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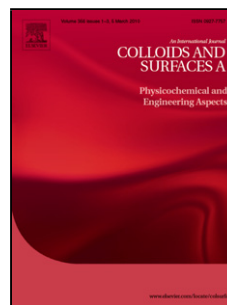
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Proppant immobilization facilitated by carbon nanotube mediated microwave treatment of polymer-proppant structures

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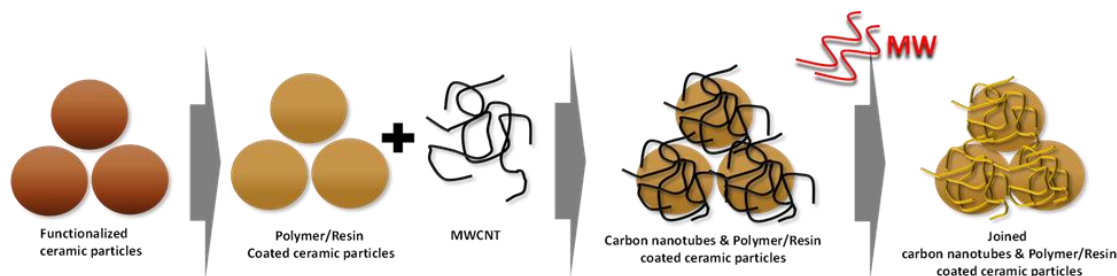
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TOC



Highlights

- MWCNTs facilitate the aggregation of coated proppants through localized microwave heating.
- Covalently functionalized proppants are used as linkage points for polymer coatings.
- MWCNTs result in melting of the coating under microwave irradiation joining the particles.

ABSTRACT

The application of multi-walled carbon nanotubes (MWCNTs) to facilitate the aggregation of ceramic particles (proppants) by embedding in the coating through localized microwave heating is reported. Thermogravimetric analysis (TGA), scanning electron microscopy (SEM) along with energy dispersive X-ray analysis (EDX) and atomic force microscopy (AFM) were used to characterize a series of covalently functionalized proppants with carboxylic acids (lysine and fumaric acid). The bi-functional acids allow for a controlled reaction with a coating (resin and polymer). The addition of carbon nanotubes results in the melting of the coating under exposure to microwave irradiation (20 s @ 100 W) joining the particles. The significant reduction in reaction time (compared to the thermal treatments of 2-24 hours) is due to the presence of the MWCNTs. The microwave heating of the MWCNTs can thus be used to create interaction and adhesion between functionalized particles subject to a specific stimulus.

Keywords: Carbon nanotubes, Epoxy resin, Tri-block copolymer, Microwave, Proppant

1. Introduction

Ceramic particles and sand are commonly used as proppants in the oil and gas industry [1]. The proppant provides a highly porous conductive pathway from the reservoir to the well by holding fractures open and so enhance the ability of fluids (oil and/or gas) to migrate through the fractures [2,3]. The loss of proppant from a fracture (flowback) can cause the reduction of the fracture conductivity reducing the production rate [4,5]. In extreme cases, misplaced or overly mobile proppant can result in back flow of debris back into the well shaft resulting in the need to either abandon the well or re-drill.

A number of methods have been investigated to improve proppant performance including modifying them with different resins, polymers, and fibers [3-10]. The use of resin coated particles is well documented method to control proppant flowback in a wide variety of oil and gas wells. Resin coatings can be used to impart a degree of adhesion to the proppant so that flow back is substantially reduced or eliminated [7,9]; however, undesirable effects can be caused if the coatings are eroded, cured prematurely or adhered to each other in a non-uniform manner. These issues may be overcome by improving the interaction between the particle and the surface coating and by designing a specific trigger such as pH, heat or microwave radiation, and response mechanism so that the adhesion can be controlled.

The use of nanomaterials for controlled self-assembly of macrostructures is a growing field of research merging chemistry, physics and biology, with implications for new technologies [11-14]. In a recent work, we have used the localized high temperatures, generated using multi-walled carbon nanotubes (MWCNTs), which are able to absorb microwaves to create a flux. They can then act as an adhesive between individual ceramic particles [15] creating dimers, trimers, and longer networks, that would mechanically interlock and provide greater resistance to flowback. Microwave absorbing properties of carbon nanotubes (CNTs) make them very attractive when used as a nexus for fast and direct heating [15-18]. We have applied the rapid heating and decreased sintering temperatures of microwave energy for chemical synthesis [19-21]. Composites with different matrix and multi-walled carbon nanotubes (MWCNTs) with microwave absorbing properties have been prepared [22-24]. Ceramic/CNT composites [18] have been also cured by using the microwave absorbing properties of carbon nanotubes. Epoxy resins containing carbon nanotubes have been used as adhesive under microwave irradiation [21,25] and have demonstrated effects on the physical performance of the resin [26,27].

Submitted to *Colloids Surf., A*.

We have previously reported that the interaction between the aluminum oxide surfaces and polymers and resins can be improved by modifying the surfaces with bi-functionalized carboxylic acids [28-32]. Using this approach we have recently reported that aggregation of proppants is observed results following the reaction of lysine and fumaric acid functionalized surfaces with an epoxy resin and polymer, respectively [33]. However, while aggregation was observed it required curing at either 150 °C for 2-3 hours or 80 °C overnight. The goal is to provide a way in which once in-location, a subset of proppants may be fused together to create a lock-and-key interaction to minimize proppant flowback. Since the use of microwaves “down hole” has been successful and widely utilized as a standard in the oil and gas industry [34-36], it offers the possibility of being applied to immobilization of proppant. In this regard, we have investigated the microwave treatment of MWCNT incorporated into functionalized proppants coated with either a resin or polymer in comparison with thermal treatment. A summary of the process is shown schematically in Fig. 1.

