A comparative study of pH and temperature on rheological behaviour between Polyacrylamide (PAM) and its modified PAM

Jin Kwei Koh[1], *Chin Wei* Lai[1,*], *Mohd Rafie* Johan[1], *Sanjay Mavinkere* Rangappa[2], *Suchart* Siengchin[2]

[1]Nanotechnology & Catalysis Research Centre (NANOCAT), Level 3, Block A, Institute for Advanced Studies, University of Malaya (UM), 50603, Kuala Lumpur, Malaysia.
[2]Natural Composite Research Group Lab, Department of Materials and Production Engineering. The Sirindhorn International Thai-German Graduate School of Engineering (TGGS), King Mongkut's University of Technology North Bangkok (KMUTNB), Bangkok, Thailand.

Abstract. Drilling waste is a problem that affects the environment, society, and health. However, the rheological additive in drilling fluid is the source of the generation of drilling waste. Hence, a suitable rheological additive became a concern in bored pile construction. Conventional bentonite has been replaced by the usage of polymer in drilling operations, this is due to the operational, environmental, and economic aspects. Unlike bentonite, polyacrylamide (PAM) has a high molecular weight, good gelling behaviour, and is eco-friendly. However, there are limitations of PAM in terms of thermal stability and pH sensitivity. Therefore, the conventional polymer-based drilling fluid requires the hybridisation of functionalised material. In this paper, PAM with its enhancement is needed for water-based drilling through modification using silica (SiO_2) and sodium dodecyl sulphate (SDS). The paper presented a comparative analysis of rheological behaviour between polyacrylamide (PAM) and modified PAM. This research involved the influence of temperature (ambient to 80 °C) and pH (9 and 10). Results revealed that modified PAM performed better at 40 °C and pH 10. Furthermore, PAM and modified PAM had a better rheological performance at pH 10. Future studies can demonstrate the modified PAM as the drilling fluid in the bored pile construction to investigate the frictional resistance of the drilling fluid.

Keyword. Polyacrylamide, functionalised, rheological, temperature, pH

1 Introduction

Drilling waste is the second-largest waste. This issue has become a concern in drilling, exploration, and offshore industry because the waste can affect the soil quality, health, water, and entire ecosystem without proper management[1], [2]. Hence, the drilling fluid is a critical component that can generate waste after excavation and exploration. Generally, drilling fluid is composed of rheological additives, water, and clay. Water-based drillings can use with various rheological additives, such as bentonite, polymer, and others [3]. Currently, the polymer is the alternative to bentonite in drilling technology due to operational, environmental, and economic aspects [4]. In addition, polyacrylamide (PAM) is commonly utilised in bored pile and diaphragm construction because it has a high molecular weight, good gelation time, inexpensive, and eco-friendly industrial usage. In contrast, the consumption of bentonite requires higher amounts of dosage, which generate more waste than PAM [5].

Nonetheless, the poor thermal stability and pH sensitivity are the limitations of PAM usage in drilling. Additionally, the polymer can degrade at a specific temperature. For example, the thermal stability of PAM can endure a temperature below 175 °C, according to Europe *et al*. [6]. However, Xie *et al*. [7] reported a detrimental effect on drilling performance when the incline of temperature with the excessive hydrolysis in the polymer. In this study, the temperature of drilling fluid was investigated from ambient conditions to 80 °C due to safety concerns on the laboratory scale and the boiling point of water acting as the heating base of fluid.

Besides, the drilling fluid is always alkaline, with a pH of 8 to 10.5. Gamal *et al*. [8] studied the bentonite-based drilling fluid that kept better rheological performance at pH 9-10. However, more acidic or basic conditions of drilling fluid can contribute to the cost of facilities in drilling, such as pumping power and equipment corrosiveness. Hence, a drilling fluid with a pH of 9 to 10 can perform well in the drilling operation. Additionally, a low dosage of nanoparticles in polymer composite influenced the rheological behaviour and pH of modified drilling marginally [9], [10]. Inversely, the pH of the drilling fluid was more acidic after graphene oxide was involved in the drilling fluid, as investigated by Kusrini *et al*. [11]. Therefore, this study investigated the rheological behaviour between PAM and modified PAM at pH 9 and 10 because the water-based drilling fluid is usually favourable at pH 9 and 10.

