Control of the effects of the concentration on the viscoelastic behavior of the aqueous Polyethylene-Oxide solution

N Lahlou¹, M Riahi¹, S Aniss¹, M Ouazzani Touhami¹

¹Laboratory of Mechanics, Faculty of Sciences Aïn-Chock, B.P.5366 Mâarif, Casablanca, Morocco.

E-mail: nouhalahlou10@gmail.com

Abstract. It is established that the rheological properties of polyethylene oxide solutions are related to the concentration, molecular weight, nature of the solvent, external stresses such as temperature and pressure and microstructural interactions. The main objective of this study is to carry out the effect of the concentration of aqueous PEO solutions on their rheological behavior. In this context, we consider quasi-stationary, transient and oscillatory flow regimes for three values of concentrations (250 ppm, 500 ppm and 1000 ppm). Except the case where the solution is Binghamian (250 ppm), we denote that for quasi-stationary mode, the observed behaviors correspond to a rheofluidifying fluids with yield stress. The model adapted from Rheowin Software is Herschel-Bulkley for which a yield stress and consistency increases and a flow index decreases when the concentration increases. The studies of these solutions under transient and subsequently under oscillating conditions are made to specify their viscoelastic properties. For a concentration less than 500 ppm the viscoelastic nature is described by the Maxwell model and by the Jeffrey model for a concentration of 1000 ppm. Otherwise, and for the oscillating test, the determination of the evolution of the critical frequency \( f_c \) (for which the conservation factor \( G' \) and the loss factor \( G'' \) are comparable) as a function of the concentration consolidates the actual control protocols of PEO aqueous solutions and allows to optimize the processes of their use in industrial environment.

1. Introduction

POLYOX Water-Soluble Resins are non-ionic poly (ethylene oxide) polymers. They are hydrophilic polymers available in a wide range of molecular weights and are supplied as white, free flowing powders. POLYOX offers a history of successful use in extended release applications, including osmotic pump technologies, packaging, construction, heavy industry, electrical and electronics, automotive and agriculture. Other applications include hydrophilic matrices, gastro-retentive dosage forms, tamper-resistant technologies and other drug delivery systems such as transdermal and muco-adhesive technologies [1]. POLYOX water-soluble resins provide a number of benefits including:

- Wide range of molecular weights for formulation flexibility
- Versatile application in direct compression and granulation
- Rapid hydration and swelling for use in osmotic pump technologies
- Fast hydration and gel formation for use in hydrophilic matrices
- Extreme hardness and virtually crush-proof for tamper-resistant technologies

Most of these solutions exhibit a complex rheological behavior associating their viscoelastic and thermal properties to their mechanical history as well as memory effects that result in thixotropic
behaviors. An earlier study [2], the viscosity of the solutions increases with the concentration of PEO and the flow curves obtained don’t exhibit a yield stress. Otherwise, the concentrations are considered to verify that G ‘and G” modules increase with the frequency [3]. The rheofluidifying character was confirmed by Bahlouli at al. [4] at different concentrations and the rheological parameters have been calculated from the Cross’s model. These conclusions are the results of many studies carried out [5].

In this work, we make a contribution to this study in order to better understand the rheological behavior of PEO aqueous solutions at low concentrations, mainly through the diversification of flow regimes.

2. Materials and Experimental Procedure

The tests are carried out with a Rheostress 1 Rheometer from Haake. It is a rotating rheometer operating at imposed speed and imposed stress, provided with several measuring cells. For our study, the coaxial cylinders cell called Z-41 is retained, and the samples used are solutions based on polyethylene oxide POE incorporated as a powder in distilled water. Three concentrations were prepared: 1000 ppm, 500 ppm and 250 ppm. The mixture is stirred through a rod rotating at a constant angular velocity for 24 hours.

It should be noted that each test is the result of the implementation of a procedure specified in the Rheowin software. This procedure is used to determine the nature and duration of the excitations imposed.

Firstly, the quasi-stationary tests are done to determine the yield stress of the prepared samples as well as their flow curves. The fluid is subjected to a constrained flow ramp imposed in a given range for a long time.

To carry out the viscoelastic properties, the solution is solicited by a sufficiently low stress (less than the yield stress to respect the linear behavior) for 5 min, this test allows to have a creep function of these solutions.

To complete the characterization of the viscoelastic behavior [3] (determination of the loss and conservation modules), oscillating mode tests were conducted.

3. Results and Discussion

3.1. In quasi-stationary mode

From the procedure mentioned above concerning the determination of the yield stress [5], Figure 1 shows the evolution of the deformation as a function of the shear stress, and Figure 2 represents two curves; (a) and (b) concerning respectively the rheograms of the PEO solution for different concentrations and the Variation of the viscosity in function of the shear rate.

