

## Surface activity and flocculation behavior of polyethylene glycol-functionalized silica nanoparticles

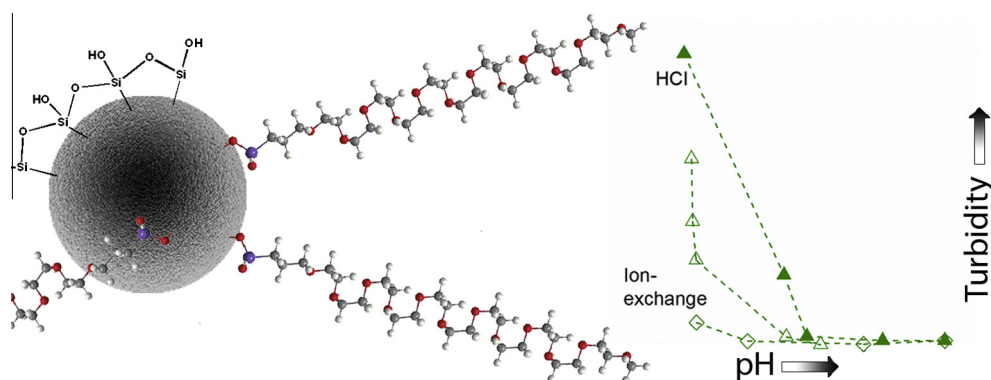


Sanna Maria Sofi Björkegren<sup>a,b,\*</sup>, Lars Nordstierna<sup>a</sup>, Anders Törncrena<sup>b</sup>, Michael E. Persson<sup>a,b</sup>, Anders E.C. Palmqvist<sup>a</sup>

<sup>a</sup> Chemistry and Chemical Engineering, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

<sup>b</sup> AkzoNobel Pulp and Performance Chemicals AB, SE-445 80 Bohus, Sweden

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 23 February 2015

Accepted 20 April 2015

Available online 27 April 2015

#### Keywords:

PEGylated colloidal silica

NMR diffusometry

Surface activity

Dynamic light scattering (DLS)

### ABSTRACT

Colloidal silica nanoparticles have been functionalized with methyl polyethylene glycol silane (mPEG silane) and the PEGylated particles have been characterized with focus on exploring their surface chemical properties. The degree of surface functionalization was quantified using NMR diffusometry, and the measurements showed that the silane binds covalently to the silica surface. Samples with surface coverages ranging from 0.068 to 0.315  $\mu\text{mol silane}/\text{m}^2$  have been analyzed. The functionalized particles proved to be surface active and showed a significant reduction in surface charge and zeta potential with increasing degree of PEG functionalization. All samples showed colloidal stability at neutral pH and above within the range studied. At lower pH, the samples with low surface coverage displayed a reversible flocculation behavior, while samples with a high surface coverage and samples without functionalization remained stable. This suggests that steric stabilization is effective at low pH when the surface coverage is high enough; electrostatic stabilization is effective for samples without functionalization; and that inter-particle PEG–silica interactions cause flocculation of particles with too low degrees of PEG functionalization.

© 2015 Elsevier Inc. All rights reserved.

## 1. Introduction

Dispersions of colloidal silica, also referred to as silica sols, are utilized in numerous industrial processes and commercial products, such as retention aid in paper making, as additives in paints,

\* Corresponding author at: Chemistry and Chemical Engineering, Chalmers University of Technology, SE-412 96 Göteborg, Sweden.

E-mail address: [sanna.bjorkegren@chalmers.se](mailto:sanna.bjorkegren@chalmers.se) (S.M.S. Björkegren).

as binder in foundry applications, for beverage clarification, and in polishing applications [1]. In all these applications the nature of the silica surface and the ability to control the aggregation of the colloidal particles are of great importance. Studies concerning the surface chemistry of amorphous silica have previously been undertaken [2–4]. The surface chemistry is complex and further characteristics remains to be understood. To further expand the uses of silica, and to improve the use in existing applications, development of new composite silica materials has been extensively explored. Surface modification is a common approach to customizing the silica material properties, which requires further investigations of the material in terms of characterization and evaluation methods. Publications addressing the grafting of poly(ethylene glycol) (PEG) or poly(ethylene oxide) (PEO) onto silica surfaces are frequently appearing, often with uses in biomedical applications due to the biocompatibility of the material [5–9]. PEG-containing coatings is another field of interest, where for example Malmsten et al. [10] found that a high enough interfacial density of PEG on flat silica surfaces results in efficient protein rejection. Leckband et al. studied intermolecular forces and show that grafted PEG chains can exist in both protein-repulsive and protein-attractive states, depending on factors such as compression and polymer chain length [11]. The grafting of PEO onto the surface of silica particles was reported already in the 1980s by Bridger and Vincent [12]. They investigated two methods for terminal grafting of PEO chains of which one was suitable for aqueous conditions, using *in situ* grafting of isocyanate-capped PEO during particle formation (by Stöber method [13]). However, the modified particles obtained had a low colloidal stability in water [12]. Other examples are Zhang et al. [14] who prepared PEGylated silica particles in methanol addressing both chemical and colloidal stability issues in water and Xu et al. [15] who obtained PEG-coated silica through synthesis in a methanol–ammonia mixture. Joubert et al. [16] prepared PEO-grafted silica through graft polymerization; the polymerization of EO was initiated from the silica surface, onto which alcohol groups had been attached. Still, the grafting of PEG onto silica particles where the synthesis is carried out by a simple process in purely aqueous conditions is not as recurrent.

