Herschel-Bulkley Rheological Parameters of a Novel Environmentally Friendly Lightweight Biopolymer Drilling Fluid from Xanthan Gum and Starch

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ABSTRACT: This article summarizes a concise investigation on the effect of concentration of the four main components of a novel lightweight drilling fluid, i.e., glass bubbles, xanthan gum, starch, and clay, to the Herschel-Bulkley rheological model parameters. The three parameters of Herschel-Bulkley model, i.e., yield stress, fluid consistency, and fluid index were calculated by fitting the experimental data of shear stress as a function of rate of shear to the model. Results indicate that the increment of the amount of four main components increase the yield stress of the final fluid as the flow resistance is increased. Furthermore, the result also showed that the calculated fluid consistency of the drilling fluid appears to be strongly dependent on the presence of glass bubbles, xanthan gum, and clay. However, the fluid consistency appears not to be affected by the presence of starch. It is also concluded that the presence of glass bubbles, xanthan gum, and clay in the fluid tends to determine the final fluid to behave as pseudoplastic. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 595–606, 2012

Key words: rheology; biopolymers; polysaccharides; drilling fluid; underbalanced drilling (UBD); Herschel-Bulkley model

INTRODUCTION

The desire to extract more hydrocarbons has driven scientists to develop new techniques in exploration and production including drilling technology. In drilling, one of the current technologies widely applied to improve hydrocarbon production is underbalanced drilling (UBD). Technically, UBD is conducted by keeping the wellbore pressure lower than the reservoir during drilling process.[1] UBD has been proven to bring many benefits such as increasing rate of penetration, reducing or eliminating perforation damage and loss circulation problems, reducing drilling time, elongate bit life, ensuring a rapid indication of productive reservoir zone, and the potential for dynamic flow testing while drilling, etc.[2]

Generally, common practices make use of compressible fluids, such as pure gas, gas-liquid mixtures, and foams to create sufficient degree of underbalanced in the wellbore.[3] However, such treatments often cause UBD challenging and difficult. The treatment usually requires special additional instruments and posts additional works. In addition, with regards to environmental issues, at the moment, most of the drilling fluids that is used in UBD compose of either oil, crude or synthetic oil which are toxic and considered not environmentally friendly.[4] Toxic substances such as polyacrilate are also frequently used as an additive to improve the fluid's properties. Thus, it would be very attractive to have UBD fluid with not only has low to very-low density value but also consists of environmentally friendly additives.

In a previous study, Khalil and Badrul[5,6] have successfully formulated a novel lightweight biopolymer drilling fluid composed of water-based mud system with glass bubbles as density reducing agent and two types of biopolymers which are xanthan gum and starch as additives. The lowest achievable density of the new drilling fluid is 6.3 lbm gal^{-1} (754.5 kg m^{-3}). The application of the new incompressible lightweight biopolymer drilling fluid is expected to facilitate the UBD procedures and reduces environmental impact of the existing toxic drilling fluid.

Xanthan gum and starch are nontoxic natural based exocellular polysaccharides that have been extensively used in broad range of industrial applications including in the upstream oil and gas industry. These water-soluble biopolymers are used mostly in the enhanced oil recovery (EOR) processes and in the formulation of drilling fluids.[7–10] In EOR, both xanthan gum and starch are frequently used in polymer flooding and oil displacement processes to improve oil production.[11–13] In drilling fluid

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formulation, these polysaccharides are frequently used as a rheological-controlling agent in aqueous system and as a stabilizer for emulsions and suspensions, either in combination with traditional thickener, bentonite clay, or alone in clear muds.[4,14,15] In addition, starch and xanthan gum are also frequently used as a fluid loss controlling agent in the formulation of both oil-based and water-based drilling muds.[7]

This article presents a continuation study of our previous work on the fluid formulation.[5,6] In this study, the effect of the concentration of drilling fluid's four main components, i.e., glass bubbles, biopolymers (xanthan gum and starch), and clay to the rheological properties of the fluid was investigated. Herschel-Bulkley model was used to describe the rheological properties of the formulated fluid. The model has been widely used to describe the viscoplastic behavior of fluids used in the upstream oil and gas industry including drilling fluids. Studies have shown that rheological behavior of most of the drilling/completion fluids or cement slurries can be satisfactorily described using Herschel-Bulkley model.[16–18] Herschel-Bulkley model was developed originally to accommodate the poor result given by the Ostwald-De-Weale model at extremely low shear rate. The model of Herschel-Bulkley is a combination of Bingham-plastic and power-law models, in which it provides three parameters to describe the relation between shear rate and shear stress.[19] With the use of three-parameters, the model has been presented a good agreement most of the drilling fluids, especially at low shear rates. The Herschel-Bulkley model is defined by the following equation:

$$\tau = \tau_0 + k(\gamma)^n \tag{1}$$

where τ, τ_0 are the shear stress and the yield stress respectively, k, n are the fluid consistency and index flow respectively, and γ is the shear rate.

As discussed earlier, the main objective of this study is to present a concise investigation on the effect of the fluid main fluid components, such as glass bubbles, xanthan gum, starch and clay, on the three parameters of Herschel-Bulkley model. The information on the three parameters of Herschel-Bulkley is essential in selecting the appropriate drilling fluid in drilling operation. Herschel-Bulkley yield stress (τ_0) data allows drilling engineers to predict the minimum force required to initiate fluid flow. Meanwhile, the knowledge on the other two fluid parameters, the fluid consistency (k) and index flow (n), give field engineers information on the type of fluid, i.e., on Newtonian, non-Newtonian with shear thinning (pseudoplastic) behavior, or non-Newtonian fluid with shear thickening (dilatant) behavior. Thus, in this study, experimental viscoplastic data, i.e., shear rate and shear stress, of the fluid at different concentration of glass bubbles, xanthan gum, starch, and clay were measured and fitted to the Herschel-Bulkley model. The mathematical experimental data fitting process allows the model to calculate the three Herschel-Bulkley parameters for drilling fluid at different concentration of its main components.

