Cross-linked polymer nanocomposite networks coated nano sand light-weight proppants for hydraulic fracturing applications

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ABSTRACT

Three-dimensionally cross-linked polymer nanocomposite networks coated nano sand light-weight proppants (LWPs) were successfully prepared via ball-milling the macro sand and subsequently modifying the resultant nano sand with sequential polymer nanocomposite coating. The modified nano sand proppants had good sphericity and roundness. Thermal analyses showed that the samples can withstand up to 411 °C. Moreover, the proppant samples’ specific gravity (S.G.) was 1.02–1.10 g/cm³ with excellent water dispersibility. Therefore, cross-linked polymer nanocomposite networks coated nano sand particles can act as potential candidates as water-carrying proppants for hydraulic fracturing operations.

Keywords: proppants; nano sand; polymer; nanocomposites; graphene; hydraulic fracturing

1. Introduction

In general, proppants are milli- or micrometer-sized solid particles with specific crush resistance employed to keep open the cracks and enhance oil production from a wellbore[1–5]. Since the proppants are used in downhole a few kilometers deep, they must be stable at harsh conditions of high temperature and high pressure (HT-HP), high temperature-high salinity (HT-HS) coming from either groundwater in deep wells or the strong acid mixtures (hydrofluoric and hydrochloric acids) that are pumped into wellbore to clear blockages, and corrosion from the fracturing fluid itself[6–22]. Therefore, the nature and quality of the proppant are vital to a successful hydraulic fracturing operation and subsequent oil production. Frac sand and modified frac sands are widely employed as proppants[23–26]. Even though the frac is abundantly available and has a low cost due to its high density, low crush resistance (6000 psi), and relatively decreased sphericity and roundness, it often causes poor fracture permeability[2,27,28]. Conversely, although the ceramic proppants have very high crush resistance (up to 20,000 psi) and thermal stability, the settling rate in fracturing fluid is high, which is ascribed to their high specific gravity values (3 g/cm³)[2,28–33]. Hence, various conventional hydraulic fracturing operations exploit large volumes of water-based hydraulic fluid to enhance the well permeability, potentially producing large amounts of wastewater as flow back and pose severe environmental threats[33–39]. Therefore, water-based fracturing technology has recently attracted the attention of scientists, and it
requires the development of ultra-lightweight proppant\textsuperscript{[40–44]}. At the same time, the ultra-lightweight proppants should possess excellent crush resistance, thermal stability, acid resistance, and higher roundness and sphericity.

Polymeric composite microspheres have been recently employed as low-density proppants for water-based hydraulic fracturing operations\textsuperscript{[4,42,44–47]}. For instance, Chen et al.\textsuperscript{[48]} reported polymethylmethacrylate (PMMA)/graphite composite microspheres with SG of 1.055–1.135 g/cm\textsuperscript{3} and can withstand crushing stress up to 69 MPa. They have also reported polystyrene (PS)/graphite microspheres with SG of 1.025–1.185 g/cm\textsuperscript{3} with a crush resistance of 68 MPa\textsuperscript{[49]}. The primary preparation methods of the polymeric microspheres are emulsion polymerization, suspension polymerization, dispersion polymerization, and so on\textsuperscript{[50–52]}. However, this method involves multi-step syntheses with yield limitations and is most often not scalable to meet the growing industrial demands\textsuperscript{[53–64]}. Therefore, we conceived the idea of making nano sand particles by ball-milling the abundant and low-cost frac sand and suitably modifying them to withstand high temperature-high pressure-high salinity (HT-HP-HS) downhole conditions\textsuperscript{[17]}. Incorporating nanofillers like graphene can potentially increase the final material’s thermal and mechanical properties\textsuperscript{[65,66]}. To our knowledge, no publications exist on nano sand particles as lightweight proppants in hydraulic fracturing applications. We have recently reported different surface modification techniques using various polymers, resins, and their combinations to improve the crush resistance of frac sand. The existing modification techniques are majorly of one-layer coating, and there is still space for improvement in thermo-mechanical and structural integrities in the coated sand proppants\textsuperscript{[45,67]}. Our group has recently introduced a two-layer coating approach for the surface modification of frac sand using sequential coating polymer nanocomposites with graphene or boron nitride nanosheets. Interestingly, the two-layer coating sand proppants exhibited a crush resistance to a maximum of 10,000-14,000 psi\textsuperscript{[2,28,33,68–70]}. However, practical applications of these proppants are limited due to their high specific gravity values and poor dispersibility in water-based fracturing fluid. Also, pumping the high-density proppants into formations may result in discontinuous structures that may have an adverse impact on oil production. Therefore, the proppants with ultra-low density, good water dispersibility (low-settling rate), and enhanced thermal properties are highly preferred.

