Urethane based nanocomposite coated proppants for improved crush resistance during hydraulic fracturing

T Qian¹, A S Muhsan¹*, L Htwe¹, N Mohamed² and O Hussein³

¹Petroleum Engineering Department, Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak, Malaysia.
²Fundamental and Applied Sciences Department, Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak, Malaysia.
³Mechanical Engineering Department, Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak, Malaysia.

*E-mail: ali.samer@utp.edu.my

Abstract. Hydraulic fracturing is one of the stimulation techniques that has been used to increase the hydrocarbon flow in unconventional reservoirs. Proppants are normally used to maintain the fracture conductivity and increase the permeability to oil. Due to high closure stress of the fractured formation, the conventional or uncoated proppants are easily crushed. Therefore, this project aims to increase the compressive strength of proppants by coating it with urethane based nanocomposite. Glass beads and fracking sands are coated with urethane resin and mixed with reduced graphene oxide (rGO) and carbon nanotubes (CNTs) respectively. Analysis testing using optical microscopy (OM) was conducted to study the morphology and microstructures of the coated proppants before and after crush test. Results showed remarkable improvement in proppants compression strength up to 41% and 35% after adding only 0.5% of CNTs and 0.1% of rGO respectively to the urethane resin coating. Therefore, it is recommended to utilize this material for coating the proppant with the optimized concentration to prevent pore plugging and proppant from flowing back, achieving the objective and solving both problem statements.

1. Introduction

Hydraulic fracturing is a commonly used stimulation technique to further increase the hydrocarbon fluid production from unconventional reservoirs [1]. Unconventional reservoirs are reservoirs that have permeability of less than 1mD. Hydraulic fracturing helps to increase the reservoir permeability by inducing fractures around the near wellbore region. To prevent the fractures from closing, proppants are introduced to maintain the fracture width after the fracturing fluid has been removed [2]. Proppant is a solid particle that is pumped into the formation by suspending in the fracturing fluid. The proppant will then deposit in the fracture together with other proppants to form a “proppant pack” [3]. Proppants also comes in different sizes, shapes and types to provide an optimum production of hydrocarbon fluids.

Proppants can be divided to uncoated and coated proppants. Uncoated proppants are also known as traditional proppants. For instance, glass bead proppants. Glass bead proppants was once known as the strongest proppant as it is round in shape and are well sorted [4]. However, glass bead proppants were found to be easily crumbled in brine at high temperature and hence, not suitable to be used in formation with high temperature as it will create fines, reducing the permeability to oil [5]. Coated proppants on the other hand is mostly resin based coated proppants. Resin coated proppants is a further modification...
of both sand and ceramic proppants by coating resin on the uncoated proppants. There are two types of resins can be used, which are curable resin and pre-cured resins. Curable resins are used to prevent proppant flowback by consolidating the proppants whereas pre-cured resins are used to trap the fines generated by the proppants [7]. According to Palisch [6], both resins have the function of encapsulating the fines generated by the proppant but doesn’t improve the proppant compressive strength. The proppant may be crushed by high closure stress, but the fines will not be migrated to the wellbore. Resins are also easily degraded at low softening temperature, approximately above 121 °C [2]. In the case where resin is being heated above 121 °C, resin will change its surface to a rubbery state and migrate to the wellbore, leaving uncoated proppants with low compressive strength.

Therefore, this work aims to investigate the compressive strength of different concentration of CNTs and rGO reinforced resin/urethane based coated proppant. To mimic the actual proppants, glass beads were chosen as it has higher compressive strength of 5,000 psi compared to sand proppants 4,000 psi. The resulting compressive strength for both nanomaterials coated proppants with resin will then be compared and the optimum concentration of nanomaterials that gives the highest compressive strength will be reported. By incorporating resin with rGO and CNTs as a proppant coating, it is expected that the coated glass bead proppants will be able to withstand at higher temperature condition since both rGO and CNTs have great thermal properties [8]. As shown in figure 1, it is also expected that the fines generated by both resin with rGO and resin with CNTs coated glass bead proppants are low as rGO and CNTs are known to have high mechanical properties [8]. This allowing the proppants to withstand high closure stress as well as preventing fines from generating. The figure also shows the fines generated are captured by the resin with CNTs or resin with rGO coatings after applied the formation pressure.

