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Comparative study of correction methods of wall slip effects for CMC solutions

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ABSTRACT

In this paper, an experimental analysis has been carried out in order to characterize the rheological properties of non-Newtonian CMC fluids (carboxymethylcellulose CMC solutions). Two solutions at low and medium concentrations, respectively 0.5 and 1.5%, have been tested. A comparative study of the three methods proposed by Mooney, Wiegreffe, and Geiger has been carried out. It was found that the two solutions follow the rheological power-law model of Ostwald/de Waele-type for the studied experimental range. The diameter of the flow channel influences the rheological behavior of the CMC solution and highlights the wall slip effects. For a 0.5% concentration, the methods of Mooney and Wiegreffe could not be used as they gave results that could not be explained physically. However, for a 1.5% concentration, the three of them gave satisfactory results.

1. Introduction

The flow of complex fluids often shows wall effects because of the interaction between the particles and the solid boundary lines. These effects lead to inhomogeneous distributions of particles in the less viscous (solvent) fluid, which plays a role as lubricant. The analyses of rheological measurements do not take into account these fluid–wall interactions and then lead to erroneous results [1]. The wall slip depends on three parameters: the test conditions (shear stress at the wall, pressure and temperature), the fluid–wall contact (physicochemical fluid–wall interactions, roughness of the wall), the fluid composition and its rheological properties (viscosity, molecular structure, additives). This complex phenomenon is still an open topic for both its interpretation and quantification [2].

To find the real rheological law of the fluid, we must use the correction of walls effect. Several correction methods exist in the literature for the wall slip effects and the aim of the present work is to make a comparative study of the three methods of Mooney, Wiegreffe and of that of Geiger for CMC solutions at low concentration (0.5%) and a medium one (1.5%).

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Nomenclature

Q	Total volumetric flow rate (m^3/s)
R	Pipe radius (m)
V	Velocity (m/s)
h	Thickness of the flat die (m)
d	Capillary diameter (m)
L	Capillary length (m)
ΔP	Pressure drop (Pa)

Greek letters

$\dot{\gamma}$	Shear rate (s^{-1})
τ	Shear stress (Pa)

Subscripts

app	apparent
s	slip
ws	without slip
w	wall

2. Theory

The phenomenon is frequently encountered in various types of fluids among polymer solutions for which the wall slip is often an apparent slip effect resulting from the formation of a thin fluid wall layer with low viscosity, due to a preferential orientation of molecules or particles.

The slip of a real fluid on a solid wall can be defined by the existence of a tangential fluid velocity V_s, different from zero at the wall. Various authors tried to interpret this phenomenon.

According to Joshi et al. [3] for charged polymers, the wall slip mechanism looks more like a real slip: when the surface energy of the wall material is low, the wall slip mechanism appears by breaking the connections that link the macromolecular chains to the wall under the shear effect.

On the other hand, when the surface energy is high, there is a cohesive break by mess between the chains that are adsorbed at the wall and the linked chains. For concentrated suspensions, the wall slip resembles an apparent slip. This results in the formation of a thin layer of lubricating fluid on the wall.

Uhland [4] studies the phenomenon in cylindrical channels; he stipulates that the wall slip would be due to a thin layer on the wall. This layer is due to the migration of a low-viscosity product towards zones with strong gradients. The layer on the wall being more fluid, the energy dissipated during its shear is less important.

Different methods of quantification of wall slip exist [5–8]; the first one was proposed by Mooney in 1931. It is based on the fact that the relationship between stress and shear rate at the wall is independent of the geometry. The literature abounds in examples of application of this method for diverse mixtures, as shown in the papers of Kanu and Shaw [9], Karam [10,11], Jepsen and Räbiger [12], Boube et al. [13], Vergnes et al. [14], Mezry [15], Lanteri [16]. It assumes that the slip velocity V_s depends only on the single shear stress at the wall τ_w, and expresses the flow rate as the sum of two terms, as shown in Eq. (1):

