

Steric stabilization of Stöber silica dispersions using organosilanes

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Organosilanes of the general formula $R_xSi(OR')_{4-x}$ (where R is an alkyl group and $R' = CH_3$ or CH_2CH_3) were used to sterically stabilize hexane dispersions of submicrometre silica spheres. The dispersions were characterized according to sediment volume results. For $0.5\ \mu\text{m}$ silica particles, the sediment density increased by more than a factor of three up to 50 to 55% of theoretical in the presence of organosilanes with 12 or more carbons in the R group. Solid-state ^{13}C nuclear magnetic resonance was used to characterize the powder-dispersant interaction; this technique can distinguish between carbons in the R group of the organosilane and residual organic groups in the silica. Scanning electron micrographs of filter compacts were used to further characterize the dispersions and indicated the presence of primary particles as well as small agglomerates.

1. Introduction

Stöber silica is a chemically synthesized silica prepared by the controlled hydrolysis of tetraethylorthosilicate under basic conditions [1]. The monosized spheres prepared in this fashion can be dispersed electrostatically in high-dielectric-constant solvents such as water, then sedimented to produce compacts with high packing densities [2]. Because of the spherical nature and narrow size distribution of its particles, Stöber silica was selected here as an ideal model system for studying the steric stabilization of ceramic powder dispersions in non-aqueous liquids with low dielectric constants. Steric stabilization of Stöber silica in apolar solvents has previously been achieved using succinimide-capped isobutylene polymers, where the powder-dispersant interaction presumably arises from acid-base interactions between the terminal succinimide group and hydroxyl groups at the surface of the silica [3].

In this research, alkoxy silanes of the general formula $R_xSi(OR')_{4-x}$ (where R is an alkyl group, $R' = CH_3$ or CH_2CH_3 and $x = 1, 2$ or 3) were used to sterically stabilize silica dispersions in hexane. The reaction between alkoxy groups and hydroxyl groups at the surface of the silica to eliminate one or more molecules of alcohol allows the organosilane to be covalently attached to the silica. Once the dispersant is anchored to the surface, the alkyl group may extend into solution to form a steric barrier that prevents flocculation. Similar chemistry is known to occur for BaTiO_3 powders sterically stabilized with organotitanium dispersants [4, 5].

Polymeric dispersants with reactive terminal silane groups have previously been grafted to the surface of silica powders [6]. In this research, different monomeric organosilanes were used in efforts to determine the minimum hydrocarbon chain length necessary to

sterically stabilize spherical particles of a given size. The data collected in this study and related research may provide a basis for the study of the range and magnitude of steric interactions and van der Waals forces in sterically stabilized non-aqueous dispersions.

2. Experimental procedure

The organosilanes $\text{C}_8\text{H}_{17}\text{Si}(\text{OCH}_2\text{CH}_3)_3$, $\text{C}_{16}\text{H}_{33}\text{Si}(\text{OCH}_2\text{CH}_3)_3$, $\text{C}_{18}\text{H}_{37}\text{Si}(\text{OCH}_3)_3$, $\text{C}_{18}\text{H}_{37}\text{Si}(\text{OCH}_2\text{OCH}_3)_3$ and $\text{C}_{18}\text{H}_{37}\text{Si}(\text{CH}_3)_2\text{OCH}_3$ employed in this study were obtained from Petrarch Systems, Inc., (Bristol, Pennsylvania) and were used as received. Alkoxy silanes that were not commercially available were synthesized from the corresponding chlorosilanes. The chlorosilanes were refluxed in excess alcohol containing triethylamine to neutralize the byproduct HCl. After the triethylamine hydrochloride was filtered out and residual alcohol distilled away, the purity of the product was checked by ^1H nuclear magnetic resonance (NMR) in CDCl_3 solution. The hexane used to prepare the dispersions was distilled under nitrogen from LiAlH_4 .

The silica employed in this study was prepared by the Stöber method [1]. Tetraethylorthosilicate (TEOS) was purchased from Aldrich Chemical Co. (Milwaukee, Wisconsin) and Alfa Products (Danvers, Massachusetts), and was used as received. The $0.5\ \mu\text{m}$ silica was prepared in a two-litre round-bottom flask by vigorously stirring dehydrated 200-proof ethanol (1450 ml) with concentrated aqueous NH_4OH (229 ml), then adding the TEOS (121 ml). The mixture was stirred at room temperature for 4 h, refluxed for an additional 2 h, then cooled and stirred overnight at room temperature. The solvent was removed by trap-to-trap distillation on a Schlenk line. Halving the amounts of NH_4OH and TEOS in the above procedure produced $0.16\ \mu\text{m}$ silica.