MATERIALS AND METHODS

Materials

Two types of biopolymers were used in this study, namely starch and xanthan gum. Starch soluble $(C_6H_{10}0_5)_n$ (composed of two main polysaccharides, amylase, and amylopectin; estimated MW of amylose: 20,000–225,000 g mol^{-1}; estimated MW of amyopectin: 200,000–1,000,000 g mol^{-1} or more) [CAS No. 9005-25-8] was purchased from *ChemAR*® (purity: 99%), while xanthan gum $(C_{35}H_{49}O_{29})_n$ (estimated MW: 15 million g mol^{-1}) (from *Xanthomonas campestris*) [CAS No. 11138-66-2] was purchased from Sigma-Aldrich® (purity: 99%). To reduce the density of the mixture, 3M Scotchlite hollow-glass sphere (HGSs) [3M, St. Paul, Minnesota, USA] (rating: 4000 psi) was added in the formulation. Glass bubbles are unicellular, perfectly formed sphere made from soda-lime borosilicate glass. The diameter of glass bubble is in the range of 30–70 μm, with density as low as 0.32 g cm^{-3} (2.67 lbm gal^{-1}). A bactericide known as paraformaldehyde $OH(CH_2O)_nH$ (MW: 600 g mol^{-1}) [CAS No. 30525-89-4], purchased from Sigma-Aldrich® (purity: 96%) was used to protect the biopolymers against parasites. In the fluid formulation, clay was used to improve the fluid rheological properties as well as its stability. In this study, typical montmorillonite clays with high content of calcium samples were taken from Wyoming (Lovell, WY). Sodium chloride (NaCl, MW: 55.44 g mol^{-1}), purchased from R&M Chemicals [CAS No. 7647-14-5] (purity: 99.5%), was used as an additive to improve fluid properties.

Formulation of lightweight biopolymer drilling fluids

To formulate water based lightweight biopolymer drilling fluid, all of the raw material, i.e., distillated water, glass bubbles, starch, xanthan gum, clay, paraformaldehyde, and sodium chloride were mixed together using IKA RW 20 digital mixer at 500 rpm. In the first test, the concentration of glass bubbles was varied at four different values, i.e., 12.5%, 18.75%, 21.25%, and 25% w/v, while the amount of other components are fixed (clay: 2.5% w/v; xanthan gum: 0.5% w/v; starch: 1.5% w/v; NaCl: 0.75% w/v; paraformaldehyde: 0.125% w/v). To profoundly understand the effect of glass bubbles concentration to the Herschel-Bulkley parameters and the rheological properties of the fluid, a control test was performed by formulating a fluid with 0% w/v of glass bubbles concentration. In the second step, the concentration of xanthan gum concentration was varied at four different concentrations, i.e., 0.25%, 0.5%, 0.75%, and 1%. Other components are fixed (clay: 2.5% w/v; starch: 1.5% w/v; glass bubbles: 21.25% w/v; NaCl: 0.75% w/v; paraformaldehyde: 0.125% w/v). Here, a control test was also conducted at 0% w/v of xanthan gum concentration. Next step, the concentration of starch was varied at five different concentrations, i.e., 1%, 1.25%, 1.5%, 1.75%, and 2% w/v, while other component are fixed (clay: 2.5% w/v; xanthan gum: 0.5% w/v; glass bubbles: 21.25% w/v; NaCl: 0.75% w/v; paraformaldehyde: 0.125% w/v). In addition to the previous experiments, a control test was also performed at 0% w/v of starch concentration. Finally, in the last test, along with a control test that was conducted at 0% w/v of clay concentration, the amount of clay was varied at four different concentrations, i.e., 2.5%, 5%, 7.5%, and 10% w/v, while other component are fixed (xanthan gum: 0.5% w/v; starch: 1.5% w/v; glass bubbles: 21.25% w/v; NaCl: 0.75% w/v; paraformaldehyde: 0.125% w/v). All the experiments were conducted at ambient pressure and temperature.

Rheological properties measurement

In this study, the viscoplastic parameters, i.e., shear stress as the function of shear rate, were measured using a rotational viscometer equipped with MV2P spindle (Haake viscotester model VT 550, with repeatability and accuracy: ± 1%, comparability: ± 2%). Herschel-Bulkley parameters were estimated by plotting shear stresses versus various applied shear rates. The experimental data were fitted to the Herschel-Bulkley equation using commercial statistical software, Matlab version 7.9. The applied shear rate applied in this study ranging from 2.639 to 264 s^{-1}. To gain repeatability and accuracy of the measurement, reading was taken three times, and the average of the three readings was adopted in calculation. Moreover, to gain reproducibility of the measurement a newly fresh-made sample was used in each test and measurement. To assess the adequacy of Herschel-Bulkley model in describing the rheological properties of the fluid, statistical parameters such as *R*-square, sum of square error (SSE), and root mean square error (RMSE) were calculated using Matlab.

RESULTS AND DISCUSSION

Effect of glass bubbles

The motivation to embark on UBD using incompressible drilling fluid was triggered since there is enough evidence to indicate that the density of drilling fluid could be further reduced with the addition of glass bubbles. With its super low density value (0.32 g cm^{-3}), glass bubbles have been used widely as a filler and density reducing agent in vast areas from space shuttle research to polymer industry. In the oil and gas industry, glass bubbles have been used as preferable fillers in formulating so-called lightweight drilling/completion fluid or cement slurries.[20] However, beside its promising advantages in reducing fluid density, fluid system with glass bubbles often time show challenges especially in fluid homogeneity and stability. It is observed that fluid with glass bubble tends to separate to form a two or three distinct layer after certain period of time. This phenomenon is due to super low density value of glass bubbles that it tends to stay afloat in the fluid system.[21,22] This phenomenon may be reduced by the addition of stabilizing agent such as clay and emulsifier to improve the fluid stability. Study conducted by Khalil et al.[22] on the stability of super lightweight completion fluid from glass bubbles and synthetic oil-based completion fluid, shows that there is significant improvement in terms of fluid stability whenever natural clay is introduced in the fluid system. The study shows that the fluid containing glass bubbles and clay as its stabilizing agent is relatively homogenous, and it is stable up to more than one and a half months. Fluid without the presence of clay started to show significant separation in a matter of days. Generally, in the case of our lightweight biopolymer drilling fluid, similar challenges are observed in which the fluid is only stable less than 3 months in its static condition. After 3 months, the drilling fluids start to separate, forming a distinct two layers system where a thicker layer suspected as glass bubbles stay on the top and watery phase suspected as water and other components like clay and biopolymer stay on the bottom. However, agitation would bring the fluid back to it homogenous and stable form. Unlike completion fluid which is left static during completion process, drilling fluid is always in motion during drilling process.[23] In the field, drilling fluid would be pumped down from reservoir to the wellbore and back up again to the surface to carry drill cuttings. As fluid separation could be prevented by stirring the fluid, the problem of fluid stability and glass bubbles settlement in our lightweight biopolymer drilling fluid is not a critical issue.

