.2766
SS10	13.76	1.2759
SS15	21.59	0.8560
SS16	70.19	0.4688
SS18	17.44	1.1913

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6. Conclusions

In this study, silica particles of aqueous silica sols were modified by covalently grafting silanes to the silica surface in order to provide varying hydrophobic and/or hydrophilic character. Surface and interfacial tension was measured to increase knowledge of the factors affecting the character of the particles. The surface modified silica particles were evaluated as emulsifier in model oil-water systems.

The hydrophilic silane was synthesized by reacting a hydrophilic poly (ethylenglycol) methylether (MPEG) with a coupling agent, (3-Glycidyloxypropyl) triethoxysilane (GPTES), and an acid catalyst, TFA. The efficiency of the synthesis was estimated from the measured amount of unreacted GPTES by HPLC. In the most efficient synthesis 32.2 % of the GPTES remained after reaction.

Grafting of the hydrophobic isobutyl (trimethoxy) silane to Bindzil$^®$ 40/130 silica particles was efficient with yields around 96 %. The maximum degree of surface coverage of isobutyl silane was 3 μmol/m^2.

Due to the inefficient synthesis of the hydrophilic silanes and indication of low efficiency when grafting the silane in previous work, the modification of the silica particles with the hydrophilic silane was performed with a large excess of purified silane. The amount of covalently bond hydrophilic silane to the silica surface was evaluated by NMR diffusometry. The highest surface coverage of covalently bond MPEG-GPTES obtained was 0.105 μmol/m^2.

Particle size measurements by dynamic light scattering showed an increase in particle size by 10 nm in diameter when MPEG-GPTES was grafted and 3 nm in diameter when isobutyl silane was grafted. An increase of 5 nm in particle radius indicates a coiled PEG chain attached to the silica surface.

The silica sol of particles with MPEG-GPTES covalently attached to the surface, corresponding to a surface coverage of 0.105 μmol/m^2, showed no sign of flocculation or change in appearance in the pH-interval 2-10. The stability of the sol indicates that a sufficient grafting of MPEG-chains is achieved to provides steric stabilization.

Measurements of surface tension showed that the most surface active silica sol was the one grafted with both 0.105 μmol/m^2 MPEG-GPTES and 1 μmol/m^2 isobutyl silane. This sol also achieved the lowest interfacial tension value between paraffin oil and water. Bare silica particles with free MPEG added showed the lowest interfacial tension values in the oil-water systems; squalane and n-heptane.

The surface modified particles seem to work differently in the three model oil-water systems. At low particle concentration Bindzil$^®$ 40/130 with free MPEG seems to work best in comparison with the surface modified silica particles for all three oil-water systems. Increased particle

concentration to 2 wt% showed opposite results indicating an advantage of having the MPEG covalently attached to the particles.

The different results for the surface modified particles in the three model oil-water systems makes correlation to the surface and interfacial tensions difficult. The surface activity is however affected by the different surface modifications and further studies regarding correlations between the emulsifying properties and the surface activity are needed.

7. Future studies

Future studies regarding the synthesis of the hydrophilic silane are interesting. The current work showed low yield when synthesizing the MPEG-GPTES silane and the uncertainty of the exact products forms are of great importance in the proceeding of the work with this silane. Different lengths of the MPEG chain and the use of other coupling agents e.g. 3-(triethoxysilyl)propyl isocyanate (IPTES) [47] could be examples of future studies.

In addition the grafting of the hydrophilic silane to the silica particles could be investigated with focus on the yield. The reasons to the low yields in this work are interesting. Further studies of surface modifications of silica particles include using particles of different sizes and optimizing the amphiphilic character by two distinct parts, one hydrophobic and one hydrophilic.

Furthermore studies including correlations between the emulsification properties of the surface modified silica particles and the surface and interfacial tensions are needed.

The particles should also be optimized as emulsifiers for the model oil/water systems achieving stable emulsion droplets of suitable size. The emulsions could also be studied under stress conditions to evaluate their storage stability, thermal stability and mechanical stability.

Optimizing the surface modified silica nanoparticles toward a specific field of application could also be an interesting area of further studies.

References

[1]   H.E. Bergna, W.O. Roberts, *Colloidal Silica: Fundamentals and applications,* Taylor & Francis group, Boca Raton, **2006**

[2]   R.K. Iler, *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry*, Wiley, Hoboken, **1979**

[3]   E.F Vansant, P. van der Voort, K.C. Vrancken, *Characterization and Chemical Modification of the Silica Surface*, Elsevier, Amsterdam, **1995**

[4]   L.T. Zhuravlev, *Surface characterization of amorphous silica – a review of work from the former USSR,* Colloids and Surfaces A: Physiochemical and Engineering Aspects, **1993**, 74, pp 71-90

[5]   F. Orgaz, H. Rawson, *J. Non-Crystalline Solids*, **1986**, 82, pp 57-68

[6]   W. Stöber, A. Fink, E. Bohn, *J. Colloid Interface Sci.*, **1968**, 26, 62

[7]   R.M. Pashley, M.E. Karaman, *Applied colloid and surface chemistry*, Wiley, Chichester, **2004**

[8]   K.S. Birdi, *Surface and colloid chemistry*, Taylor & Francis group, Boca Raton, **2010**

[9]   M. Kobayashi et.al. *Aggregation and Charging of Colloidal silica particles*, Langmuir, **2005**, 21, 5761

[10]   J. Rubio, J.A. Kitchener, *J. Colloid Interfacial Sci.*, **1976**, 57, 1, pp 132-142

[11]   B. Wind, E.Killman, *Colloid Polym Sci*, **1998**, 276, pp 903-912

[12]   F. Giordano-Palmino, R. Denoyel, J. Rouquerol, *J. Colloid Interfacial Sci.,* **1994**, 165, pp 82-90

[13]   K. Holmberg, B. Jönsson, B. Kronberg, B. Lindman, *Surfactants and Polymers in Aqueous Solution*, 2nd ed., Wiley, Chichester, **2003**, pp 451-471

[14]   J. Lyklema, *Fundamentals of Interface and Colloid Science*, Volume V, Elsevier, **2005**, pp 8.91-8.92

[15]   F. Leal-Calderon, J. Bibette, V. Schmitt, *Emulsion Science Basic Principles*, 2nd ed., Springer, New York, **2007**

[16]   W.D. Bancroft, *The theory of emulsification V*. J. Phys. Chem., **1913**, 17, pp 501-519

[17]   I.D. Morrison, S. Ross, *Colloidal dispersions: Suspensions, emulsions and foams*, Wiley, New York, **2002**

[18]   S.U. Pickering, *J. Chem. Soc.*, **1907**, 91, 2001

[19]   S. Levine, B.D Bowen, S.J. Partridge, *Colloids Surf.*, **1989**, 38, pp 325-343

[20]   D.N. Petsev, *Emulsions: Structure stability and Interactions, Elsevier*, **2004**, pp 641-642

[21]   P. Finkle, H.D. Draper, J.H. Hildebrand, *J. Am. Chem. Soc.*, **1923**, 45, pp 2780-2788

[22]   B.P. Binks, S.O. Lumsdon, *J. Am. Chem. Soc.*, Langmuir, **2000**,16, pp 8622-8631

[23]   B.P. Binks, S.O. Lumsdon, *J. Am. Chem. Soc.*, Langmuir, **2000**,16, pp 2539-2547

[24]   B.P. Binks, S.O. Lumsdon, *Phys. Chem. Chem. Phys.*, **1999**, 1, pp 3007-3016

[25]   B.R. Midmore, *Colloids Surf. A*, **1998**, 145, pp 133-143

[26]   B.R. Midmore, *Colloids Surf. A*, **1998**, 132, pp 257-265

[27]   H. Hassander, B. Johansson, B. Törnell, *Colloids Surf.*, **1989**, 40, pp 93-105

[28]   P. Greenwood, *Surface modifications and applications of aqueous silica sols, D*octoral thesis, Chalmers University of Technology, **2010**

[29]   F.D. Osterholtz, E.R. Pohl, *J. Adhesion Sci. Technol.*, **1992**, 1, pp. 127-149

[30]   N. Nishiyama, T. Asakura, K. Horie, J. Colloid Interface Sci., **1987**, 124, 1, pp. 14-21

[31]   D.C. Harris, *Quantitative Chemical Analysis*, 7th ed., W.H. Freeman and Company, New York, **2007**, pp. 556-583

