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VISCOMETRIC PERFORMANCE EVALUATION OF OIL WITH RESPECT TO SHEAR RATE, TEMPERATURE AND SHEARING TIME

GOH, E. G.[1*], KOW, C.S.[2] & W. B. WAN NIK[3]

Abstract. In this study, we evaluate the fundamental behaviour of mineral oil (Mobil Extra 2T) that was stressed from stagnant condition to a shear rate of 1900 1/s in different shearing time (60, 300 and 900 s), remained at constant shear rate of 1900 1/s between 30 to 60 s, and continued by decreasing shear rate to stagnant condition at specific shearing time of 60, 300 and 900 s. This process was repeated from 40 to 100 °C with an interval of 20 °C. Viscosity measurement was carried out by ThermoHaake (Rheometer model RS600) and temperature control (Haake - Phoenix model C1 35P). Failure of rheological models in modeling the relationship of viscosity-shear rate was demonstrated and alternative model i.e. Fourier series was proposed as a substitution with a high R-squared value of 0.99. Integration of Fourier series from 0 to 1900 1/s was carried out on increasing and decreasing shear rate-generated curves. Results showed a consistent trend of lost-shear stress (τ_L), represented by the difference of integration value of increasing and decreasing shear rate-generated curves, at specific temperature and shearing time. This method is proposed to evaluate the performance of oil on viscosity recovery after historical treatment of shear rate.

Keywords: Viscosity; temperature; shear rate; rheological models; Fourier series

Abstrak. Dalam kajian ini, kami menilai kelakuan asas minyak mineral (Mobil Extra 2T) yang dikenakan tekanan daripada keadaan pegun ke 1900 1/s keterikan pada masa keterikan yang berlainan (60, 300 dan 900 s) dan dikekalkan pada 1900 1/s keterikan di antara 30 dan 60 s, dan kemudiannya dengan pengurangan keterikan sehingga keadaan pegun pada masa keterikan 60, 300 dan 900 s. Proses ini diulangi daripada 40 ke 100 °C dengan peningkatan suhu 20 °C. Pengukuran kelikatan dilakukan dengan ThermoHaake (Rheometer model RS600) dan pengawal suhu (Haake - Phoenix model C1 35P). Kegagalan persamaan reologi dalam permodelan hubungan kelikatan-keterikan dikenalpasti dan persamaan alternative iaitu siri Fourier dicadang sebagai pengganti dengan nilai R^2 bersamaan 0.99. Integrasi siri Fourier daripada 0 ke 1900 1/s telah dilakukan pada lengkung peningkatan dan penurunan keterikan. Keputusan menunjukkan

[1&2] Department of Engineering Science, Faculty of Science and Technology, Universiti Malaysia Terengganu, Mengabang Telipot, 21030 Kuala Terengganu, Terengganu, Malaysia
[3] Department of Maritime Technology, Faculty of Maritime Studies and Marine Science, Universiti Malaysia Terengganu, Mengabang Telipot, 21030 Kuala Terengganu, Terengganu, Malaysia
[*] Corresponding author : sunny.goh@gmail.com

lesapan-keterikan (τ_L) boleh diwakili dengan perbezaan nilai integrasi di antara lengkung peningkatan dan penurunan keterikan, pada satu suhu dan masa keterikan. Kaedah ini dicadangkan untuk menilai prestasi minyak pada pemerolehan semula kelikatan selepas dikenakan keterikan.

