CHARACTERISTIC STUDY OF GRAPHENE OXIDE (GO) COATED SAND PROPPANT

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***Abstract*— Hydraulic fracturing is a well stimulation method performed on reservoirs with low permeability to improve the flow of hydrocarbon into wellbore. Certain chemicals are injected into the well under very high pressure; propping agent, such as sand is added to the fracturing fluid to keep the fracture open [1]. In order to study the performance of GO coated sand used in application of hydraulic fracturing, local sands are improved by surface modification using Graphene Oxide (GO). The interaction of GO and sand are confirmed through Fourier-transform infrared (FTIR). Scanning electronic microscopy (SEM) showed the present of GO had modified the surface of the rough and uneven of uncoated sand. In order to study the performance of GOS, a series of laboratory tests were performed according to the API recommended practice (ISO 13503-2). The clay content, roundness and sphericity, acid solubility, crush resistance and grain size were measured for all samples. The results of sphericity and roundness showed that only sample 4 satisfied with the requirement. Acid solubility of sample 4 and sample 5 for both 1st and 2nd layer of GO do not exceed 2.0 % which is satisfy with requirement for hydraulic fracturing. The turbidity of whole samples is varies from 21-80 FTU, agreed with the ISO recommended.**

I. INTRODUCTION

Stimulation techniques are commonly applied to encourage production to flow from the reservoir rock. Today, hydraulic fracturing is commonly used to stimulate the flow of natural oil and gas by producing fractures in the rock formation. During fracturing process, fracturing fluid is injected at high pressure to break down the rock [1]. The proppant agent is used to keep the fracture to open, resulting the improvement of production. There are many materials have been used as proppant agent such as natural sand, glass, resin coated sand, walnut hull and fused zirconia [2].

In 1947, the first fracturing operation was done using 20,000 lbs of uncoated fracture sand. However, the job was not successful because the uncoated fracture sand did not providing enough strength to keep the fracturing opened. The discovery of several type of proppant was continues in 1950's and natural fracture sand such as white and brown sand was widely used as proppant agent until today. White sand and brown sand are two types of fracturing sand. Because of their brownish surface color, the sand is known as brown sand. Basically, brown sand has low price and more prone to crush at lower stress [2].

Quartz sand is one of natural proppant that widely used today. However, proppant is mostly produces from overseas and there is no supplier in Malaysia. Malaysia has potential to produce own proppant because there are abundant sources of sand in Malaysia. Besides, an alternative of producing proppant locally can reduce the well stimulation cost and also help to increase Malaysia economy. In industry today, various surface modification of sand has been observed to improve the performance of sand during hydraulic fracturing process for example is resin coated sand (RCS) [3].

Graphene Oxide is a layered nano-material that contains graphene sheets and oxygen bearing functional group. Graphene oxide can easily spread in organic solvent, such as water and different matrixes because of the existing oxygen functional group [4]. Graphene Oxide can combine with polymer or ceramic matrixes to enhance the mechanical and chemical properties [4].

New modification of sand is introduced in this research study to improve the characteristic of proppant. This research is focused on the study the characteristic of GO coated sand as a proppant.

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II. METHODOLOGY

2.0 MATERIALS

2.1 Sand

In this study, local sand is used as proppant due to abundance of sand resource in Malaysia. The location field of sand used is located in Terengganu coastal area because Terengganu is the largest states in Malaysia that produced silica sand. The samples sand are collected 3 meter from shore line and 0.5 meter depth from the surface. Hobben Ceramic proppants are used as commercial proppant in this study. The properties of commercial ceramic proppant are obtained from literature review for comparison purpose. Table 2.1 below shows the labels and the location of the sample sand.

Table 2.1 Location of the samples

Labels	Location
Sample 1	Pantai Teluk Ketupang , Terengganu (Malaysia)
Sample 2	Pantai Seberang Takir, Terengganu (Malaysia)
Sample 3	Pantai Seberang Takir, Terengganu (Malaysia)
Sample 4	Pantai Marang, Terengganu (Malaysia)
Sample 5	Pantai Marang, Terengganu (Malaysia)
Sample 6	Pantai Rusila, Terengganu (Malaysia)
Sample 7	Pantai Batu Buruk, Terengganu (Malaysia)
Sample 8	Lombong, Perak Malaysia