In the first test, the effect of glass bubbles concentration on the Herschel-Bulkley rheological parameters of the mixture was investigated. The concentration of the glass bubbles was varied in the range of 12.5% to 25% w/v. In addition to those tests, one additional experiment at the glass bubbles concentration of 0% w/v was also conducted as a control run in which to investigate the effect of glass

TABLE I
The Measured Average Shear Stress as a Function of Applied Shear Rates for Lightweight Biopolymer Drilling Fluid at Different Concentration of Glass Bubbles

	Glass bubbles concentration (% w/v)				
	0 (control)	12.5	18.75	21.25	25
Shear rate, γ (s^{-1})	Shear stress, τ (Pa) ± sd				
2.639	0.38 ± 0.01	2.37 ± 0.25	4.17 ± 0.81	4.40 ± 0.97	13.70 ± 0.51
5.279	0.46 ± 0.03	2.99 ± 0.11	4.95 ± 0.74	5.54 ± 1.06	15.15 ± 0.42
26.4	0.69 ± 0.12	4.17 ± 0.12	6.47 ± 0.37	7.90 ± 1.85	18.34 ± 1.41
52.71	1.08 ± 0.08	6.40 ± 0.48	8.15 ± 0.11	9.72 ± 1.73	20.44 ± 1.09
79.28	1.35 ± 0.06	7.45 ± 0.79	9.85 ± 0.12	11.21 ± 1.83	22.67 ± 1.04
88.17	1.51 ± 0.11	8.17 ± 0.34	10.79 ± 1.14	12.14 ± 1.98	23.46 ± 1.14
158.3	2.54 ± 0.17	11.24 ± 1.51	13.44 ± 1.24	15.87 ± 2.16	28.33 ± 1.29
176	2.97 ± 0.13	11.97 ± 1.11	14.97 ± 0.92	16.75 ± 2.07	29.76 ± 2.37
264	5.15 ± 0.54	14.67 ± 0.97	18.63 ± 0.86	20.49 ± 2.03	36.36 ± 2.06

sd, standard deviation.

bubbles concentration to the Herschel-Bulkley parameters and the rheological properties of the fluid at the absent of glass bubble itself. Table I presents the measured experimental data of the shear stresses as a function of fluid shear rate at different concentration of glass bubbles.

Table I shows the result of shear stresses at different shear rates of fluids containing various concentrations of glass bubbles. The data of the shear stress at different shear rate were fitted to the Herschel-Bulkley model [Eq. (1)] to determine the three Herschel-Bulkley parameters. Figure 1 illustrates the plot of experimental shear rate data as well as the one that predicted using Herschel-Bulkley model against shear stress of the mixture at different concentration of glass bubbles including for the control. Table II presents the result of the experimental data of Herschel-Bulkley model fitting and its statistical parameters, as well as the three Herschel-Bulkley parameters of the mixture at different concentration of glass bubbles and for the control.

Figure 1 and Table I show that the stresses from the application of shear tend to increases with the concentration of glass bubbles. It appears to increase significantly as the concentration of the glass bubbles reaches 21.25% w/v. This is because the particles dispersed in the system may disturb the stream line flow of the liquid and resulting to additional energy/stress required to make the fluid flow.[24] Furthermore, unlike other tests, shear stress vs. shear rate plot for control test in Figure 1 shows that the increase of shear rate did not seem to change the stress significantly. Based on this result, it shows that the presence of large amount of dispersed particles (glass bubbles) in the fluid system increases the stress as the application of shear. The greater amount of dispersed particle in the fluid system, the greater the stress occurred. In contrast, in the absence or in the presence of very-small amount of glass bubble, the measured stress is small and less dependent on the applied shear rate.

Table II shows that the model of Herschel-Bulkley performs satisfactorily well in describing the rheological behavior of all mixtures at various concentration of glass bubbles including the control fluids. This is shown from high value of R^2 (close to 1) and the low values of error (below 2), i.e., the SSE and RMSE. Furthermore, the results also showed that the yield stress (τ_0) increases with the concentration of glass bubbles. The increase is profound when the concentration of the glass bubbles reaches 21.25% w/v or higher. This result seems similar to the effect of glass bubble concentration on the stress discussed earlier. Apparently more power/stress is required to initiate fluid flow as more glass bubbles are added to the system. Hence, it leads to higher yield stress. In drilling operation, fluid with high yield stress is desirable since it has a better drill cutting carrying

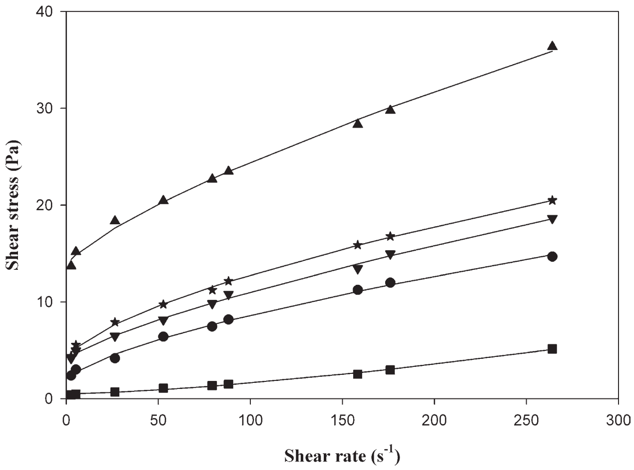

Figure 1 Shear stress vs. shear rate plot for the mixture at glass bubbles concentration of ■: 0% w/v (control); ●: 12.5% w/v; ▼: 18.75% w/v; ★: 21.25% w/v; ▲: 25% w/v; — : predicted with Herschel-Bulkley model.

TABLE II
Herscel-Bulkley Parameters at Different Concentration of Glass Bubbles

Glass bubbles concentration (% w/v)	Herschel-Bulkley parameters τ_0 (Pa)	k (Pa·s^n)	n	R^2	SSE	RMSE
0 (control)	0.489	0.001	1.443	0.9961	0.074	0.111
12.5	1.794	0.314	0.669	0.9971	0.424	0.266
18.75	3.892	0.230	0.746	0.9968	0.596	0.315
21.25	3.879	0.462	0.643	0.9983	0.399	0.258
25	13.65	0.346	0.747	0.9962	1.616	0.519

capacity. However, as yield stress represents the minimum amount of force need to be applied to the fluid before it would start to move, drilling fluid with extremely high yield stress would require large horse-power pump to pump the fluid down to the wellbore and/or up to lift the drilling cuttings to the surface. In this study, in terms of Herschel-Bulkley's yield stress, we concluded that the fluid is considered appropriate candidate for a good drilling fluid. This is because the value of yield stress of the fluid is between 0.489 to 13.65 Pa. This is a good range for drilling fluid criteria (below 15 Pa).[4]