The dispersions employed in this study were prepared by sonicating the Stöber silica (2 g) and the organosilane with hexane (8 ml) in a graduated cylinder on its side in an ultrasonic bath. The concentration of organosilane was always based on the weight of the powder. Neat organosilane was injected by syringe and the graduated cylinder was capped with a rubber serum cap prior to sonication. The dispersions were allowed to gravity-sediment to constant volume and the packing density was calculated as a percentage of theoretical using 2.0 g ml^{-1} as the density of the Stöber silica.

Filter-cake compacts were prepared by filtering the dispersions through submicrometre filter paper using house vacuum. The sonicated dispersion was pipetted into a polypropylene Econocolumn 17 mm in diameter (Bio-Rad Laboratories, Richmond, California). Generally, two pieces of No. 596 filter paper and two pieces of $0.45 \mu\text{m}$ BA85/23 membrane filter (both from Schleicher and Schuell, Keene, New Hampshire) were placed on the frit in the column. Scanning electron micrographs (SEMs) of the dried compacts were obtained using an ISI-DS130 dual-stage scanning electron microscope. Solid-state cross-polarization/magic-angle spinning (CP/MAS) ^{13}C NMR spectra were recorded on a Nicolet S-100 instrument. Crushed samples of dried compacts were spun at approximately 3000 r.p.s. in a boron nitride rotor. Spectra were acquired using a 2 sec delay and a contact time of 2 msec.

3. Results

The most commonly used dispersants in this research were trifunctional alkoxyxilanes with the general formula $\text{RSi}(\text{OR}')_3$. Fig. 1 summarizes the results of dispersion experiments in hexane with $0.5 \mu\text{m}$ Stöber silica and the alkoxyxilanes $\text{C}_8\text{H}_{17}\text{Si}(\text{OCH}_2\text{CH}_3)_3$, $\text{C}_{12}\text{H}_{25}\text{Si}(\text{OCH}_3)_3$ and $\text{C}_{18}\text{H}_{37}\text{Si}(\text{OCH}_2\text{CH}_3)_3$. These data indicate that the packing density of the silica increased with increasing silane concentration, then levelled off at a maximum value for each silane. The data also indicate that this maximum packing density was attained at lower silane concentrations as the

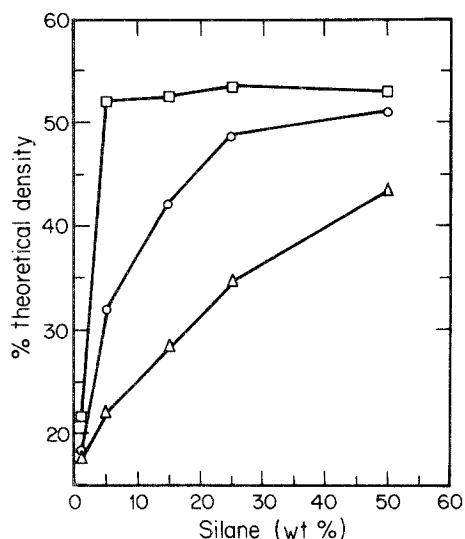


Figure 1 Packing density of $0.5 \mu\text{m}$ Stöber silica against weight percentage of C_8 , C_{12} and C_{18} alkoxyxilane dispersants. (\square) $\text{C}_{18}\text{H}_{37}\text{Si}(\text{OCH}_2\text{CH}_3)_3$, (\circ) $\text{C}_{12}\text{H}_{25}\text{Si}(\text{OCH}_3)_3$, (\triangle) $\text{C}_8\text{H}_{17}\text{Si}(\text{OCH}_2\text{CH}_3)_3$.