In this study, we aimed to fabricate cross-linked polymer nanocomposite networks modified nano sand particles as a potential proppant candidate for successful hydraulic fracturing. In addition, the present study also reports the successful co-polymerization of styrene (S), methyl methacrylate (MMA), and divinylbenzene (DVB) into a cross-linked nanonetwork onto the nano sand particles. The first-layer modified nano sand particles were further subjected to another modification using an epoxy-CG (commercial graphene) composite layer. In contrast to the conventional resin coating approaches, this method applies a direct co-polymerization onto the nano sand surfaces and subsequent second-layer modification. In an alternative approach, nano sand particles were pre-modified with zirconia nanoparticles (ZrO\textsubscript{2}) as an attempt to enhance the inter-layer interaction of an inorganic component (nano sand surface) to a polymer layer (organic component). The nano sand-based lightweight proppants with reinforced thermo-mechanical properties and high crush resistance can be potential water-carrying fracturing proppants. The novelty of the work is the utilization of nano sand derived from the abundant natural source of macro sand through ball-milling and its successful surface modification with a two-layer polymer composite layer.

2. Experimental

2.1. Chemicals

The monomers styrene with a purity of >99% (S), methyl methacrylate with a purity of 99% (MMA), and divinylbenzene with a purity of >99% (MMA) were purchased from Sigma Aldrich. The monomers were used as received. Azoisobutyronitrile (AIBN) was obtained from Aldrich and recrystallized using methanol. Saudi Aramco provided us with sand samples, epoxy resin, and the curing agent. The commercial graphene (CG)
was procured from XG Sciences. ZrO₂ samples were prepared in our laboratory[15].

2.2. Preparation of nano sand and ZrO₂ modified nano sand

Nano sand samples were prepared by ball milling the frac sand particles for 12 h. To prepare the ZrO₂-modified nano sand, the nano sand sample is mixed with a specific amount of ZrO₂ nanoparticles and ball-milled for another hour. The experimental preparation for ZrO₂ can be found elsewhere[14,15].

2.3. Preparation of dual-coated nano sand proppants

A sequential coating of cross-linked PS-PMMA/DVB nanonetworks (layer 1) and epoxy-CG composite (layer 2) onto the nano sand surface was used to prepare lightweight nano sand proppants. The cross-linked PS-PMMA/DVB nanonetworks onto nano sand particle surfaces were prepared by carrying out an in-situ cross-linking and one-step copolymerization of S and MMA monomers (1:1 wt%), with DVB (10 wt% to S: MMA mixture) as a cross-linker with AIBN as an initiator (0.01 wt% to the monomer and cross-linker mixture). To carry out the surface polymerization, the monomer, cross-linker, and initiator mixture (5 wt% to the nano sand weight) is well-mixed with nano sand samples and heated to 70 ℃. Cross-linked co-polymer networks’ modified nano sand was mixed with 4:1 wt% of epoxy resin, curing agent, and CG (0.001 wt% to epoxy resin) and treated at 150 ℃ for curing of the epoxy. The curing reaction is optimized to be 5 min. The PS-PMMA coating on the nano sand was carried out using the same procedure but without adding the DVB.