2. Materials

Fumaric acid (FA, Fig. 2a) and lysine (K [37], Fig. 2b), 1-methylimidazole, epoxy resin DER-332 (Fig. 2c), 2-propanol, and acetone were obtained from Sigma Aldrich. Jeffamine® ED900 polyetheramine (Fig. 2d) was provided kindly by Huntsman (UK). Carbolite (16-20 mesh, $d \approx 1000 \mu\text{m}$) was obtained from CARBO Ceramics (USA). All materials were used as received. MWCNT were prepared using a Nanotech Innovations SSP-354 tabletop horizontal tube reactor as previously reported [38].

The synthesis of the lysine functionalized proppants (K-P) and the epoxy resin coated derivative (EP-K-P) were according to previous methods [33], using DER332 epoxy resin (EP) with 1-methylimidazole as the curing agent. To 100 mg of EP-K-P was added 2.0 mL of a dispersion of MWCNTs (0.5 mg/mL) in 1 wt% SDS aqueous solution formed by 30 min in an ultrasonic bath. The mixture was placed in an ultrasonic bath for 5 min and then stirred for 30 min. The sample (MWCNT-EP-K-P) was then washed with water (3 x 5 mL) to remove the excess of MWCNTs and SDS, and dried under ambient indoor conditions ($\sim 20 \text{ }^\circ\text{C}$, 1 atm). The polyetheramine (PEA) coated fumaric-functionalize proppant (PE-FA-P) were prepared as reported [23] using Jeffamine® ED900, and the MWCNTs were attached using the same method as described above, to give MWCNT-PE-FA-P. Both samples with and without MWCNTs were subjected to microwave irradiation using a microwave oven

(Panasonic NN-CT579SBPQ) with an irradiation frequency of 2.45 GHz. We have previously reported successful heating of MWCNTs using the same system [15,19]. In all microwave reactions the sample was placed in a glass vial and microwaved for 20, 40 or 80 s periods at 100 W, 250 W or 600 W power. The microwave oven incorporated inverter technology allowing control of oven power between 0 and 1000 W. Rotating the sample on the standard turntable enabled a uniform distribution of power. A summary of the sample compositions studied is given in Table 1.

3. Techniques

Samples were characterized by scanning electron microscopy (SEM) using an Ultra-High Resolution FE-SEM S-4800 coupled with an energy dispersive X-ray analyzer (Inca X-ray analysis system, Oxford Instruments, Abingdon, UK) for the EDX analysis. Samples were placed as powders on a carbon based, electrically conductive, double sided adhesive discs. For sample imaging 2 kV and 10 μ A were selected as beam voltage and current, probe current was in normal mode and a fast scan mode (TV mode) was selected to collect the images. The JPK NanoWizard II AFM and non-contact cantilevers (RTESP, Bruker) were used for surface imaging. Images for each sample were obtained using intermittent contact mode, at a scan rate of 0.5-1 Hz and an image resolution of 512 x 512 pixels. Images were obtained with a scan size of 10 x 10 μ m. The captured images were analysed using JPK offline-processing software to determine the surface roughness from the AFM scans. The mean roughness measurements determined the average (R_a), root-mean-square (R_q), and peak-to-valley roughness (R_t) for each sample type. Thermogravimetric analyses (TGA) of the samples were performed on a TA Q600 instrument. The samples were heated under flowing air (100 mL/min) from room temperature to 1000 $^{\circ}$ C with a heating rate of 20 $^{\circ}$ C/min.

4. Results and discussion

Prior work with MWCNTs as reinforcing elements in epoxies to achieve better mechanical properties has shown that a homogeneous dispersion is required [26,28,39]. This may be achieved through either pre-mixing dispersible MWCNTs with the polymer or adding the MWCNTs to the surface of the polymer with some form of post-treatment. In order to avoid the issues associated with the dispersion of the MWCNTs in the resin or polymer mixture the second approach has been chosen in this work. It was hoped that the

homogeneous dispersion of the MWCNTs with the resin or polymer would occur as a result of the microwave treatment. Adding the CNTs once the particles are coated also reduce the amount of nanotubes required. Microwave irradiation of both resin and polymer coated proppants, both with and without carbon nanotube, have been studied using different exposure times (20 - 80 s) and powers (100 - 600 W). The best results were observed at 20 s and 100 W, as the coatings started to burn at higher energy and longer times.

4.1 Appearance by SEM

The base proppants used in this study have a nominal particle size in the range 16-20 mesh (i.e., 0.841-1.190 mm). This was confirmed by SEM, which indicated that they have a diameter of 1.0 ± 0.2 mm (Fig. 3). Representative images of the unfunctionalized surface of the proppant are shown in Fig. 4a and b. These images should be compared to those in Fig. 4c and d, which show the surface of lysine functionalized proppant particle after reaction with the epoxy resin DER332 (EP-K-P) through a ring opening reaction [30,31]. There is a significant difference in the surface morphology and roughness in comparison with the unmodified particles; in particular the resin appears to cure as ca. 10 μ m features. The morphology of the fumaric acid functionalized proppant after reaction with ED900 (PE-FA-P) is rough (Fig. 4e and f), but not as uniform in feature type as EP-K-P. The assembly process of the particles coated with pH responsive polymers is reversible and this may account for the smoother surface features [40].

The globular morphology seen for EP-K-P (Fig. 4c and d) is unaffected by the addition of the MWCNTs (Fig. 5a). The MWCNTs are clearly seen resting on the surface; however, upon microwave heating (20 s, 100 W) the MWCNTs become embedded in the coatings (Fig. 5b). A similar behavior under microwaves has been previously observed on plastic substrates [41,42]. It is interesting that while the MWCNTs are embedded, and there is obviously localized melting around the nanotubes, the overall morphology of the resin itself appears little changed upon microwave irradiation. This is confirmed by exposing EP-K-P to microwave irradiation in the absence of MWCNTs (Fig. 5c). In contrast, the surface morphology of EP-K-P heated to 400 °C appears smooth the globular morphology due to overall softening of the resin (Fig. 5d).