$$Q = Q_s + Q_{ws} \tag{1}$$

The apparent shear rate is then given by Eq. (2):

$$\dot{\gamma}_{app} = A(\tau_w) + \frac{4V_s}{R} \tag{2}$$

By plotting $\dot{\gamma}_{app}$ versus $(\frac{1}{R})$ for a given stress τ_w, a straight line is obtained. Its intercept is $\dot{\gamma}_{ws}$ (the apparent shear rate with no slipping) and the slope $4V_s$. By repeating this procedure for different values of τ_w, one obtains a series of straight lines with the corresponding values of V_s and $\dot{\gamma}_{ws}$. Hence, one can deduce both the slip velocity and the corrected flow behavior of the fluid.

Wiegreffe [7] has modified the Mooney method by linking the slip velocity to the geometry. Assuming that $V_s = V_s(\tau_w, R)$, this is inversely proportional to the radius and one admits that the total volume rate is the sum of two components: the first one is due to the slip and the second one to the shear flow. The apparent shear rate is then written as:

$$\dot{\gamma}_{app} = A(\tau_w) + \frac{4a(\tau_w)}{R^2} \tag{3}$$

The apparent shear rate is then plotted as a function of R^{-2} and not against R.

Geiger assumes that the slip velocity depends not only on the stress, but also on the radius and agrees with the idea of Wiegreffe. He assumes that the apparent shear and the slip rates (with no apparent shear) $g(\tau_w)$ are connected by the relation:

$$\dot{\gamma}_{app} = g(\tau_w) \cdot f(h, \tau_w) \tag{4}$$

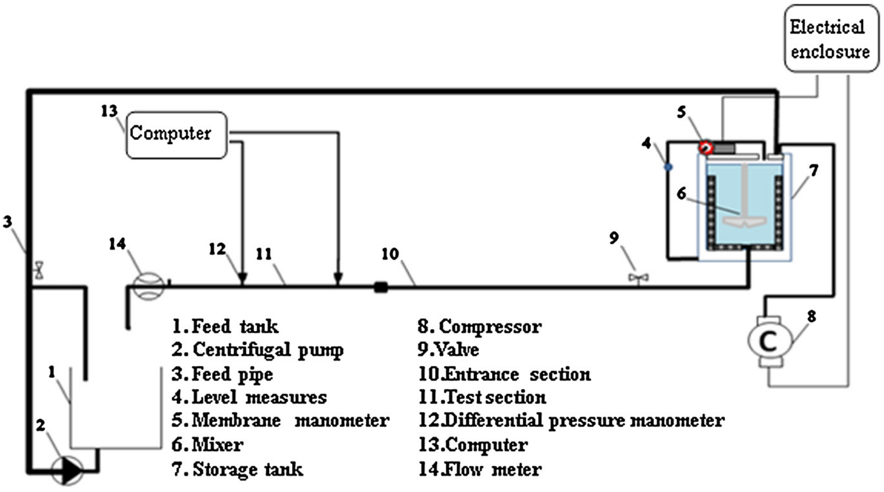

Fig. 1. (Color online.) Schematic diagram of the experimental setup.

Geiger assumes that the function f obeys an exponential law of h and τ_w:

$$f(h,\tau_w) = \exp\left[\frac{a(\tau_w)}{h}\right] \tag{5}$$

He developed a quantification method assuming that the total flow rate is the sum of the slip rate and the shear flow, written as a product of the shear rate by the function f depending on the thickness of the flat die h and the wall shear stress according to:

$$Q = Q_{ws} + Q_s = f(h,\tau_w)\cdot Q_{ws} = f(h,\tau_w)\cdot wh^2 g(\tau_w) \tag{6}$$

or in logarithmic form it becomes

$$\log(\dot{\gamma}_{app}) = \log\left[\frac{Q}{w\cdot h^2}\right] = \frac{f(h,\tau_w)}{h} + \log\big(g(\tau_w)\big) \tag{7}$$

For an imposed constraint at the wall, the plot $\log(\dot{\gamma}_{app})$ versus $f(\frac{1}{h})$ is a straight line whose slope is $f(h,\tau_w)$ and whose intercept with the $\log(\dot{\gamma}_{app})$ axis is $\log(g(\tau_w))$.