Kata kunci: Kelikatan; suhu; keterikan; persamaan reologi; siri Fourier

1.0 INTRODUCTION

Fluid under shearing condition generates friction which acts against the shearing forces. Shearing stress could be resulted by gravity flow, mechanical stirring, temperature generates stress, etc. In a general perspective, it is the flow of the fluid body that is causing the stress. Shear stress over the rate of deformation is known as viscosity. Viscosity is a direct indication on stickiness of the fluid under studied. Higher viscosity indicates greater stickiness of a fluid, and vice versa. Viscosity is a constant parameter as a result of the relationship between shear stress and deformation rate (or shear rate) as summarized below:

$$\eta = \tau \Big/ \frac{du}{dx} \tag{1}$$

where: τ is the shear stress (Pa); du/dx is the shear rate (1/s); and η is the viscosity (or dynamic viscosity) (Pa.s). An applied shear stress generates greater shear rate is an indication of viscosity reduction which is better known as shear-thinning (or pseudoplastic behaviour) and conversely, lesser shear rate generated from a similar shear stress is known as shear-thickening (or dilatant behaviour).

Shear-thinning behaviour can be modelled by various models. They are Power Law, Cross, Carreau, Herschel-Bulkley, Casson, Sisko, etc. These equations are presented in sequence as followings [1-2]:

$$\eta = K_P \gamma^{n_P - 1} \tag{2}$$

$$\eta = \eta_{\infty,\gamma} + \frac{\eta_{o,\gamma} - \eta_{\infty,\gamma}}{1 + (\alpha_c \gamma)^m} \tag{3}$$

$$\eta = \eta_{\infty,\gamma} + \frac{\eta_{o,\gamma} - \eta_{\infty,\gamma}}{\left[1 + (\lambda_c \gamma)^2\right]^N} \tag{4}$$

$$\eta = K_H \gamma^{n_H - 1} + \eta_{\infty,\gamma} \tag{5}$$

$$\sqrt{\eta} = \frac{K_C}{\sqrt{\gamma}} + \sqrt{\eta_{\infty,\gamma}} \tag{6}$$

where: K_P and K_H are consistency index (Pa.s^n); K_C is consistency index (Pa$^{1/2}$.s); n_P and n_H are flow behaviour index (dimensionless); $\eta_{\infty,\gamma}$ is viscosity at infinite-shear rate (Pa.s); $\eta_{o,\gamma}$ is viscosity at zero-shear rate (Pa.s); m and N are constant (dimensionless); and λ_c and α_c are characteristic relaxation time (s).

Equation 1 is the very foundation of viscosity measurement and Equations 2-6 are models that can be used to summarize non-Newtonian behaviour in the relationship between shear stress and shear rate. Other influences on viscosity are additional factors which affecting the shear rate. They are shear-time, composition, moisture, pressure, oil degradation, molecular weight, density [3-11], and etc. Apart from these, viscosity measurement is also measured under the influence of temperature [12].

The current work is limited to measurement of viscosity under the influence of shear rate at specific temperature and shearing time. The objectives of the work are: (1) to evaluate changes of viscosity under the influence of shear rate, temperature and shearing time; (2) to model viscosity as a function of shear rate at specific temperature and shearing time; and (3) to propose alternative quantitative method in comparing liquid property from the perspective of viscosity.

2.0 MATERIAL AND METHODS

Mobil Extra Two-Stroke engine oil was selected and subjected to viscosity measurement at different shear rate, shearing time and temperature. This is a commercial mineral oil that should have a good representation of oil's general behaviour under stress condition. Its properties are tabulated in Table 1.

Table 1 Typical properties of mobile extra 2T [13]