2.2 *Graphene Oxide.*

2.2.1 Synthesize of Graphene Oxide

Graphene Oxide is obtained from graphite powder by applying modified Hummer method [5]. 5 g of graphite powder and 2.5 g of sodium nitrate (NaNO3) are mixed together in a 1000 ml beaker at low temperature (ice bath condition). Next, 200ml of sulphuric acid (H2SO4) is added into the mixture with constant stirring for 1 hour. 30 g of potassium permanganate (KMnO4) is added slowly into the mixture .The mixture is continued stirred for 2 hour and temperature is kept below 15°C. The ice bath is removed and the mixture is continued stirred for another 20 hour at room temperature and the resulting solution is heated to 70°C and continues stirred for another 2 hours. The solution is diluted by adding 100ml of water gradually. The temperature of reaction is increased to 90°C and kept stirred for another 1 hour. Then, the mixture is added with 30 mL hydrogen peroxide H2O2 to stop the reaction in the mixture. The resulting mixture is washed by hydrochloric acid (HCL) and distilled water several times until it gel solution is formed gel. This gel like solution is dried in the oven for 24 hour at temperature of 60°C, GO powder is thus obtained.

2.2.2 *Characterization techniques*

The analysis of element and function groups of graphene oxide is determined by using Fourier transform infrared (FTIR) and X-ray diffraction analysis (XRD)

2.2.2. *Preparation of GO coated sand proppant [7]*

The samples sand are thoroughly cleaned with tap water and followed by using 0.1 M nitric acid HNO3 (70%) for 3 hour to ensure the surface impurities of samples sand are removed. The samples are rinsed with distilled deionized water, then placed in 0.1 M Na OH for 3 hour. The samples sand are rinsed with distilled deionized water again. Finally, the samples sand are 150 dried in an oven at 80 °C. GO attached on surface of the sand are prepared in this study. Clean and dried sand (10 g) are put in a petri dish with 5 mL 0.35 % GO dispersion using ultrapure water. The sample are heated up to 150 ◦C in a drying oven for 2 h Figure 2.1 shows the GO coated sand proppant after drying in oven for 2 h. In this research study, the process is repeated to obtain different thickness of GO- coating on sand. The sand is weighted before and after GO coating to evaluate the amount of GO coated on sand.

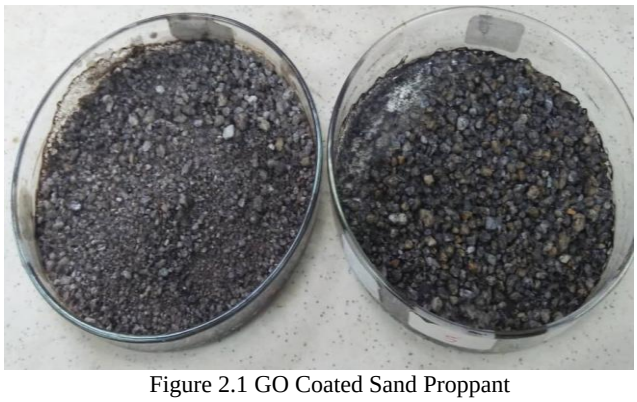

Figure 2.1 GO Coated Sand Proppant

2.3 Method Performance

2.3.1 Characteristic of GO coated sand proppant

The properties of sand and GO coated sand proppant will be characterized by using recommended (ISO 13503-2) procedure [8] to quantify performance of proppant.

Sieve analysis and grain size

The prepared sample is test by using 16 to 100 mesh of sieve sizes. The sieves then shaking for 10 minutes. The weight of sample sand retained has been recorded. The graph are plotted based on calculation percentage of passing and total of percentange retained.

Sphericity and roundness measurements

The sphericity and roundness of sand particles is observed by using SEM machine with 15x magnification. The result obtain is compared with the Krumbein Chart to estimate both roundness and sphericity

Turbidity test

5 g of each sample is placed in the sample cell and then filled by 100 ml of distiled water. The cell is capped and has been shaken for 30 second to suspend the particles in the sample. Turbidimeter is used to read the turbidity of the sample. Turbidity test is the measurement of soft particles and clay content in the sample.

Acid solubility

Samples sand is washed and then is placed in a HCI with a concentration of 10 % for 24 hour with stirring every 2 hour. After 24 hour immersed in HCI, sample is washed again and dried at 105ºC until constant weight is obtained. Acid solubily is measured by using following equation (Equation 1.1).

$$AS\% = \frac{ms - ms_{after}}{ms}$$

Equation 1.1 Acid Solubility

ms = The mass of dry sample (gram)
ms_{after} = The mass of remaining sample after the acid bath (grams)
AS = Acid Solubility (%)

Crush resistance test

Crush resistance test is conducted to measure the amount of produced fines under certain stress. The steel crush cell is filled by the sieved sand with mesh size of (-20/40+*)* . Uniform stress is applied to the crush cell to reach the stress level (500, 1000, 1500 2000and 2500 Psi) within 2 minute before released. Lastly, the sand is sieved again after the crush resistance test is completed. The amount of crush material are calculated and recorded.