3. Experimental studies

To characterize the rheological properties of non-Newtonian fluids, we adopted a method based on the measurement of pressure drop and flow rate. The experimental set-up conceived for this purpose, which served as support for the present study, is illustrated in Fig. 1. It consists essentially of:

The storage bins up- and downstream, the fluid is thus aspirated from the upstream tank by a downstream pump unit equipped with a speed regulator toward the upstream tank with overpressure with respect to atmospheric pressure, a compressor, with circular horizontal pipes of different internal diameters (8, 10 and 12 mm) placed at the end of a 3-m-long cylindrical pipe, used to establish the flow regime. The test lines are equipped with pressure sensors for measuring pressure. Flow measurement is carried out by means of an electromagnetic flowmeter.

The solutions are prepared from carboxymethylcellulose (CMC) at pH 10.5 and degree of substitution 0.51, and are mixed slowly with gradually demineralized water under stirring for 2 h, in order to prelude the formation of aggregates and thus to ensure a good homogenization [17]. The aqueous samples of CMC solutions at 0.5 and 1.5% (wt%) remain unstirred for 24 h before use.

4. Results and discussion

The wall shear stress (τ_w) and the apparent wall shear rate ($\dot{\gamma}_{app}$) were obtained from Eqs. (8) and (9):

$$\tau_w = \frac{d}{4}\frac{\Delta P}{L} \tag{8}$$

$$\dot{\gamma}_{app} = \frac{32Q}{\pi d^3}\left(\frac{3n'+1}{4n'}\right) \tag{9}$$

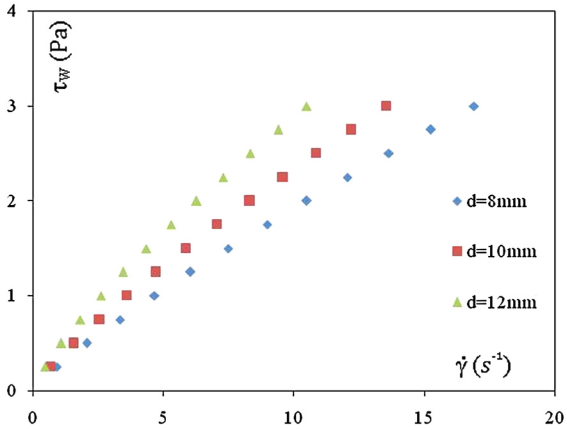

Fig. 2. (Color online.) Variation of the shear stress as a function of shear rate for a 1.5% CMC solution.

where Q is the volumetric flow rate, d the capillary diameter, L the capillary length, and ΔP the pressure drop between capillary ends. No corrections were applied to the flow data.

Where n' is not a real material (rheological) parameter, only an approximation parameter for further evaluation steps of the wall slip correction:

$$n' = \frac{\mathrm{d}\log(\frac{\Delta P}{L})}{\mathrm{d}\log Q} = \frac{\mathrm{d}(\log \tau_\mathrm{w})}{\mathrm{d}(\log \dot{\gamma}_\mathrm{app})} \tag{10}$$

4.1. Phenomenon of wall slip

For better understanding the wall slip phenomenon of CMC solutions over the concentrations ranges (0.5–1.5%) in flow inside cylindrical pipes, we studied the variation of the shear stress as a function of shear rate for different diameters of pipes. Fig. 2 reports the variation of the shear stress as a function of shear rate for a solution of 1.5% CMC at 24 °C.

From Fig. 2, one can describe the behavior of the CMC solution (1.5%) by an Ostwald/de Waele-type power-law model over the investigated range of shear rates. One also notes that the pipe diameter has an effect on the rheological behavior of the CMC solution. This dependence of the rheological behavior on the diameter of the flow highlights the effects of wall slip. To determine the actual rheological properties of the CMC solution, one must take into account the wall slip effects.