In this paper we report on the characterization of colloidal silica particles functionalized with methyl end-capped tri-methoxy poly(ethylene glycol) silane (mPEG silane) prepared via a simple water-based route. A direct measurement of the mPEG silane attached to the silica particles has been employed using NMR diffusometry, providing quantitative information of the grafting efficiency. The aggregation behavior of the PEGylated particles has been studied with dynamic light scattering (DLS) and UV–Vis spectroscopy. Further, the modified silica surface has been characterized through polyelectrolyte adsorption and zeta potential measurements. In addition, surface activity of the particles has been assessed, since the use of particles as stabilizers for emulsions has recently gained much interest [17,18]. This full study and characterization provides both quantitative information concerning the degree of surface functionalization and surface activity as well as qualitative information concerning flocculation behavior of surface modified colloidal silica.

## 2. Experimental section

### 2.1. Materials

Sodium ion-stabilized colloidal silica particles with the trade name Bindzil 40/130 were provided by AkzoNobel Pulp and Performance Chemicals. These anionic particles have a surface area of 130 m<sup>2</sup>/g, as measured by Sears titration [19], corresponding to an equivalent spherical diameter of 21 nm [4]. The suspension has

a native pH of 9.1 and a concentration of 40 wt% silica. Silquest A-1230 (from Momentive), a tri-methoxy poly(ethylene glycol) silane end-capped with a methyl group and denoted mPEG silane, was used for the functionalization. The chemical structure of the mPEG silane is shown in Fig. 1 and was derived from standard high-resolution NMR studies (COSY, HMQC, HMBC), giving an average molecular weight of 679 g/mol. The polydispersity index of the mPEG is less than 1.2, as verified with HPLC measurements. For salt and pH adjustments reagent grade sodium hydroxide, sodium chloride and hydrochloric acid from Sigma–Aldrich were used. In addition, Amber-Jet 1500H from Dow was used for pH adjustments, a strong cation-exchange resin with sulfonic acid groups in the hydrogen form.

### 2.2. Methods

#### 2.2.1. Functionalization with mPEG silane

The mPEG silane was added to the silica suspension during agitation and at constant temperature (70 °C or room temperature) using a syringe pump. The synthesis was carried out at pH 9–10, since at this pH interval the desired condensation reaction as well as hydrolysis of the silane are fast [20]. In addition, this pH provides an electrostatically stabilized colloidal system where aggregation of the silica particles is avoided [4]. When the mPEG silane is added to alkaline water, the methoxy groups are hydrolyzed. The formed Si–OH groups of the mPEG silane become available for reaction with the silanol groups of the silica particle surface and through condensation reactions, siloxane bonds form. This results in covalent attachment of the mPEG silane to the silica surface. The mPEG silane has three functional groups, however, only up to two siloxane bonds to the surface can be formed [21], and adjacent silanes may well bind to each other. Hydrolyzed mPEG silane can also react in solution with one another. The samples were purified either by dialysis or by using an ultrafiltration cell from Millipore with an applied N<sub>2</sub> pressure of 1.6 bar. The dialysis membranes (from Sigma–Aldrich) were of cellulose with a cut-off of 14 kDa. The ultrafiltration membranes of regenerated cellulose (from Millipore) had a cut-off of 100 kDa, removing free unreacted silanes from the suspensions.

### 2.3. Characterization and evaluation

#### 2.3.1. NMR diffusometry

NMR self-diffusion measurements were conducted on a Bruker Avance 600 spectrometer, equipped with Diff30 diffusion probe with a maximum gradient strength of 1200 G/cm and with a 5 mm RF insert. Using the conventional stimulated spin-echo sequence [22], the diffusion experiments were performed at 25 °C with diffusion time  $\Delta = 100$  ms, gradient pulse length  $\delta = 1.5$  ms, gradient ringing delay  $\tau_r = 1$  ms and the gradient strength,  $g$ , ramped in at least 16 steps from 5 to 1200 G/cm. At each gradient step, the <sup>1</sup>H spectrum was collected from 8 to 16 acquisitions dependent on sample concentration. The relaxation delay was set to 5 s. It was however noted that full longitudinal relaxation was not achieved during this time, why this was

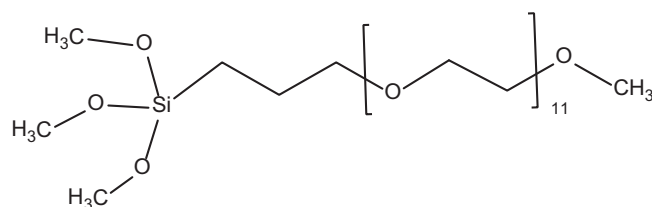


Fig. 1. Chemical structure of tri-methoxy poly(ethylene glycol) silane (mPEG silane) as derived from high resolution NMR spectroscopy.

Download English Version:

<https://daneshyari.com/en/article/606692>

Download Persian Version:

<https://daneshyari.com/article/606692>

[Daneshyari.com](https://daneshyari.com)