Fig. 6a shows the SEM micrograph of the MWCNTs on the surface of the polymer coated fumaric acid functionalized ceramic proppant (MWCNT-PE-FA-P). The MWCNTs may be clearly seen resting on the surface of the highly textured surface. However, after microwave irradiation (Fig. 6b) not only are the MWCNTs embedded within the polymer, but there appears to be a densification of the surface. Such a change is clearly due to the presence of the heating due to the MWCNTs since microwave irradiation on PE-FA-P (Fig. 6c) shown only a small change in the texture. Again it is possible to judge the difference between localized MWCNT facilitated heating and thermal effects by observing the dramatic change that occurs when PE-FA-P is heated to 400 °C for at 20 °C/min rate. It appears that volatiles are removed from the polymer since the surface is highly porous (Fig. 6d).

The changes in the surface morphology are a good indication that the MWCNTs provide localized heating of both the resin and the polymer. However, it is observation at the inter particle scale that shows the greatest effect. Fig. 7 shows images of untreated proppant after exposure to microwaves in comparison to those of MWCNT-EP-K-P and MWCNT-PE-FA-P after the same treatment. Uncoated proppant is unaffected (Fig. 7a and b), but resin coated samples have been effectively joined together after being irradiated with microwave radiation during 10 s at 100 W (Fig. 7c and d). It is apparent that during the microwave treatment, where coatings of particles are in contact they become fused together due to the localized heating process generated by microwave treatment of the MWCNTs creating junctions among the proppant pack. This is a significant improvement in time and energy compared to both our previous thermal annealing of MWCNT-EP-K-P [33] and our previous microwave treatment of MWCNT impregnated silica coated proppant which required 2 mins at 1000W [15]. A similar fusing of the proppant particles is observed for the polymer coated samples, MWCNT-PE-FA-P (Fig. 7e and f). In both cases the neck between the proppant particles appears to be bridged by resin/polymer imbedded with MWCNTs.

4.2 Surface morphology by AFM

Additional characterization of carbon nanotube coated proppant surfaces was undertaken by AFM (Fig. 8). It was not possible to obtain any good images for untreated proppants (P), due to the exceedingly high rough nature of the proppant, and resin coated proppant (EP-K-P)

was selected as a model example. Height measurements on EP-K-P revealed an uneven surface with peak to valley profiles of 1.4 μm (Fig. 8c and Table 2). The addition of MWCNTs is clearly seen on both the surface image (Fig. 8b) and the height profile (Fig. 8d and Table 2). The roughness data and the 3D image illustrate that the MWCNTs appear to make the surface smoother by both fill up and bridge across surface features.

4.3 Composition by EDX

The EDX analysis of the coated particles shows the significant coverage of the surface with resin and polymer as indicated by an increase in the carbon content from ca. 6% (P) to an average of 63.5% and 18% for EP-K-P and PE-FA-P, respectively (Table 3). Upon the addition of MWCNT, the EDX analysis of both coated particles shows the sufficient coverage of the surface with MWCNT before and after the microwave treatments. However, it can be concluded that the distribution of MWCNTs is inhomogeneous since the range of values for the C content (and hence remaining elements) varies dramatically (see Table 3). For example, the C% in MWCNT-PE-FA-P varies from 5.5% to 43.1% across the surface. The coverage of the particles with carbon nanotubes is highly irregular, and in this work the formation of polymer/resin bridges between adjacent particles is not affected by it. However, for other applications of the carbon nanotubes resin or polymers mixtures, different strategies should be explored (i.e. use functionalized carbon nanotubes) to provide a better dispersion of the nanotubes in the resin/polymer surfaces.

4.4 Thermal analysis by TG/DTA

The thermogravimetric analysis of the untreated proppant (P), the coating materials (MWCNT, EP and PE), and the functionalized proppants (FA-P and K-P), are given in Table 4. As was expected, proppant particles do not show a significant mass loss within the temperature range (0 – 700 $^{\circ}\text{C}$), whereas proppant functionalized with both lysine and fumaric carboxylic acids show weight loss curves above 200 $^{\circ}\text{C}$. As can be observed in Table 4, small weight losses of 0.02% and 0.05% were obtained for samples K-P and FA-P respectively, due to the proppants small surface area of $\sim 3.81 \times 10^{-3} \text{ m}^2/\text{g}$ (based on average diameter of 1000 μm and density of 1.57 g/cm^3). Our previous results for the functionalization of aluminum wafers [28,33] revealed multilayer surface coverage, especially for fumaric acid functionalized surfaces, because this functional group can react with itself via an esterification reaction. This is in agreement with our data for functionalized

proppants as a higher percentage of weight loss was obtained for FA-P particles compared to K-P.

Both PE and EP decompose with complete weight loss at around 400 °C, while MWCNT decomposition occurs at higher temperatures and there appears a residue that is related to the catalyst used to grow the tubes [18]. As can be observed in Fig. 9, 10 and Table 4, the thermal stability (and final decomposition point) of the EP-K-P and PE-FA-P is higher compared to the both pure PE and EP. The change in temperature decomposition is due to the bonding interactions between polymer/resin and the functional groups on the surface (fumaric acid and lysine). The presence and identity of the surface functionalization affect the thermal stability of the resulting resin and polymer as it was shown in our previous studies [31,33].