2.4. Characterizations

2.4.1. X-ray diffraction (XRD)

The Rigaku MiniFlex 600 instrument was used to record the XRD patterns for the samples. The diffraction measurements were recorded in the range of 5°–80°.

2.4.2. Thermal analysis

Thermogravimetric analyses (TGA, Hitachi STA7200) evaluated the samples’ degradation temperatures (T_{deg}). The measurements were conducted from 30 ℃ to 500 ℃ at a heating rate of 10 ℃/min under a constant inert gas (N₂) flow.

3. Results and discussion

3.1. Preparation of cross-linked PS-PMMA/DVB nanonetworks and Epoxy-CG nanocomposite modified nano sand particles

Figure 1 shows a sequential two-layer coating of cross-linked PS-PMMA/DVB layer followed by an Epoxy-CG layer onto nano sand surfaces. The first layer of cross-linked PS-PMMA/DVB nanonetworks onto the surface of nano sand was prepared by polymerizing monomers mixture of S and MMA, cross-linker DVB, with the aid of AIBN at 70 ℃. The detailed formation and the mechanistic pathway for the cross-linked PS-PMMA/DVB nanonetworks can be found in our previous reports[2,28,33,68,70]. At 70 ℃, the AIBN produces free radicals, and the monomers are converted into free radicals instantaneously. Then, the monomer radicals reacted randomly with other monomers, and the polymeric chain propagated. At the same time, the growing polymer chains also randomly reacted with the DVB molecules, resulting in the cross-linking of polymer chains[2,39,71]. Therefore, a cross-linked PS-PMMA/DVB nanonetwork is formed on the surface of the nano sand. The second layer of Epoxy-CG was prepared using an epoxy resin, curing agent, and CG that was cured at 150 ℃ for 5 min.
3.2. XRD

**Figure 2** shows the XRD of micro sand (100 mesh) and nano sand samples that were prepared by ball-milling for various times ranging from 1 to 12 h. The peaks detected at 21°, 26.5°, 42°, 44°, 51°, 58°, 68°, 77° are assigned to SiO$_2$ (quartz phase). As for the micro sand, two major peaks were observed: one is at 21° (100), and the other is at 26.5°. When the micro sand is subjected to ball-milling for 1 h, the intensities of 100 and 101 peaks are slightly reduced. The decrease in the peak intensities is more evident when the ball-milling time is increased, for instance, from 2 h to 12 h. The reduction in the intensities of the characteristic peaks of frac sand can directly be related to the particle size of the resultant ball-milled nano sand particles. Using Debye-Scherer’s equation, the particle sizes can be calculated for each hour of ball-milling. The nano sand’s average particle size was 9 nm for the sample ball-milled for 12 h.

**Figure 3** shows the XRD for the nano sand (ball-milled for 12 h), epoxy-CG (commercial graphene) composite coating layer, and modified nano sand with one- or two-layer polymer composite coating layers with and without ZrO$_2$ cross-linker modification of the nano sand. As for the nano sand, the characteristic peaks detected at 21°, 26.5°, 42°, 44°, 51°, 58°, 68°, and 77° correspond to the quartz phase of SiO$_2$. For the epoxy-CG, peaks were detected at 15°, 18°, and 26° and attributed to CG; for the samples of NS-(Epoxy-CG), NS-(PS-PMMA-CG-ZrO$_2$)-(Epoxy-CG), NS-(PS-PMMA-ZrO$_2$)-(Epoxy-CG), NS-ZrO$_2$-(PS-PMMA)-(Epoxy-CG), NS-ZrO$_2$-(PS-PMMA-CG-ZrO$_2$)-(Epoxy-CG), and NS-ZrO$_2$-(PS-PMMA)-(Epoxy-CG), the characteristic peak position and their relative intensities of the nano sand were not altered. This indicates that the relative weight ratio of the coating layers to nano sand particles is low enough as the peak position or the intensities are unchanged.