[32]   W.S. Price, *Concepts Magn. Reson.*, **1997**, 9, pp. 299-336

[33]   C.S. Johnson Jr., *Progress in Nuclear Magnetic Resonance Spectroscopy*, **1999**, 34, pp. 203-256

[34]   A. Einstein, *Ann. Phys.*, **1905**, 17, pp. 549-560

[35]   C. Urban, P. Schurtenberger, J. Colloid Interface Sci., **1998**, 207, pp 150-158

[36]   H.G. Merkus et. Al., J. Aerosol Sci., **1994**, 25, Suppl. I., pp. 319-320

[37]   U. Foerter-Barth, U. Teipel, Mineral and material characterization, **2000**, pp C1-1 – C1-8

[38]   Malvern Intruments 2012 *Google search: Mastersizer microplus (First hit)* URL: http://www.malvern.com/common/downloads/campaign/MRK343-01_LR.pdf   Retrieved on 2012-02-16

[39]   C. G. Masi, *Test & Measurement World*, **2000**, 20, 5, pp 36-46

[40]   I.Lo et.al., Ann. Pharm. Fr., **1972**, 30, 3, pp. 211-222

[41]   Lotioncrafter LLC 2012 *Home, Emollients, Lotioncrafter Olive Squalane* URL: http://www.lotioncrafter.com/lotioncrafter-olive-squalane-p14.html, Retrieved on 2012-03-13

[42]   F. Oesterhelt, M. Rief, H. E. Gaub, New Journal of Physics, **1999**, 1, 6.1-6.11

[43]   C.S. Chern, C.K. Lee, K.C. Lui, J. Polym. Research, **2006**, 13, pp. 247-254

[44]   E.M. Johansen, *Industrial and engineering chem.*, **1924**, 16, 2, pp. 132-135

[45]   F.M. Fowkes et.al., *Colloids Surf.*, **1990**, 43, pp 367-387

[46]   M. Alpaz, A. Bilgezü, O, Tutkun, *Commun. Fac. Sci. Univ. Ank. Serie B,***1988** ,34, pp 103-112

[47]   Y-J Hwang et.al., *J. Ind. Eng. Chem.*, **2006**, 12, 3, pp 380-386

Appendix A

As references the surface tension of the reactants for the synthesis of the hydrophilic silane was measured at the different pH. The result is presented in figure A1. The result of GPTES show only a slight decrease in surface tension compared with pure water. The surface tension decreases as the added amount of MPEG increases and the decrease are probably valid until the surfaces are completely saturated with MPEG. There is no sign of any synergy effect when both GPTES and MPEG are added and the surface tension is approximately the same as for the same amount of MPEG alone. There is no sign of any of the starting materials or the hydrophilic silane to be dependent of the pH.
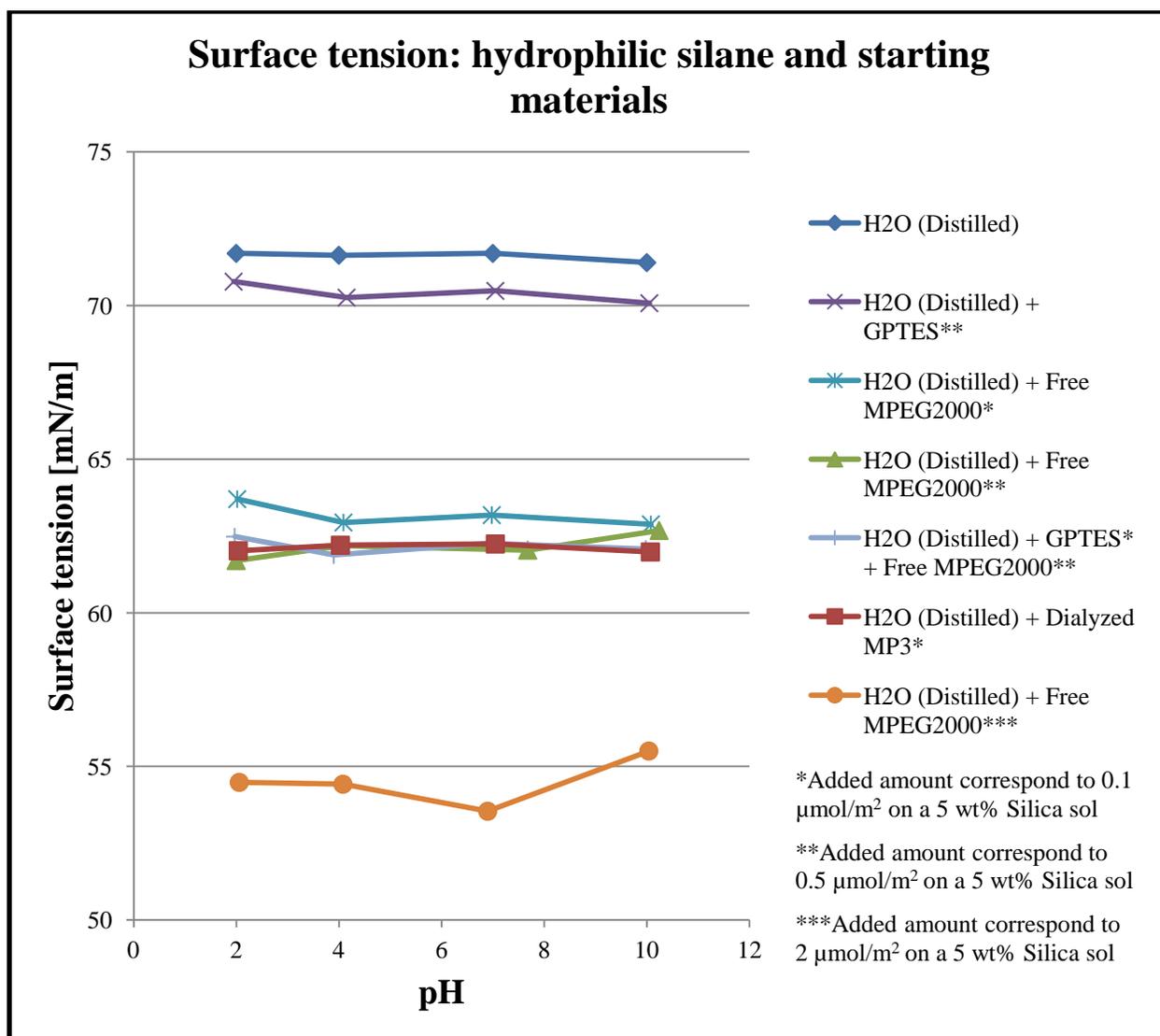
Figure A1. Surface tension of the hydrophilic silane and starting materials at different pH. The lines are only added as visual help.
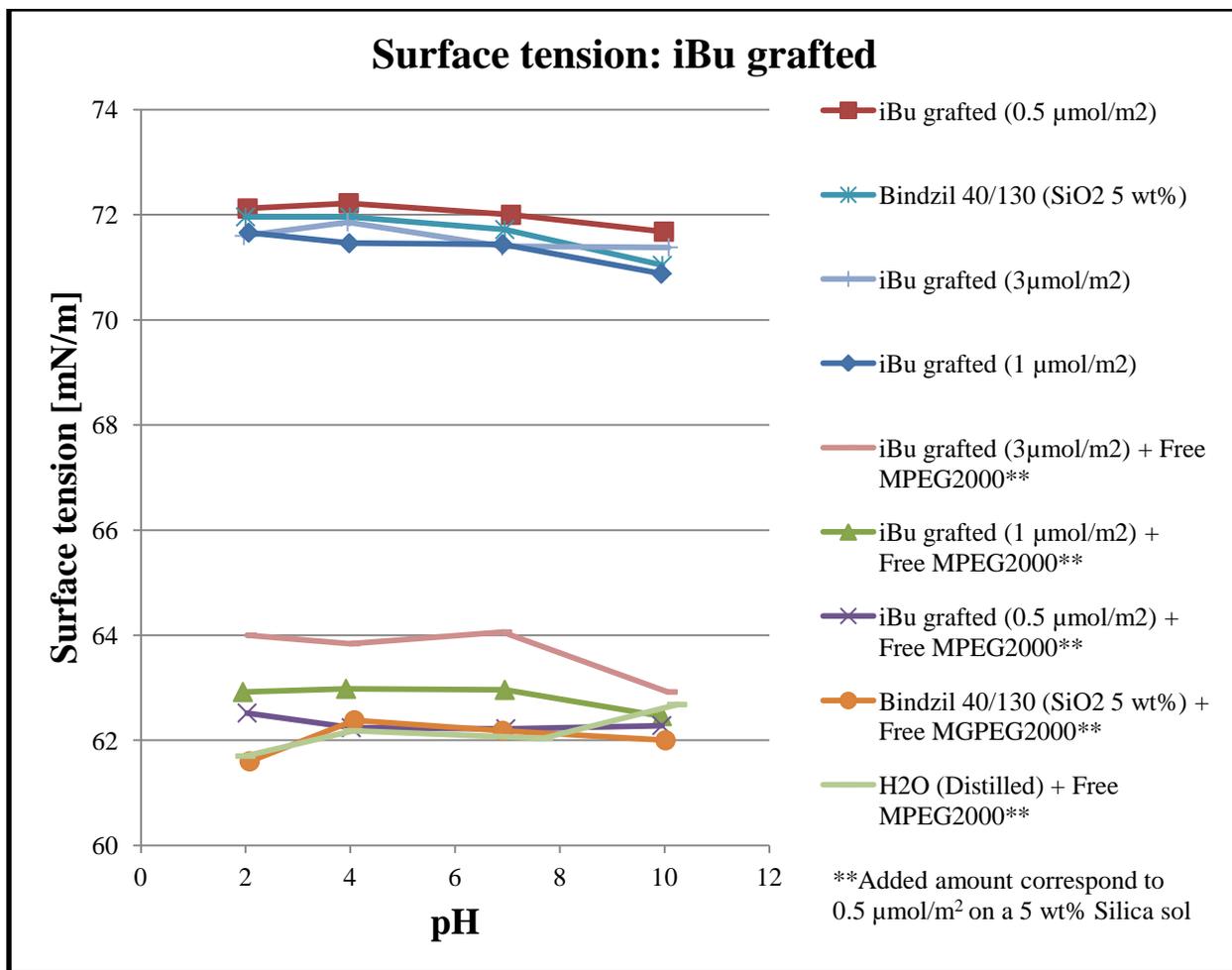
Figure A2. Surface tension of isobutyl silane modified silica sols at different pH. The lines are only added as visual help.