TGA analyses of both EP-K-P and PE-FA-P, along with the MWCNT containing samples, are shown in Fig. 9 and 10, respectively [33]. The TGA of PE-FA-P shows a mass loss associated with water, presumably due to the hydrophilic nature of the polymer. Both MWCNT-EP-K-P and MWCNT-PE-FA-P samples shown a first loss step below 300 °C related to the loss of adsorbed SDS used to disperse the MWCNTs. The SDS appears to be evaporated/decomposed upon microwave irradiations. Even though the MWCNT are either dispersed on the surface of the particles (Fig. 5a and Fig. 6a) or agglomerated as patches on the surface of the proppants (Fig. 7c and e), no significant differences in the thermogravimetric analysis are observed after microwave treatment of the samples.

No significant losses in the polymer or resin coverage has been found for 20s 100 Watt microwave treatments which is in agreement with the EDX analysis results (Table 3). The residue values at 700 °C for MWCNT-EP-K-P before and after being microwaved are 98.8 and 97.7 respectively. The weight losses differences between them are explained due to a not homogeneous distribution of MWCNT agglomerates in the samples. The samples with a greater amount of MWCNT agglomerates have greater mass losses below 300 °C and 600 °C because of the greater presence of SDS and nanotubes.

4. Conclusions

Aluminum oxide ceramic proppants have been functionalized using carboxylic acids, as molecular anchors, before being coated to improve the interaction between the particles and the coating of the proppants. Multiwall carbon nanotubes were successfully added to the surface of the proppants and after MW treatment at 20 s 100 W were embedded in the coatings. However, the most important observation was that the presence of the MWCNTs allows for the formation of polymer/resin bridges between adjacent particles in a similar manner to that resulting from thermal treatment [33], but with a significant reduction in reaction time. Down hole use of microwaves could allow the oil and gas industry to actively controlled bonding and adhesion between proppant particles and effectively switch on immobilization of the proppants. This application has a great interest since a microwave

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source can be used to initiate and assist the interaction between the particles [15] and can be positioned and operated within well shafts using currently available technology employed in the oil and gas industry. This system can avoid the effects of conventional heating, where undesired temperature gradients are frequently generated.

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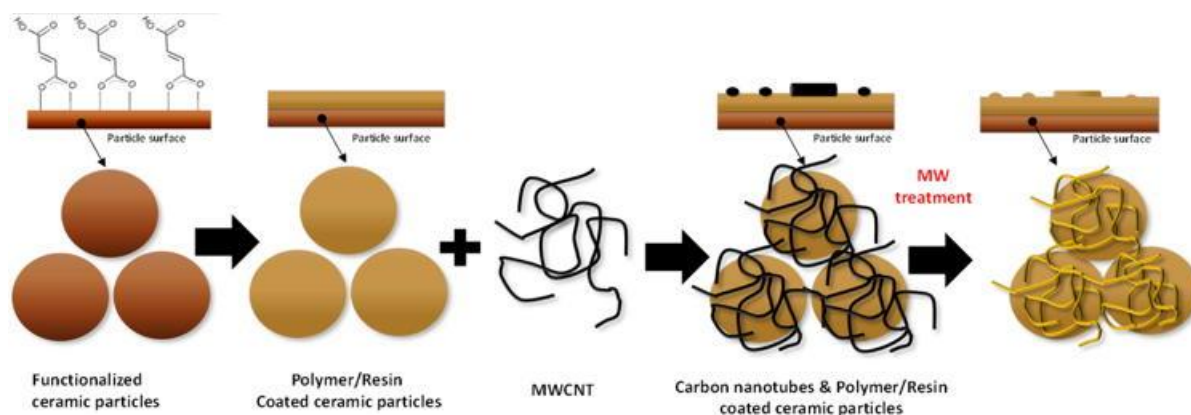
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Fig. 1. Schematic of the approaches used to modify the surface of the ceramic particles.

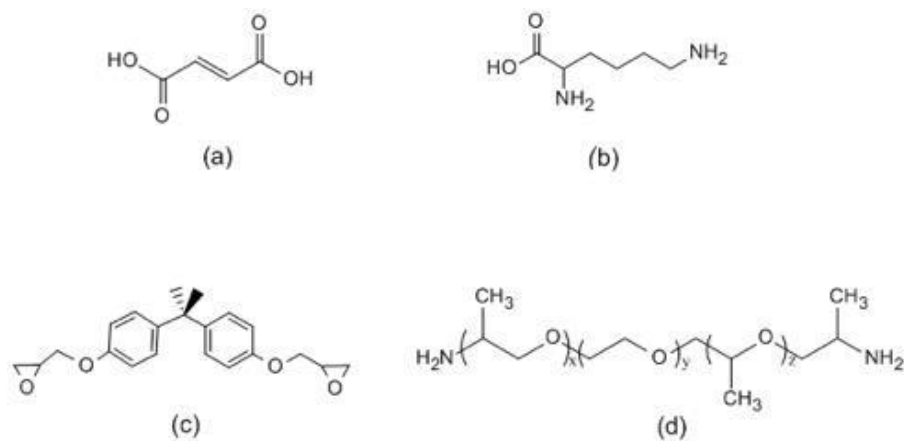


Fig. 2. Structures of (a) fumaric acid (FA), (b) lysine (K), (c) epoxy resin DER-332 (EP), and (d) Jeffamine® ED900 polyetheramine (PE).