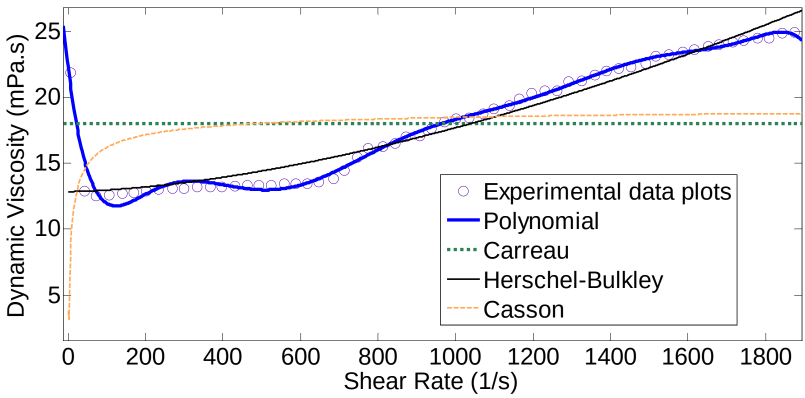
Physical Property	**Unit**
Viscosity, ASTM D 445	
cSt @ 40ºC	55
cSt @ 100ºC	8.8
Viscosity Index, ASTM D 2270	135
Sulfated Ash, wt%, ASTM D 874	0.06
Pour Point, ºC, ASTM D 97	-24
Flash Point, ºC, ASTM D 92	110
Density @ 15ºC kg/L, ASTM D 4052	0.867

2.1 Viscosity Measurements

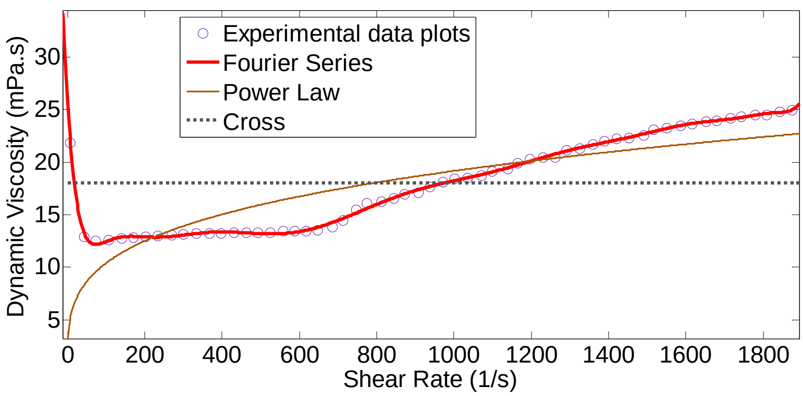
A ThermoHaake (Rheometer model RS600) rotational-type rheometer was used to carry out viscosity measurements. An oil sample was placed into a sample holder where a spindle was fully submerged into the oil sample. A Haake (Phoenix model C1 35P) thermo controller was used to control the temperature of the oil sample with an accuracy of ± 1 °C. The oil sample was sheared from 0 to 1900 1/s, which is the maximum rheometer capacity, to obtain an increasing shear rate-generated curve in 60 s of shearing time. It was then subjected to a constant shear rate at 1900 1/s for a shearing time of between 30 and 60 s. To complete a thixioloop test, the shear rate was reduced from 1900 to 0 1/s to obtain a decreasing shear rate-generated curve in 60 s. This test was carried out at 40 degree Celsius. The viscosity measurements were then carried out separately at 300 and 900 s of shearing time at 40 degree Celsius. Similarly, viscosity measurements were carried out separately at shearing time of 60, 300 and 900 s at 60 degree Celsius before increase the temperature to 80 degree Celsius and finally, at 100 degree Celsius. In each complete thixioloop test, a new oil sample was used. This is to ensure a minimum deviation of oil physical quality in terms of viscosity, because sheared-oil sample requires considerable amount of time to fully recover its molecular arrangement to recover its original viscosity-shear rate relationship. Overall, twelve thixioloop tests were completed.

2.2 Mathematical Modeling

Each thixioloop test generated two curves that were increasing and decreasing shear rate-generated curves. The increasing shear rate-generated curve was curve-fitted by various models as shown in Figures 1(a) and (b). They were Power Law (Equation 2), Cross (Equation 3), Carreau (Equation 4), Herschel-Bulkley (Equation 5) and Casson (Equation 6).