III. RESULTS AND DISCUSSION

3.1 Synthesis and characterization of GO

Modified Hummer method produced Graphene Oxide from graphite powder. Graphene Oxide was analyzed by using X–ray diffraction analysis (XRD) and fourier transform infrared (FTIR). Figure 4.1(A) and 4.2(B) showed the XRD paterns of GO and raw graphite. Based on the Figure 4.1(A), the peak were observed at $2\theta = 10.0°$ due to reflection from the plane [5]. Figure 4.2(B), peak were observed at $2\theta = 26.0°$ for raw graphite.

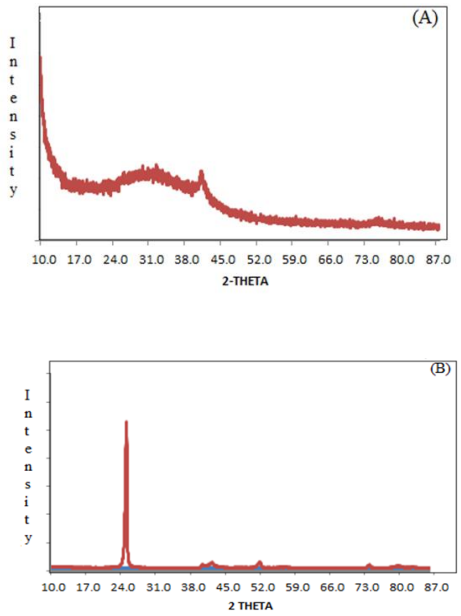

Figure 3.1 (A) X-ray diffraction (XRD) analysis of graphite, (B) X-ray diffraction (XRD) of graphene oxide (GO)

Figure 3.1(A) and 3.1(B) showed the FTIR spectra result for GO and graphite. Based on FTIR spectra of GO, its showed a smooth peak approximately at 3200-3300 cm^{-1} due to weak hydroxyl group C-OH. The peak at 1630cm^{-1} was corresponding to the present of C=C vibration of the graphene plane [8]. Next the peak at 1760cm^{-1} was due to the present of carbonyl group C=O. Finally, the peak at 1220cm^{-1} represent the streching vibration of C-O-C group. All these peaks were not appear in the Figure 3.2(B), spectrum of graphite.

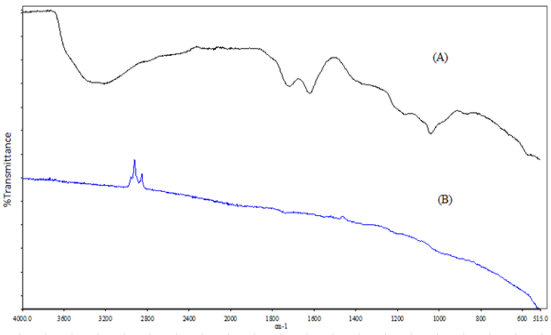

Figure 3.2 (A) FTIR spectra of GO, (B) FTIR spectra of graphite

3.2 Synthesis and characterization of Graphene Oxide Coated Sand Proppant

Figure 3.3 corresponds to SEM images of uncoated sand, sand with 1st layer of GO, sand with 2nd layer of GO. Figure 3.4(A) shows that the uncoated sand have uneven and extremely rough of surface. Based on Figure 3.4(B), the surface are modified due to a first layer of GO on the surface. The surface become more smooth compared to Figure 3.4(A). In the Figure 3.4(C), the tiny pores was observed on the surface of sand. This indicated that the present of GO had modified the surface of the rough and uneven of uncoated sand.