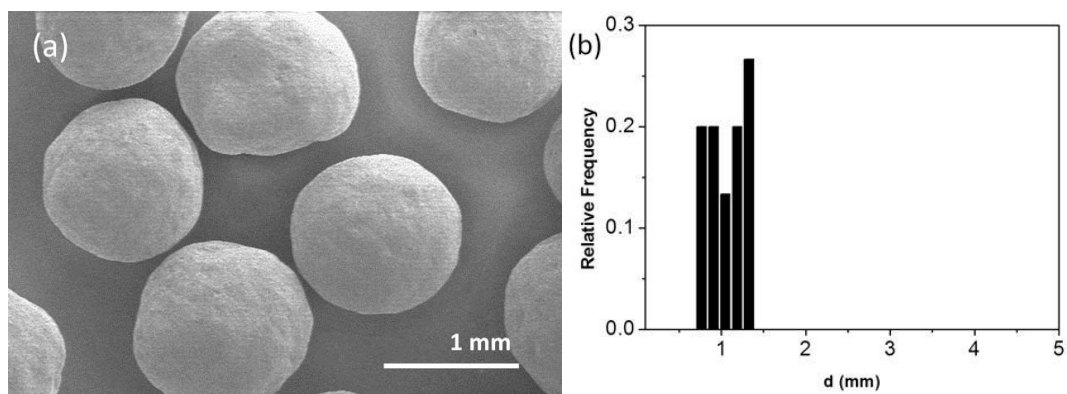
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Fig. 3. SEM micrograph (a) of as received Carbolite proppant (P) with (b) the calculated particle size distribution.

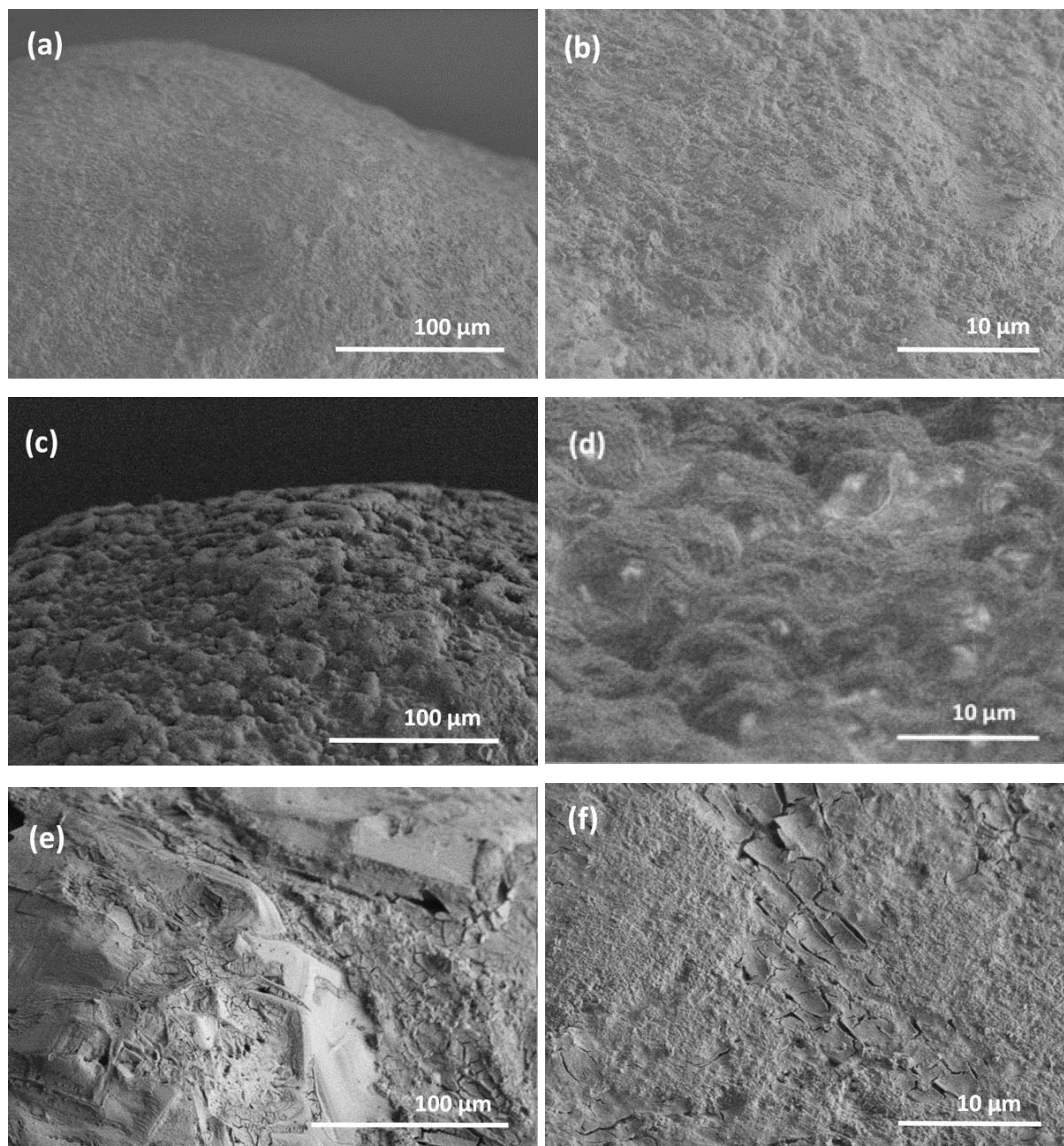
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Fig. 4. SEM micrograph of (a and b) the surface of the unfunctionalized Carbolite proppant (P) in comparison with (c and d) epoxy resin coated lysine-functionalized proppant (EP-K-P) and (e and f) polymer coated fumaric acid-functionalized proppant (PE-FA-P).