![Figure 1. Fines are captured with resin, CNTs and GNPs coating.](image)

2. Materials and methods

2.1. Materials

Different concentration of CNTs and rGO such as 0.1%, 0.5%, and 1%, resin, acetone and glass bead proppants are required in this experiment. Water also is required for the ultrasonic bath to ensure the uniform dispersion of nanomaterials in resin.

2.2. Apparatus and procedure

2.2.1. Carbon nanotubes coated proppants with resin. The CNTs is mixed with acetone and it is soaked into the ultrasonic bath to ensure the uniform dispersion of the CNTs in the solution. The purpose of using acetone is to dilute the resin or to reduce resin usage since resin has low thermal stability. The great thermal properties of CNTs will help to increase the overall thermal stability of proppants in the formation. The first step is then repeated by adding Urethane Part B and followed by Urethane Part A. The uncoated glass bead proppants are prepared by placing it on a siever. By using a pipette or a dropper, the well mixed CNTs and resin solution is then dripped onto the uncoated glass bead
proppants. The excessive coatings will then flow to the bottom of the strainer and are wiped off. This is to ensure only a thin layer of coatings are coated on the proppants as well as to prevent any agglomeration on the proppants coating.

2.2.2. Reduced graphite oxide coated proppants with resin. The coating process is similar with CNTs but without the usage of ultrasonic bath as the reduced rGO is already well mixed in a solution form. The first step is to mix the rGO with the Urethane Part B. Then, another mixture of acetone with Urethane Part A is mixed. The purpose of adding acetone to Urethane Part A is to dilute the resin instead of mixing acetone with rGO as rGO is already well dispersed in a solution. Both mixtures are mixed together to form a rGO with resin coatings. The dropper will then drip the coatings onto the surface of the uncoated glass bead proppants and the excessive coatings are wiped off.

2.2.3. Compressive strength testing with Universal Testing Machine (UTM). Due to the limitation of compressive equipment, Universal Testing Machine (UTM) is used to perform crush test on all coated and uncoated glass bead proppants according to ISO 13503-2. The UTM machine exerts vertical stress onto the proppants to determine the compressive strength of the coated and uncoated proppants. A stainless-steel mold will be used together with the compression test. Once all of the proppants are fully crushed, the top plate is then released the load applied. A layer of proppants is prepared inside the mold and close it with a plunger. Then it is placed in between the top and bottom plate of the UTM machine. It is critical to ensure that only one even layer of proppants is placed in the mold as extra proppants will affect the compressive strength of the proppants. The results were presented in a stress vs deformation graph, with the maximum load (kN) and compression strength (MPa).

2.3. Measurement of fines Percentage (%) generated using 400 mesh siever
A 400 mesh siever is used to determine the amount of fines generated by each coated and uncoated glass bead proppants after the crush test. Any crushed proppants that are smaller than 40 mesh size are considered as fines. The % of fines generated here refers to the mass percentage and it is determined using equation (1):

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\% \text{ of fines generated} = \frac{\text{Mass of crushed proppants (g)}}{\text{Total Mass (g)}} \times 100
\]  

where the total mass is the mass of proppants used before the crush test and the mass of crushed proppants are the mass of fines that are smaller than 40 mesh size. After sieving the fines, the fines that are smaller than 40 mesh size are weighted, and the % of fines generated for each coated glass bead proppants and uncoated glass bead proppants is obtained.

2.4. Optical microscope on all coated proppants
Each coated proppant will undergo Optical Microscopy to observe any agglomeration on the proppant coatings. According to figure 2, it is noticed that there is agglomeration of CNTs on the surface of the 1% CNTs coated proppant. Also, from figure 3, it is noticed that after 0.1% rGO coated proppants agglomeration of rGO is noticed on the proppant’s coatings.

