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Rheological Properties Determination of Wax Oil Using Fractal Scaling Theory

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Abstract

Wax blockages due to gelation of waxy oil in subsea pipelines represent a high-cost problem for the oil industry. Determining its rheological properties has been a challenging problem for scientists and engineers, especially yield stress determination. To address this rheological complexity, the waxy gels formed by model oils containing 2.5, 5.0 e 7.5 wt % under three cooling rates (i.e. 0.50, 0.75, and 1.00 °C/min) were investigated using the fractal framework of scaling laws. Thus, the weight fraction of wax obtained from DSC experiments was conciliated with rheological data from oscillatory stress sweep, elastic modulus, critical stress, and strain. The results showed that the influence of the cooling rate in the gel strength changes with their microstructural regime, which is strongly dependent on the precipitated mass of paraffin.

Keywords

Yield stress; waxy oil; fractal objects.

Introduction

Waxy oils under gelation represent a serious problem for the oil industry due to their high yield stress and the complex thixotropic elastoviscoplastic behavior [1].

These gels have been recognized in the literature as fractal structures, according to Shih et al. [2] theory, which allows the application of scaling models to describe the elastic modulus and the critical elastic strain.

The theory proposed by Shih et al. [2] states that the volume spanning network of a colloidal gel can be understood as a set of clusters with fractal characteristics. These gels can be classified into two groups according to their microstructure. In the first one, called strong-link, the force between clusters is predominant over the bond between particles, then the breakage tends to happen intraclusters. When the situation is opposed, the breakage occurs between clusters and is called a weak-link regime.

Generalizing the theory, Wu and Morbidelli [3] proposed a modification to the previous approach, stating that the gel can have an intermediate behavior defined by a factor α, ranging from 0 to 1. When α is equal to 0, it is said that the gel has a pure strong-link behavior and, when it is equal to 1, the pure weak-link behavior dominates. Between these limits, a combination of these characteristics is found.

This theory has been applied to wax gels since Silva and Coutinho [4] applied Wu and Morbidelli's [3] model to describe the elastic modulus and the critical elastic strain of three crude oils finding fractal dimensions (D) in the range of 1.7 to 2.2.

Visitin et al. [5] also apply this model to paraffinic crude oils with a slight modification. They proposed that the backbone fractal dimension x can be calculated through a direct relation with the fractal dimension (i.e., $x = 0.7278\ D$). Visitin et al. [5] also reveal that there is a relation between the value of α with the rigidity of the gel. For α close to 0, the flow restart occurs with some recompacting in the structure, while for α close to 1, the fracture tends to be more brittle. In a later work, Visitin et al. [6] used the framework of the model to discuss the structural properties of some crude oil emulsions.

Yang et al. [7] and Yang et al. [8] applied Shih et al. [2] model to study the gelation behavior in model oils [7] and crude oils [8]. In these works, the authors divided the gel behavior into three parts for some oils: two strong-link regions with decreasing critical elastic strain, and a weak-link region with an increasingly critical elastic strain. The lack of the capability of the model to predict the strong-link can be related to the use of α as 0 or 1 only.

More recently Xue et al. [9] use the mentioned theory to show that the increase in the amount of asphaltene in the oil is responsible to diminish the weak-link regime in the gel.

A summary of the results found by Xue et al. [9] is presented in Table 1. The results show that just a few works applied the scaling law framework to waxy oil and some inconsistencies should be discussed. One example is the value of fractal dimension under 1 for a volume spanning network, which is not reliable. Another example is the pre-exponential value and the limit values of x in the models, an issue that has been little addressed. Finally, to the best of our knowledge, no previous work has been presented discussing the effect of cooling rate on the parameters. Therefore, this work aims to present a study of the Wu and Morbidelli [3] reasoning applied to a model waxy gel, using an experimental design composed of two variables: the wax mass fraction (ϕ) and the cooling rate (q).

Table 1. Scaling parameters find in some works

Author	ϕ (wt %)	D	x	α
[4]	6.8	1.7	n.m	n.m
	23	2.2	n.m	n.m
	21	1.9	n.m	n.m
[5]	4	2.6	n.m	0.7
	30	2.1	n.m	0.8
[7]	5	0.6/2.5/2.7	n.m	0/0/1
	10	0.5/2.3/2.7	n.m	0/0/1
	15	0.9/2.6	n.m	0/1
	20	0.9/2.7	n.m	0/1
[8]	8.1	2.4/2.7	n.m	0/1
	11.5	2.3/2.7	n.m	0/1
	17.3	0.8/1.8/2.5	n.m	0/0/1

n.m.: not measured by the authors.