On the other hand, with regards to the effect of glass bubbles concentration on the fluid consistency, the results show no obvious difference for this parameter as the concentration of glass bubbles is varied, except for the control test with 0% of glass bubbles. In the presence of glass bubbles (in the range of tested glass bubbles concentrations), the values of fluid consistency (k) lie between 0.2 to 0.4 Pa·s^n. Meanwhile, in the absence of glass bubbles, the fluid consistency dropped to 0.001 Pa·s^n. Mathematically, the parameter of fluid consistency in the Herschel-Bulkley model is a simple constant of proportionality that shows the degree of significant changes of dependent variables (in this case shear stress) as the result of changes in the independent variable (in this case shear rate). Greater fluid consistency infers greater changes of shear stress resulted from the variation of the applied shear rate. Thus, in the case of our fluid, the result confirms previous hypothesis that in the absence or in the presence of very-small amount of particles (glass bubbles), the stress is small and it is not a strong function of the applied shear rate. The calculated fluid consistency of the fluid with no glass bubbles ($k = 0.001$ Pa·s^n) is very small compared with fluids with glass bubbles ($k =$ in the range of 0.2 to 0.4 Pa·s^n).

Furthermore, in terms of fluid flow index (n), the result shows that in all the tested concentration of glass bubbles (except for control test), the fluid appears to follow a typical pseudoplastic (shear thinning) behavior as the calculated flow indexes (n) at any given glass bubbles concentrations values are less than 1 ($n =$ in the range of 0.6 to 0.7). According to literature, pseudoplastic or rather known as shear thinning fluid refers to fluid that presents a lower apparent viscosity at higher shear rates and high viscosity at low shear rate.[25] In general, in fluid rheological studies, pseudoplastic behavior is always associated to a fluid system with large (commonly polymeric materials) molecules in a solvent with smaller molecules. A typical pseudoplastic fluid shows that at lower shear, most of the large molecular chains tumble and randomly entangled resulting in a high resistance for fluid to flow. In contrast, at higher shear rate, fluid will gradually align themselves in a certain direction and produce less resistance. In the area of drilling fluid, most effective drilling fluids are shear thinning (pseudoplastic), even though it also presents some gel-binding characteristic.[23] In its application, drilling fluid with pseudoplastic behavior has few advantages in drilling processes such as higher drilling rate and improved cutting lifting. Pseudoplastic behavior phenomenon is commonly observed in a typical drilling fluid with long-chain polymer suspensions like xanthan gum.[26] This type of fluid, in static state, the polymers chains are randomly entangled. However, it does not set up a structure because its electrostatic forces are predominately repulsive. When the fluid is in motion, the chains tend to arrange themselves parallel to the direction of the flow resulting in the increase of shear rate and reduction of the effective viscosity.[27]

In the fluid tested in our study, the bulk presence of glass bubbles is believed to be the one responsible for the pseudoplastic behavior of the fluid. This is supported from the result in Table II which shows that whenever glass bubbles is introduced to the fluid system, regardless of its concentration, the calculated value of flow index is always lower than 1. Meanwhile, the calculated flow index of the control fluid, where glass bubbles was not introduced (0% of glass bubbles) in the system, is greater than 1 ($n = 1.443$). Indicating the fluid follows a dilatant (shear thickening) behavior. Based on this result, the presence of the bulk large molecular particles of glass bubbles (diameter: 30–70 μm) leads the fluid to behave as pseudoplastic. The presence of glass bubbles in the fluid seems to produce higher resistance whenever the fluid is moved at low shear rate. This is because the bulk dispersion of glass bubbles that

TABLE III
The Average Measured Shear Stress as a Function Applied Shear Rates of the Lightweight Biopolymer Drilling Fluid at Different Concentration of Xanthan Gum

Shear rate, γ (s^{-1})	Xanthan gum concentration (% w/v)				
	0 (control)	0.25	0.5	0.75	1
	Shear stress, τ (Pa) ± sd				
2.639	1.61 ± 0.11	2.13 ± 0.02	4.40 ± 0.97	8.19 ± 0.72	10.16 ± 1.11
5.279	1.67 ± 0.94	2.88 ± 0.12	5.54 ± 1.06	9.14 ± 1.02	11.32 ± 0.93
26.4	1.84 ± 1.01	4.17 ± 0.75	7.90 ± 1.85	12.11 ± 0.92	14.14 ± 0.92
52.71	2.15 ± 1.09	6.50 ± 0.94	9.72 ± 1.73	14.81 ± 0.24	16.64 ± 0.94
79.28	2.49 ± 0.87	7.98 ± 1.11	11.21 ± 1.83	16.84 ± 1.11	18.55 ± 0.71
88.17	2.57 ± 1.04	8.36 ± 0.75	12.14 ± 1.98	18.09 ± 0.99	19.64 ± 2.10
158.3	3.30 ± 0.91	11.81 ± 1.06	15.87 ± 2.16	22.68 ± 0.86	25.31 ± 0.85
176	3.53 ± 0.87	12.81 ± 1.03	16.75 ± 2.07	23.48 ± 2.03	26.84 ± 2.02
264	5.38 ± 1.13	16.48 ± 2.08	20.49 ± 2.03	28.87 ± 2.02	35.41 ± 1.11

sd, standard deviation.

has a large dimension in the fluid system tends to tumble at random direction and causing the fluid to behave as pseudoplastic behavior. This is a positive effect because it would improve drill cuttings lift and drilling rate. In contrast, the absence of glass bubbles in the fluid system would change the fluid to follow a shear thickening (dilatant) behavior. In this type of fluid, at low rate of shear, the fluid tend to flow easily because the liquid would easily fills the gaps between the particles inside the system. This is true because in the absence of bulk amount of glass bubbles which has a large dimension (diameter: 30–70 μm) in the fluid system, the fluid will allow its continuous phase to flow easily. In contrast, when the velocity of the shear is increased, the viscosity of the fluid tends to increase because the friction between the liquid and particles (clays and biopolymers, i.e., xanthan gum and starch) greatly increase due to the inability of the liquid in the continuous phase to fill up the gaps created between particles. Thus, due to its bulky volume, it could be stated that the presence of glass bubbles is one of the most critical factors that determine the type of the final fluid behavior, i.e., pseudoplastic (shear thinning) behavior or dilatant (shear thickening).

Effect of xanthan gum

In the second test, the effect of the concentration of xanthan gum on the three parameters of the Herschel-Bulkley model was investigated. The concentration of xanthan gum was varied from 0.25% to 1% w/v. In addition, the additional control test was also investigated by formulating a fluid with 0% w/v of xanthan gum concentration. Table III presents the average experimental data of shear stress of the lightweight biopolymer drilling fluid at various concentration of xanthan gum as a function of the applied shear rate.