![Figure 2](image_url).
3. Results and discussion

Universal Testing Machine (UTM) was used to carry out crush test on all coated and uncoated glass bead proppants. Table 1 and figure 4 show the results from the UTM crush test showed that the uncoated glass bead proppants give the lowest compressive strength compared to the other CNTs coated proppants. This is because of the uncoated proppants are not protected by any coatings and hence, it is easily crushed with low load applied. The 0.5% CNTs coated proppants shows the highest compressive strength compared to the 0.1% CNTs and 1% CNTs coated proppants. In the beginning, the compressive strength of proppants increases as the concentration of CNTs increase. However, after 0.5% CNTs, it is noticed that the compressive strength of CNTs coated proppants starts to decline due to the agglomeration on the surface of the proppant coating. Agglomeration means there are uneven surface of coatings on the proppants and when pressure is applied on the proppants, the surface that has thinner coating than the agglomerated side tends to break first. This will cause the proppants have lower compressive strength. Thus, the most suitable CNTs concentration for proppant coatings is 0.5%.

Table 1. Compressive strength of each concentration of CNTs coated glass bead proppants.

| Concentration of CNTs (%) | Fines generated (%) | Compressive Strength (MPa) |
|---------------------------|--------------------|----------------------------|
| Uncoated                  | 9.183              | 2923.125                   |
| 0.1                       | 12.847             | 4089.387                   |
| 0.5                       | 16.868             | 5369.251                   |
| 1                         | 13.536             | 4308.56                    |

Figure 3. Optical microscope of (a) 0.1% rGO, (b) 0.5% rGO and (c) 1% rGO.

Figure 4. Compressive strength of uncoated proppants with different concentration of CNTs coated proppants.
For rGO coated proppants, it is noticed that 0.1% rGO gives the highest compressive strength compared to other concentration of rGO coated proppants as shown in Table 2 and Figure 5. It is also noticed that the uncoated proppants still have the lowest compressive strength among all the rGO coated proppants. Furthermore, the compressive strength of rGO coated proppants starts to decrease after 0.1% rGO coated proppants also due to the agglomeration of rGO on the proppants coating, which causes uneven stress exerted around the proppants surface. Usually, the side of the proppants that are agglomerated have protruding ends, which could increase the pressure applied on the agglomerated side and crush faster.

Table 2. Compressive strength of each concentration of rGO coated glass bead proppants.

| Concentration of rGO (%) | Fines generated (%) | Compressive Strength (MPa) |
|--------------------------|---------------------|---------------------------|
| Uncoated                 | 9.183               | 2923.125                  |
| 0.1                      | 12.957              | 4124.395                  |
| 0.5                      | 11.832              | 3766.278                  |
| 1                        | 11.285              | 3592.18                   |

4. Conclusion
In conclusion, 0.5% Carbon Nanotubes (CNTs) is the most suitable for proppants coating because it provides the highest compressive strength of 5369.25 MPa compared to 0.1% reduce Graphite Oxide (rGO) coated proppants as well as other concentration of CNTs coated proppants. This 0.5% CNTs coated proppants is able to improve the compressive strength of the uncoated glass bead proppants by almost 84%, which is twice the percentage of compressive strength improvement for 0.1% rGO coated proppants. Moreover, 0.5% CNTs coated proppants generate fines slightly more than the fines generated by 0.1% rGO coated proppants. With similar amount of fines generated but with different compressive strength, it is preferable to choose the coatings that are able to provide the highest compressive strength. By using 0.5% CNTs coated proppants, it is able to maintain the fracture width and fracture conductivity with its high compressive strength and prevent fines from migrating towards the near wellbore region, allowing more hydrocarbons to be produced. Therefore, it helps to prevent pore plugging and proppant from flowing back, achieving the objective and solving both problem statements.

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