(a)



(b)

Figure 1 Viscosity data generated after Mobil Extra 2T being sheared from 0 to 1900 1/s in 60 s shearing time at 100 degree Celsius. The experimental data were curve-fitted by (a) Polynomial, Carreau, Herschel-Bulkley and Casson models, and (b) Fourier, Power Law and Cross models

The curve-fitting shows that Cross and Carreau gave the worst estimation. This is simply because both equations model only shear-thinning liquid. Herschel-Bulkley model shows a better estimation compared to Power Law and Casson models. Overall, Fourier series and polynomial equations gave the best curve-fitting result with respective R-squared of 0.999 and 0.990. Apart from its accuracy, it is observed that polynomial equation generates "bumps", as shown in Figure 1(a) at shear rate approximately 150, 300 and 550 1/s, which is an indication of over-fitting on experimental data. For this reason, Fourier series was chosen over polynomial equation.

Fourier series equation implemented in the curve-fitting is shown below:

$$\begin{aligned}\eta &= a_o + a_1\cos(\gamma w) + b_1\sin(\gamma w) + a_2\cos(2\gamma w)\\ &+ b_2\sin(2\gamma w) + \ldots\ldots\ldots + a_8\cos(8\gamma w) + b_8\sin(8\gamma w)\end{aligned} \tag{7}$$

where: a_o, a_1, ..., a_8, b_o, b_1, ..., b_8 and w are equation constants.

Equation (7) was integrated over an interval as shown below:

$$\begin{aligned}\int \eta d\gamma &= \int a_o d\gamma + \int a_1\cos(\gamma w)d\gamma + \int b_1\sin(\gamma w)d\gamma\\ &+ \int a_2\cos(2\gamma w)d\gamma + \int b_2\sin(2\gamma w)d\gamma + \ldots\ldots\ldots\\ &+ \int a_8\cos(8\gamma w)d\gamma + \int b_8\sin(8\gamma w)d\gamma\end{aligned} \tag{8}$$

Solving Equation (8) gives the following form:

$$\begin{aligned}\eta\gamma &= a_o\gamma + \frac{a_1\sin(\gamma w)}{w} - \frac{b_1\cos(\gamma w)}{w}\\ &+ \frac{a_2\sin(2\gamma w)}{2w} - \frac{b_2\cos(2\gamma w)}{2w} + \ldots\ldots\ldots\\ &+ \frac{a_8\sin(8\gamma w)}{8w} - \frac{b_8\cos(8\gamma w)}{8w}\end{aligned} \tag{9}$$

Equation 9 was used to estimate an area encompassed by increasing and decreasing shear rate-generated curves over *x*-axes (or shear rate-axes) from 0 to

1900 1/s. Viscosity (η) multiplied by shear rate (γ) to give shear stress (τ). The difference of area, as shown below, is an indication of lost-shear stress (τ_L):

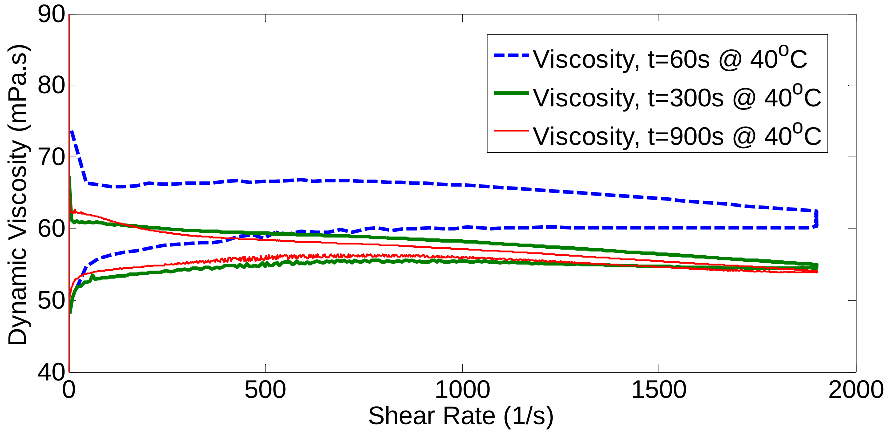
$$\tau_L = [\eta\gamma]_i - [\eta\gamma]_f \tag{10}$$

where: i is representing the increasing shear rate-generated curve; and f is representing the decreasing shear rate-generated curve.

