Proceedings of the 9th International Conference on Heat Transfer and Fluid Flow (HTFF'22)
Prague, Czech Republic – July 31, 2022 - August 02, 2022
Paper No. HTFF 166
DOI: 10.11159/htff22.166

Analysis of Carbopol And Triethanolamine Concentration in The Viscoplastic Properties of Aqueous Solution

Daiane Mieko Iceri[1], Jorge Luiz Biazussi[1], Charlie van der Geest[1], Roney Leon Thompson[2], Marcelo Souza de Castro[3]
[1]Center for Petroleum Studies, University of Campinas
Campinas, São Paulo, Brazil
[2]Department of Mechanical Engineering, COPPE, Federal University of Rio de Janeiro, Centro de Tecnologia, Ilha do Fundão, 21945-970, Rio de Janeiro, RJ, Brazil
[3]School of Mechanical Engineering, University of Campinas
Campinas, São Paulo, Brazil
daianemiceri@gmail.br

Abstract – Materials with viscoplastic characteristics have being widely studied due to their applicability in industries, but also because of their common presence in nature. Fluids with such characteristic can be modelled by the equation known as Herschel-Bulkley. This type of fluid has a yield stress property, which is extremely important to characterize it. Carbopol solution is the most common fluid used for experimental studies involving this type of fluid. However, the Carbopol solution needs a neutralizing agent, which acts as a pH regulator, prevents the formation of fungus, but it also affects the yield stress. In the present work, measurements of the yield stress from flow curve tests, performed in a rheometer, were made for different combinations of Carbopol and Triethanolamine (neutralizing agent) concentrations. The yield stress increased with the increment in the concentration of both, Carbopol and Triethanolamine (TEA), in addition, it was observed that TEA concentrations must be greater than 500 *ppm* to avoid the formation of fungi and less than 700 *ppm* to obtain a homogeneous solution.

***Keywords*:** Non-Newtonian fluid, Herschel-Bulkley fluid, Carbopol solution, Triethanolamine

1. Introduction

Materials that do not follow the Newtonian constitutive equation are common in natural and industrial processes and these are known as non-Newtonian materials. The specific non-Newtonian behavior studied here is called viscoplastic behavior and a classic example is described by the Herschel Buckley (HB) constitutive equation. These types of fluids present an interesting property called yield stress, i.e., the material presents a strength threshold below which there is no flow. In addition, at steady state, the relation between shear stress and shear rate is non-linear. The evaluation of the yield stress is critical for several industrial processes, such as when pumping viscoplastic materials. This property is crucial to predict the minimum pressure that should be applied on the system to guarantee the desired flow rate and to estimate performance losses [1].

When such a material is flowing in a pipeline, there is a core region with uniform velocity (plug flow) since the shear stress at the centerline is zero and it achieves the yield stress value at some radial position. The estimation of the plug flow region is important because it affects the relation between flow rate and pressure losses. The flow rate is directly proportional to the yield stress, in addition to the Herschel-Bulkley parameters, pipe diameter, and plug flow size, as shown by [2]:

$$Q = \pi R^3 n \left(\frac{\tau_y}{k}\right)^{1/n} (1-\phi)^{(n+1)/n} \left\{\frac{(1-\phi)^2}{3n+1} + \frac{2\phi(1-\phi)}{2n+1} + \frac{\phi^2}{n+1}\right\}, \tag{1}$$

where Q is flow rate, R radius tube, τ_y yield stress, ϕ is the ratio of the plug radius to the pipe radius, k is the consistency index, and n is the flow behavior index. All units are in SI. For this, the Herschel-Bulkley equation to be considered for analysis is given by [3],

$$\tau = \tau_y + k\dot{\gamma}^{1/2} + \eta_\infty \dot{\gamma}, \tag{2}$$

where $\dot{\gamma}$ is the shear rate, τ is the shear stress, τ_y is the yield stress and η_∞ is the viscosity at high shear rates.

However, characterizing yield stress of such fluid still lacks a standard methodology, mainly because yield stress obtained experimentally can vary in an order of magnitude for different tests. According to [4], the protocol used for the yield stress determination is still not well defined. It can be obtained by different types of rheological tests, such as:

1. Steady state flow curves.
2. Oscillatory experiments at a fixed frequency of oscillation.
3. Creep tests (constant shear stress) where the transient response of the shear rate is evaluated.

This work presents the initial characterization (since the tests were started by the flow curve tests and the other tests will be carried out later) of the yield stress in HB-type viscoplastic materials. Since aqueous solutions of Carbopol (Carbomer 940) are known for such behavior and Triethanolamine (TEA) is commonly used as fungicidal agent, we develop a characterization map of the yield stress of these mixtures as a function of Carbopol and Triethanolamine concentrations. One should not the difficulty to obtain the yield stress and the importance associated with its estimation given the advancement of studies involving viscoplastic material flow.