Methodology

Differential scanning calorimetry (DSC) and oscillatory rheology were employed to assess the data obtained. The samples were composed of a mineral oil kindly provided by Petrobras S.A and a predominantly linear wax bought from Sigma-Aldrich, with a mean carbon number of 29. Both materials were previously characterized by Marinho et al. [10], [11], [12]. The experimental design is presented in Table 2 along with the gelation temperature (T_{gel}) of each oil.

Table 2. Experimental design and T_{gel}.

Number of experiments	q (°C/min)	ϕ (wt %)	T_{gel} (°C)
1	0.50	2.5	20.1
1	0.50	7.5	16.0
1	1.00	2.5	29.9
1	1.00	7.5	20.1
2	0.75	5.0	23.7

DSC tests

The DSC tests were performed in a microcalorimeter 7 EVO from SETARAM instruments, according to the following protocol: (i) previous solubilization for 15 min; (ii) 5 min of thermal equilibration at 50°C in the DSC instrument; (iii) cooling from 50°C to -20 °C (cooling rates are presented in Table 2). The thermograms results enabled obtaining the precipitated mass fraction, which was calculated from the Chen et al. [13] method using the crystallization enthalpy of the pure wax of 217.45 J/g.

Oscillatory stress amplitude sweep

ARG-2 (TA Instruments) rheometer was employed. The oscillatory stress amplitude sweeps were made using the following protocol: (i) 15 min of previously solubilization of the sample in a magnetic stirrer; (ii) 5 min of thermal equilibration at 50 °C; (iii) cooling in quiescent condition until the final test temperature; (iv) 30 min aging for structure buildup using oscillatory stress of 0.1 Pa and 0.2 Hz frequency; (v) Stress sweep from 0.1 to 2,500 Pa using 15 points per decade and an oscillation frequency of 1 Hz. This protocol was applied to temperatures below the sample gelation point, until 4°C.

Mathematical model

To fit the data, the Wu and Morbidelli [3] model was applied to the storage modulus in the linear viscoelasticity region (G'_{LVR}) and for the critical elastic strain (γ_c). Also, a relation for the critical stress (τ_c) was applied, according to Khalkhal and Carreau [14], as is shown in Equations (1) to (6). ϕ is the precipitated wax mass fraction, D is the fractal dimension, x is the backbone fractal dimension and α is the homotopy factor.

$$G'_{LVR} = C_G \phi^A \tag{1}$$

$$\gamma_c = C_\gamma \phi^B \tag{2}$$

$$\tau_c = C_\tau \phi^{(A+B)} \tag{3}$$

$$A = \beta/(3-D) \tag{4}$$

$$B = (2-\beta)/(3-D) \tag{5}$$

$$\beta = 1 + (2+x)(1-\alpha) \tag{6}$$

The expected value of fractal dimensions is in the range of 1 and 3 and x was fixed as 1.3 because it can also be interpreted as the tortuosity of the main ramification inside the cluster. Therefore, values in the range of 1 to 1.3 are expected (Wu and Morbidelli [3]). Holding x as a constant also avoids the possibility of multiple optimum values in the parameter estimation procedure, once multiple combinations of x and α can lead to the same results.

The parameter estimation procedure was done by the estimation of the pre-exponential factors (C_G, C_γ, C_τ), D, and β using the ESTIMA software [15], employing the weighted least squares function. The error was calculated as a pooled standard deviation in the central point of the experimental design and distributed according to the magnitude of the rheological variables to the others conditions.

Results and Discussion

Concerning the adjustments with Wu and Morbidelli's [3] model, Figs. from (1) to (5) show the resultant curves along with the experimental data and α and D parameters. According to the values of the homotopy factor in Fig. (1) to Fig (5), no gel presented a pure strong-link behavior (i.e., α = 0). The closest value to this limit was obtained for the model oil with 2.5 wt % of wax cooled at 0.50 °C/min which, in Fig. (1), presents an α equal to 0.17. On the other hand, the gel with the same initial wax mass fraction (cooled at 1.00 °C/min) in Fig. (2) and the gel with 5.0 wt % of wax (c.f. Fig. (3)) presented values of α close to 0.5, which corresponds to an intermediate behavior. This result shows that, although the values of critical elastic strain decreased as a function of the crystallized wax fraction, the transition behavior (from a decreasing to an increasing critical elastic strain) does not occur for a value of α equal to 0.5. In the other extreme, the gels which presented an increasing critical elastic strain (Fig. (3) to (5)) had α values of approximately 1 which corresponds to the pure weak-link gels.