Due to the poor thermal stability and chemical stability of PAM, the modification of PAM is popular with the hybridisation with additives, such as functionalised materials, organic modifiers, cross-linking

* Corresponding author: cwlai@um.edu.my.

agents, and others. Among all the functionalised materials, silica is the most simple and economical material as it is easy to access and less harmful to the environment. Hence, this study enhanced PAM by using sodium dodecyl sulphate (SDS) and silica (SiO_2) as the modifiers. Furthermore, several researchers investigated the synergistic effect of SDS and SiO_2 involved in PAM-based drilling applications, contributing the better viscosity, surface tension, and others [10], [12]–[15]. The paper studied the rheological behaviour with the effects of temperature and pH between bare PAM and modified PAM. Further, chemical and surface characterisations were studied to investigate the surface properties between PAM and modified PAM.

2 Experimental

2.1 Materials

Polyacrylamide was provided by Synergy Lite Sdn Bhd. Sodium dodecyl Sulphate was purchased from Merck. Silica was purchased from Sigma-Aldrich. Soda Ash was purchased from Solvay S.A.

2.2 Synthesis of PAM and modified PAM

Bare PAM fluid was mixed in 1000 ppm. Besides, 0.5 wt % SiO_2 and 0.2 wt % SDS were mixed with 1000 ppm PAM as a modified PAM fluid. These were mixed well at a relative speed with Joanlab overhead stirrer.

2.3 Characterisation

PAM and modified PAM were characterised using Fourier Transform Infrared Spectroscopy (FTIR) and tensiometer.

2.4 Rheological testing

PAM and modified PAM were characterised using HST-6ST 6-speed rotational viscometer, Qingdao Heng Taida. This test was further analysed with the effect of pH (9, 10) and the influence of temperature (ambient, 40, 60, and 80 °C) on both polymers. The procedure of testing is followed, according to American Petroleum Institute (API).

3 Results and discussion

3.1. Appearance of fluid

As depicted in **Fig. 1**, the appearance of PAM is transparent. However, the colour shifted from transparent to milky white after modification, indicating the addition of SiO_2 and SDS in the PAM solution. Additionally, the top layer of modified PAM formed with white foam, which is attributed to SDS dispersion in SiO_2/PAM solution. This also indicates that SDS increases the surface activity of SiO_2 in drilling fluid [16].

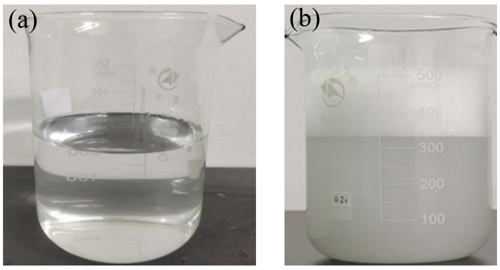

Fig. 1. The appearance of (a) PAM and (b) modified PAM doped with SiO_2 and SDS.

3.2 FTIR analysis

The FTIR spectra of bare PAM and the modified PAM are illustrated in **Fig. 2**. A spectrum of PAM exhibited the stretching vibration of the carbonyl group at the peak of 1650 cm^{-1} and the stretching vibration of the amide group at the peak of 3424 cm^{-1}. The stretching vibration of the C-H bonds is shown in two consecutive peaks at 2905 cm^{-1} and 2974 cm^{-1}. The ring structure vibration of the methyl C-H bond is observed at the peak of 1449 cm^{-1}, while the peak at 1378 cm^{-1} is C-N stretching vibration [17], [18].

Due to their low concentration of SiO_2 and SDS applied in surface modification, the functionality of both modifiers is poorly identified in the spectra of modified PAM. However, a prominent peak in the range 3200 – 3400 cm^{-1} is the silanol -OH vibration in all modified PAM spectra. Furthermore, the bending vibration of H-O-H is indicated at a sharp peak at 1630 cm^{-1} in the modified PAM spectra. Both peaks in modified PAM spectra exhibited a stronger linking between the -OH groups and the modified SiO_2 functionalised particles [17]. Moreover, the peak observed at 3424 cm^{-1} and 1650 cm^{-1} in PAM are shifted towards the lower peaks at 3280 cm^{-1} and 1630 cm^{-1} in modified PAM, showing stable dispersion of SiO_2 in PAM.