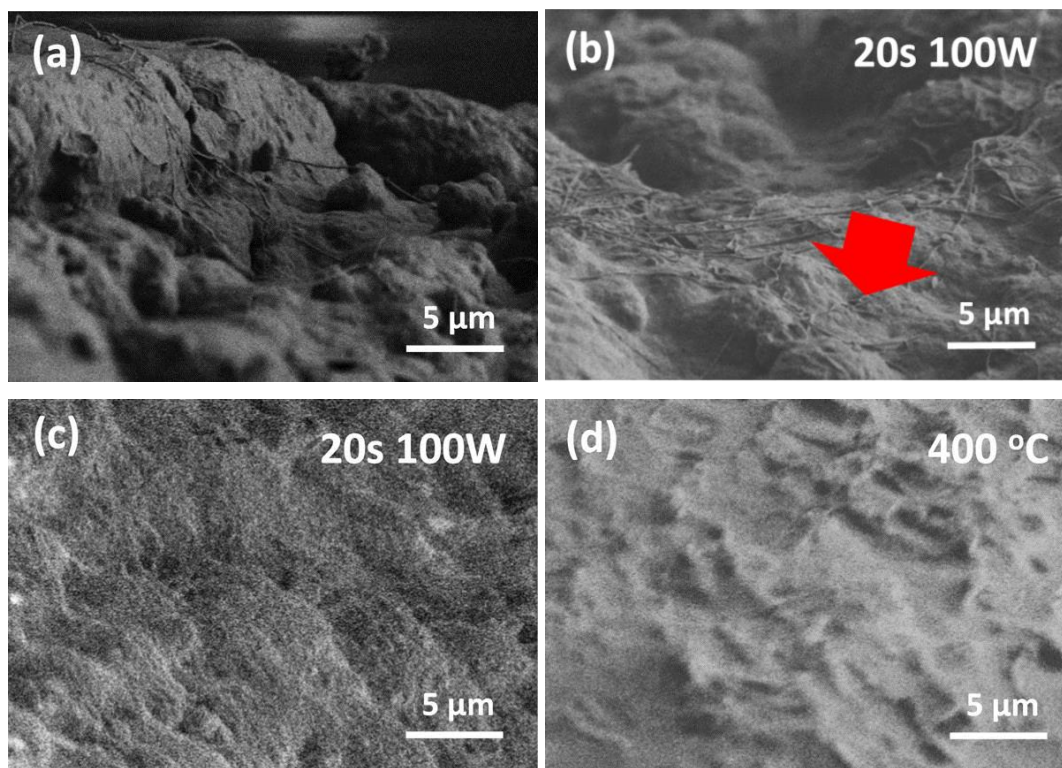
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Fig. 5. SEM micrographs of MWNTs on the surface of resin coated lysing functionalized proppant (MWCNT-EP-K-P) before (a) and after (b) microwave irradiation (20 s @ 100 W), to be compared to (EP-K-P) heated by microwaves under the identical conditions (c) and thermally heated to 400 °C at 20 °C/min rate (d).

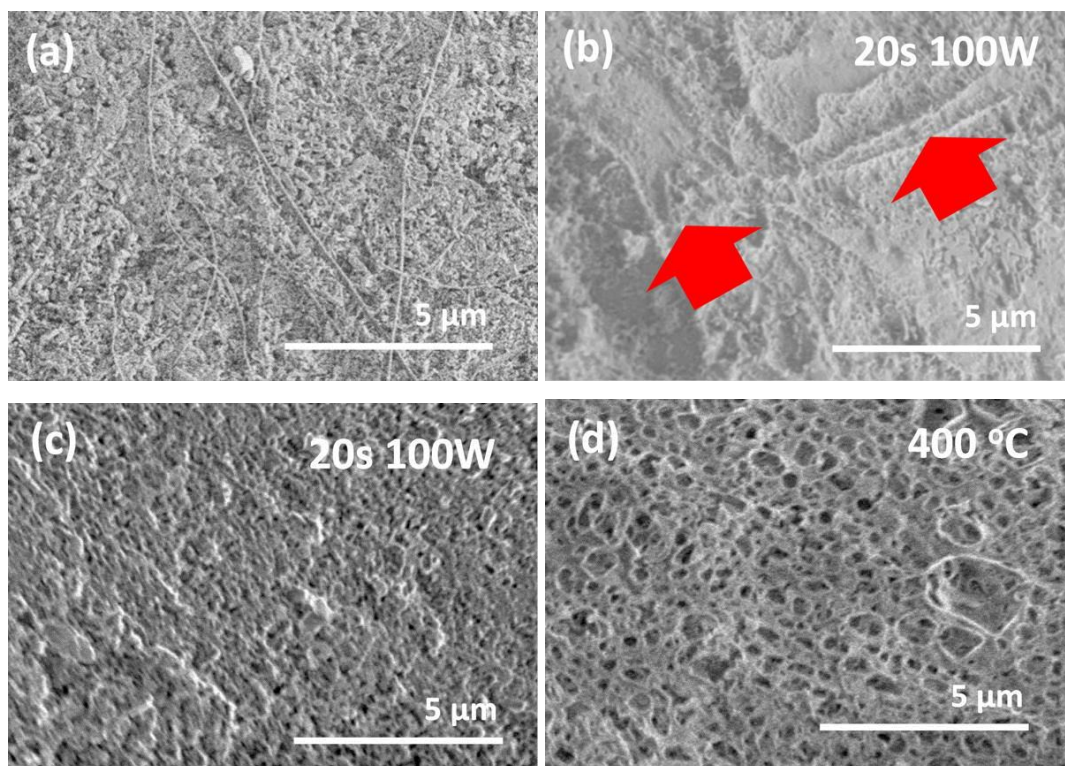
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Fig. 6. SEM micrographs of MWNTs on the surface of polymer coated fumaric acid functionalized proppant (MWCNT-PE-FA-P) before (a) and after (b) microwave irradiation (20 s @ 100 W), to be compared to (PE-FA-P) heated by microwaves under the identical conditions (c) and thermally heated to 400 °C for at 20 °C/min rate mins (d).