Measured experimental data in Table III were fitted to the Herschel-Bulkley model to calculate its three main parameters as well as the statistical parameters for fitting goodness evaluation. Figure 2 shows the plot between the shear stress obtained from the measurements and calculated from the Herschel-Bulkley model versus shear rate applied to the fluid. The results of the data fitting to the Herschel-Bulkley model at different concentration of xanthan gum and its control test are presented in Table IV.

Based on Table III and Figure 2, results show similar outcome as in earlier tests. In this test, shear stresses also tend to increase with the concentration of xanthan gum. It shows that at higher shear rate, the increase of stress as a function of xanthan gum concentration seems to be more profound than in the lower velocity of shear. Data also shows that at the lowest tested shear rate (2.639 s^{-1}), the increase

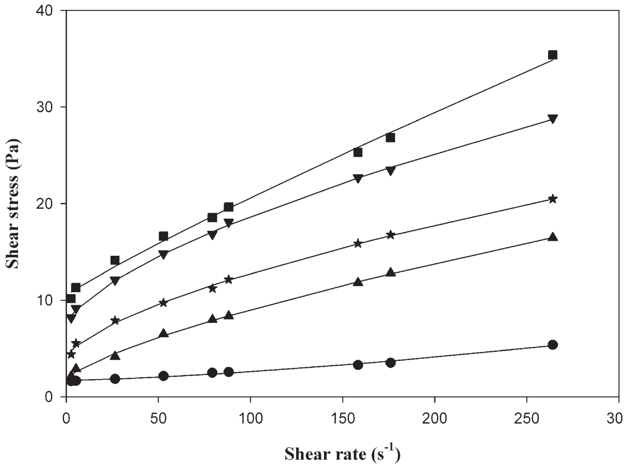

Figure 2 Shear stress vs. shear rate plot for the mixture at xanthan gum concentration of ●: 0% w/v (control); ▲: 0.25% w/v; ★: 0.5% w/v; ▼: 0.75% w/v; ■: 1% w/v; — : predicted with Herschel-Bulkley model.

TABLE IV
Herschel-Bulkley Parameters at Different Concentration of Xanthan Gum

Xanthan gum concentration (% w/v)	Herschel-Bulkley parameters τ_0 (Pa)	k (Pa·s^n)	n	R^2	SSE	RMSE
0 (control)	1.705	0.001	1.428	0.9904	0.111	0.136
0.25	1.751	0.255	0.728	0.9985	0.274	0.214
0.5	3.879	0.462	0.643	0.9983	0.399	0.258
0.75	7.309	0.562	0.653	0.9992	0.308	0.227
1	10.47	0.157	0.905	0.9962	1.997	0.577

of stress when the amount of xanthan gum is increased from 0% (τ = 1.61 Pa) to 1% w/v (τ = 10.16 Pa) is less profound compared with fluid measured at high shear rate (264 s^{-1}) where the stress (τ) dramatically increases from 5.38 Pa at 0% of xanthan gum to 35.41 Pa at the fluid with 1% of xanthan gum. This is true as the calculated yield stress (τ_0) of the fluid also increased as the amount of xanthan gum added to the fluid is increased. However, unlike the previous test where the presence of glass bubbles in the fluid dramatically increases yield stress of the fluid by almost 40% (0.489 Pa at 0% of glass bubbles and 1.794 Pa at 12.5% of glass bubbles, see Table II), the presence of xanthan gum at lower concentration does not alter the yield stress of the fluid significantly. Based on the result in Table IV, the calculated yield stress for the control fluid with no xanthan gum (τ_0 = 1.705 Pa) in the fluid is about the same magnitude with the fluid with 0.25% of xanthan gum on it (τ_0 = 1.751 Pa). However, when the amount of xanthan gum is gradually increased to 1% w/v, the yield stress increases significantly to 10.45 Pa (see Table IV).

Furthermore, in the case of the fluid consistency (k), similar result as previous test is observed. In this test, a very low value of calculated fluid consistency (0.001 Pa·s^n) for the control test is also observed. The number increases dramatically whenever xanthan gum is introduced into the fluid. This is true because the changes of dependent variables (in this case shear stress) as the result of the changes of independent variable (in this case shear rate) for the control fluid is less significant than the fluid with xanthan gum where the fluid consistency is greater. In addition, it is also found that the fluid consistency of the fluid appear to be less dependent on the amount of xanthan gum added to the system. Among the three fluids at different concentration of xanthan gum (varied from 0.25% to 1% of xanthan gum), the fitting process gave similar magnitude of fluid consistency (k = in the range of 0.1 to 0.5 Pa·s^n).

Moreover, similar result as previous test is also observed with regards to the effect of xanthan gum concentration on the third parameters of Herschel-Bulkley model, i.e., the flow index (n). Based on the result obtained from the previous test, the presence of glass bubble leads to the pseudoplastic behavior, regardless the concentration of the glass bubbles. In contrast, the absence of glass bubbles in the fluid system leads to dilatant behavior. It is believed that the large bulky volume of glass bubbles randomly tumble in a disordered direction. This increases the resistance for fluid to flow. In this test, as the concentration of glass bubbles is fixed at 21.25% w/v and the concentration of xanthan gum is varied, the phenomenon of dilatant behavior is also observed in the control fluid. This is supported by the calculated value of the flow index (n) of the drilling fluid formulated with 0% of xanthan gum is greater than 1 (n = 1.428). However, whenever xanthan gum is introduced in the fluid system, regardless of its concentration, the fluid follows a pseudoplastic behavior. This is supported by the value of calculated flow indexes (n) for all the fluids with xanthan gum which are less than 1 (see Table IV). Hence, based on this result, it is noted that the presence of xanthan gum plays a pivotal role to ensure pseudoplastic behavior of fluid which is beneficial for drilling operations such as improving cuttings lift and drilling rate. Without xanthan gum, the fluid will behave as dilatant (shear thickening behavior).