The surface tension values of the isobutyl silane modified silica sols are displayed in figure A2. As for the previous result of the hydrophilic silane and starting materials, no effect in surface tension when altering the pH is detected. When no MPEG is added, there is no significant decrease in surface tension compared to pure water and the surface coverage of grafted isobutyl silane does not seem to affect.

When MPEG is added there seem to be some correlation between the surface coverage of isobutyl silane and the decrease in surface tension, the higher the surface coverage of isobutyl silane the higher the surface tension.

Appendix B

To increase knowledge of the surface modified silica as emulsifier, model oil water systems was investigated. Three oils with different polarity were evaluated as suited model system for the modified silica particles as emulsifier. Squalane (HLB 12-12.9 [40]), paraffin oil (HLB 10 [13]) and n-heptane (HLB 10.5-11 for hexane [39]).

The emulsification conditions; particle concentration, energy input, added amount of MPEG, pH of the water phase were altered to study the correlations to texture and droplet size distribution. The latter was evaluated by microscopy and laser light diffraction.

B1 Screening of different oils

A suitable model oil water system was required to be able to investigate effects of the different modifications of the silica particles. Table B1 illustrates specifications of the different emulsion samples tested with three different oils. All the emulsion tests for screening of different oils were performed at an operation speed of 11000 rpm for 5 minutes.

Table B1. The sample number and content of the emulsion tests for screening of different oils are displayed. All the samples contain 50 wt% oil and 50 wt% water. The silica content is 0.5 wt% of the oil mass.

Squalane		N-Heptane		Paraffin oil	
Sample	**Emulsifier**	**Sample**	**Emulsifier**	**Sample**	**Emulsifier**
1	Bindzil	9	Bindzil	13	Oil water 50/50
2	Bindzil + $0.1 \mu mol/m^2$ MPEG	10	Bindzil + 0.1 $\mu mol/m^2$ MPEG	14	Bindzil
3	Bindzil + 0.5 $\mu mol/m^2$ MPEG	11	SS1 iBu-mod 1 $\mu mol/m^2$ + 0.1 $\mu mol/m^2$ MPEG	15	Bindzil + 0.1 $\mu mol/m^2$ MPEG
4	SS1 iBu-mod 1 $\mu mol/m^2$	12	SS9 iBu-mod 1 $\mu mol/m^2$	16	SS1 iBu-mod 1 $\mu mol/m^2$ + 0.1 $\mu mol/m^2$ MPEG
5	SS1 iBu-mod 1 $\mu mol/m^2$ + 0.1 $\mu mol/m^2$ MPEG			17	SS9 iBu-mod 1 $\mu mol/m^2$
6	SS1 iBu-mod 1 $\mu mol/m^2$ + 0.5 $\mu mol/m^2$ MPEG				
7	No Bindzil, only 0.5 $\mu mol/m^2$ MPEG				
8	oil water 50/50				

The results of the emulsions are displayed in figure B1, B2 and B3. A picture of the emulsions the same day as emulsification and a picture three days after emulsification are shown to investigate the destabilization. The emulsion type was determined by a conductivity test and by diluting the emulsion in water. If the emulsion show conductivity and the droplets remain stable after dilution, the emulsion type is o/w and vice versa.

The squalane was tested with bare silica particles, silica modified with isobutyl silane and only water without any silica particles, see figure B1. Different amounts of MPEG2000 were added as to see if it could help to create the emulsions. Sample 1, 7 and 8 showed that only energy input, free MPEG or bare silica particles alone was insufficient to create an emulsion.