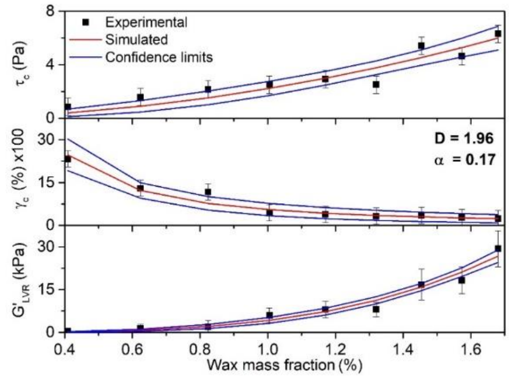

Figure 1. Parameter estimation results for the oil 2.5 wt % cooled at 0.50 °C/min.

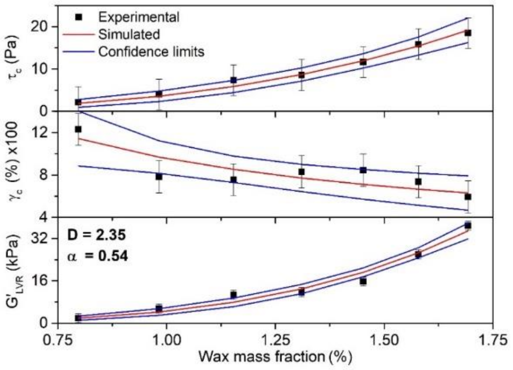

Figure 2. Parameter estimation results for the oil 2.5 wt % cooled at 1.00 °C/min.

Concerning the accuracy of the nonlinear adjustments, Figs. (1) to (5) also show a good model agreement with the experimental data obtained. This result can be verified mathematically by the value of objective functions (F_{obj}) obtained in Table 3, which also presents the parameters estimated with their respective lower and upper confidence limits (LL and UL, respectively).

Table 3. Objective function and estimated parameters (LL = lower limit, UL = upper limit).

2.5 wt% at 0.50 °C/min			
F_{obj}/ param	Value	LL	UL
F_{obj}	27.92	10.98	36.78
D	1.96	1.26	2.27
B	3.73	2.84	5.00
$C_G(kPa)$	4.15	2.48	6.24
$C_\tau(Pa)$	2.21	1.53	3.23
$C_\gamma(Pa)$	0.056	0.022	0.093
2.5 wt% at 1.0 °C/min			
F_{obj}	13.72	6.91	28.87
D	2.35	2.01	2.53
B	2.51	2.01	3.39
$C_G(kPa)$	4.53	2.64	6.83
$C_\tau(Pa)$	3.78	2.05	6.22
$C_\gamma(Pa)$	0.096	0.072	0.119
5.0 wt% at 0.75 °C/min – Decreasing γ_c			
F_{obj}	0.08	1.69	16.01
D	2.19	2.01	2.31
B	2.52	2.24	2.92
$C_G(kPa)$	8.00	5.73	11.26
$C_\tau(Pa)$	2.10	1.08	3.43
$C_\gamma(Pa)$	0.035	0.029	0.043
5.0 wt% at 0.75 °C/min – Increasing γ_c			
F_{obj}	16.13	6.91	28.84
D	2.70	2.51	2.75
B	0.88	0.63	0.87
$C_G(kPa)$	9.59	4.27	25.41
$C_\tau(Pa)$	0.034	0.006	0.868
$C_\gamma(Pa)$	4.5×10^{-4}	6.5×10^{-4}	9.6×10^{-4}
7.5 wt% at 0.50 °C/min			
F_{obj}	13.66	8.91	32.85
D	2.68	2.56	2.71
β	0.63	0.55	0.89
$C_G(kPa)$	22.92	12.94	36.98
$C_\tau(Pa)$	0.024	0.007	0.362
$C_\gamma(Pa)$	1.2×10^{-4}	3.2×10^{-5}	1.7×10^{-3}
7.5 wt% at 1.00 °C/min			
F_{obj}	18.96	10.98	36.78
D	2.40	2.24	2.50
β	0.69	0.51	0.93
$C_G(kPa)$	71.20	44.36	111.43
$C_\tau(Pa)$	1.27	0.44	4.36
$C_\gamma(Pa)$	1.9×10^{-3}	5.1×10^{-4}	6.7×10^{-3}