Apparently, the result on calculated value of flow indexes in Table IV supports the idea that pseudoplastic behavior is frequently a result of the presence of large and bulky molecules like polymer or large dispersant particles in the fluid system. As in the previous test, it is also shown that xanthan gum also exhibit the same phenomenon as observed in glass bubble. Large and bulky structure of polymeric molecule of xanthan gum (with molecular weight approximately up to 15 million gram mol^{-1}) is believed to produce high resistance whenever the fluid is moved at low shear rate. This is because of the large polymeric structure of xanthan gum tends to entangle at random direction and causing the fluid to behave as pseudoplastic, which is beneficial in improving cuttings lift and drilling rate. Large dimension of polymer structure of xanthan gum is mostly used in drilling fluid as thickener or suspending agent to formulate a stable pseudoplastic fluid with gel-like properties.[23] In addition, xanthan gum is usually preferred not only because of its

TABLE V
The Average Measured Shear Stress as a Function Applied Shear Rates of Lightweight Biopolymer Drilling Fluid at Different Starch Concentration

	Starch concentration (% w/v)					
	0 (control)	1	1.25	1.5	1.75	2
Shear rate, γ (s^{-1})	Shear stress, τ (Pa) ± sd					
2.639	0.72 ± 0.72	1.34 ± 0.53	3.14 ± 0.99	4.40 ± 0.97	8.14 ± 0.54	12.50 ± 0.72
5.279	0.82 ± 0.92	1.42 ± 0.91	3.95 ± 0.76	5.54 ± 1.06	9.14 ± 0.94	14.32 ± 0.64
26.4	2.15 ± 1.04	3.46 ± 0.78	5.14 ± 0.82	7.90 ± 1.85	13.05 ± 1.08	17.84 ± 0.91
52.71	3.82 ± 0.25	5.01 ± 0.87	7.14 ± 0.61	9.72 ± 1.73	15.90 ± 1.11	20.28 ± 1.11
79.28	5.28 ± 0.11	6.19 ± 0.71	8.46 ± 0.59	11.21 ± 1.83	16.97 ± 1.16	22.62 ± 1.10
88.17	5.59 ± 1.07	6.45 ± 0.86	9.18 ± 0.31	12.14 ± 1.98	18.05 ± 1.13	23.46 ± 2.08
158.3	8.24 ± 1.13	9.15 ± 0.67	12.64 ± 0.88	15.87 ± 2.16	22.19 ± 2.10	28.01 ± 2.09
176	8.96 ± 1.12	10.12 ± 0.95	13.67 ± 1.11	16.75 ± 2.07	23.04 ± 2.01	29.34 ± 2.02
264	12.42 ± 1.10	13.65 ± 1.07	17.44 ± 1.02	20.49 ± 2.03	28.18 ± 2.01	35.11 ± 2.03

sd, standard deviation.

natural degradability, but also for its compatibility with other filtration-reducing agent such as bentonite clay or carboxymethylcellulose.[7] Moreover, fluid flow index corresponds to the fluid carrying capacity to lift drill cuttings from the bottom hole up to the surface. Caenn and Chillingar[7] reported that a critical concentration of xanthan gum must be established to provide adequate drill cutting carrying capacity. The critical concentration is usually between 1.25 to 1.5 lb bbl^{-1} (0.35% to 0.43% w/v).[23] Apparently, this critical concentration range is still inside the range of our working range (0.25% to 1% w/v). Thus, our formulated fluid is still in the appropriate and adequate range in the terms of its carrying capacity.

Effect of starch

In the third part of this study, as a continuation from the previous two tests, the concentration of starch was varied to determine its effect to the three Herschel-Bulkley parameters as well as on the rheological behavior of the formulated fluid. The concentration of starch was varied between 1% to 2% w/v, while keeping other components constant. Moreover, a control test was also conducted by formulating a fluid with 0% w/v of starch concentration. Table V summarizes the experimental data of the measured shear stress as a function of applied shear rate of formulated fluids at various starch concentration.

Experimental data in Table V were fitted to the Herschel-Bulkley model to calculate the three important parameters as well as the statistical parameters to determine the goodness of fitting process. Figure 3 presents the plot of both the measured shear stress data and the one obtained from the Herschel-Bulkley model versus the applied shear rate at various starch concentration. The result of the experimental data obtained from the fitting measurement process to the Herschel-Bulkley model at different concentration of starch as well as its control test are presented in Table VI.

Based on the plot of shear stress versus shear rate on Figure 3, a unique pattern is observed. It is shown that for all of the fluid formulated either with or without the addition of starch, regardless of its concentration, they seem to have a similar slope. In other words, the dependency of shear stress as the result of the applied shear rate remains the same regardless of the presence or absence of starch. The dependency appears to be less dependent on the concentration of starch in the fluid system. This is because the main objective of starch in the drilling fluid is as fluid loss controlling agent. It is known that starch gelatinization properties is the one that is responsible for its ability to control fluid viscosity and fluid loss control in drilling mud.[28] According to Atwell et al.,[29] gelatinization is a process of the collapse (disruption) of molecular order within the

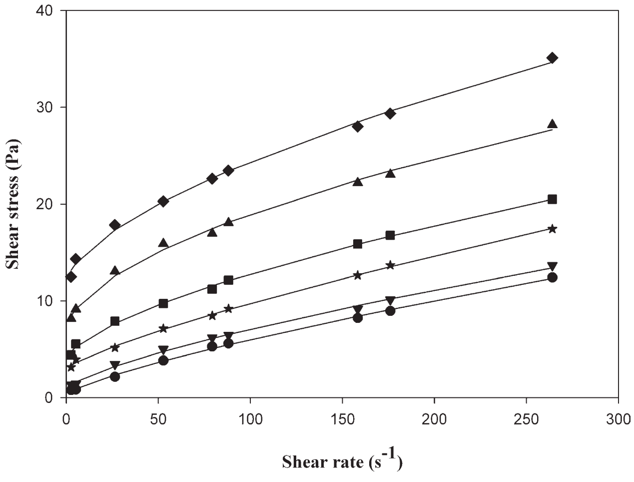

Figure 3 Shear stress vs. shear rate plot of the mixture at various starch concentration of ●: 0% w/v (control); ▼: 1% w/v; ★: 1.25% w/v; ■: 1.5% w/v; ▲: 1.75% w/v; ◆: 2% w/v; — : predicted with Herschel-Bulkley model.