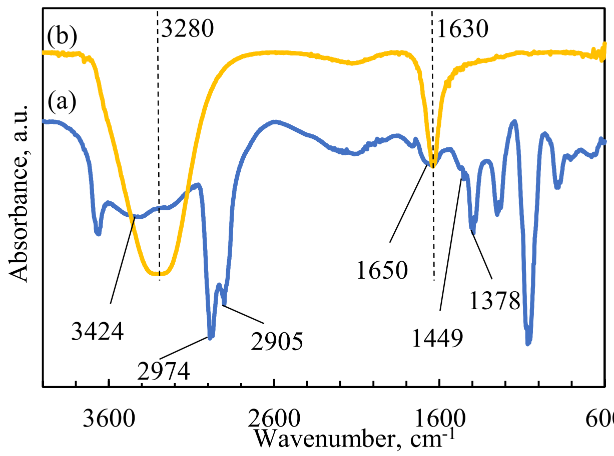

Fig. 2. FTIR spectra of (a) PAM and (b) modified PAM doped with SiO_2 and SDS.

3.3 Surface characteristic

Table 1 shows the surface tension and surface contact angle of PAM and modified PAM. Modified PAM

 https://doi.org/10.1051/e3sconf/202235502005

showed less surface tension mean than PAM, indicating the modified PAM can enhance the rheological properties of drilling. The lesser surface tension can reduce the rheological risk, such as pipe sticking, wellbore issue, and others [19], [20].

Meanwhile, the surface contact angle of modified PAM was lower than that of PAM, demonstrating the modified PAM is more hydrophilic than PAM. Based on the wettability theory, both have hydrophilic properties as their contact angles were below 90°.

Table 1. The surface characteristic of PAM and modified PAM.

Surface characteristic	PAM	Modified PAM
Surface tension mean, mN/m	43.83	30.11
Surface contact angle mean, °	42.19	24.58

3.4. Rheological test

3.4.1 Effect of temperature on rheological properties between PAM and modified PAM

As depicted in **Fig. 3**, overall showed the fluctuation in apparent viscosity (AV), plastic viscosity (PV), and yield point (YP) between PAM and modified PAM. In ambient conditions, the modified PAM had an incline of YP by 2.2 % but AV and PV reduced by 17.7 % and 25.8 %, respectively. After heating at 40 °C, modified PAM showed a reduction of AV, PV, and YP by 20.9 %, 15.1 %, and 30.2 %, respectively. After heating at 60 and 80 °C, the modified polymer demonstrated the incline of AV and PV with the decline of YP. When compared to the gel strength of PAM, modified PAM demonstrated lower over all the temperatures in **Fig. 4**. In conclusion, modified PAM can withstand temperatures up to 40 °C because modified PAM exhibited better rheological performance, especially the reduction of PV in this study.

Generally, the heating of the polymer can enhance the flocculation and adsorption capacity. This situation can affect the rheological performance of the drilling fluid. Additionally, the endothermic process also enhances the flocculation rate. Flocculation can change the chemical conformity and functionality of the polymer [21], [22]. Therefore, high PV in drilling fluid due to flocculation is undesired, which can influence the wellbore performance [23], [24]. This paper showed that the inclination of PV is affected by higher heating temperatures. The large gel-like floc formation that occurs at high temperatures potentially contributes to the higher viscosity with high pumping energy during drilling. Therefore, aggregation and flocculation can cause poor rheological performance at higher temperatures [24]–[26].

