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 reservoirs. 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 ~2.65 g/cm³ (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 (SiO₂) proppant particles by controlling their bulk density. This is achieved by...
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 (Ramby 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; Río-Echevarría et al., 2010).

2. Materials and methods

2.1. Materials

Granular silica (SiO₂) particles (4–20 mesh), Poly (ethylene glycol) diacrylate (PEG-DGA) 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 μ) 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
crosslinked structure. They have been widely used for various applications, primarily in the biomedical arena owing to high biocompatibility and similarity to soft tissue (Nguyen and West, 2002). These 3D networks of hydrogels can also be used in industrial applications, since the swelling of the grafted hydrogel layer can create “self-suspending” proppant particles that have a reduced density and settling velocity (Ahmed, 2015). This has enormous implications in reducing pumping loads and associated energy and environmental costs (Gu et al., 2015). Herein, poly (ethylene glycol) diacrylate (PEG-DA) is used as a proof-of-principle photocrosslinkable hydrogel that can be attached to the silica surface using a facile and rapid process. PEGDA and other acrylate polymers have been widely used for several decades as swellable hydrogels for a number of applications (Priola et al., 1993). The high reactivity of acrylate monomers, together with the large choice of acrylate functionalized oligomers provide a ready route for photoinitiated polymerization and crosslinking using UV radiation. The advantage of using UV radiation to initiate the chain reaction lies in the high polymerization rates and reaction rate, such that the liquid to solid phase change can occur within a fraction of a second (Decker, 1996). As we show, even short chain PEGDA (MW 575) can form a highly crosslinked, yet swellable network on the surface of the particle. By suitable control of the degree of crosslinking, chain length and nature of the oligomer, we can control the density change of the particle.

### 3.1. Synthesis of functionalized particles

Via amination, PEGylation and polymerization, the hydrogel layer was successfully bonded to each particle surface (Scheme 1) (Guibal,
alkene (C=C) peak, suggesting the C=C bonds ruptured and formed a cross-linked hydrogel shell around the particles.

Imaging was also utilized to verify that the polymer was successfully bonded on the particle surfaces. The first grafted hydrogel layer was too thin for optical microscopy to capture (consider that the hydrogel layers are essentially optically transparent). Fluorescein isothiocyanate (FITC) dye was therefore mixed into the precursor polymer that was then grafted to the silica particles. The dye was captured inside the hydrogel shell and remained on the particle surface as can be seen in Fig. 2c (expectedly, the unmodified particle showed no fluorescence – Fig. 2b). On addition of the second hydrogel layer, the imaging is similar as seen in Fig. 2d. The addition of the second hydrogel layer permitted optical microscopy of the particles as seen in Fig. 1c and d. Optical microscopy images show the attached hydrogel layers on the surface of the particles in dry and fully hydrated condition. The highly hydrated polymer shell is clearly observed in the wet condition. The formation of the grafted hydrogel shell using PEGacrylates or -methacrylates is based upon the UV initiated free-radical polymerization of acrylate or methacrylate end groups on PEG derivatives. The photoinitiator used in these studies dissociates upon exposure to UV radiation, creating reactive free radicals, which then attack unsaturated carbon-carbon double bonds of (meth)acrylate functionalities on the macromer, initiating free radical polymerization. Since two reactive centers per macromer are created, propagation results in the formation of a poly (meth)acrylate network that is highly cross-linked with PEG. This network represents a three-dimensional, insoluble structure, capable of absorbing large quantities of water and providing a “self-suspension” behavior.

3.2. Characterization of functionalized proppant particles

The surface area of the particles was estimated before and after grafting (and polymerization) using optical microscopy followed by software analysis. As observed in Fig. 3, the increase in surface area is ~16% following grafting of two hydrogel layers. The particles...
themselves were polydisperse (calculated value 1.12) resulting in higher error bars. As noted above, the grafting of a single layer was not easily observed using optical microscopy. However, on fully hydrating the particles, an increase of ~35% of surface area was observed owing to the high degree of hydration of the particles. Hydrogels swell in water without dissolution due to their hydrophilic but crosslinked structure. The % of hydration was calculated by weighing the particles before and after suspension in water. % hydration is estimated as \( \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \). For a single hydrogel layer, the hydration was 23.06%, whereas on addition of the second hydrogel layer, the hydration was 33.2%. The particles were also stable in both dry and hydrated conditions. In the dry condition, they could be stored for weeks without any loss of hydration (i.e. they had the same level of hydration as measured prior to storage). In the hydrated condition, the particles did not aggregate over time.