3.0 RESULTS AND DISCUSSION

It is commonly agreed that viscosity decreases with increasing shear rate. This is observed on various liquids including polymer-oils solution, mineral oil-in-water emulsions, waxy oils, [3, 14-15] and many others. This observation is a single direct relationship as most of the studies generally categorized viscosity-shear rate relationship into either shear-thinning (pseudoplastic) behaviour or shear-thickening (dilatant) behaviour. The current study found out that the measured oil neither falls into these categories. The measured Mobil Extra 2T motor oil was found rather consists of both pseudoplastic and dilatant behaviours at intermittent. This observation is rather unique since it has not been reported by researchers on motor oil/vacuum residue blends and aged bitumen at high shear rate [16-17].

Mobil Extra 2T exhibits shear-thinning at the initial stage of shear rate ($\gamma < 100\,\mathrm{s}^{-1}$). As the shear rate continues to increase, a mild shear-thickening was found. Further increasing shear rate, $\gamma > 700\,\mathrm{s}^{-1}$, mild shear-thinning was observed. This observation was found at 60 s of shearing time, except at 300 and 900 s (Figure 2(a)), but a frequent intermittent between pseudoplastic and dilatant behaviours were observed in Figures 3(a) to (c). The intermittent observation was not a result of inconsistent increase of shear rate, as proven by the approximate value between slope (m) and γ / t value (Table 2), but rather the natural phenomenon of the oil itself. Note that a sudden increase of shear rate would be visible in Figure 2(b) or indicated by a large deviation slope (m) value from γ / t value, in Table 2.



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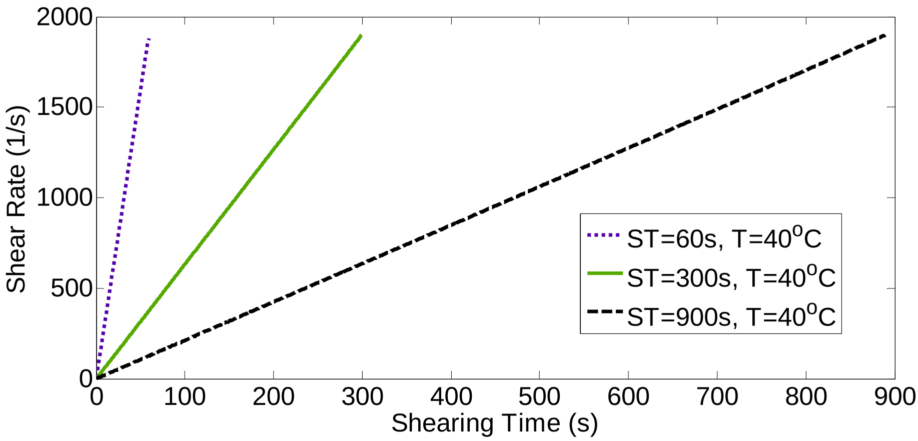
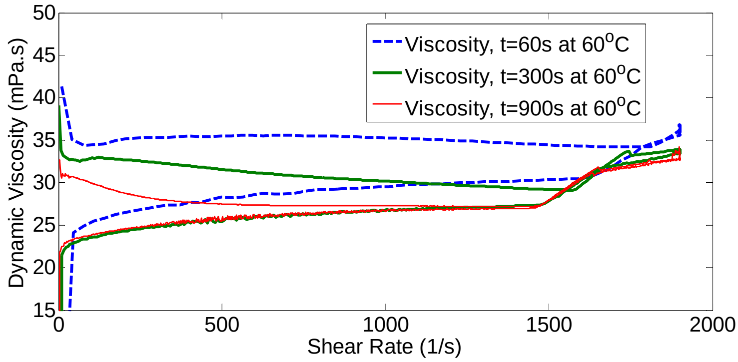
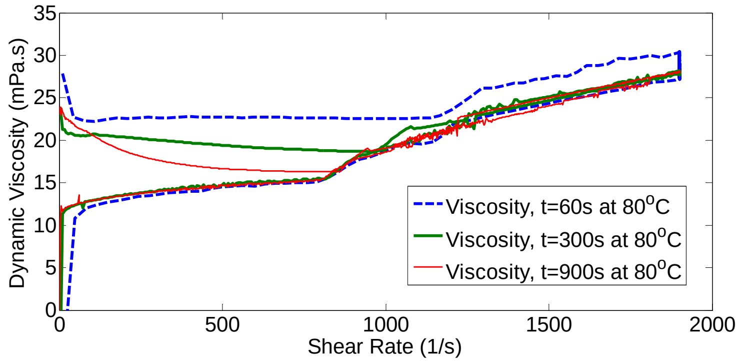