2. Materials and Methods

Carbopol is an acrylic acid cross-linked polymer with high molecular weight, commonly used in water that presents HB behavior. Given its non-toxic characteristics, it is compatible with human and environmental activities and has been used in pharmaceutical and cosmetic products [5]. However, a neutralizing agent is necessary (TEA), initially as a fungicidal agent and secondly to make the mixture pH neutral (close to 7) since the aqueous solution of Carbopol has an acidic pH (around two or three).

Before preparing the Carbopol/TEA solutions, it was necessary to check the viable limits of TEA concentration. The minimum TEA concentration needed to guarantee the prevention of fungi was found to be 500 *ppm*. Below this value, fungi occurred after 15 days. The upper limit in TEA was the maximum concentration that allowed a homogeneous solution (a solution that does not form granules). Since TEA expands the bonds between the carbomer molecules, which also results in an increase in the yield stress, it is necessary to investigate how different concentrations of TEA affects the yield stress values. Three concentrations of Carbopol were used (0.1, 0.15, and 0.2wt%), which were combined with three concentrations of TEA (500, 600, and 700 *ppm*), totalizing nine samples.

The solution preparation procedure consisted of the following steps:

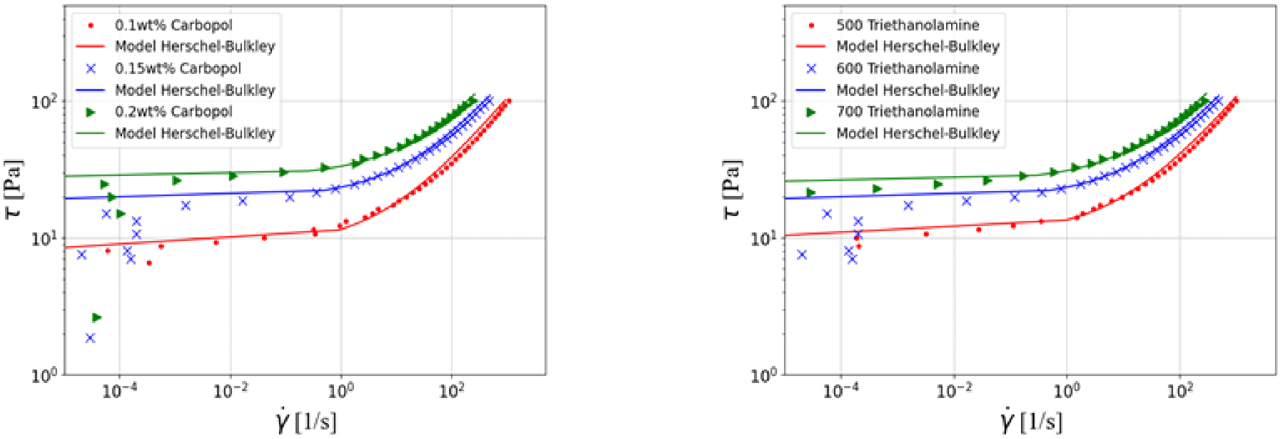
- Separately weigh the quantities of each component.
- Heat deionized water on a magnetic stirrer device at 200 rpm and up to 40°C.
- Slowly add Carbopol to the center of the stirrer.
- Stir solution on a magnetic stirrer for 10 minutes at 200 rpm.
- Carefully add TEA, drop by drop, in the center.
- Stir solution on a magnetic stirrer for one hour at room temperature to homogenize the mixture.

The next step was the experimental procedure for measuring the flow curves definition. First, the air trapped during the preparation process was removed in a centrifuge device from Hettich, model Rotanta 460R, at a rotation of 4000 rpm, for two minutes. This period was enough to guarantee the removal of air bubbles dispersed in the sample.

The tests were carried out in triplicates, at room temperature (25ºC) on the rheometer from Thermo Scientific, model Haake Mars III, with a serrated plate (to avoid slip) of 35 mm diameter, with a gap of 1 mm (as indicated by the manufacturer). The flow curves were obtained with a shear stress ramp ranging from 10^{-1} up to 100 Pa, with a logarithmic distribution, with 15 s steady-state time. The flow curve experiments were executed with two methods: (i) from low to high shear stress and (ii) from high to low shear stress, to check hysteresis effects.

3. Results and Discussion

Hysteresis was not observed in any of the flow curves for all nine samples tested and very small deviations were observed between triplicates. Since up and down curves did not present hysteresis, only the results for increasing shear rate are presented in Fig. 1. In Figure 1(a), the TEA concentration was fixed at 600ppm and the Carbopol concentrations were set at 0.1, 0.15, and 0.2wt%. In Figure 1(b), the Carbopol concentration was kept constant at 0.15wt% and the TEA concentrations were 500, 600, and 700 *ppm*. The increase in TEA, for the same concentration of Carbopol, caused an increase increase of the linked Carbomer molecules, while the increase in Carbopol increased the amount of Carbomer molecules. Both influences lead to higher values of the yield stress.



(a) (b)

Figure 1. Carbopol flow curves (a) for different Carbopol concentration and 600 ppm of TEA and (b) different TEA concentration and 0.15wt% of Carbopol.