**Figure 4** shows the XRD patterns for the nano sand modified with epoxy-CG, NS-(PS-PMMA)-(Epoxy-CG), NS-(PS-PMMA-CG)-(Epoxy-CG), NS-(PS-PMMA/DVB)-(Epoxy-CG), and NS-(PS-PMMA/DVB-CG)-(Epoxy-CG). As evident from the unaltered the characteristic peak position and intensities of the nano sand weight ratio of the nano sand to coating layers particles are much lower.
Figure 2. XRD of Ball-milled sand samples for 0–12 h. (a) 0–4 h, (b) 5–8 h, and (c) 9–12 h.

Figure 3. XRD patterns of coated nano sand proppants with ZrO$_2$ as a cross-linker in comparison to neat nano sand and epoxy-CG.
3.3. Thermal stability analyses

Thermal degradation temperatures (T\textsubscript{deg}) of the modified nano sand proppant samples were evaluated using their respective TGA curves. Figure 5 shows the TGA of neat-nano sand, epoxy-CG, nano sand-(ZrO\textsubscript{2})-(Epoxy-CG), nano sand-(ZrO\textsubscript{2})-(PS-PMMA)-(Epoxy-CG), nano sand-(ZrO\textsubscript{2})-(PS-PMMA-ZrO\textsubscript{2})-(Epoxy-CG), nano sand-(ZrO\textsubscript{2})-(PS-PMMA-CG)-(Epoxy-CG), nano sand-(ZrO\textsubscript{2})-(PS-PMMA-CG-ZrO\textsubscript{2})-(Epoxy-CG), and nano sand-(PS-PMMA-CG-ZrO\textsubscript{2})-(Epoxy-CG). The T\textsubscript{deg} was calculated using a differential thermal curve for the samples with clear degradation steps. However, for the samples with no clear degradation patterns, the temperature at which half of the weight loss was observed was considered to be their T\textsubscript{deg}[72]. The nano sand lost weight at 500 °C, while the epoxy-CG layer had a degradation peak at 362 °C. When the ZrO\textsubscript{2}-modified nano sand is coated with an epoxy-CG layer, the T\textsubscript{deg} is increased to 365 °C, and this thermal stability enhancement is a clear indication of cross-linking of ZrO\textsubscript{2} to the epoxy layer. For the samples of nano sand-(ZrO\textsubscript{2})-(PS-PMMA)-(Epoxy-CG), nano sand-(ZrO\textsubscript{2})-(PS-PMMA-ZrO\textsubscript{2})-(Epoxy-CG), nano sand-(ZrO\textsubscript{2})-(PS-PMMA-CG-ZrO\textsubscript{2})-(Epoxy-CG), and nano sand-(PS-PMMA-CG-ZrO\textsubscript{2})-(Epoxy-CG), the T\textsubscript{deg} was calculated using a differential thermal curve for the samples with clear degradation steps. The T\textsubscript{deg} was considered to be their T\textsubscript{deg}[72].
(PS-PMMA-CG)-(Epoxy-CG), nano sand-(ZrO$_2$)-(PS-PMMA-CG-ZrO$_2$)-(Epoxy-CG), T$_{\text{deg}}$ values are 368 °C, 369 °C, 371 °C, and 371 °C, respectively. From these results, it can be noted that polymer and polymer composite coating of PS-PMMA and PS-PMMA-CG, in addition to the epoxy-CG coating onto the ZrO$_2$-modified nano sand, would further enhance the stabilities of the respective proppant samples. Interestingly, for the sample of nano sand-(PS-PMMA-CG-ZrO$_2$)-(Epoxy-CG), the T$_{\text{deg}}$ value is 375 °C. This can be attributed to the higher cross-linking ability of ZrO$_2$ between PS-PMMA-CG and epoxy-CG layers. Therefore, it is more desirable to have cross-linked dual-coating of copolymer-2D nanofiller composite and cured resin composite onto nano sand particles for the successful hydraulic fracture operation with modified nano sand as proppants.