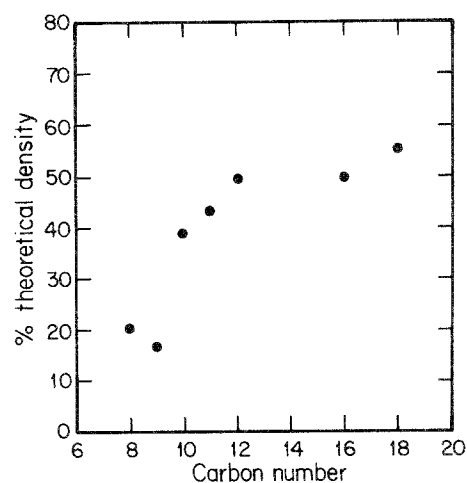


Figure 2 Packing density of $0.5 \mu\text{m}$ Stöber silica against carbon chain length in the silane alkyl group.

carbon chain length increased. For example, greater than 50% theoretical density was obtained using only 5 wt % of the C_{18} organosilane, whereas the packing density still had not reached its maximum with 50 wt % of the C_8 derivative.

Fig. 2 illustrates the packing density of $0.5 \mu\text{m}$ Stöber silica as a function of carbon chain length in the silane alkyl group. For this series of experiments, the concentration of $\text{C}_{18}\text{H}_{37}\text{Si}(\text{OCH}_3)_3$ was set at 15 wt % to ensure that the maximum packing density for this organosilane would be achieved. Then, to allow a valid comparison, the concentrations of silanes with smaller chain lengths were set such that the mole percentage of silane remained constant throughout the entire series.

Under these conditions, a steady increase in the silica packing density was observed with increasing chain length up to the C_{12} derivative. Beyond this point, increasing the chain length did little to improve the packing density; sediment densities typically ranged between 50 and 55% of theoretical. Experiments comparing $\text{C}_{18}\text{H}_{37}\text{Si}(\text{OCH}_3)_3$, $\text{C}_{18}\text{H}_{37}\text{Si}(\text{OCH}_2\text{CH}_3)_3$ and $\text{C}_{18}\text{H}_{37}(\text{CH}_3)_2\text{Si}(\text{OCH}_3)_3$ also produced packing densities in this range, indicating that the identity (methoxy or ethoxy) or number of alkoxy groups had little effect on the dispersion and packing behaviour of the silica.

Fig. 3 compares the solid-state CP/MAS ^{13}C NMR spectrum of the as-prepared $0.5 \mu\text{m}$ Stöber silica with the spectrum for the same powder dispersed with

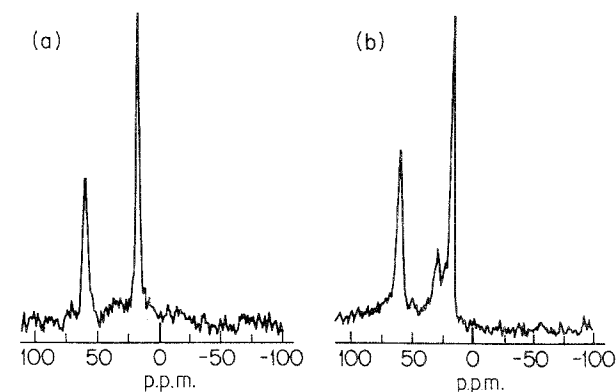


Figure 3 Solid-state CP/MAS ^{13}C NMR spectra of $0.5 \mu\text{m}$ Stöber silica: (a) as-prepared, (b) stabilized with $\text{C}_{18}\text{H}_{37}\text{Si}(\text{OCH}_3)_3$.

TABLE I Effect of sonication time on sedimentation velocity and packing density of 0.5 μm Stöber silica using $\text{C}_{18}\text{H}_{37}\text{Si}(\text{OCH}_3)_3$ as the dispersant

Sonication time	Sedimentation velocity, Particle Front 1	Sedimentation velocity, Particle Front 2	Packing density (% theoretical)
5 min	7.69 cm sec^{-1}	3.33 cm h^{-1}	52.6
30 min	2.5 cm h^{-1}	0.25 cm h^{-1}	55.0
3 h	1.62 cm h^{-1}	0.32 cm h^{-1}	55.0

$\text{C}_{18}\text{H}_{37}\text{Si}(\text{OCH}_3)_3$. In Fig. 3a, the resonances at 60 and 18 p.p.m. are due to $-\text{OCH}_2$ and $-\text{CH}_3$ carbons in residual ethoxy groups in the starting powder [7]. The new resonances at 30 and 20 p.p.m. in Fig. 3b can be attributed to the octadecyl chain of the organosilane dispersant [8]. These results illustrate the power of solid-state NMR for characterizing chemically derived ceramic powders and their interactions with dispersant molecules. Using Fourier transform infrared spectroscopy, it was very difficult to determine if the organosilane was present due to its low concentration as well as overlap in the C-H stretching frequencies. Solid-state NMR could readily distinguish between carbons in residual alkoxy groups and the hydrocarbon chain in the organosilicon dispersant.