From the flow curves data, considering strain rates above 10^{-3} 1/s, the HB parameters were obtained from a least square adjustment. The traditional Herschel-Bulkley model does not consider the viscous effects at high rates and this non-physical characteristic can be corrected by the addition of a viscous parameter at high shear rates, η_∞. We adopted the modified HB proposed by [3], where the exponent index n is equal to 0.5 (see Eq. (2)). Experimental data presented a good fit for the modified Herschel-Bulkley model, with covariance lower than 0.05. The results obtained for yield stress, viscosity at high rates and Hershel-Bulkley constants are presented in Table 1.

With the data from Table 1, a yield stress map as a function of the TEA and Carbopol concentrations was elaborated, as shown in Fig. 2. We highlight the possibility of using this map as a guideline to predict yield stress for different values of Carbopol and TEA concentration.

Table 1. Experimental results for nine different Carbopol and Triethanolamine concentrations.

Total sample [g]	Carbopol [%]	Triethanolamine [ppm]	Yield stress (1) [Pa]	n [-]	K [Pa.s^n]	η_∞ [Pa.s]
179.2	0.10	500	5.0	0.5	1.8	0.001
179.2	0.10	600	10.6	0.5	2.0	0.001
179.2	0.10	700	15.7	0.5	3.1	0.001
179.2	0.15	500	13.9	0.5	2.1	0.001
179.2	0.15	600	21.4	0.5	3.7	0.001
179.2	0.15	700	27.8	0.5	4.5	0.001
179.2	0.20	500	21.2	0.5	3.1	0.001
179.2	0.20	600	28.3	0.5	4.7	0.001
179.2	0.20	700	37.2	0.5	6.4	0.001

(1): measured at 25°C

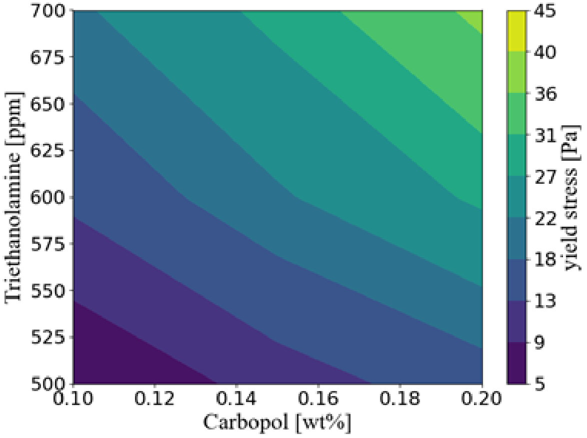


Figure 2. Yield stress map for Carbopol and Triethanolamine samples.

4. Conclusions

The results show that higher concentrations of Carbopol and Triethanolamine induce higher values of yield stress because of the increase in the amount of Carbomer molecules and/or the increment of links between these molecules, with a consequent swelling of their chains. Furthermore, the Carbopol and Triethanolamine aqueous solution behavior can be estimated from a Herschel-Bulkley model.

An important aspect of the analysis conducted was the determination of the minimum TEA concentration to prevent fungi (500 *ppm*) and the maximum TEA concentration (700 *ppm*) to guarantee a homogeneous mixture. Since within this range, the yield stress can significantly change, the results reported here are important for applied problems where TEA is employed in combination with Carbopol solutions.

5. Acknowledgment

We gratefully acknowledge the support of TotalEnergies EP Brazil and ANP. The results presented in this document were obtained through a Research, Development and Innovation (R,D&I) project carried out in partnership with the company TotalEnergies EP Brazil and financed with resources from the R,D&I Clause regulated by the National Agency of Petroleum, Gas and Biofuels - ANP. Acknowledgements are extended also to the Center for Petroleum Studies (CEPETRO), School of Mechanical Engineering (FEM-UNICAMP), Alberto Luiz Coimbra Institute (COPPE-UFRJ) and ALFA Research Group for the collaborative efforts to achieve the objective of this publication.

References

[1] Shakeel, A., Kirichek, A., Chassagne, C., “Yield stress measurements of mud sediments using different rheological methods and geometries: An evidence of two-step yielding,” *Marine Geology*, Vol. 427, pp. 427-434, 2020.

[2] Vajravelu, K., Sreenadh, S., Devaki, P. and Prasad, K., "Mathematical model for a Herschel-Bulkley fluid flow in an elastic tube," *Open Physics*, vol. 9, no. 5, pp. 1357-1365, 2011.

[3] Caggioni, M., Trappe, V., Spicer, P. T., “Variations of the Herschel-Bulkley exponent reflecting contributions of the viscous continuous phase to the shear rate-dependent stress of soft glassy materials,” *Journal of Rheology*, vol. 64, pp. 413-422, 2020.

[4] Dinkgreve, M., Paredes, J., Denn, M. and Bonn, D., “On different ways of measuring “the” yield stress,” *Journal of Non-Newtonian Fluid Mechanics*, vol. 238, pp. 233-241, 2016.

[5] Jaworski, Z., Spychaj, T., Story, A. and Story, G., "Carbomer microgels as model yield-stress fluids," *Reviews in Chemical Engineering*, pp. 000010151520200016, 2021.