Sample 2-6 showed that free MPEG in combination with silica particles created oil in water emulsions with excess water. Both unmodified and isobutyl modified silica particles created emulsions which look equally good and the amount of added MPEG did not seem to have any effect. The isobutyl modified particles did however manage to create an emulsion without free MPEG present (sample 4) in comparison to unmodified Bindzil® particles (sample 1). The reason could be that a more hydrophobic character of the isobutyl modified particles lead to a contact angle to the oil droplet closer to 90°. This would improve the stability of the emulsion since the particles will be drawn to the oil-water interface and be more wetted by the oil phase.
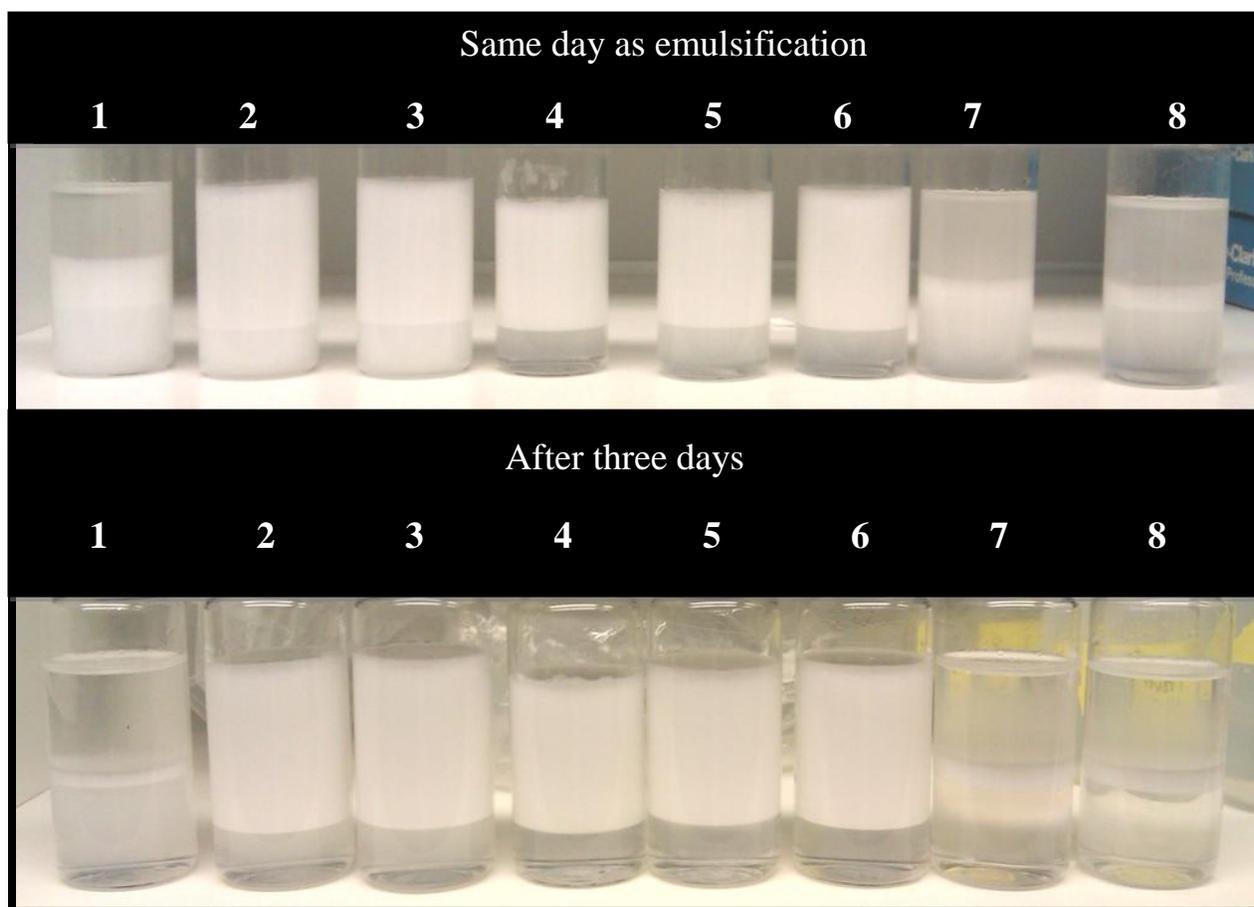
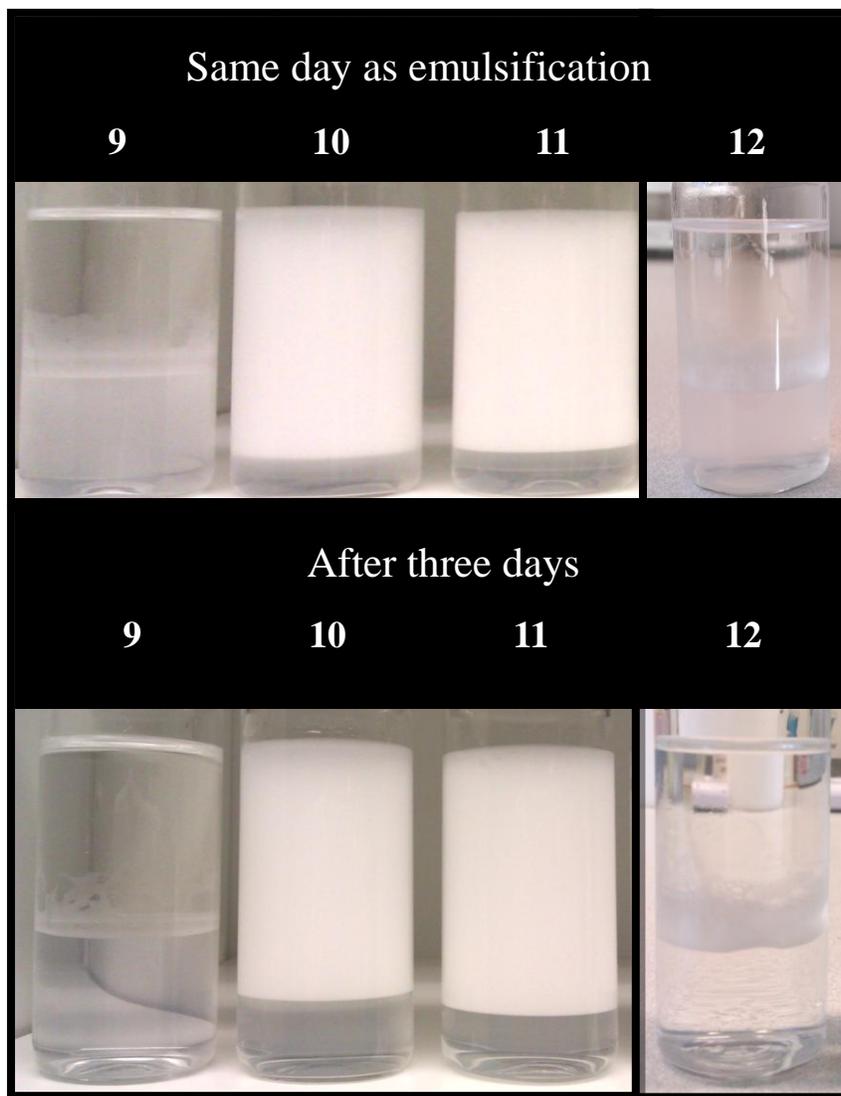*Figure B1. Emulsion tests with Squalane 50 wt% and 50 wt% water. The silica content is 0.5 wt% of the oil mass. The emulsions are o/w with visual creaming.*

The emulsion tests with n-heptane, see figure B2, were performed with bare and isobutyl silane modified silica particles with or without free MPEG added. The amount of added free MPEG was set to 0.1 μmol/m^2 since no effect of the amount added was visual for squalane. According to figure B2, the free MPEG was needed to create an emulsion. No difference in appearance of the emulsions created with unmodified and the isobutyl modified silica particles was visual.

Figure B2. Emulsion tests with n-heptane 50 wt% oil and 50 wt% water. The silica content is 0.5 wt% of the oil mass. The emulsions are o/w with visual creaming.
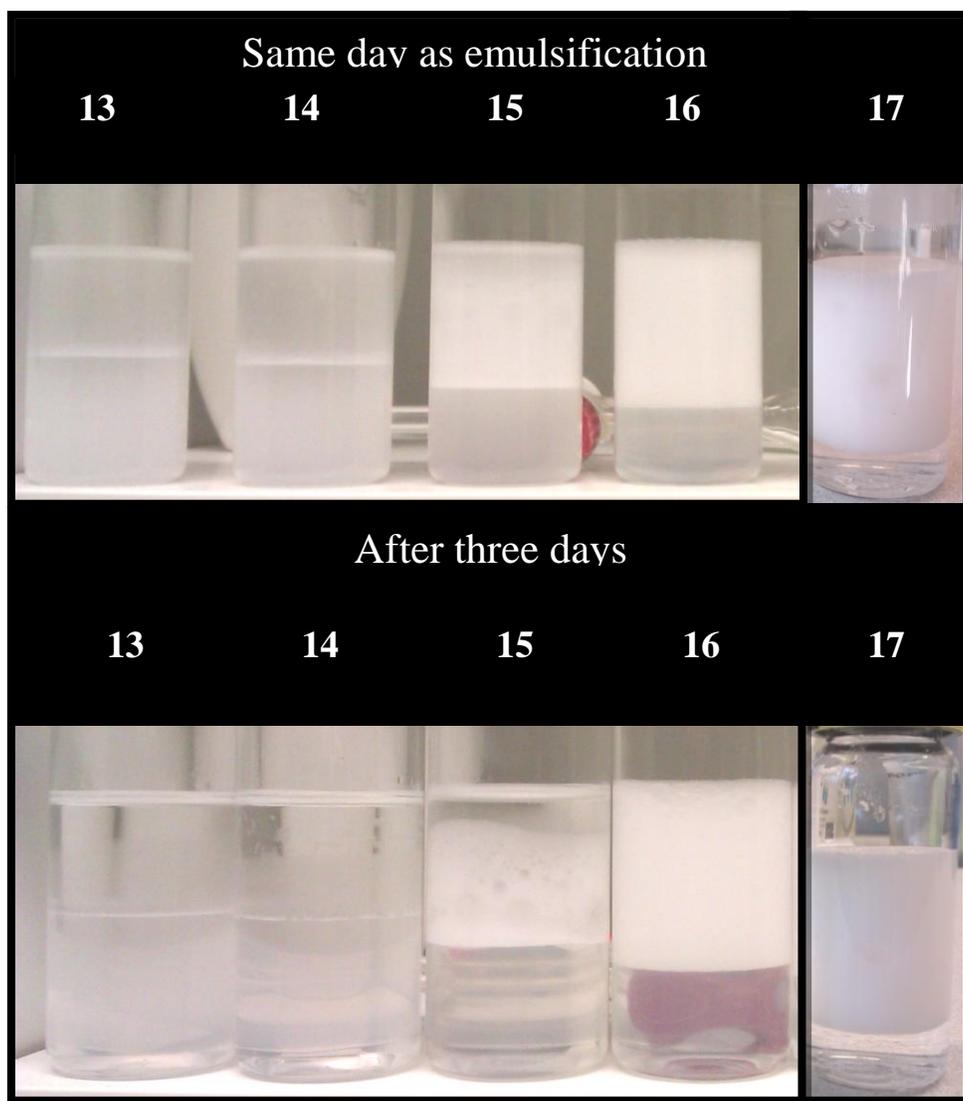
Figure B3. Emulsion tests with paraffin oil 50 wt% oil and 50 wt% water. The silica content is 0.5 wt% of the oil mass. The emulsions are o/w with visual creaming.