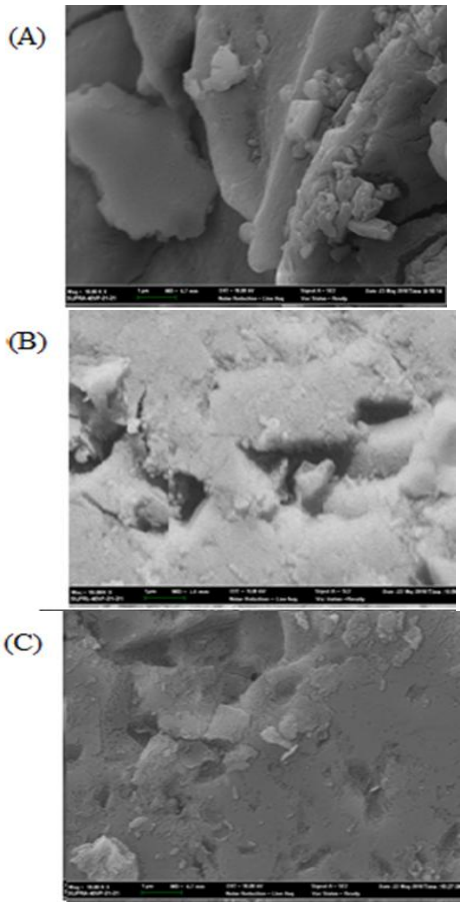

Figure 3.3 Image of SEM

3.3 Performance of Graphene Oxide Coated Sand Proppant

3.3.1 Sphericity and roundness

The sphericity and roundness were determined by using 15x magnification microscope. Based on requirement ISO 13503-2 and the graphical visual assessment using Krumbein and Sloss chart, typical sand proppant should exceed the value of 0.6 for both sphericity and roundness respectively. As shown in Table 3.1 and Figure 3.4, samples 4 exceed the value of 0.6 for both sphericity and roundness respectively. Meanwhile, the other samples do not meet the desired value required. However, sample 1,2,4,7 and 8 have a desired sphericity but not for roundness. As a result obtained, only sample 4 satisfied the requirement for sphericity and roundness. The sphericity of proppant is the important parameters because it has a direct relationship to the conductivity of the fracture propped by the respective proppant [10]. Besides, particles with higher sphericity will result in better conductivity of the fracture [10].

Table 3.1: Sphericity and roundness

Sample	Roundness	Sphericity
Sample 1	0.5	0.7
Sample 2	0.5	0.7
Sample 3	0.3	0.5
Sample 4	0.7	0.7
Sample 5	0.5	0.7
Sample 6	0.3	0.5
Sample 7	0.5	0.7
Sample 8	0.3	0.7

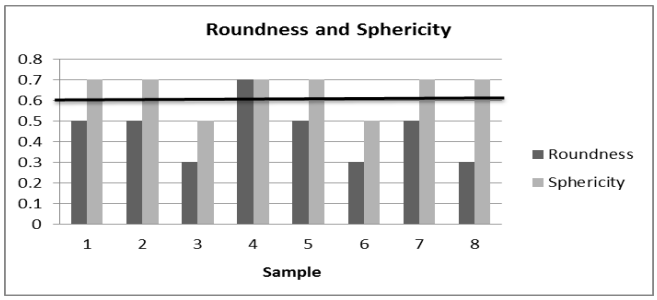

Figure 3.4: Sphericity and roundness

3.3.2 Acid Solubility Test

Figure 3.5 showed the result of acid solubility of sample after test was conducted. Regarding to recommended requirement, the acid solubility should not excess 2.0%. Based on the Figure 3.5, sample 4 and sample 5 for both 1st and 2nd layer of GO do not exceed 2.0 %. However, second coating of sample 6, 7 and 8 showed that the acid solubility do not exceed 2.0%. The decreasing of acid solubility can proved that the surface of the sample may effect on the result gained. The layer of GO coating on sand can prevent the sand to dissolve in these solutions.

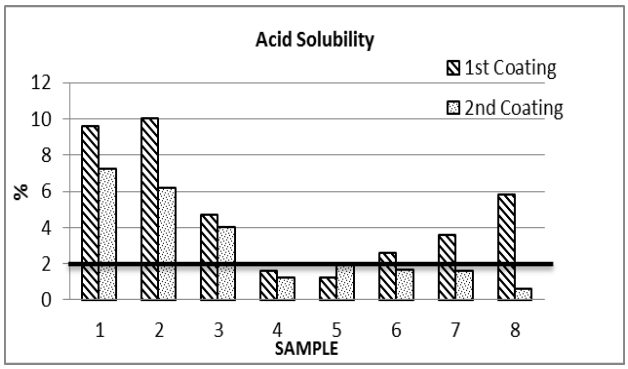

Figure 3.5 Acid Solubility

3.3.3 Crush Resistance Test

Based on API standard requirement, the sand only allows to produces 10% by weight of fine produce after pressure 2500psi is exerted on it. As shown in figure 3.6 and 3.7, sample 2 for both first and second layer of GO shows really high crush resistance compare to other sample, where it produce less than 10% of fines until 2500 psi exerted on it. However, after second layer of GO, sample 3 shows decreasing in fine produce percentage, where it produce 10% of crush after 2500 psi is applied, compared to first layer of Go where produce 10% of crush after 2000 psi exerted on it. From the result, GO can increased the resistance of the sand. The more layer of GO coating on sand, less fines is produced when high stresses are applied. The particles shape also gives impact to the sand. The angular grains tend to crush easily compare to rounder one [11].