Figure 6 shows the TGS curves for nano sand-(PS-PMMA)-(Epoxy-CG), nano sand-(PS-PMMA-CG)-(Epoxy-CG), nano sand-(PS-PMMA/DVB)-(Epoxy-CG), and nano sand-(PS-PMMA/DVB-CG)-(Epoxy-CG) in comparison to nano sand-(Epoxy-CG) and neat-nano sand. Table 1 summarizes all the degradation temperatures of the samples. As shown in Figure 6, the T$_{\text{deg}}$ values are found to be 372 °C, 375 °C, 396 °C, and 411 °C for nano sand-(PS-PMMA)-(Epoxy-CG), nano sand-(PS-PMMA-CG)-(Epoxy-CG), nano sand-(PS-PMMA/DVB)-(Epoxy-CG), and nano sand-(PS-PMMA/DVB-CG)-(Epoxy-CG) respectively. This increase can be explained by forming 3D-nanonetworks of PS-PMMA/DVB. This can be credited to the higher thermal stability of the epoxy-CG composite layer. Interestingly, a synergistic increase in the degradation temperature values for the samples with a two-layer coating of cross-linked PS-PMMA/DVB followed by Epoxy-CG coating was observed. Therefore, these proppant samples would be highly suitable for high-temperature wells.

![Figure 6](image_url)

**Figure 6.** Compared to neat nano sand and epoxy-CG, TGA curves for coated nano sand proppants with DVB as a cross-linker.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T$_{\text{deg}}$ (°C)</th>
<th>SG (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nano sand</td>
<td>-</td>
<td>1.02</td>
</tr>
<tr>
<td>Epoxy-CG</td>
<td>362</td>
<td>-</td>
</tr>
<tr>
<td>Nano sand-(ZrO$_2$)-(Epoxy-CG)</td>
<td>365</td>
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</tr>
<tr>
<td>Nano sand-(ZrO$_2$)-(PS-PMMA)-(Epoxy-CG)</td>
<td>368</td>
<td>1.07</td>
</tr>
<tr>
<td>Nano sand-(ZrO$_2$)-(PS-PMMA-ZrO$_2$)-(Epoxy-CG)</td>
<td>369</td>
<td>1.09</td>
</tr>
<tr>
<td>Nano sand-(ZrO$_2$)-(PS-PMMA-CG)-(Epoxy-CG)</td>
<td>371</td>
<td>1.08</td>
</tr>
<tr>
<td>Nano sand-(ZrO$_2$)-(PS-PMMA-CG-ZrO$_2$)-(Epoxy-CG)</td>
<td>372</td>
<td>1.10</td>
</tr>
<tr>
<td>Nano sand-(PS-PMMA-CG-ZrO$_2$)-(Epoxy-CG)</td>
<td>375</td>
<td>1.08</td>
</tr>
<tr>
<td>Nano sand-(Epoxy-CG)</td>
<td>336</td>
<td>1.04</td>
</tr>
<tr>
<td>Nano sand-(PS-PMMA)-(Epoxy-CG)</td>
<td>372</td>
<td>1.06</td>
</tr>
<tr>
<td>Nano sand-(PS-PMMA-CG)-(Epoxy-CG)</td>
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<td>1.07</td>
</tr>
<tr>
<td>Nano sand-(PS-PMMA/DVB)-(Epoxy-CG)</td>
<td>396</td>
<td>1.07</td>
</tr>
<tr>
<td>Nano sand-(PS-PMMA/DVB-CG)-(Epoxy-CG)</td>
<td>411</td>
<td>1.09</td>
</tr>
</tbody>
</table>
3.4. Specific gravity (SG) and water suspension analyses