(b)

Figure 2 Viscosity measurements separately at 60, 300 and 900 s shearing time at 40 degree Celsius. Graph (a) represents viscosity versus shear rate, and graph (b) represents shear rate versus shearing time



(a)



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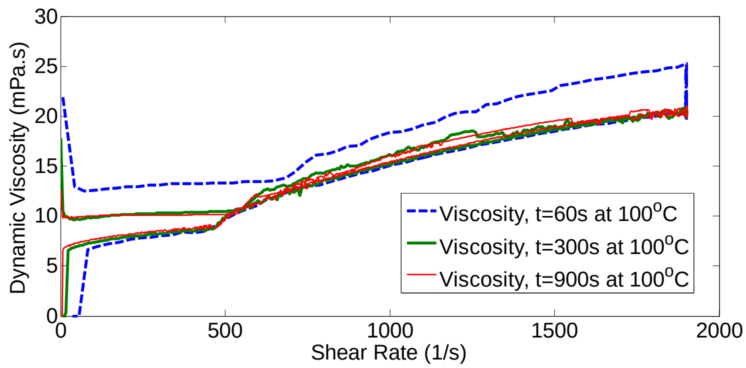

(c)

Figure 3 Viscosity measurements separately at 60, 300 and 900 s shearing time at: (a) 60 degree Celsius; (b) 80 degree Celsius; and (c) 100 degree Celsius

Table 2 Linear equation ($\gamma = mt + c$) curve-fitted on experimental data from Figure 2(b)

Shearing time (t), Temperature (T)	**Slope (m)**	**Intercept (c)**	$\frac{\gamma}{t}$
60 s, 40 °C	31.56	8.085	1900/60 = 31.66
300 s, 40 °C	6.339	0.1606	1900/300 = 6.33
900 s, 40 °C	2.133	-3.423	1900/900 = 2.11

Decreasing shear rate-generated curve was approximately identical to increasing shear rate-generated curve at high shear rate region. The former curve is indicating the recovery of oil's stickiness after being shear. From Figures 2(a), 3(a) to (c), viscosity recovery was indeed greater at high shear rate region, for instance, $\gamma \geq 1000\,\mathrm{s}^{-1}$ at 80 degree Celsius. As the shear rate continues to decrease, the viscosity recovery becomes slower and it leads to a larger decoupling between decreasing and increasing shear rate-generated curves. Further decreasing of shear rate until approximately zero, viscosity approximates zero value in which it indicates a longer time was required to fully recover its viscosity at low shear rate region.

A sudden increase of viscosity was apparent at 60 degree Celsius and above, at high shear rate region, for instance, $\gamma \geq 1500\,\mathrm{s}^{-1}$ at 900 s shearing time at 60 degree Celsius. This phenomenon occurred at much earlier stage of increasing shear rate as the shearing time and temperature increases. We hypothesize that increasing shear rate supply incremental energy to the liquid body to breakdown any attraction forces between molecules. At some point when the attraction forces between molecules are weakened, any additional supply of energy whether contributed by increasing shear rate and/or temperature will cause a transition of flow from laminar to turbulence.

