



Synthesis of self-suspending silica proppants using photoactive hydrogels



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ABSTRACT

Micro and mesoscale particles in fluids are widely used from hydrocarbon extraction to drug delivery applications. Of interest are silica particles that are used as proppants for the extraction of natural gas from underground reserves. These particles have the tendency to settle out or aggregate in slurries, resulting in hindered transport. This in turn, necessitates requires high pressure pumping or additives, resulting in various environmental concerns and increased costs. As an alternative to using lighter proppant particles, here we report on a facile procedure to create self-suspending particles formed by a water swellable hydrogel shell. We graft photoactive polyethylene glycol hydrogels to large, non-spherical silica particles using a UV polymerization procedure. The proppant particles formed are stable with a high degree of hydration and reduced apparent density. A significant drop in density in comparison to unmodified particles is shown that can reduce the settling velocity and thereby, reduce hindered transport. The experimentally obtained settling velocities are in good agreement with theoretical models. The ability to tune particle density has implications in industrial applications to improve environmental impact, efficiency and productivity.

1. Introduction

Particles of silicon dioxide, also known as silica, are widely used in a variety of industrial processes. These can range from fillers in rubbers and plastics, drug delivery vehicles, to hydrocarbon extraction. In the latter operations, silica particles (sands) ranging in size from 100 to 2000 μm are known as proppants used to support open underground fractures, allowing for natural gas flow via hydraulic fracturing techniques (Breval et al., 1987; Hellmann et al., 2014). The micro and mesoscale proppant particles are typically transported using a fluid consisting of water and other additives. In some industrial applications, it is necessary to remove suspended silica particles from the process stream (Wang et al., 2009). However, in other cases such as during fracturing, the settling of the particles is considered to be a major challenge. For instance, silica proppants with a density of $\sim 2.65 \text{ g/cm}^3$ (exceeding that of the transport fluid) have the propensity to settle out over time, requiring the use of high pressure pumping or toxic additives to the sand slurry in hydrocarbon extraction operations (Hammond, 1995). These hindered transport properties can lead to environmental concerns and increased costs. There is a continuous need to improve the compatibility of these operations with an eye to their environmental impact. For instance, an outstanding research question involves the viability of creating additive-free transport fluids or slurries (ideally,

water + particles only). The ability to tune the density of particles is therefore of critical importance in such applications to improve efficiency and productivity.

While using lighter proppant materials such as alumina is an option, these lighter materials are expensive and often have reduced mechanical properties. Functionalization of the surfaces of the cheaper silica proppant particles is therefore a promising strategy to tune properties to address specific needs (Zoveidavianpoor and Gharibi, 2015). Several techniques have been used as lightweight proppants or to reduce the specific gravity of proppants as summarized in a recent comprehensive review (Liang et al., 2016). In particular, organic-inorganic composite particles have been long studied in order to combine properties of the inorganic material (e.g. rigidity, thermal stability) with the organic surface functionalization (e.g. flexibility, surface charge, processability) (Kango et al., 2013). Physically or chemically modified silica particles have been used for improved optical, mechanical or rheological properties, and also to improve their integration with polymeric matrices to form novel composites (Zou et al., 2008). On the other hand, controlling the settling of proppants by tuning their apparent density (without fundamentally altering the core itself) has not been well explored from a fundamental perspective. In this study, we focus on the control of transport properties, specifically the settling velocity of silica (SiO_2) proppant particles by controlling their bulk density. This is achieved by

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controlling the *effective* specific gravity by engineering the surfaces of the particles with the use of hydrogel coatings that can swell in aqueous environments.

We report on covalently bonding a swellable hydrogel layer to the silica proppant surface using a rapid UV-based photopolymerization process. The grafted hydrogel layer creates a shell around the particle that results in “self-suspension” and a significant drop in density due to swelling in water. The idea of self-suspending proppants via hydrogel coatings is relatively new. (Kincaid et al., 2013) This work has been discussed in recent patent filings (e.g. Fairmount Santrol) but not extensively in the technical literature (Pangilinan et al., 2016). Indeed, the use of UV polymerization to graft hydrogels to the proppant surface has not been widely reported. While a few reports have presented the surface modification of microparticles of silica using UV-graft polymerization (Kim et al., 2005; Shin et al., 2008), to the best of our knowledge, this is the first report of highly stable, multilayer modification of relatively large (several mm size), industrially relevant and irregularly shaped, non-spherical particles. The method is a facile and scalable process that can be used to form multiple layers following three main steps: amination, PEGylation and polymerization. Earlier works have reported the formation of clusters due to agglomeration of particles during the modification process, coupled with the formation of ungrafted polymer (Perruchot et al., 2001). To address these issues, we use a surface-grafting reaction initiated by ultraviolet (UV) irradiation (Ranby et al., 1986). Such reactions tend to be fast and efficient, and are limited to the surface without affecting the bulk properties (Wang et al., 2008).