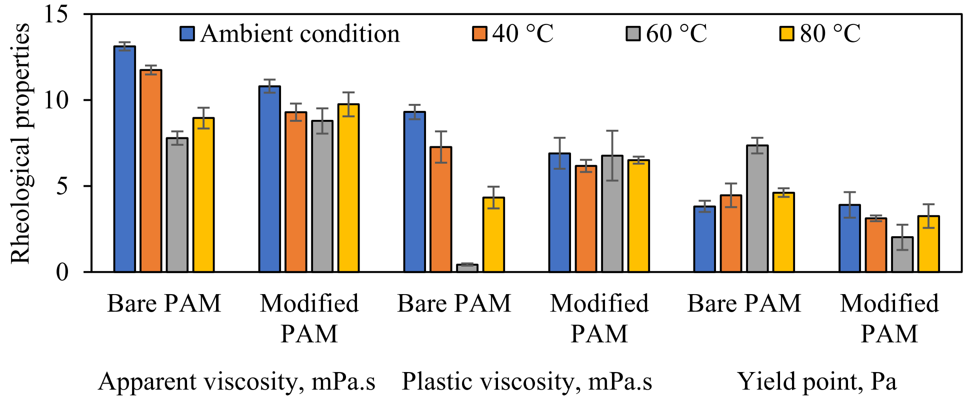

Fig. 3. Effect of temperature on the rheological properties between PAM and modified PAM doped with SiO_2 and SDS.

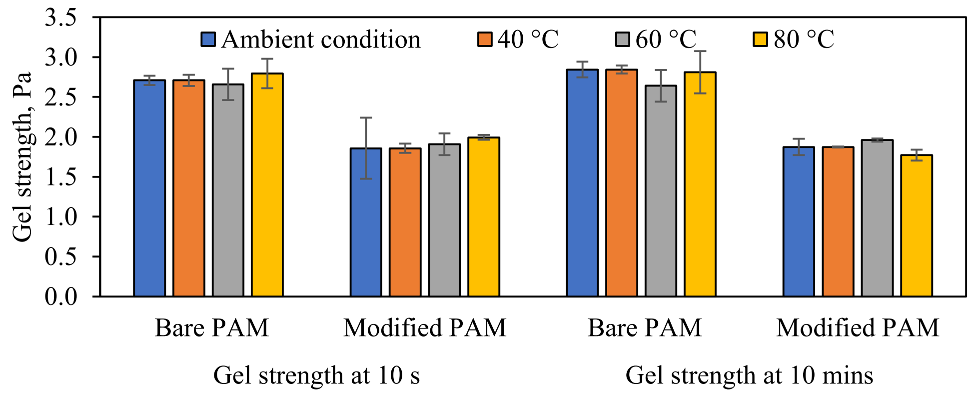

Fig. 4. Effect of temperature on the gel strength between PAM and modified PAM doped with SiO_2 and SDS

https://doi.org/10.1051/e3sconf/202235502005

3.4.2 Effect of pH on rheological properties between PAM and modified PAM

The effect of pH on the rheological properties between PAM and modified PAM is compared in **Fig. 5** and **Fig. 6**. At pH 9, the modified PAM reduced AV and YP by 11.6% and 79.8%, respectively. However, modified PAM showed an incline of AV by 6.3% and a decline of YP by 48.1%, respectively, at pH 10. For PV, modified PAM inclined by 48%, and 89.4%, at pH 9 and 10, respectively. Although the rheological performance of modified PAM was not ideal than PAM, the plastic viscosity of modified PAM was lower at pH 10.

The gel strength of modified PAM was inclined at pH 9 -10. Hence, modified PAM had higher gel strength than bare PAM. Higher gel strength can promote better cutting in drilling [23], [27]. Further, modified PAM and PAM performed a flat gel strength at pH 10 due to a negligible difference in gel strength between 10 seconds and 10 minutes. Therefore, the drilling fluid performed with better rheological behaviour at pH 10.