4.2. Correction of wall-slip effect

We have chosen three methods for quantifying the wall slip effects mentioned above, and applied them for low CMC (0.5%) and medium CMC concentrations (1.5%).

4.2.1. Method of Mooney

According to the Mooney method for quantifying the shift of the apparent viscosity curves, one can easily deduce the slip velocity and the apparent shear rate without wall slip, by plotting the apparent shear rate as a function of the reciprocal radius of the pipe at a constant wall shear stress τ_w for low (0.5%) and medium CMC concentrations (1.5%).

a. 0.5% CMC solution

The results of the Mooney examination are given in Fig. 3. It is helpful to outline from Fig. 3 that the Mooney method could not be used for the low CMC concentration (0.5%), because it gives a negative intercept with the ordinate axes, i.e. a negative shear flow, which is physically impossible.

b. 1.5% CMC solution

The results of the Mooney examination for a 1.5% CMC solution are given in Fig. 4. Unlike low-CMC-concentration solutions, the Mooney correction method could be used for a concentration of 1.5%.

We determine by linear regression the wall-slip velocity (slope) as well as the apparent shear rate (intercept with the apparent shear rate axis) without slipping. Therefore, one determines the real rheological behavior of CMC solutions and the results show only one rheological law for different diameters (Fig. 5, geometry-invariant flow curves).

4.2.2. Method of Wiegreffe

Wiegreffe assumes that the wall-slip velocity depends on the wall shear stress and on the pipe diameter and, in this way, on the geometry. Wiegreffe proposes to draw the shear stress as a function of the reciprocal square radius.

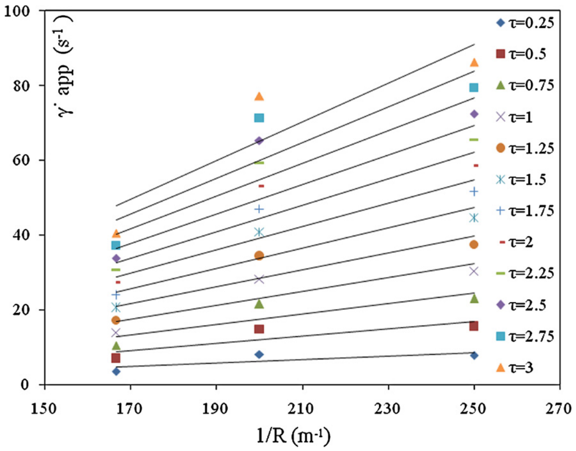

Fig. 3. (Color online.) Variation of apparent shear rate as a function of $1/R$ for a 0.5% CMC solution.

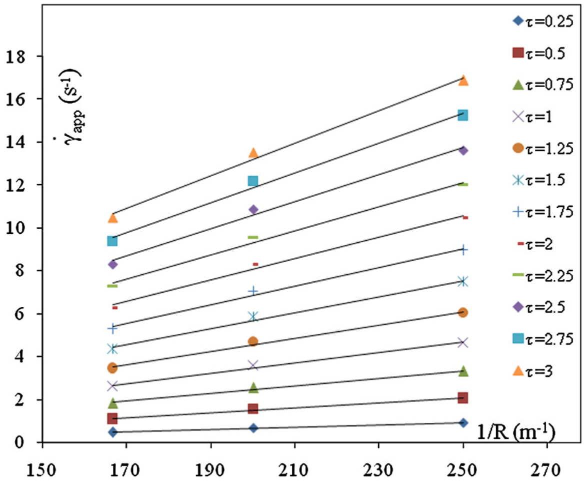

Fig. 4. (Color online.) Variation of apparent shear rate as a function of $1/R$ for a 1.5% CMC solution.