According to figure B3, the emulsion tests using paraffin oil showed that samples 13-15 with only energy input and bare silica particles with or without free MPEG added did not create stable emulsions. Sample 15 indicates that the added MPEG helped to create the emulsion but not enough stability was provided. The isobutyl silane grafted silica particles created stabile o/w-emulsions with excess water both when free MPEG was added or not. This could be because of the more hydrophobic particles probably had an improved contact angle to the oil droplets compared to the bare silica particles. The improved contact angle in combination with the increased hydrophobic interactions between the particles helps to stabilize the particles at the o/w interface.

B2 Droplet size

The droplet size and droplet size distribution of the emulsion affects the appearance, texture, stability and viscosity of the emulsion. Different factor affecting the emulsification was altered to investigate the effects of the correlations to these properties. The emulsions were evaluated through microscopy and laser light diffraction.

The emulsification conditions; particle concentration, energy input, added amount of MPEG, pH of the water phase were altered to study the correlations to texture and droplet size distribution.

B2.1 Effect of particle concentration

Emulsions of paraffin oil and isobutyl grafted silica particles with free MPEG2000 added were prepared with different concentration of silica particles to study the effect of particle concentration. The o/w-ratio was set to 70/30 wt% and particles used were grafted with isobutyl silane corresponding to a surface coverage of 1 µmol/m^2. The amount of free MPEG2000 added equaled a surface coverage of 0.1 µmol/m^2. All the emulsions were prepared at pH 9.6 and an operating speed of 11000 rpm for 5 min. The particle concentrations were 0.5, 1, 2.5, and 5 wt% of the oil mass.

All emulsions created were concentrated viscous oil-in-water emulsions. The texture of the emulsions resembled a cream which got thicker with increasing particle concentration.

The results from the laser light diffraction are presented in figure B4. The mean droplet diameter of the emulsion tends to decrease as the particle concentration increases. Increasing the particle concentration gives the potential of stabilizing an increased surface area of smaller droplets.
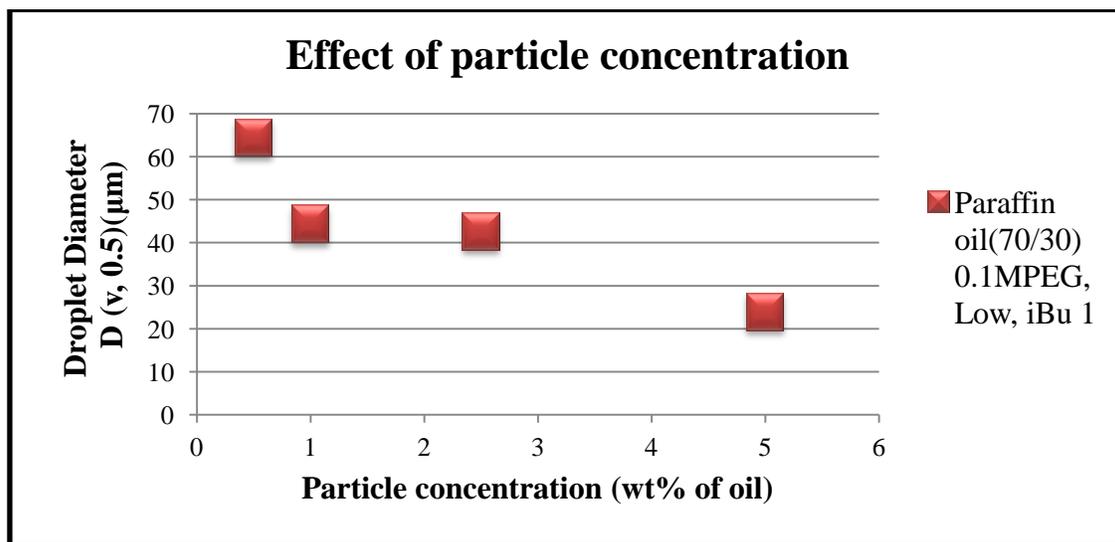

Figure B4. Results from the laser light diffraction of emulsions with paraffin oil 70 wt% oil and 30 wt% water. The silica concentration is varied from 0.5 to 5 wt% of the oil mass. All the emulsions are o/w.

All of the emulsions consisted of polydisperse oil droplets according to both the laser light diffraction and the microscopy pictures, see figure B5. From the microscopy pictures it is also visual how the mean oil droplet diameter decreases with the increased particle concentration

Assuming that the particles would form a 90° contact angle (measured through the water phase) with the emulsion oil droplets they would occupy the largest possible surface area on the oil droplet. Based on the assumption that they also pack in a hexagonal close-packed structure on the surface of the oil droplets they would be able to occupy an even slightly larges surface area. In figure B6 this is illustrated with hexagonal close-packed silica spheres showing the projected surface area occupied. The degree of area coverage by the particles can be calculated using the red triangle and the particle radius. An example of calculation of the theoretically smallest paraffin oil droplet diameter that could be stabilized by 5 wt% Bindzil® 40/130 silica particles is demonstrated in appendix C.

The calculation for 5 wt% particles gave a theoretical smallest droplet diameter of 3.9 μm. This represents monodispersed oil droplets which is not the case, but it gives an idea of the theoretical limit of emulsion droplet size in this case. In the microscopy picture, figure B5, of the emulsion containing 5 wt% of silica particles indicates that droplets in that size range are formed. The size distribution of the emulsion from the laser light diffraction, presented in figure B7, shows a comparable range of the smallest droplet size.
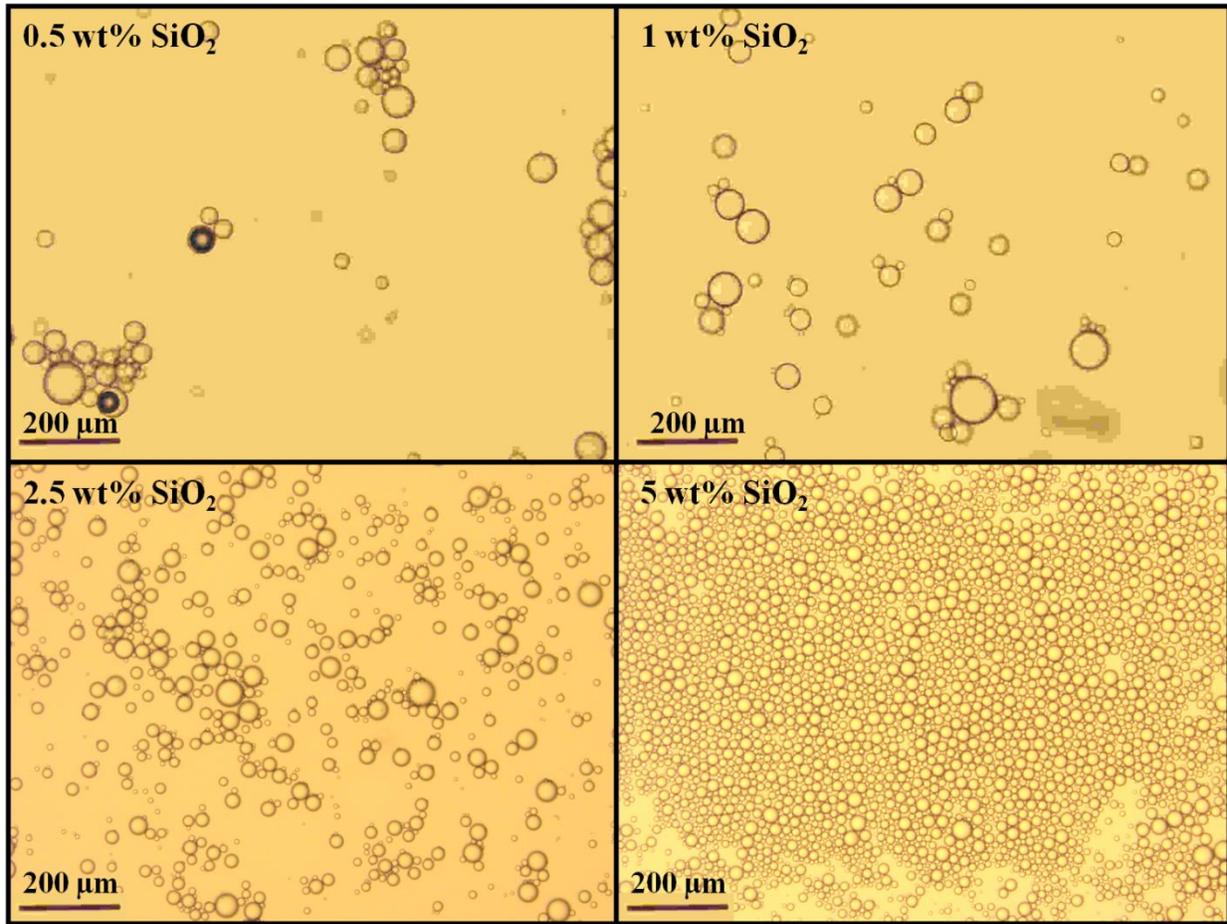
Figure B5. Microscopy pictures of emulsions with paraffin oil 70 wt% oil and 30 wt% water. The silica concentration is varied from 0.5 to 5 wt% of the oil mass. All the emulsions are o/w.
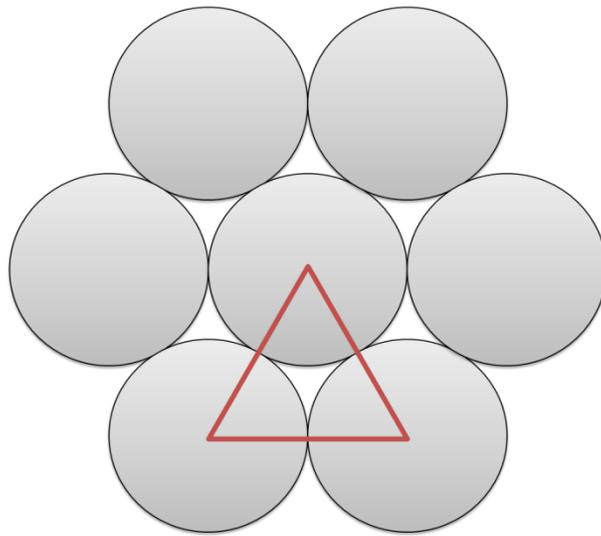