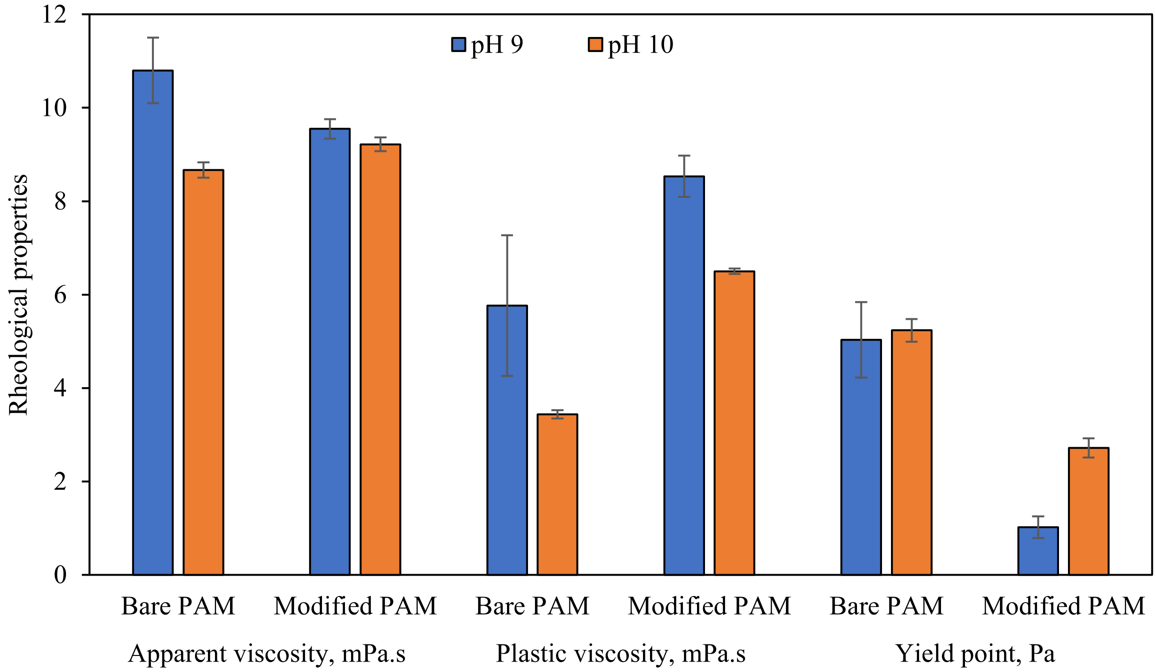

Fig. 5. Effect of pH on the rheological properties between PAM and modified PAM doped with SiO_2 and SDS.

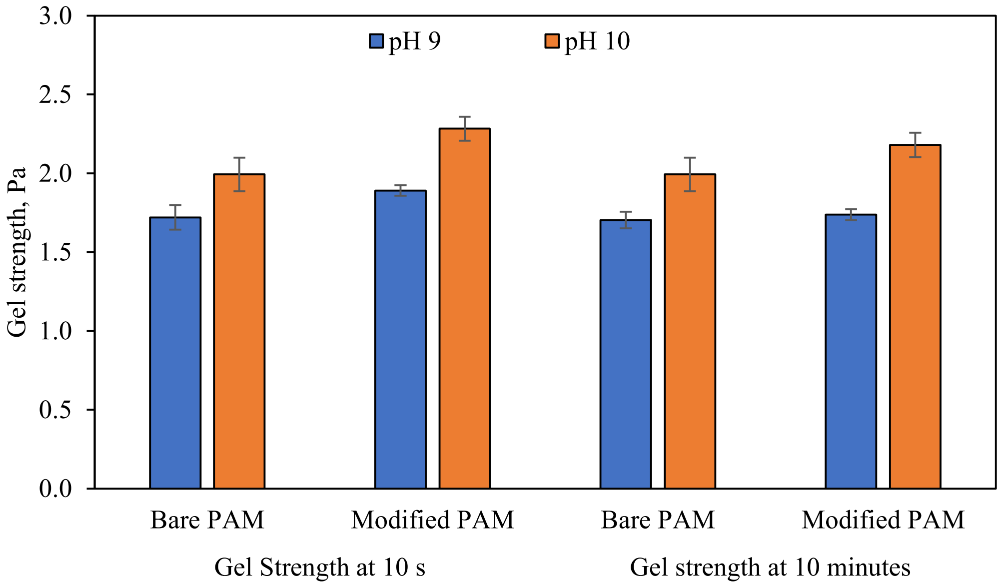

Fig. 6. Effect of pH on the gel strength between PAM and modified PAM doped with SiO_2 and SDS.