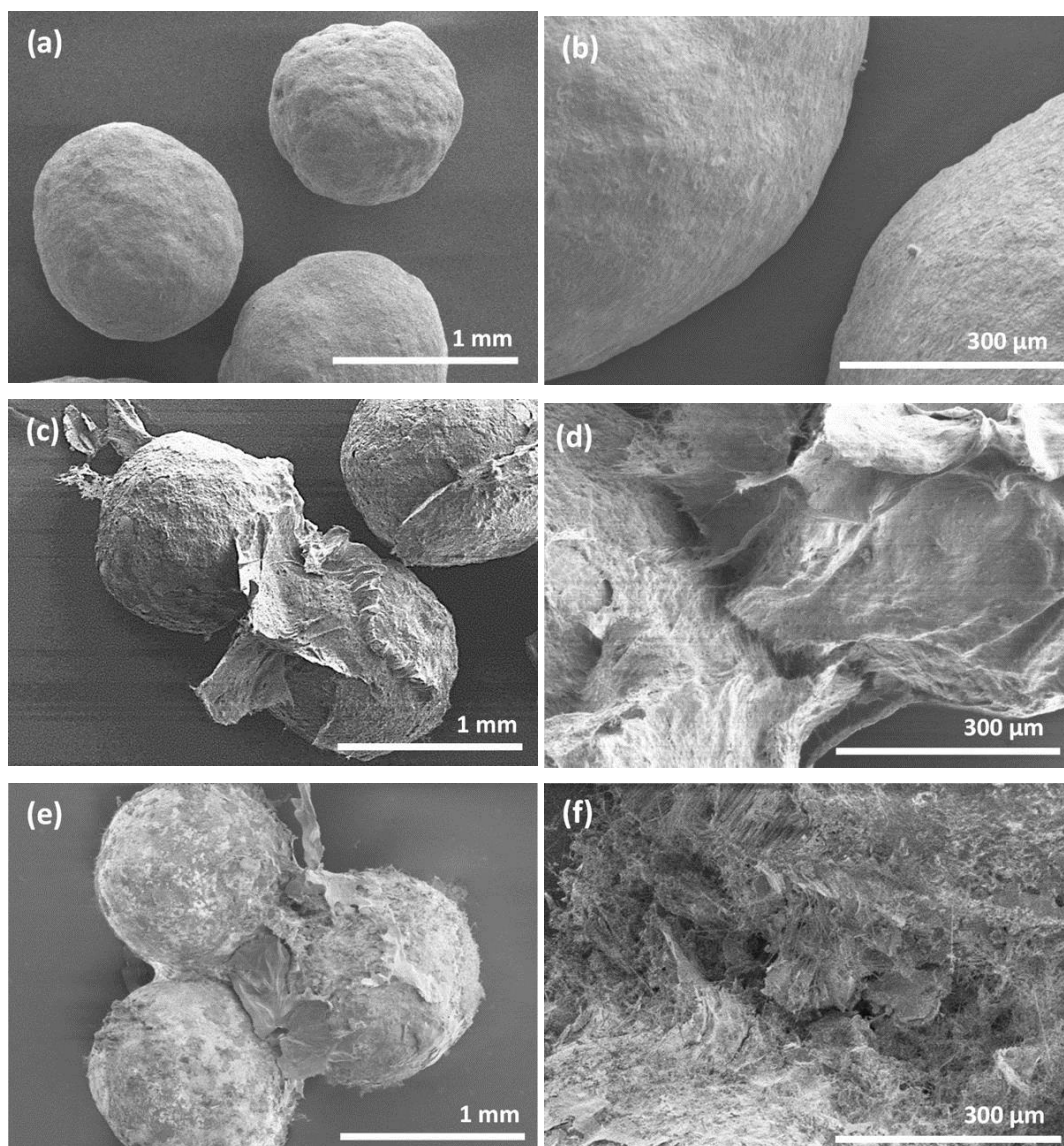
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Fig. 7. SEM micrographs of (a and b) untreated proppant particles (P), (c and d) MWCNT impregnated resin coated lysine functionalized proppant (MWCNT-EP-K-P), and (e and f) MWCNT impregnated polymer coated fumaric acid functionalized proppant (MWCNT-PE-FA-P) after microwave irradiation during 10 s at 100 W.

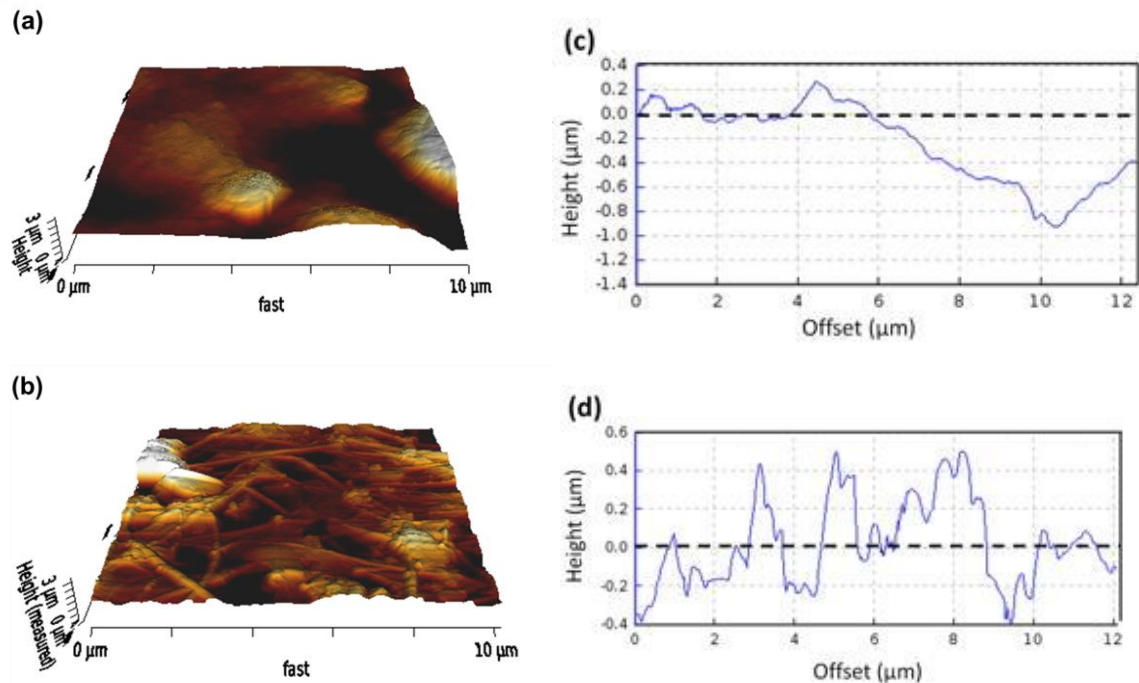
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Fig. 8. 3D-AFM images of (a) resin coated particle (EP-K-P) and (b) MWCNTs coated sample (MWCNT-EP-K-P) surfaces. The height profiles associated with the white line are shown in (c) and (d), respectively. Images were obtained with a scan size of 10 x 10 μm.