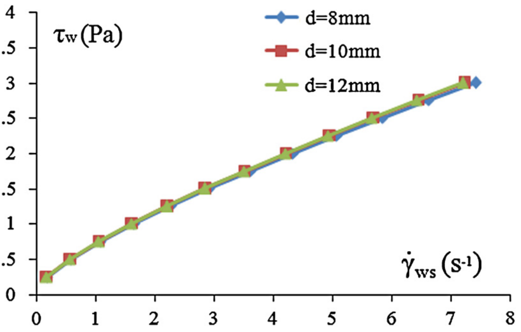

Fig. 5. (Color online.) Evolution of the wall shear stress as a function of corrected shear rate (with no slip) for a 1.5% CMC solution (according to the Mooney method).

a. 0.5% CMC solution

The results of the Wiegreffe examination for a 0.5% CMC solution are given in Fig. 6.

The same remark as for the Mooney correction is valid; this method cannot be applied because it gives negative corrected rates.

b. 1.5% CMC solution

The results for the concentrated CMC solution (1.5%) at 24 °C are shown in Fig. 7.

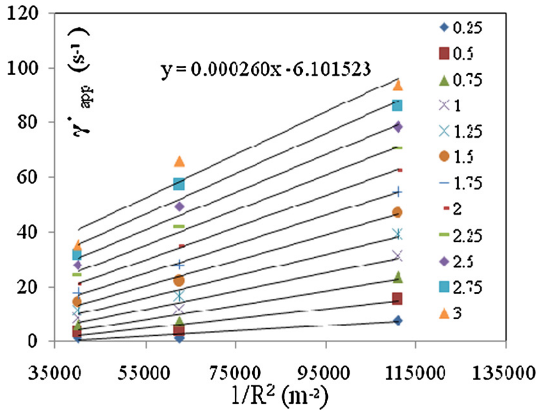

Fig. 6. (Color online.) Variation of apparent shear rate versus $(1/R^2)$ for a 0.5% CMC solution.

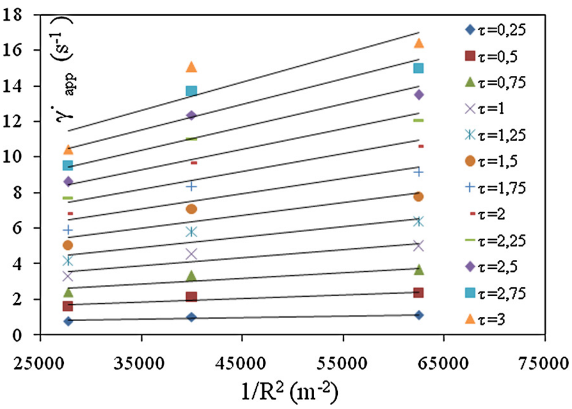

Fig. 7. (Color online.) Variation of apparent shear rate versus $(1/R^2)$ for a 1.5% CMC solution.

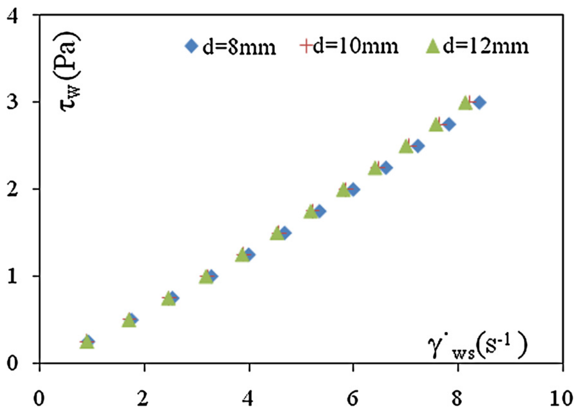

Fig. 8. (Color online.) Evolution of the wall shear stress as a function of the corrected shear rate (with no slip) for the 1.5% CMC solution, according to Wiegreffe's method.