TABLE VI
Herschel-Bulkley Parameters at Various Starch Concentration

	Herschel-Bulkley parameters					
Starch concentration (% w/v)	τ_0 (Pa)	k (Pa·s^n)	n	R^2	SSE	RMSE
0 (control)	0.317	0.163	0.771	0.9981	0.178	0.172
1	0.901	0.216	0.728	0.9973	0.363	0.246
1.25	2.948	0.182	0.786	0.9987	0.244	0.202
1.5	3.879	0.462	0.643	0.9983	0.399	0.258
1.75	6.837	0.917	0.560	0.9959	1.420	0.487
2	11.82	0.728	0.618	0.9968	1.385	0.481

starch granule manifested in irreversible changes in properties such as granular swelling, native crystallite melting, loss of birefringence, and starch solubilization. Besides its gelatinization property, starch is also added to the mixture to minimize disposal problem and maximize its thermal stability.[28] However, the functional performance of this biodegradable material often time is less effective compared to its synthetic counterparts. This is due to its vulnerability to parasites. Tatarka[30] reported that starch can easily be destroyed by bacteria during its application in drilling process. Thus, to address this problem, a bactericide (paraformaldehyde) was added in the formulation to protect starch granules against the parasites.[30]

Furthermore, this phenomenon could also be explained from the calculated value of fluid consistency (k) at different starch concentration in this study. The result shows that, unlike the previous two tests, the calculated fluid consistency (k) values of all the fluids remain in the same magnitude including the control test. Based on the result in Table VI, regardless of the absence/presence of starch, the calculated fluid consistency (k) of the fluid remains in the range of 0.1 to 0.9 Pa·s^n. Fluid consistency is a parameter indicating significant dependency of stress occurred to the fluid as the result of the applied shear. The result confirms that this dependency is not significantly affected by either the presence/absence of starch or its concentration in the fluid system.

In terms of the minimum power required to initiate fluid flow, the >Herschel-Bulkley yield stress (τ_0) show similar result as the previous two tests. Fluid with higher starch concentration gives higher yield stress. The calculated Herschel-Bulkley yield stress (τ_0) gradually increased from 0.317 Pa for fluid with no starch to 11.82 Pa as the amount of starch is increased to 2%. This phenomenon is expected because more resistance is predicted with the presence of additional dispersants, thus resulting in higher power required to overcome the additional resistances.

In contrast, in the effect of starch concentration on the value of fluid flow index (n), a slightly different result was found. Unlike the previous two tests where the presence and absence of the component is considered crucial to determine the fluid behavior i.e., pseudoplastic or dilatant, it appears that all the fluid tested at various concentration of starch, from 0% to 2% w/v, behave as pseudoplastic (shear thinning) behavior. This is based on the calculated value of flow index (n) for the entire tested fluid, including the controlled fluid, which are less than 1 (in the range of 0.5 to 0.7) (see Table VI). Dilatant behavior was not detected in fluid with no starch due to the presences of large molecules in the fluid such as glass bubbles (21.25% w/v), xanthan gum (0.5% w/v), and clay (2.5% w/v). In fluid with no starch, the presence of large and bulky volume of glass bubbles, clay and long-chained polymeric structure such as xanthan gum tend to produce higher resistance whenever fluid is in motion at low shear rate. This is because of materials entanglement at random direction and causing the fluid to behave as pseudoplastic behavior. Thus, regardless of starch content, the fluid would still behave as pseudoplastic because of its large molecules of fluids/solid. The physical bulk volume of starch is comparatively smaller than other components in the fluid. Thus, the presence/absence of this material would not significantly affect the spacing (gaps) between dispersed particles that allow continuous phase to fill the gaps and shows a dilatant behavior.

Effect of clay

Finally, in the last test of this study, the effect of clay concentration on the rheological behavior as well as the three parameters of Herschel-Bulkley model was also investigated. Clay concentration was varied from 2.5% to 10% w/v, while keeping other components constant. In addition to those tests, a control test was also conducted by formulating a fluid with 0% w/v of clay concentration. Table VII presents the measured experimental data of the stresses as a function shear rate of the fluids formulated at different clay concentration. In this test, the measured experimental data of shear stress in Table VII were also fitted to the Herschel-Bulkley model and its corresponding parameters were calculated.

TABLE VII
The Average Measured Shear Stress as a Function Applied Shear Rates for Lightweight Biopolymer Drilling Fluid at Different Concentration of Clay

	Clay concentration (% w/v)				
	0 (control)	2.5	5	7.5	10
Shear rate, γ (s^{-1})	Shear stress, τ (Pa) ± sd				
2.639	1.46 ± 0.74	4.40 ± 0.97	15.21 ± 1.06	26.65 ± 1.08	37.63 ± 0.95
5.279	1.76 ± 0.91	5.54 ± 1.06	17.12 ± 1.08	27.19 ± 1.07	40.93 ± 0.81
26.4	2.99 ± 0.52	7.90 ± 1.85	20.42 ± 1.11	31.44 ± 1.07	46.54 ± 1.11
52.71	3.84 ± 0.92	9.72 ± 1.73	22.49 ± 1.04	35.64 ± 1.12	53.63 ± 0.99
79.28	5.07 ± 0.81	11.21 ± 1.83	24.88 ± 2.01	37.18 ± 1.04	59.44 ± 1.10
88.17	5.57 ± 0.73	12.14 ± 1.98	25.26 ± 2.01	39.79 ± 2.09	60.28 ± 2.03
158.3	9.99 ± 0.83	15.87 ± 2.16	29.71 ±± 2.07	45.47 ± 1.03	70.73 ± 2.04
176	11.12 ± 1.09	16.75 ± 2.07	31.16 ± 2.01	48.09 ± 2.11	72.09 ± 2.02
264	14.81 ± 1.02	20.49 ± 2.03	38.47 ± 2.01	54.93 ± 1.12	76.95 ± 2.11

sd, standard deviation.

The results of the fitting process are presented in Table VIII. Furthermore, Figure 4 shows the plot of both the measured shear stress and calculated stress obtained from Herschel-Bulkley model versus shear rate at various clay concentrations.

Figure 4 shows that the stress resulting from the applied shear to the fluid seems to increase with the suspended particle concentration, in this case clay. However, the increase of shear stress seems more significant (especially in the fluid with 5% of clay or more). This is supported from the calculated yield stress (τ_0) of the fluid which increases dramatically from 2–3 Pa at 0% and 2.5% of clay to more than 16 Pa at 7.5% of clay and peaks at 31.97 Pa for the fluid with 10% of clay. Drilling fluid with high yield stress is desirable as it has a better drill cutting carrying capacity. However, drilling fluid with extremely high yield stress would require large horse-power pump to lift the drilling cuttings to the surface. This is true since yield stress represents the minimum amount of force required to initiate fluid movement. In oil-well drilling fluid, besides its function as viscosity control, clay is also used to aid the transfer of drill cuttings from the bottom of the well to the surface, and for filtration control to minimize fluid invasion into the pores of productive formations.[18] Caenn and Chillingar[7,31] reported that clay has an excellent carrying capacity and suspension of cuttings due to its swelling properties.