Of specific interest in this case are the high mechanical strength of silica proppant particles required for industrial applications. Unlike typical grafting protocols, the particles present improved stability in aqueous solution without aggregation, as well as in the dry state whereby they can be transported and re-hydrated as necessary. Characterization of the particles after each step is performed using imaging and FTIR to monitor the changes on the particle surface. Our results show that the PEGylation strategy is able to decrease the effective specific gravity by more than 33% in aqueous suspensions. The concurrent decrease in settling velocity shows that this can be a relevant method to improve transport properties of industrially relevant silica proppant particles using a rapid functionalization procedure. Further, the reported strategy of PEGylation of “swellable” silica particles with high hydrophilicity and cytocompatibility can help in improving the dispersion within polymer matrices (Shin et al., 2008), or creating functional, “stealth” carriers at different length scales (nano to meso scale) for drug delivery applications (He et al., 2010; Rio-Echevarria et al., 2010).

2. Materials and methods

2.1. Materials

Granular silica (SiO₂) particles (4–20 mesh), Poly (ethylene glycol) diacrylate (PEG-DA) with reported molecular weight of 575 Da, (3-aminopropyl) triethoxysilane (APTES) were purchased from Sigma-Aldrich Co. (St Louis, MO). Photoinitiator Darocur 1173 (Hydroxy-2-methyl-1-phenyl-1-propanone) was obtained from Ciba Specialty Chemicals Corporation (Tarrytown, NY). Deionized water (resistivity 18 mΩ cm) was obtained from a MilliQ water purification system (Millipore Corporation, Danvers MA). Methanol (Alfa Aesar) and ethanol (200 proof, absolute, anhydrous, Shelbyville, KY) were used as received for experiments. Photopolymerization of the PEG polymer was performed using UV light at 365 nm (Lumen Dynamics OmniCure 1000).

2.2. Synthesis of modified particles

In a typical experiment, SiO₂ particles (0.5 g) in a beaker were mixed with APTES (185 μL) in 20 ml ethanol. The beaker was covered and agitated with a magnetic stir bar for 24 h at 50 °C and 500 rpm. The particles were then separated and washed with methanol 5 times and

deionized water 3 times. In order to record the dry weight of the particles, they were dried overnight in an oven at 60 °C, prior to recording the mass. The particles were dispersed in methanol (42 ml), heated to 40 °C, and stirred at approx. 700 rpm for 30 min. Poly (ethylene glycol) diacrylate (1 g) in methanol (8 ml) was added to the mixture and allowed to react for 24 h at the set temperature and rpm. Then, the particles were separated and washed. Some of the particles were dried overnight in an oven at 60 °C to record the dry weight of the PEGylated particles. Finally, to graft and crosslink the PEG layers to the particles, they were dispersed in photoinitiator solution (0.2% in water) and vortexed for 30 min. Crosslinking was conducted in water for 10 min using high intensity UV lamp (365 nm at 2 mW/cm²) under constant stirring to obtain the hydrogel-modified particles. In order to form a second layer of hydrogel, grafting was performed by repeating the above procedure.

2.3. Particle characterization - imaging and spectroscopy

Imaging of the particles was conducted using an Olympus IX-71 fluorescence microscope (Olympus, Japan). Fourier Transform Infrared (FTIR) spectroscopy was conducted on particles using a Nicolet iS10 FTIR (ThermoFisher Scientific, Waltham MA) spectrometer.

2.4. Settling velocity

Settling velocities were measured in water by measuring their fall in a graduated cylinder. Each particle was dropped in a tall graduated tube and the velocity was measured between two markings once terminal velocity was attained. This was performed at least five times for each set and each experiment was repeated at least three times. Further analysis of the silica particles was conducted through water displacement experiments, size data, and settling velocity experiments. Water displacement density experiments were conducted for the hydrated polymerized particles (1- and 2-layer) and the unmodified particles to quantify the decrease in density. Size data of hydrated and dried (1- and 2-layer) and unmodified particles was collected through the images captured and JMicroVision software (Roduit, 2008).

3. Results and discussion

Developing strategies for the control of physico-chemical properties of particles has vital implications in diverse areas ranging from energy extraction to drug delivery. For particles in flow, this can affect their transport properties and behavior in solution. In several industrial applications, settling of particles in two-phase flows is a major challenge, for example as proppants in hydrocarbon extraction. As calculated using Stokes' Law, the settling rate of a particle is proportional to the square of the particle diameter and the density difference between the particle and the suspending fluid (Bird et al., 2002). Therefore, if our objective is to increase particle travel in water for instance, at a given density, decreasing particle diameter in half can increase traveling distance four-fold. Similarly, given same sized particles, reducing the density in half can increase the traveling distance by five times. Thus, decreasing density or size or both are options to improve transport properties. However, decreasing particle size can lead to other issues such as clogging. While replacement with lighter proppant particles is always possible, lighter materials usually have a reduced mechanical strength or tend to be more expensive. Given these design constraints, a viable alternative is to modify the surface of currently used particles to reduce their *effective* density and achieve similar benefits in transport properties as lighter particles.

In these experiments, a water swellable polymer (hydrogel) was covalently bonded to silicon dioxide (silica) particles, to control the effective density of the particles in water suspensions, while maintaining their mechanical strength. Hydrogels, which are crosslinked hydrophilic polymers, are an important class of materials can also swell in water without the dissolution of the polymer due to their hydrophilic but

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