The Wiegreffe variables are determined by a simple linear regression from the above results: $4a(\tau_w)$ is deduced from the slope, while $A(\tau_w)$ is obtained from the intercept with the ordinate axis. Taking into account the correction of the wall slip effects, the real rheological behavior of the CMC solution can be elucidated by applying the Wiegreffe treatment to the corrected experimental data. Fig. 8 shows the real rheological behavior of the CMC solution after correcting the wall slip effects.

4.2.3. Method of Geiger

Geiger has proposed a correction method that depends on the geometry, thus agreeing with the Wiegreffe method. Geiger assumes that the apparent shear rate and the wall shear stress τ_w are related by an exponential function. The plot $\ln(\dot{\gamma}_{app}) = f(\frac{1}{R})$ permits to determine the variables of the method, as shown in Fig. 9.

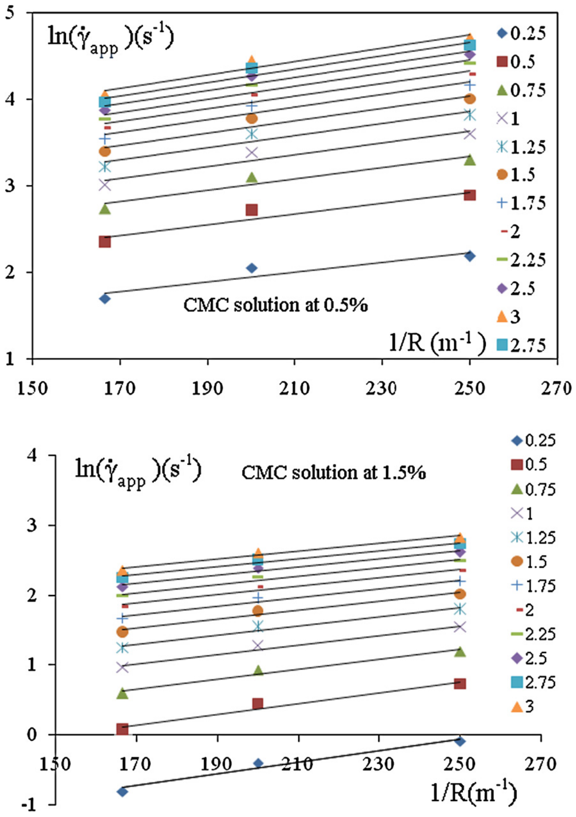

Fig. 9. (Color online.) Variation of the logarithm apparent shear rate versus ($1/R$) (Geiger method).

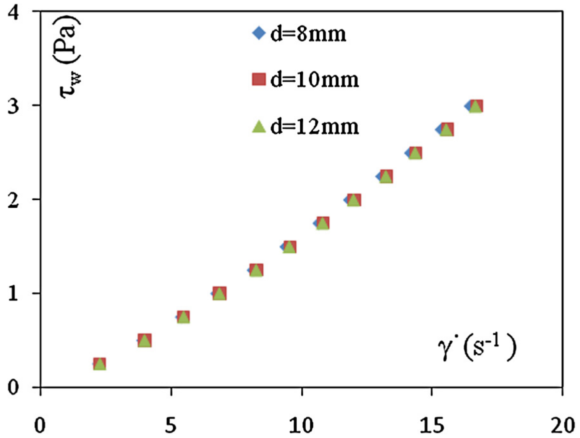

Fig. 10. (Color online.) Evolution of the wall shear stress as a function of the corrected shear rate (with no slip) for a 0.5% CMC solution, according to the Geiger method.

The Geiger variables: $f(\tau_w)$ and $\log(g(\tau_w))$ can be obtained on the basis of the above results, by a simple linear regression from the slope and the intercept with the ordinate axis of the $\ln(\dot{\gamma}_{app}) = f(\frac{1}{R})$ diagram.

Taking the correction of the wall slip effects into account, the rheological properties of the CMC solution can be elucidated by applying the Geiger treatment to the experimental data. The intercept of the straight lines with the ordinate of the $\ln(\dot{\gamma}_{app}) = f(\frac{1}{R})$ diagram leads to the apparent shear rate of the shear flow without wall slip. The evolution of the shear stress as a function of shear rate corrected for both studied CMC concentrations is given in Figs. 10 and 11.