In addition, Figure 4 also shows that the slope of the plot of shear rate against shear stress increases with clay concentration and it seems to be more profound at the highest tested clay concentration (10% w/v). It is also showed that the increase is more profound at higher shear rate. The addition of clay would increase the dependency of shear stress to the shear rate the mixture. This is supported by the calculated value of fluid consistency (k) of the fluid formulated at different clay concentration. Based on the result in Table VIII, within the tested range, the calculated fluid consistency can be divided into three categories and it tends to increase with the amount of clay, i.e., low (at control fluid, $k = 0.05$ Pa·s^n), moderate (at the fluid with the amount of clay, i.e., 2.5%–7.5% of clay, $k =$ in the range of 0.2 to 0.6 Pa·s^n) and high (at high concentration of clay, i.e., 10%, $k = 3.683$ Pa·s^n). In the control fluid, the calculated fluid consistency is low because the dependency of stress resulted from the application of different shear rate is considerably low. However, when clay is introduced into the fluid system, the fluid consistency tends to increase because of the additional resistance due to the presence of clay as dispersant in the fluid system. Higher clay concentration leads to higher fluid resistance. In addition, swelling property also has a great influence on the dramatic increment of fluid consistency (k) with clay concentration. In the presence of water, high

TABLE VIII
Herschel-Bulkley Parameters at Various Clay Concentrations

	Herschel-Bulkley parameters					
Clay concentration (% w/v)	τ_0 (Pa)	k (Pa·s^n)	n	R^2	SSE	RMSE
0 (control)	1.356	0.050	1.009	0.9938	1.066	0.421
2.5	3.879	0.462	0.643	0.9983	0.399	0.258
5	15.44	0.368	0.735	0.9896	4.413	0.858
7.5	25.40	0.618	0.693	0.9968	2.363	0.628
10	31.97	3.683	0.456	0.9918	13.01	1.473

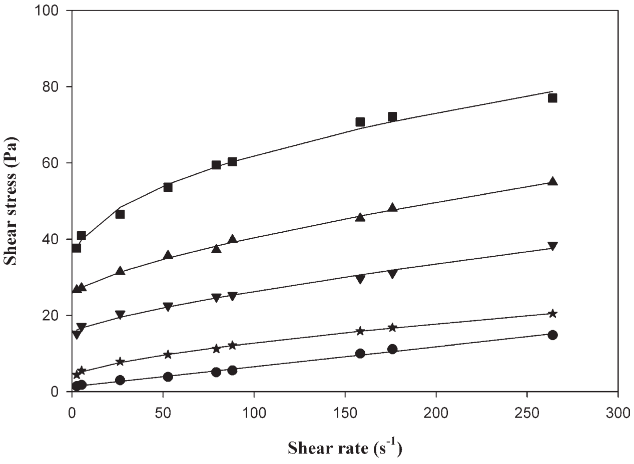

Figure 4 Shear stress vs. shear rate plot of the mixture at various clay concentration ●: 0% w/v (control); ★: 2.5% w/v; ▼: 5% w/v; ▲: 7.5% w/v; ■: 10% w/v; — : predicted with Herschel-Bulkley model.

concentration of clay may also lead to gelling phenomenon resulting in very thick mud slurries due to swelling.[23] To minimize this problem, salt (in this case sodium chloride) was added to aid the stabilization of shales and control swelling of the clays. The chloride ion (Cl^-) from sodium chloride prevents water from entering the clay matrix.[4] In addition, salt is also needed to stabilize the biopolymers structure. Without salt, most polysaccharides will be denatured. This is due to the reduction of contour length of the biopolymers, where the macromolecules tend to adopt more coiled conformation.[4]

Furthermore, the result also shows that the presence of clay plays an important role in fluid behavior. It is also observed that the presence of clay also caused the fluid to behave as pseudoplastic (shear thinning). This is supported by the fact that all the fluids mixed with clay in the fluid system show calculated values of fluid index (n) less than 1 ($n =$ in the range of 0.4 to 0.7). The bulky volume and large dimension of clay and its swelling ability is the reason of the observed pseudoplastic behavior. Thus, higher fluid resistance results from the presence of bulky clay structure whenever the fluid is moved at low shear rate as clay is entangled at random direction and causing the fluid to behave as pseudoplastic. This behavior is good for lifting of drill cutting and increases of drilling rate. However, in the absence of clay, fluid tends to follow a Newtonian behavior. This is based on the calculated value of fluid flow index (n) for fluid with 0% clay is very close to 1 ($n = 1.009$). Thus, based on the result from the previous three tests and this test, it is concluded that the presence of the three main component, i.e., glass bubbles, xanthan gum, and clay, in the lightweight biopolymer drilling fluid plays an important synergic role in determining the fluid behaves, i.e., pseudoplastic, dilatant, or Newtonian. The result shows that the absence any one of the three main components would result the fluid to follow either dilatant or Newtonian behavior.

In addition, Table VIII also showed that the ability of the Herschel-Bulkley model to describe the rheological behavior of the fluid weakens with the increase of clay concentration. Even though the calculated value of R^2 is essentially high, the error (SSE and RMSE) seems to increase as the amount of clay is increased. This may be due to the failure of sodium chloride to control the clay from swelling. As a result, fluid rheological properties tend to change whenever the amount of clay is increased. Thus Herschel-Bulkley model is no longer adequate to describe the formulated fluid viscoplastic properties.

CONCLUSION

The effect of concentration of the four main components of a novel lightweight biopolymer drilling fluid, i.e., glass bubbles, xanthan gum, starch, and clay to the three Herschel-Bulkley rheological parameters, i.e., yield stress (τ_0), fluid consistency (k), and fluid index (n) are presented in this work. The study was conducted by fitting experimental data of shear stress as a function of applied shear rate to the Herschel-Bulkley model of fluids formulated at various concentrations of the four main components. Results show that the model of Herschel-Bulkley is reliable to describe the relationship of shear stress as a function of shear rate (except for high concentration of clay). In terms of fluid yield stress (τ_0), the effect of the concentration of the fluid's four main components is similar. Fluid yield stress appears to increase with the addition of higher amount of glass bubbles, xanthan gum, starch, or clay. This is essentially true because more resistance is predicted due to the presence of additional dispersants, thus resulting in higher stress to initiate fluid flow. Furthermore, it is also showed that the calculated fluid consistency (k) of the drilling fluid is a strong function of the presence of glass bubbles, xanthan gum, and clay. However, it is not affected by the presence of starch. This is proven by the value of fluid consistency of fluid containing neither glass bubbles nor xanthan gum nor clay which are very small compared with fluid containing all of the three materials. In contrast, the fluid consistency value for the fluid with or without starch tends to remain the same. It can be concluded that the presence of three out of four main components of the drilling fluid, i.e., glass bubbles, xanthan gum, and clay, play a synergic pivotal role in determining whether the fluid behaves as pseudoplastic or either dilatant or Newtonian. Whenever one of the three above component is absence, the fluid would not show pseudoplastic behavior.

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