The hydrated shell around the particles is responsible for imparting a “self-suspension” behavior to the modified proppant particles, whereby their effective density is reduced. Using a displacement method, the density of the particles was noted to be significantly different before (2.6 g/cm³) and after modification (1.8 g/cm³). Fig. 4a shows this drop in density of 24% following addition of one hydrogel layer and 33% after addition of the second hydrogel layer. This drop by nearly a third is manifested by a concomitant reduction in settling velocity (Fig. 4b). Settling velocity experiments resulted in a drop from 12.3 cm/s to 10.9 cm/s. In order to compare the experimentally obtained values with theoretical estimations of settling velocity, a number of different correlations were studied for settling of regular and irregular particles. The correlation proposed by Tsakalakis and Stambolzis to predict the settling of irregularly shaped particles (e.g. crushed solids) in water was used. (Tsakalakis and Stambolzis, 2001) This correlation is valid for a wide range of Archimedes numbers, and was verified for crushed quartz which is very similar to the material was used in this work. The proposed correlation allows for the calculation of the settling velocity of the particles via the equation:

\[
Re_t = 0.059 \times Ar^{ \left[ \frac{0.084041 - 0.04005 \times \ln(Ar) + 0.000095 \times (\ln(Ar))^2}{C_1} \right]}
\]

where \( d \) is the particle size (diameter), \( g \) is the acceleration of gravity, \( \rho_f \) is the fluid density, \( \rho_p \) is the particle density, \( \mu \) is the fluid viscosity, and \( u_t \) is the settling velocity of the particle. Using these equations, the settling velocity for a particle with a density of 1.8 g/cm³ and 2.1 mm is 12.2 cm/s. Thus, the values are well within the range of experimentally obtained results of 12.3 cm/s and 10.9 cm/s before and after modification (note that the swelling of the particle due to the hydration of the attached PEG-layer results in an increase in diameter). To approximate proppant settling in fracturing fluid, similar calculations can be performed for non-Newtonian fluids, for instance using the Chien correlation to estimate the settling velocity for non-spherical particles of given sphericity. (Chien, 1994; Eltilib et al., 2011) For the results obtained in this work, this correlation was not applied since the settling experiments were conducted in water. Such calculations can be of great assistance when predicting the settling time and distance as well as the pumping loads. The lower settling velocity will also result in a longer travel time (theoretically estimated to be around 4 times higher than the unmodified particles) and therefore lower pumping loads in hydraulic fracturing operations.

This is the first study showing such a significant drop in particle density owing to a self-suspending hydrogel shell. Owing the facile and scalable nature of the process which can be conducted using rapid photopolymerization, large numbers of particles can be simultaneously, and inexpensively modified in an industrial setting. It may be noted that since the core of the silica particle is unchanged, this process does not affect the mechanical properties of the particles in any way. Here that we only showed the grafting of 2 hydrogel layers using a relatively short chain PEG-DA (MW 575). As shown before, higher molecular weight PEG-acrylates with longer chains show higher rates of hydration (Mellott et al., 2001; Russell et al., 2001) (likely on account of the larger “shell” around the particles) and would therefore be expected to show much higher drops in effective density. Grafting of additional layers could also be used to reduce the apparent density of the particles further, although
this needs to be optimized with regard to throughput and the expected gain in performance.

4. Conclusions

In summary, here we have demonstrated a facile and scalable strategy for the UV-grafting of acrylate monomers to irregular silica proppant particles. The PEG hydrogel was observed to form a thin shell around the particles that swells by around 33% in aqueous media. Attachment of the PEG hydrogel was verified by optical and fluorescence microscopy in addition to FTIR measurements at each step. Both one and two-layer grafting was demonstrated. The particles are stable over long periods of time, with no loss in mechanical properties as the grafted shell does not affect the underlying material. The swelling of this shell causes a self-suspension of the particles resulting in a decrease of their apparent density by around one-third, which is significant. The reduction in settling velocity were verified experimentally and theoretically. For example, if applied as proppants in hydrocarbon extraction applications, the decrease in density and accompanying settling velocity can effectively increase the total efficiency of the process. Not only is the pumping load reduced, but also the total amount of materials (proppant particles + additives) is lowered, resulting in environmental and economic benefits. Similar chemistries can be used for the modification of materials such as alumina, while functionalization methods can potentially enable continuous synthesis to form scalable processes. Current investigations are focusing on the use of hydrogels with longer chain lengths to form a larger “hydration shell” and thereby achieve a larger drop in density and settling velocity in aqueous media.

References