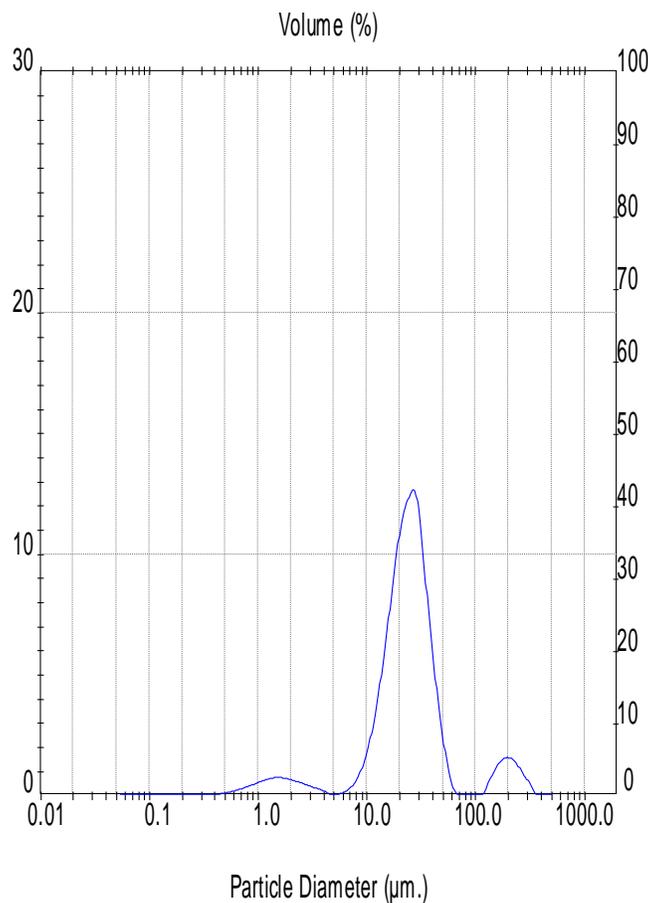*Figure B6. Hexagonal close packed silica particles.*

Figure B7. Size distribution of emulsions droplets from emulsion with 70 wt% paraffin oil and 30 wt% water. The silica concentration is 5 wt% of the oil mass.

B2.2 Effect of energy input

The effect of energy input on the emulsion droplet size and droplet size distribution were studied by creating emulsions at two different operating speeds. The o/w-ratio was set to 70/30 wt% and particles used were grafted with isobutyl silane corresponding to a surface coverage of 1 $\mu mol/m^2$. The amount of free MPEG2000 added equaled a surface coverage of 0.1 $\mu mol/m^2$. All the emulsions were prepared at pH 9.6 and the operating speed of either 11000 or 24000 rpm for 5 min. The particle concentrations were 2.5 and 5 wt% of the oil mass.

All emulsions created were concentrated viscous oil in water emulsions. The texture of the emulsions resembled a cream which thickened with increasing particle concentration and operating speed.