![Figure 1](image-url)
Figure 2. Rheograms of the PEO solution for different concentrations (a), the variation of the viscosity in function of the shear rate (b)

According of these curves, the yields stress are other than zero for the three cases and they increasewith the concentrations (Figure 1). Moreover, for 250 ppm, the fluid has a constant viscosity, and for 500 ppm and 1000 ppm, the viscosities decrease with shear rate (Figure 2 (b)).

On the following table, we present the behavior law’s corresponding of these evolutions; it’s about a Bingham model for 250 ppm and Herschel-bulkley model for the other cases (Figure 2 (a)).

| Concentration | Rheological models | Model settings |
|---------------|--------------------|----------------|
| 1%            | $\tau = \tau_o + K \dot{\gamma}^n$ | $\tau_o = 1.832$ | K=0.9262 |
|               |                     | n=0.4996       |           |
| 0.5%          | $\tau = \tau_o + K \dot{\gamma}^n$ | $\tau_o = 1.441$ | K=0.578  |
|               |                     | n=0.5593       |           |
| 0.25%         | $\tau = \tau_o + \eta \dot{\gamma}$ | $\tau_o = 0.45$ | $\eta = 0.009$ |

3.2. In transient mode
The viscoelastic properties are determined from the different expressions of their creep function. For 250ppm, this function is an affine one (Figure 3 (a)) similar to that of a Maxwell fluid:

$$ f(t) = J_0 + \frac{1}{\eta_0} t . $$

Which has an instantaneous elasticity $J_0 = 3.404 \text{ Pa}^{-1}$, a viscosity $\eta_0 = 0.009 \text{ Pa.s}$, close to that obtained in quasi-stationary mode ($\eta_0 = 0.01 \text{ Pa.s}$), and a relaxation time $\lambda = J_0 \eta_0 = 0.034 \text{ s}$.

A behavior identical to this one is observed for a concentration of 500ppm where $J_0 = 0, 1789 \text{ Pa}^{-1}$, $\eta_0 = 0.38 \text{ Pa.s}$ and $\lambda = 0.0696 \text{ s}$.

For 1000 ppm (Figure 3 (b)), the creep function is approximated by:

$$ f(t) = J_0 + \frac{1}{\eta_0} t + J_1 \left(1 - e^{-t/\lambda_1}\right) ,$$

which corresponds to that of a fluid of Jeffrey. This has an instantaneous elasticity $J_0$, a delayed elasticity $J_1$, a delay time $\lambda_1$ and a relaxation time $\lambda_2 = J_1 \eta_1$. 
3.3. In Oscillation mode

To complete the description of the viscoelastic behavior, the evolutions of conservation modules $G'$ and loss $G''$ are presented for 500 ppm and 1000 ppm, and for a frequency range varying from 1 to 10 Hz (Figure 4).

According to the figure 4 (a), the loss factor is greater than the conservation factor across the frequency range. The solution then has a rather viscous character which becomes even more accentuated when the frequency is greater than a critical value, $f_c \approx 3.6$ Hz.

A behavior similar to this one is observed for a concentration of 500 ppm where $f_c \approx 4.6$ Hz as shown in Figure 4 (b).

4. Conclusion

In conclusion, we first confirm that these solutions behave as threshold fluids, as already noted [4] even at low concentrations furthermore all the rheological parameters are related to the concentrations. Otherwise, the evolution of the value of $f_c$, which corresponds to the case where $G'$ and $G''$ are comparable, is inversely proportional to the concentration. This last result consolidates the control protocols of aqueous solutions of Polyox oscillating regime and optimizes the processes of their use in industrial environment.
Acknowledgement
The research was conducted as a part of a PhD thesis at the laboratory of mechanics - Faculty of Science Aïn Chock University Hassan II Casablanca.

5. References
[1] Niedzwiedz K, et al. 2008 Macromolecules 41 (13) 4866
[2] Ebagninin K W, Benchabane A, Bekkour K 2009 Journal of Colloid and Interface Science 336 360
[3] Niedzwiedz K, Wischnewski, A, Pyckhout-Hintzen, W, Allgaier J, Richter D, Faraone A, 2008 Macromolecules 41 4866
[4] Bahlouli M I, Bekkour K, Benchabane A, Nemdili A 2011 Comportement thermo-rhéologique des solutions aqueuses de Polyéthylène Oxyde Institut de Mécanique des Fluides et des Solides. Université de Strasbourg-CNRS, Strasbourg, France
[5] Ortiz M, Kee D De, and Carreau P J, 1994 Journal of Rheology 38 (3) 519