* Corresponding author: cwlai@um.edu.my.

4 Conclusion

In this paper, PAM and modified PAM were synthesised, characterised, and utilised in drilling fluid at a specific temperature (ambient to 80 °C) and pH (9 – 10). The modified PAM was investigated to enhance drilling fluids' performance, especially in bored pile drilling. The surface characterisation of modified PAM showed more hydrophilic than that of PAM. Besides, the rheological investigation showed that modified PAM performed better than PAM at 40 °C. Further, modified PAM had a better rheological performance at pH 10. In the future, modified PAM can be further tested in the bored pile construction to validate the frictional resistance of drilling fluid.

Acknowledgement

This research study was financially supported by Synergy Lite Sdn. Bhd. (No. PV027-2021).

References

[1] O. S. Onwuka, O. Igwe, S. I. Ifediegwu, and C. S. Uwom, "An assessment of the effectiveness of drilling waste treatment process in X-gas field, Niger Delta, Nigeria," *Geol. Ecol. Landscapes*, **vol. 2**, no. 4, (2018): 288–302

[2] A. R. Ismail, A. H. Alias, W. R. W. Sulaiman, M. Z. Jaafar, and I. Ismail, "Drilling fluid waste management in drilling for oil and gas wells," *Chem. Eng. Trans.*, **vol. 56**, (2017): 1351–1356

[3] J. K. Koh, C. W. Lai, M. R. Johan, S. S. Gan, and W. W. Chua, "Recent advances of modified polyacrylamide in drilling technology," *J. Pet. Sci. Eng.*, **vol. 215**, part A, (2022): 110566

[4] C. Lam, S. A. Jefferis, T. P. Suckling, and V. M. Troughton, "Effects of polymer and bentonite support fluids on the performance of bored piles," *Soils Found.*, **vol. 55**, no. 6, (2015): 1487–1500

[5] S. Jefferis, V. Troughton, and C. Lam, "Polymer systems for fluid supported excavations," in *Geotechnical issues in construction: short paper series and 2nd conference held on 2 November 2009, at CIRIA, London* (2011): 7–12.

[6] W. Europe, M. Doble, and A. Kumar, "Degradation of Polymers," in *Biotreatment of industrial effluents*, Elsevier Ltd, (2005): 101–110.

[7] B. Xie, J. Ma, Y. Wang, A. P. Tchameni, M. Luo, and J. Wen, "Enhanced hydrophobically modified polyacrylamide gel for lost circulation treatment in high temperature drilling," *J. Mol. Liq.*, **vol. 325**, (2021): 115155

[8] H. Gamal, S. Elkatatny, S. Basfar, and A. Al-Majed, "Effect of pH on rheological and filtration properties of water-based drilling fluid based on bentonite," *Sustainability*, **vol. 11**, no. 23, (2019): 6714

[9] H. Gudarzifar, S. Sabbaghi, A. Rezvani, and R. Saboori, "Experimental investigation of rheological & filtration properties and thermal conductivity of water-based drilling fluid enhanced," *Powder Technol.*, **vol. 368**, (2020): 323–341

[10] S. Medhi, S. Chowdhury, D. Kumar, and G. Aryab, "An investigation on the effects of silica and copper oxide nanoparticles on rheological and fluid loss property of drilling fluids," *J. Pet. Explor. Prod. Technol.*, **vol. 10**, (2019): 91–101

[11] E. Kusrini, F. Oktavianto, A. Usman, D. P. Mawarni, and M. I. Alhamid, "Synthesis, characterization, and performance of graphene oxide and phosphorylated graphene oxide as additive in water-based drilling fluids," *Appl. Surf. Sci.*, **vol. 506**, (2020): 145005

[12] T. Sharma and J. S. Sangwai, "Silica nanofluids in polyacrylamide with and without surfactant: Viscosity, surface tension, and interfacial tension with liquid paraffin," *J. Pet. Sci. Eng.*, **vol. 152**, (2017): 575–585

[13] S. K. Inturi, G. R. Dash, and J. Kodavaty, "Role of silica Nano particles in altering rheological properties of drilling fluid in Enhanced Oil Recovery," *Mater. Today Proc.*, **vol. 17**, (2019): 354–361