The results from the laser light diffraction are presented in figure B8. A higher operating speed means an increased energy input to the system. The effect of adding more energy seems to be a decrease of the mean droplet diameter, both for the high and low silica concentration. The increased energy input to the system helps to create more o/w interface which could be stabilized by silica particles. The microscopy pictures in figure B9 confirm this trend of decrease in mean droplet diameter when increasing the energy input.
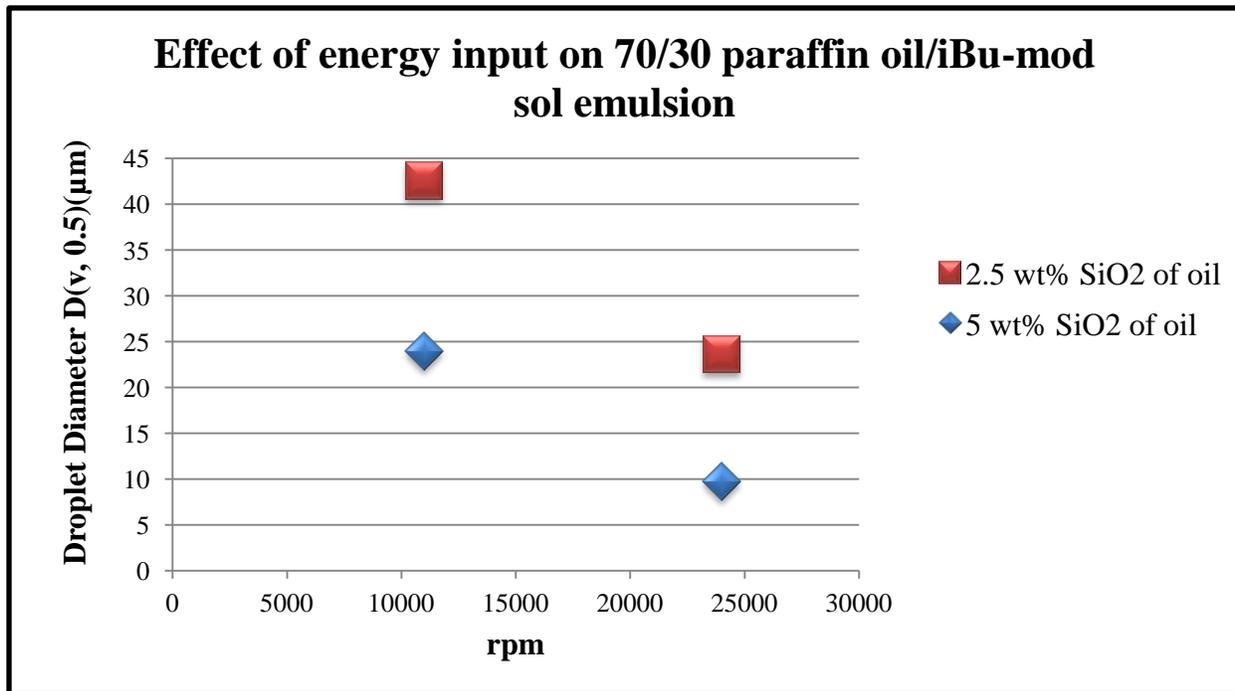
Figure B8. Results from the laser light diffraction of emulsions with paraffin oil 70 wt% oil and 30 wt% water. The operating speed is increased from 11000 to 24000 rpm for both silica concentrations of 2.5 to 5 wt% of the oil mass. All the emulsions are o/w.
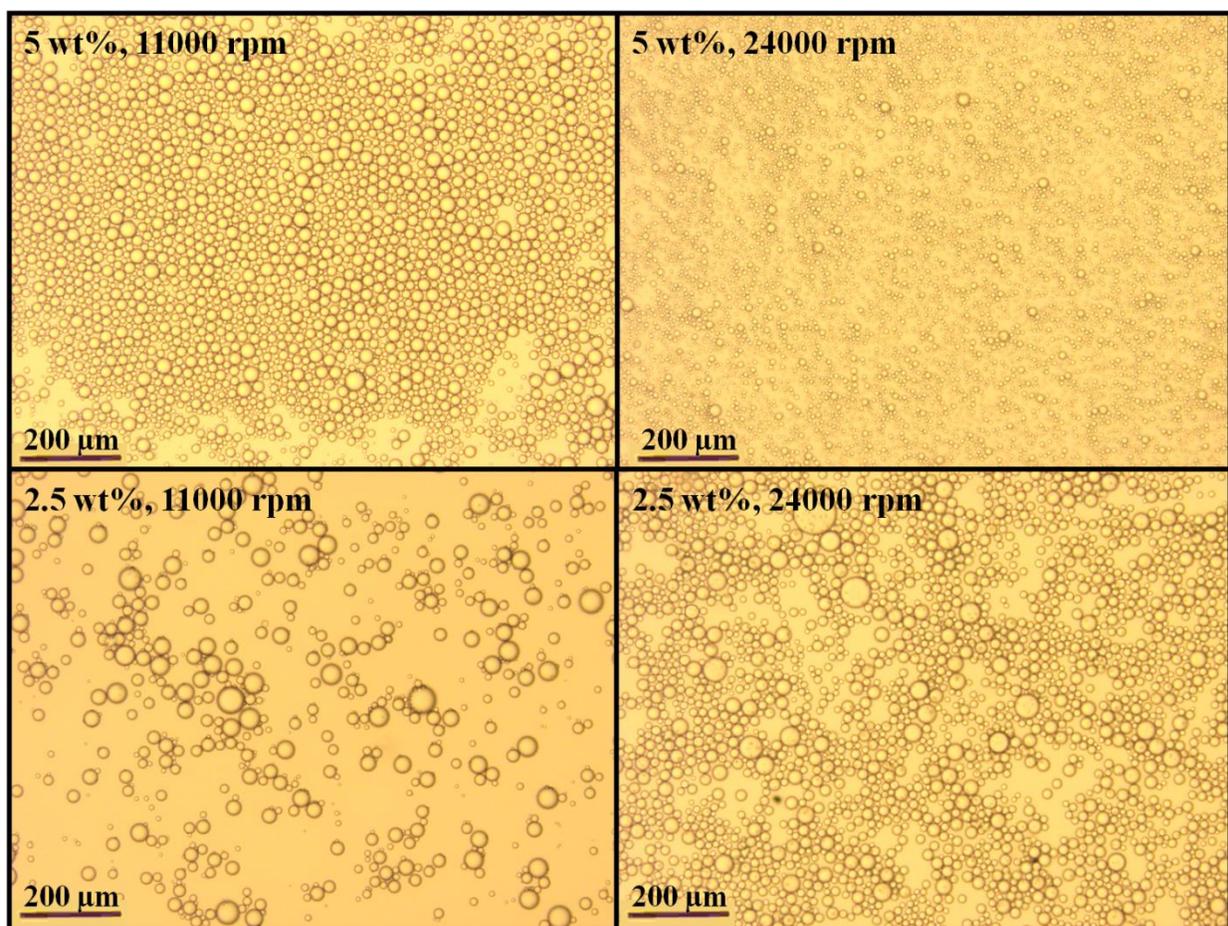
Figure B9. Microscopy pictures of emulsions with paraffin oil 70 wt% oil and 30 wt% water. The operating speed is increased from 11000 to 24000 rpm for both 2.5 and 5 wt% SiO₂ of the oil mass. All the emulsions are o/w.

B2.3 Effect of added amount of free MPEG2000

The effect of added amount of free MPEG2000 on the emulsion droplet size and droplet size distribution was studied by creating paraffin oil emulsions with increased amount of MPEG2000. The o/w-ratio was set to 70/30 wt% and particles used were grafted with isobutyl silane corresponding to a surface coverage of 3 μmol/m^2. The amounts of free MPEG2000 added equaled surface coverage of 0, 0.1 and 0.5 μmol/m^2. All the emulsions were prepared at pH 9.6 and an operating speed of either 11000 or 24000 rpm for 5 min. The particle concentration was 2.6 wt% of the oil mass.

Free MPEG2000 decreases the surface tension when added to an isobutyl modified silica sol and also the interfacial tension between for example paraffin oil and water, see figure A2 in appendix A and table 9 respectively. The decrease in interfacial tension between the oil and water helps to create the emulsion; it makes it easier to form a new interface which could be stabilized by

particles. The more MPEG added, the easier to form the emulsion. But it also means that it is easier to break the emulsion.

All emulsions created were concentrated viscous oil in water emulsions. Figure B10 shows how the increased amount of added MPEG2000 reduces the mean droplet diameter at both operating speeds. The difference in mean droplet diameter between the two operating speeds reduces as the added amount of MPEG increases. This indicates that the more MPEG added to help reducing the energy needed for creating new interfacial surface, the less difference between the two operating speeds.
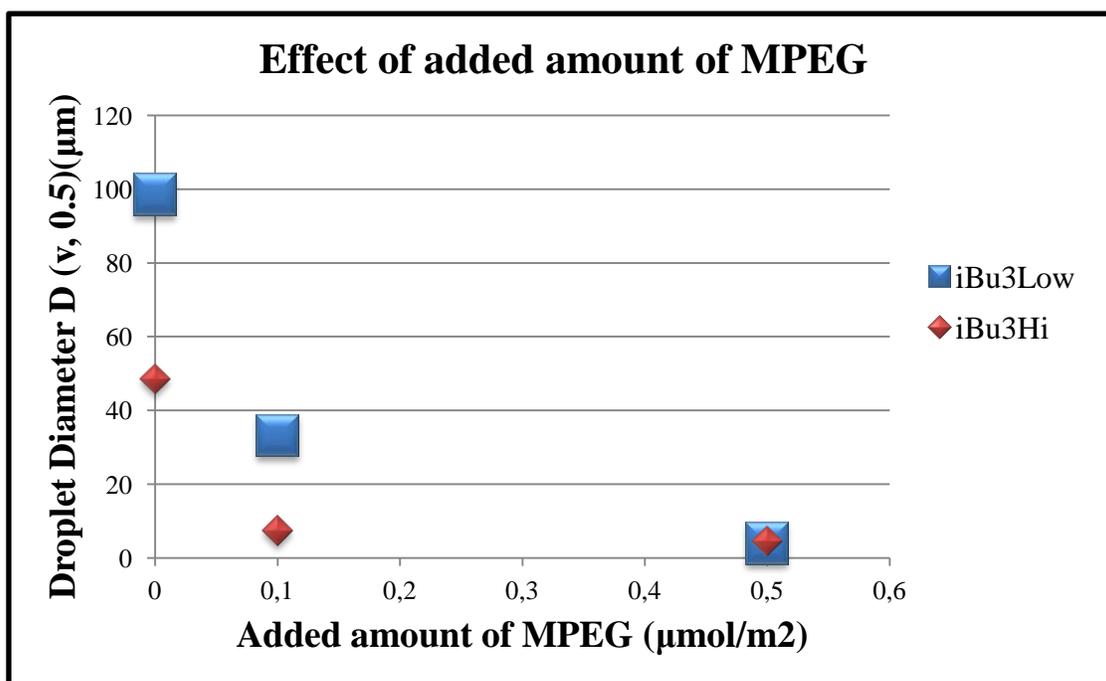

Figure B10. Results from the laser light diffraction of emulsions with paraffin oil 70 wt% oil and 30 wt% water. The silica particles are grafted with isobutyl silane corresponding to a surface coverage of 3μmol/m². The operating speed is increased from 11000(iBu3Low, blue squares) to 24000 rpm (iBu3Hi, red diamonds). All the emulsions are o/w.