The specific gravity of the nano sand proppant samples was summarized in Table 1. The neat-nano sand has an SG value as low as 1.02. At the same time, the SG values for nano sand-(ZrO2)-(Epoxy-CG), nano sand-(ZrO2)-(PS-PMMA)-(Epoxy-CG), nano sand-(ZrO2)-(PS-PMMA-ZrO2)-(Epoxy-CG), nano sand-(ZrO2)-(PS-PMMA-CG)-(Epoxy-CG), nano sand-(ZrO2)-(PS-PMMA-CG-ZrO2)-(Epoxy-CG), nano sand-(PS-PMMA-CG-ZrO2)-(Epoxy-CG), and nano sand-(PS-PMMA-CG-ZrO2)-(Epoxy-CG) are 1.05, 1.07, 1.09, 1.08, 1.08 and 1.10. The values indicate that the SG values also increase when we increase the coating layer and materials. Similarly, for the samples of nano sand-(PS-PMMA)-(Epoxy-CG), nano sand-(PS-PMMA-CG)-(Epoxy-CG), nano sand-(PS-PMMA/DVB)-(Epoxy-CG), and nano sand-(PS-PMMA/DVB-CG)-(Epoxy-CG), the SG values are found to be 1.06, 1.07, 1.07, and 1.09. The values indicate that the SG values also increase when we increase the coating layer and the coating materials.

Figure 7 shows the suspension of the nano sand proppant samples of nano sand-(PS-PMMA/DVB)-(Epoxy-CG) and nano sand-(PS-PMMA-ZrO2)-(Epoxy-CG) in gulf sea water after 1 h of dispersion in comparison neat-nano sand and correspondingly modified macro sand sample. It can be seen that the macro sand proppant particles are instantaneously settled in the water, whereas the neat nano sand remains suspended because of its low SG value of 1.02. For the modified nano sand proppant samples, the one with (PS-PMMA/DVB)-(Epoxy-CG) suspended in the seawater for a longer time in comparison to the one with (PS-PMMA-ZrO2)-(Epoxy-CG). This observation is consistent with their corresponding SG values.

![Figure 7](image)

Besides, the S.G. of the nano sand-(PS-PMMA/DVB)-(Epoxy-CG) proppant is determined to be only 1.09 g/cm³ while that of resin-coated sand proppant counterparts is 1.40g/cm³. The decrease in bulk density of the developed nano sand-(PS-PMMA/DVB)-(Epoxy-CG) proppants is an obvious indication of successful dual coating of cross-linked polymer nanonetworks and epoxy-graphene composite layer while not compromising the permeability of the fractures.

4. Conclusion

Two-layer coated nano sand particles were successfully prepared via ball-milling the macro sand and subsequently modifying the resultant nano sand with polymer nanocomposites with different surface modifications. The first layer of cross-linked PS-PMMA/DVB was prepared using S and MMA monomers, crosslinker (DVB) at 70 °C. The second layer of Epoxy-CG was prepared using a mixture of Epoxy resin, a
curing agent, and CG that was cured at 150 °C for 5 min. XRD and TGA studies confirmed successful surface coatings onto the nano sand particles. The dual-coating layer of (PS-PMMA/DVB)-(Epoxy-CG) exhibited thermal stability up to 411 °C. Nevertheless, specific gravity (SG) analysis illustrated that the density of the proppants was about 1.02–1.10 g/cm³ with good dispersion in water. Thermal studies showed that the samples can withstand up to 411 °C. Therefore, the polymer nanocomposite-modified nano sand proppant samples can act as potential candidates as water-carrying proppants in oil and gas industries. The thermally enhanced polymer nanocomposites modified nano sand proppant samples with low S.G. values and excellent water dispersibility characteristics would be highly useful for the current oil and gas industries.

Author contributions

Conceptualization, MRK, WL, and EHA; methodology, MRK; validation, WL and EHA; formal analysis, WL; investigation, MRK; resources, WL; data curation, MRK and EHA; writing—original draft preparation, MRK; writing—review and editing, MRK, WL, and EHA; supervision, WL and EHA; project administration, MRK; funding acquisition, WL and EHA. All authors have read and agreed to the published version of the manuscript.

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Conflict of interest

The authors report that there is no conflict of interest to declare.

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