Similar to shearing effect, a higher temperature implies greater energy is imposed on the liquid body to breakdown the attractive forces between molecules. For this reason, Mobil Extra 2T exhibits lesser viscosity at greater temperature (Figure 4).

As a result of shearing time, increasing shear rate and temperature effect, an interesting information can be captured on the decoupling of increasing and decreasing shear rate-generated curves. The difference of value on the integration of the curves over an interval of 0 and 1900 1/s is taken as lost-shear stress (τ_L), see Equation 10. It was found to decrease with increasing temperature and shearing time (Table 3). At greater shearing time on decreasing shear rate, a longer time is allowed for larger amount of energy transfer into the liquid body to breakdown the attractive forces that resulted in lesser viscosity. During decreasing shear rate, greater shearing time is also allowing sufficient time for energy dissipation which resulted in greater rate of viscosity recovery. Hence, lost-shear stress becomes lesser at greater shearing time. At greater temperature, viscosity reduction is further enhanced during increasing shear rate, and also, a greater viscosity recovery rate during decreasing shear rate. Hence, lost-shear stress is lesser at greater temperature.

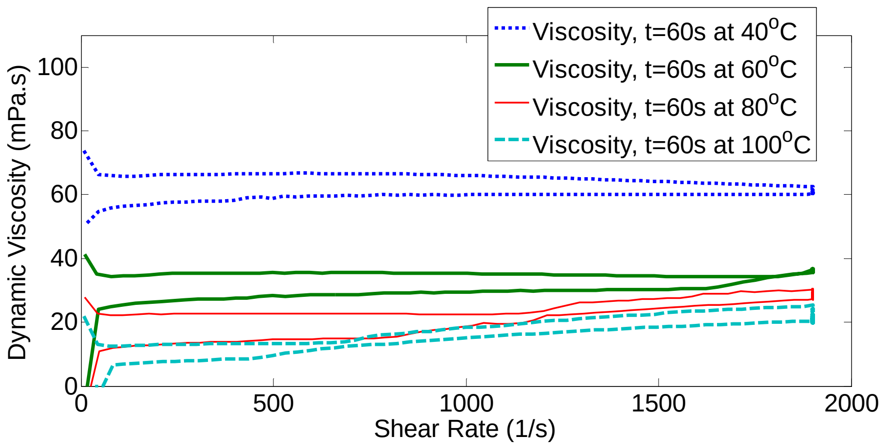

Figure 4 Viscosity versus shear rate at 60 s shearing time at respective 40, 60, 80 and 100 degree Celsius

Table 3 Lost-shear stress at 60-900 s and 40-100 degree Celsius

	Lost-shear stress, τ_L (Pa)			
Shearing Time (s)	40 °C	60 °C	80 °C	100 °C
60	11988	11940.8	11792.2	8196.9
300	6494	7958.8	5343.7	2089.7
900	4107	2889.4	2659.9	1582

4.0 CONCLUSIONS

Viscosity is apparently influenced by shearing time, temperature and shear rate. Generally, viscosity is lesser at greater shearing time, temperature and shear rate, but the current work found out that, viscosity has no single relationship with shear rate. The relationship between viscosity and shear rate is rather an intermittent behaviour of pseudoplastic and dilatant. A significant sudden increase of viscosity at 60 degree Celsius and above at all shearing time in which we hypothesize it as a transition of flow from laminar to turbulence. Lost-shear stress was found to give a consistent trend of observation on the influence of shearing time and temperature, and therefore, it could be used as an indicator on the rate of fluid viscosity recovery. Oil with greater rate of fluid viscosity recovery should possess a lower lost-shear rate value, which indicates the oil's resilient after historical treatment of shear rate. Similarly, this method can be applied on viscosity-temperature relationship.

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