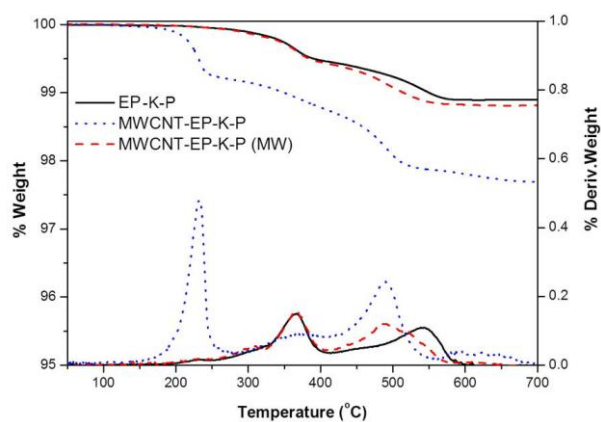
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Fig. 9. Thermogravimetric analysis and derivative weight of EP-K-P, MWCNT-EP-K-P and MWCNT-EP-K-P after microwave treatment.

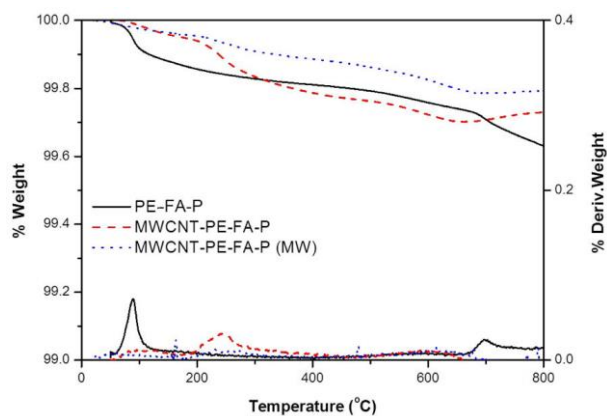


Fig. 10. Thermogravimetric analysis and derivative weight of samples PE-FA-P, MWCNT-PE-FA-P and MWCNT-FA-K-P after being microwaved.

Table 1

Summary of the proppant/carboxylic acid/cross-linker/MWCNT combinations.

Sample	Carboxylic acid	Resin/polymer	MWCNTs
EP-K-P	lysine	DER332	No
MWCNT-EP-K-P	lysine	DER332	Yes
PE-FA-P	fumaric acid	ED900	No
MWCNT-PE-FA-P	fumaric acid	ED900	Yes

Table 2

Summary of AFM height profiles data.

Sample	Averaged roughness (R_a , nm)	RMS roughness (R_q , nm)	Peak-to-valley roughness (R_t , nm)
EP-K-P	303 \pm 75	350 \pm 82	1339 \pm 369
MWCNT-EP-K-P	154 \pm 37	192 \pm 44,	906 \pm 129

Table 3Summary of EDX analysis data (given in atomic %).^a

Samples	C	Si	O	Al
P	6.3 \pm 4.5	12.5 \pm 1.5	64.7 \pm 1.7	16.5 \pm 1.5
PE-FA-P	18.2 \pm 6.3	6.1 \pm 3.1	64.8 \pm 4.2	11.0 \pm 5.1
EP-K-P	63.5 \pm 3.5	1.2 \pm 0.5	33.3 \pm 1.5	2.0 \pm 0.5
MWCNT-PE-FA-P	24.3 \pm 18.8	10.5 \pm 2.3	47.4 \pm 21.2	17.9 \pm 4.1
MWCNT-EP-K-P	81.1 \pm 5.7	0.2 \pm 0.1	13.9 \pm 10.3	0.6 \pm 0.2
MWCNT-PE-FA-P (MW)	30.3 \pm 26.7	9.9 \pm 7.73	38.8 \pm 17.1	20.6 \pm 14.7
MWCNT-EP-K-P (MW)	82.4 \pm 3.4	0.12 \pm 0.09	6.3 \pm 14.0	0.3 \pm 0.2

^a Values averaged over at least three areas per sample.

Table 4

Thermogravimetric analysis.

Sample	Oxidation Temp. (°C)	Residue @ 700 °C (%)
MWCNT	579	18
EP	409	0.0
PE	398	0.0
K-P	577	99.98
FA-P	379	99.95
EP-K-P	366, 543	98.8
PE-FA-P	696	99.5
MWCNT-EP-K-P	306, 366, 489, 519	98.8
MWCNT-PE-FA-P	243, 604	99.7
MWCNT-EP-K-P (MW)	231, 361, 489	97.7
MWCNT-PE-FA-P (MW)	230, 613	99.7