The effect of sonication time on dispersion quality and sediment density was also investigated and the results are summarized in Table I for the dispersant $\text{C}_{18}\text{H}_{37}\text{Si}(\text{OCH}_3)_3$. Lengthening the sonication time from 5 to 30 min only minimally improved the packing density but dramatically reduced the sedimentation velocities of the silica particles. During gravity-sedimentation of these dispersions, in most instances two distinct particle fronts settled out. The velocity data in the second column of Table I are for the first front, which contained an estimated 80% of the silica particles; the data in the third column are for the second front, which contained the remaining 20% of the particles.

When sonicated for 5 min the first front settled extremely rapidly, at a rate of the order of centimetres per second; the second front settled much more slowly, with a velocity of approximately 3 cm h^{-1} . In comparison, when the sonication time was lengthened to 30 min, the first front settled at essentially the same

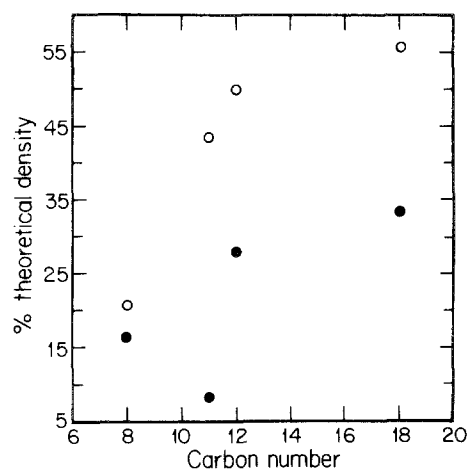


Figure 5 Packing densities of Stöber silicas with particle diameters of (○) 0.5 and (●) 0.16 μm against carbon chain length in the silane alkyl group.

velocity as that of the second front after 5 min sonication, while the second front settled at a velocity an order of magnitude smaller than that of the first front. Increasing the sonication time to 3 h had little effect on either the sedimentation velocities for the different fronts or the packing densities.

For the 30 min and 3 h sonication times, velocity calculations using the Stokes equation indicated that the second front contained primary particles. The SEM (Fig. 4a) of a thin filter-cake compact prepared using only particles from the second front indicated that some small agglomerates containing 2 to 4 particles each did exist, but the dispersion contained mostly primary particles. The SEM (Fig. 4b) of the bottom surface of a compact prepared from an entire dispersion sonicated for 30 min showed large agglomerates and poor overall packing.

Fig. 5 compares the packing behaviour of Stöber silica particles 0.16 and 0.5 μm in diameter as a function of carbon chain length in the silane alkyl group. For each silane, the packing density for the smaller silica particles was much lower, suggesting that more extensive agglomeration occurs in the 0.16 μm silica dispersions.

4. Discussion

The research has shown that the dispersion and

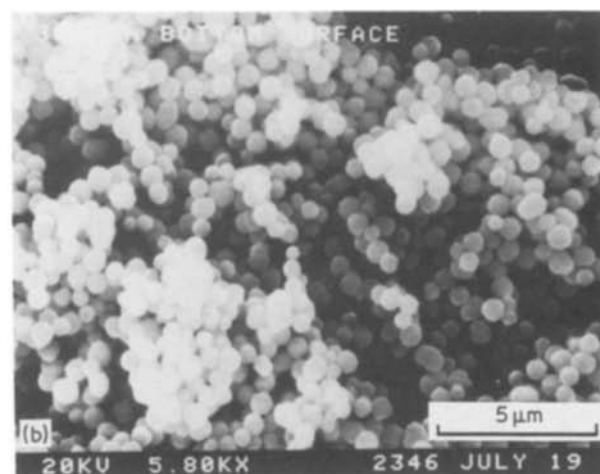
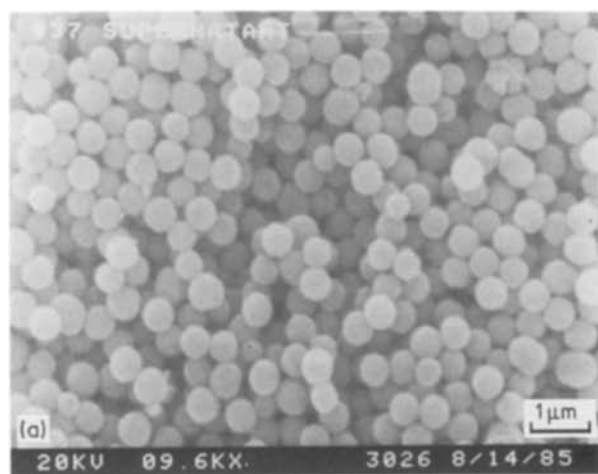