B2.4 Effect of pH
Emulsions of paraffin oil and isobutyl grafted silica particles with free MPEG2000 added were prepared at two different pH to study the effect on droplet size. The o/w-ratio was set to 70/30 wt% and particles used were grafted with isobutyl silane corresponding to a surface coverage of 1 μmol/m². The amount of free MPEG2000 added equaled a surface coverage of 0.1 μmol/m². All the emulsions were prepared at an operating speed of 11000 rpm for 5 min. The particle concentrations were 0.5 and 1 wt% of the oil mass and the emulsions were prepared at pH 9.6 and 3.9.

In figure B11 the results from the laser light diffraction measurements are presented. Emulsions prepared at pH 3.9 showed a lower mean droplet diameter compared to the emulsions prepared at pH 9.6. This is true at both 0.5 and 1 wt% SiO_2 of the oil mass. At low pH at 3.9 the affinity of the MPEG2000 is higher than at high pH at 9.6 where the surface of silica is more ionized. When the surface active MPEG2000 molecules want to go to the interface, their affinity to the silica surface could help to drag the particles to the interface which helps to stabilize the newly formed interface. Thus smaller oil droplets could be able to form since the particles are there to stabilize them before they breaks. The pH effect of the mean droplet diameter was however only studied at two different pH-values. Further studies over a larger span of pH and using other surface modification of the particles should be conducted to be able to gain more knowledge of the effects.
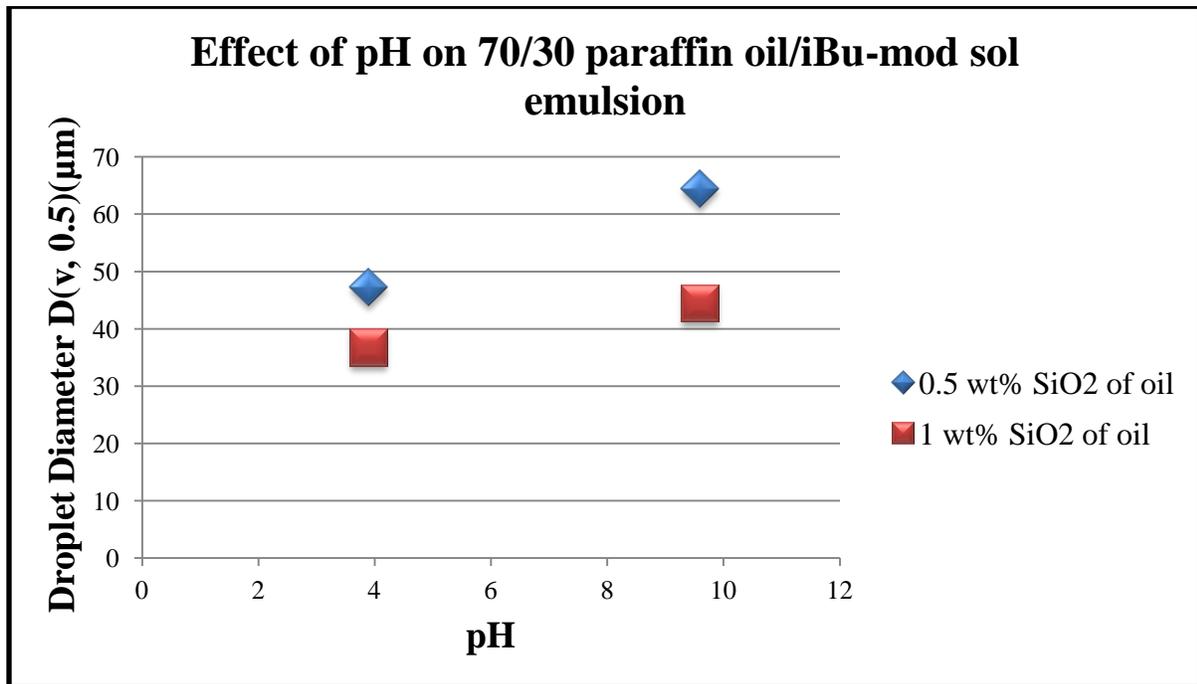

Figure B11. Results from the laser light diffraction of emulsions with paraffin oil 70 wt% oil and 30 wt% water. The silica particles are grafted with isobutyl silane corresponding to a surface coverage of 1μmol/m². The pH is increased from 3.9 to 9.6. All the emulsions are o/w and prepared at an operating speed of 11000 rpm for 5 min.

Appendix C

The calculations of the theoretically smallest possible oil droplet diameter that could be stabilized by Bindzil® 40/130 silica particles are presented.

The larges possible surface area stabilized by particles could be calculated by the following assumptions:

- The particles pack in a hexagonal patter on the emulsion droplets
- The particles forms a 90° contact angle (measured through the water phase) with the emulsion oil droplets

Figure B6 in appendix B represents a hexagonal packing of silica particles. The degree of area coverage by the particles can be calculated using the red triangle and the particle radius according to equation C1.

$$Degree\ of\ area\ coverage = \frac{Area\ of\ the\ triangle}{3 \cdot \frac{1}{6}\ projected\ area\ of\ particle} = \frac{\frac{25\ nm \cdot \sqrt{25^2 - 12.5^2}}{2}}{3 \cdot \frac{\pi \cdot 12.5^2}{6}} =$$

$$1.102657791\ (Eq.C1)$$

In the case where 5 wt% particles of the paraffin oil mass (14 g) were added, the particles have a total surface area of 91 m² according to calculations by equation C2.

$$Total\ surface\ area\ of\ silica\ particles = mass\ Bindzil \cdot 130\frac{m^2}{g} = 0.05 \cdot 14 \cdot 130 m^2$$
$$= 91 m^2 (Eq.C2)$$

The surface area of one Bindzil® 40/130 particle is calculated using equation C3.

$$Surface\ area\ of\ one\ particle = 4\pi r^2 = 4 \cdot \pi \cdot (12.5 \cdot 10^{-9})^2 m^2$$
$$= 1.96349541 \cdot 10^{-15} m^2 (Eq.C3)$$

Since the total surface area of all particles added are known, the number of added particles can be calculated according to equation C4.

$$Nr\ of\ particles = \frac{Total\ surface\ area\ of\ silica\ particles}{Suraface\ area\ of\ one\ particle} = \frac{91}{1.96349541}$$
$$= 4.634591943 \cdot 10^{16} (Eq.C4)$$

The surface area of all oil droplets formed is then calculated using equations C5 and C6.

$$Projected\ area\ of\ all\ particles = Nr\ of\ particles \cdot Projected\ area\ of\ one\ particle$$
$$= 4.634591943 \cdot 10^{16} \cdot \pi \cdot (12.5 \cdot 10^{-9})^2 = 22.75 m^2 (Eq.C5)$$

The radius of one oil droplet could then be calculated by combining equation C6 and C7 which gives equation C8.

$$Projected\ area\ of\ all\ particles \cdot Degree\ of\ area\ coverage = 22.75m^2 \cdot 1.102657791$$
$$= 25.08546475 = Surface\ area\ of\ all\ oil\ droplets$$
$$= 4\pi \cdot r_{oil\ droplet}^2 \cdot Nr\ of\ droplets\ (Eq.\ C6)$$

$$Total\ volume\ of\ oil = \frac{oil\ mass}{\rho_{oil}} = \frac{14g}{0.8585\frac{g}{cm^3}} \cdot 10^{-6}\frac{m^3}{cm^3} = 1.63075131 \cdot 10^{-5}m^3$$
$$= \frac{4\pi r_{oil\ droplet}^3}{3} \cdot Nr\ of\ droplets\ (Eq.\ C7)$$

$$d_{oil\ droplet} = 2 \cdot r_{oil\ droplet} = 2 \cdot \frac{3 \cdot Total\ volume\ of\ oil}{Surface\ area\ of\ all\ oil\ droplets}$$
$$= 2 \cdot \frac{3 \cdot 1.63075131 \cdot 10^{-5}m^3}{25.08546475m^2} \cdot 10^6\frac{\mu m}{m} = 3.9\ \mu m\ (Eq.\ C8)$$