[14] L. M. Corredor, M. M. Husein, and B. B. Maini, "Impact of PAM-Grafted Nanoparticles on the Performance of Hydrolyzed Polyacrylamide Solutions for Heavy Oil Recovery at Different Salinities," *Ind. Eng. Chem. Res.*, **vol. 58**, no. 23, (2019): 9888–9899

[15] L. M. Corredor-rojas, A. H. Sarapardeh, M. M. Husein, P. M. Dong, and B. B. Maini, "Rheological behavior of surface modified silica nanoparticles dispersed in Partially Hydrolyzed Polyacrylamide and Xanthan Gum solutions : Experimental measurements , mechanistic understanding , and model development," *Energy Fuels*, **vol. 32**, no. 10, (2018): 10628–10638

[16] R. S. Kumar, K. R. Chaturvedi, S. Iglauer, J. Trivedi, and T. Sharma, "Impact of anionic surfactant on stability, viscoelastic moduli, and oil recovery of silica nanofluid in saline environment," *J. Pet. Sci. Eng.*, **vol. 195**, (2020): 107634

[17] T. Sharma, G. S. Kumar, B. H. Chon, and J. S. Sangwai, "Thermal stability of oil-in-water Pickering emulsion in the presence of

nanoparticle, surfactant, and polymer," *J. Ind. Eng. Chem.*, **vol. 22**, (2015): 324–334

[18] M. A. Haruna, S. Pervaiz, Z. Hu, E. Nourafkan, and D. Wen, "Improved rheology and high-temperature stability of hydrolyzed polyacrylamide using graphene oxide nanosheet," *J. Appl. Polym. Sci.*, **vol. 136**, no. 22, (2019): 47582

[19] M. S. Muhamad, M. R. Salim, and W.-J. Lau, " Surface modification of SiO 2 nanoparticles and its impact on the properties of PES-based hollow fiber membrane ," *RSC Adv.*, **vol. 5**, no. 72, (2015): 58644–58654

[20] G. N. ochuwe Abang, Y. S. Pin, and N. Ridzuan, "Application of silica (SiO_2) nanofluid and Gemini surfactants to improve the viscous behavior and surface tension of water-based drilling fluids," *Egypt. J. Pet.*, **vol. 30**, no. 4, (2021): 37–42

[21] B. Xiong *et al.*, "Polyacrylamide degradation and its implications in environmental systems," *npj Clean Water*, **vol. 1**, no. 17, (2018)

[22] Y. Zhang, Z. Miao, and J. Zou, "A new cation-modified Al-polyacrylamide flocculant for solid-liquid separation in waste drilling fluid," *J. Appl. Polym. Sci.*, **vol. 132**, no. 11, (2015): 41641

[23] E. U. Akpan, G. C. Enyi, G. Nasr, A. A. Yahaya, A. A. Ahmadu, and B. Saidu, "Water-based drilling fluids for high-temperature applications and water-sensitive and dispersible shale formations," *J. Pet. Sci. Eng.*, **vol. 175**, (2019): 1028–1038

[24] M. K. Fokuo *et al.*, "Tannin-Based Deflocculants in High Temperature High Pressure Wells: A Comprehensive Review," *Adv. Chem. Eng. Sci.*, **vol. 11**, no. 04, (2021): 263–289

[25] A.-G. Guezennec *et al.*, "Transfer and degradation of polyacrylamide based flocculants in hydrosystems: a review Transfer and degradation of polyacrylamide based flocculants in hydrosystems: a review. Environ-mental Science and Pollution Title: Transfer and degradation of polyacry," *Research*, **vol. 22**, no. 9, (2015) [Online].

[26] F. A. Makinde, A. D. Adejumo, C. T. Ako, and V. E. Efeovbokhan, "Modelling the effects of temperature and aging time on the rheological properties of drilling fluids," *Pet. Coal*, **vol. 53**, no. 3, (2011): 167–182.

[27] Z. Vryzas and V. C. Kelessidis, "Nano-based drilling fluids: A review," *Energies*, **vol. 10**, no. 4, (2017)