Figure 4 SEMs of silica particles stabilized with $\text{C}_{18}\text{H}_{37}\text{Si}(\text{OCH}_3)_3$ and sonicated for 30 min: (a) filter-cake compact containing only particles from the second front, (b) bottom surface of filter-cake compact prepared from the entire dispersion.

packing behaviour of Stöber silica spheres in low-dielectric-constant liquids can be markedly improved by adding suitable quantities of alkoxy silanes with the general formula $R_xSi(OR')_{4-x}$. More than a three-fold increase in packing density was observed for sediments obtained from dispersions in hexane, and SEMs indicated the existence of primary particles in sediment compacts. The improvement in dispersion and packing is attributed to a steric-stabilization mechanism in which the alkyl groups bonded to silicon extend out into the organic medium, providing a barrier that prevents flocculation. Covalent attachment of the organosilane to the silica can occur via reaction of the alkoxy groups with hydroxyl groups at the surface of the silica to eliminate one or more molecules of alcohol. Solid-state ^{13}C NMR has provided evidence for the interaction of $C_{18}H_{37}Si(OCH_3)_3$ with the silica powder, and has also shown that in addition to hydroxyl groups, the Stöber silica contained a significant number of residual ethoxy groups that remained from the synthesis with $Si(OCH_2CH_3)_4$.

From the data in Figs 1 and 2, it is clear that the longer-chain organosilanes were considerably more effective as dispersants for the Stöber silica. For example, 52% of theoretical density was obtained using only 5 wt % of the octadecyl silane, whereas only 43% of theoretical density was obtained with 50 wt % of the C_8 derivative. The maximum packing density observed with the grafted organosilanes as steric stabilizers was 55% of theoretical density.

The goal of this research was to determine the minimum-size R group necessary to sterically stabilize spherical particles of a given size. The data in Fig. 2 indicate that the packing density of the $0.5 \mu m$ spheres remained essentially constant for organosilanes with 12 or more carbons in the R group. However, although it is apparent from the sedimentation data that the organosilanes improved the silica dispersion, it is also clear from the SEMs and Stokes velocity calculations that some agglomerates remained after sonication and grafting. It is likely that a fraction of the organosilane reacted with the surfaces of agglomerates that were not broken up during sonication, and therefore the observed differences in packing density against R group in part reflect the ability of the various silanes to disperse small agglomerates as well as primary particles. The agglomeration problem appeared to become worse as the particle size of the Stöber silica

decreased, and is thought to originate in the drying step following synthesis.

Since the overall goal of this study is to determine the minimum-size alkyl group necessary to sterically stabilize monodisperse spheres, future efforts will focus on identifying reaction conditions that allow the organosilanes to react only with the surfaces of primary particles. One approach to be investigated involves using a higher-dielectric liquid medium for the grafting reaction, such that the initial dispersion of silica particles can be improved relative to the dispersion in hexane. Once the organosilanes have been covalently attached, the silica may be isolated and transferred to a low-dielectric organic solvent for the steric stabilization studies.

Future work will also focus on the synthesis and drying of Stöber silica batches covering a broader range of particle size distributions, and on the use of chlorosilanes as dispersants. Solid-state ^{13}C and ^{29}Si NMR will be used to further characterize the silanized powders, and in conjunction with thermal gravimetric analysis, to quantify the extent of the grafting reaction.

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