From the above results, one can observe that the Geiger method is the only one that gave satisfactory results for the low concentration of CMC (0.5%).

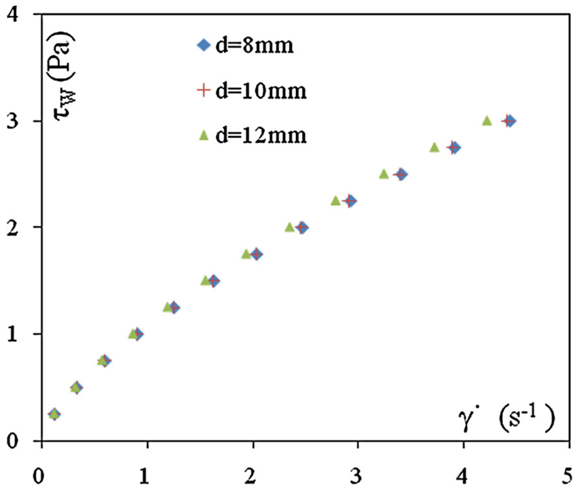

Fig. 11. (Color online.) Evolution of the wall shear stress as a function of the corrected shear rate (with no slip) for a 1.5% CMC solution according to the Geiger method.

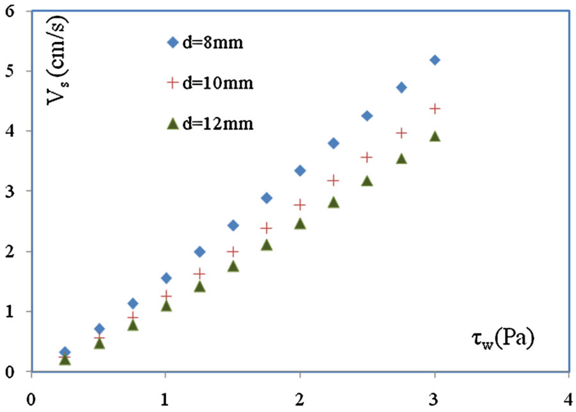

Fig. 12. (Color online.) Wall-slip velocity versus wall shear stress for a 1.5 wt% CMC content.

4.3. The wall-slip velocity function deduced by the method of Geiger

The wall-slip velocity according to Geiger is not only a function of the shear stress, but also of the diameter of the channels, as shown in Fig. 12.

From the previous figure, we notice that:

- wall-slip velocity consistently increased with increasing the wall shear stress and, at a constant wall shear stress, it increased with decreasing pipe diameter. As the diameter of the channels decreases, the surface area to volume ratio increases, implying that smaller channels have a relatively larger interfacial area, making them more pronounced to the slippage;
- wall-slip velocities are less sensitive to changes in pipe size, at low values of the shear stress; but when the shear stress increases, wall-slip velocities are more sensitive. It is possible that wall slippage was promoted by migration of the polymer molecules to the wall.

5. Conclusion

The aim of the present study is the real rheological characterization of carboxymethylcellulose solutions (CMC). The latter is determined through correcting the wall slip effects on the wall. Three methods of correction of the wall slip effects have been applied (methods of Mooney, Wiegreffe, and Geiger) for solutions of two concentrations (0.5% and 1.5%).

The two solutions follow an Ostwald/de Waele-type rheological power model in the studied shear rate range.

The findings also showed that the diameter of the flow channel has an effect on the rheological behavior of CMC, and that this dependence highlights wall-slip effects.

For a concentration of 0.5%, neither the Mooney method nor that of Wiegreffe could be used. They gave physically unexplainable results. On the other hand, for a concentration of 1.5%, the three methods gave satisfying results.

To our knowledge, no study in the literature was conducted on the comparison between the methods of corrections of the effects of slip, and on the application of these methods to two carboxymethylcellulose solutions of 0.5% and 1.5% concentrations.

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