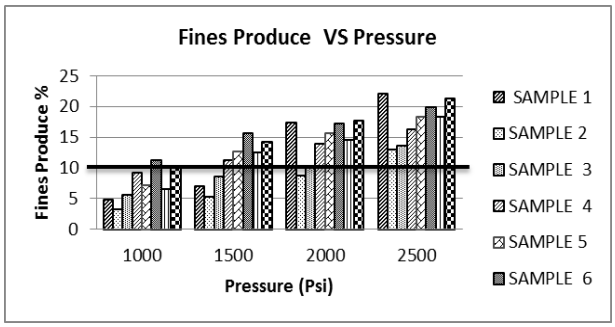

Figure 3.6 Crush Resistance 1st layer of GO

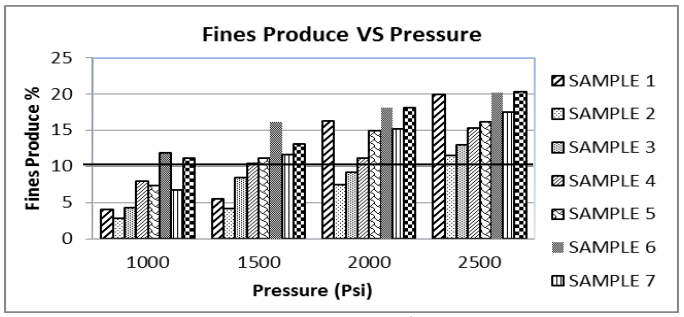

Figure 3.7 Crush Resistance 2nd layer of GO

3.3.4 Grain Size

Figure 3.8 represented the results of the grain size analysis for every sample. There are four different range used in this test which are 16/20, 20/40, 40/70, and 70/140. Only samples 6 have more than 90% of the mass retained between the sieves sizes. It showed that sample 6 meet the requirement of ISO 13503-2. All the samples was collected from 0.5 meter from depth. However, the particles size of the sample maybe influenced by weathering and stripping [12]. In order to obtained accurate values and small size of sand, the deep depth sample are required. Its is recommended to used smaller proppant to increased the conductivity of sand and prevent the fluid loss into the formation [12].

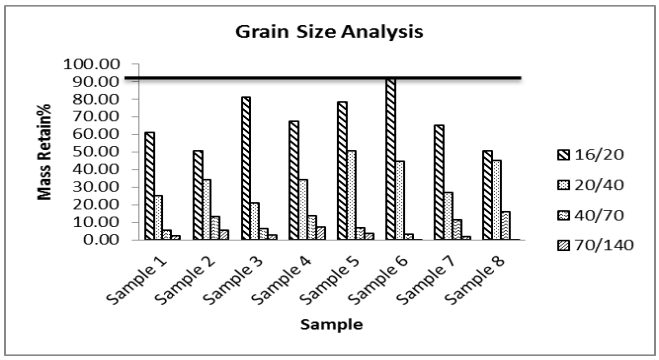

Figure 3.8 Grain Size Analysis

3.3.5 Turbidity

Table 3.2 showed the designation FTU which is represent the amount of suspended particles of the samples. From the result gained, designation FTU for each sample was varies from 29-65 FTU. It showed that all the samples have satisfied with recommended FTU reading which is not exceeds 250 FTU. Table 4 also showed that the FTU reading were increasing for 2nd layer of GO, still not exceed 250 FTU. From the results, the FTU reading were affected by the amount of GO coated on the sand. GO contributed to the amount of suspended particles.

Table 3.2 Designation FTU

Sample No	Designation FTU	
	1st layer of GO	2nd layer of GO
1	48	65
2	45	59
3	29	41
4	39	53
5	41	50
6	47	60
7	42	57
8	40	52

IV. CONCLUSIONS

In this study, GO were synthesized from Hummer Method. Based on the result of XRD and FTIR, it shows that graphite is fully oxidized with the forrmation of peak at 2θ =10.0° and the present of functional group C=O, C-H, COOH and C-O-C at graphite layer. GO produced are used to coat the surface of uncoated sand by using deep coating method. Through a test of sphericity and roundness, samples 4 exceed the value more than 0.6 for both. Turbidity of whole sample is less than 250 FTU. Sample 2 started to produce more than 10% fine under pressure of 2500 psi and layer of GO can improve the strenght of sand. The grain size analysis result shows that only sample 6 meet the requirement and to obtained accurate values and small size of sand, the deep depth sample is required. In conclusion, GO significantly can increased the resistance, improve the surface roughness, and decreased the acid solubilty of sand. In other word, GO coated sand have a potential characteristic as a proppant..

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