Based on the value of the parameters obtained in Table 3, one can observe that the fractal dimension D and the parameter β presented inversion in their dependence on the colling rate when the signal of critical elastic stress changes. As an example, the fractal dimension for the model oil with 2.5 wt % wax was 1.96 for the cooling rate of 0.50 °C/min and 2.35 for the cooling rate of 1.00 °C/min. This result indicates that the gel structure was more intricate at the highest rate applied. On the other hand, for the model oil with 7.5 wt % of wax, for the cooling rate of 0.50 °C/min, a value of *D* equal to 2.68 was obtained, while for the cooling rate of 1.00 °C/min a value of 2.40 was estimated, pointing out a more complex structure for the lowest cooling rate. Lastly, the pre-exponential factors C_G, C_{τ}, and C_{γ} were similar for the model oil with 2.5 wt % wax, regardless of the cooling rates applied. However, for the model oil with 7.5 wt %, these parameters exhibit a more pronounced difference comparing the cooling rate. As an example, C_{τ} was two orders of magnitude greater for the cooling rate of 1.00 °C/min (1.27 Pa) as compared with the value for the cooling rate of 0.50 °C/min (0.024 Pa). Therefore, there is evidence of a major cooling rate dependence of these parameters for higher wax mass fractions in the oil.

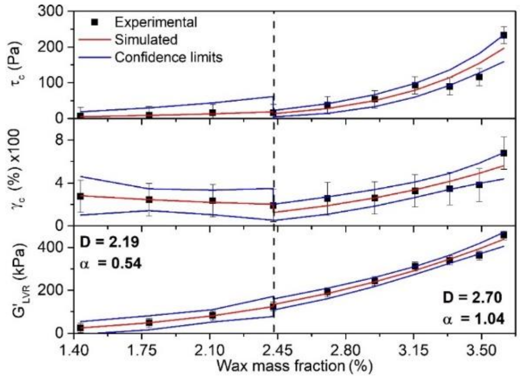

Figure 3. Parameter estimation results for the oil 5.0 wt % cooled at 0.75 °C/min.

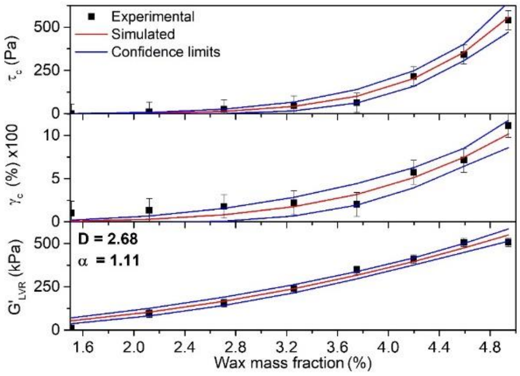

Figure 4. Parameter estimation results for the oil 7.5 wt % cooled at 0.50 °C/min.

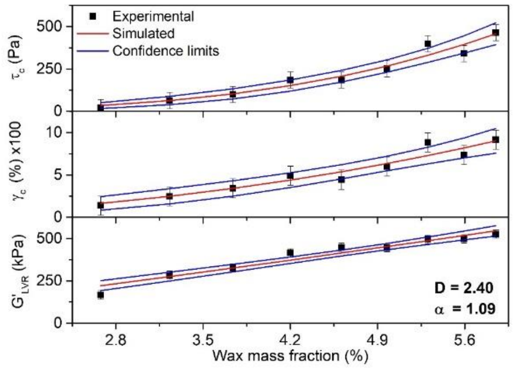

Figure 5. Parameter estimation results for the oil 7.5 wt % cooled at 1.00 °C/min.

Conclusions

The framework of the model of Shih et al. [2] and Wu and Morbidelli [3] model can be applied as a useful tool to understand some aspects of the rheological behavior of waxy oils. The homotopy factor, which is capable of capturing the effect of precipitated wax, and the fractal dimension, which is sensitive to the cooling rate, are two points of interest explored in this work. In future works, the importance of a kinetic model running together with the scaling laws, aiming the prediction of yield stress in field pipelines, will be addressed.

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Responsibility Notice

The authors are the only ones responsible for the paper content.

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