EXPERIMENTAL INVESTIGATIONS AND MODELING OF EMULSIONS RHEOLOGY IN PRESENCE OF ADDITIVATED POLYMERS

Diana BROBOANA, Assoc. Prof.  
Department of Hydraulics  
“Politehnica” University of Bucharest

Daniela SUSAN-RESIGA, Assoc. Prof.  
Department of Physics  
“Politehnica” University of Timisoara

Corneliu BALAN*, Prof.  
Department of Hydraulics  
“Politehnica” University of Bucharest

*Corresponding author: Splaiul Independentei 313, 060032, Bucharest, Romania  
Tel.: (+40) 21 4029705, Fax: (+40) 21 4029865, Email: balan@hydrop.pub.ro

ABSTRACT

The paper is concerned with the experimental investigations of the rheological behavior of emulsions water-in-oil additivated with polymers. The probes used in experiments are based on two Romanian crude (pure) oils: probe A (PA) is an asphaltic crude oil with 30% water volumic concentration, respectively probe B (PB) is a paraffine crude oil with 6% water volumic concentration. Rheological characterisations of the samples are obtained at 5°C constant temperature, as function of polymers concentration (polymer NSF for probe PA, respectively polymer AF for probe PB). Creeping and oscillatory tests have been performed in order to characterise the rheology of the samples (i.e. dependences of viscosity and elasticity on the shear rate, respectively frequency) and to evidence the polymer concentration at which these rheological properties reach minimum values. The present experimental studies, performed for the first time in Romania, bring a better understanding of flow properties of Romanian oils and have a direct application in optimization of oil transport in pipes.

KEYWORDS

rheology, emulsion oil-water, viscoelasticity, creep flow, oscillatory test

NOMENCLATURE

\[ \dot{\gamma} \] [1/s] shear rate  
\[ \tau \] [Pa] shear stress

\[ \omega \] [1/s] oscillatory frequency  
\[ G' \] [Pa] elastic oscillatory modulus  
\[ G'' \] [Pa] viscous oscillatory modulus  
\[ \eta^* = \frac{\sqrt{G'^2 + G''^2}}{\omega} \] [Pas] dynamic viscosity  
\[ \eta(\dot{\gamma}) = \frac{\tau}{\dot{\gamma}} \] [Pas] shear viscosity function  
\[ \eta_0 = \lim_{\dot{\gamma} \to 0} \eta(\dot{\gamma}) \] [Pas] zero shear viscosity  
\[ \eta_\infty = \lim_{\dot{\gamma} \to \infty} \eta(\dot{\gamma}) \] [Pas] infinite shear viscosity  
\[ \rho \] [kg/m³] mass density  
\[ \lambda \] [s] shear thinning reciprocal rate  
\[ n \] [-] shear thinning exponent  
\[ a \] [-] constitutive constant

ABBREVIATIONS

PA probe A  
PB probe B  
NSF, AF polymers used as additives

1. INTRODUCTION

Emulsions oil-water are viscoelastic fluids which disclose a complex rheological behavior. The rheological properties of an emulsions at constant water concentration, temperature and pressure (e.g. viscosity, elasticity, thixotropic character) are mainly determined by two factors: (i) composition of the crude oil and (ii) the interfacial tension between oil and water (see for details [1, 2, 5]). In the presence of surfactants, in our case special designed polymer solutions, the interfacial tension is modified and, as consequence, the rheological properties of emulsions are changed, [6, 8].
The aim of the present study is to predict, for well defined water-in-oil emulsions and flow regime, the polymer solution concentration which determines the minimum viscosity and elasticity of the samples under investigations. The control and influence of rheological properties of oil-water emulsions are of great importance for the design of pipes transport oil systems. Viscosity of emulsions, in correlation to the flow regime (laminar or turbulent), determines the pressure loss in the pipes, therefore the necessary input power into the transport system of the oil.

The correlation of rheological properties with the flow regime, in order to minimize the energy for the oil transport in pipes, represents one of the major scientific target of today applied fluid mechanics. The present study is a premiere in Romania; it is a first step in understanding of a complex scientific problem with a very positive economical impact.

2. EXPERIMENTAL

The samples under investigations are water-in-oil emulsions, based on two Romanian crude (pure) oils: probe A (PA) is an asphaltic crude oil with 30% water volumic concentration, respectively probe B (PB) is a paraffine crude oil with 6% water volumic concentration.

Rheological characterisations of the samples are obtained at temperature of 5°C and normal pressure, as function of additive polymers concentration (polymer NSF for probe PA, respectively polymer AF for probe PB). For each oil-water emulsion were tested the influences on rheology of three polymer mass concentrations: $C_1 = 0.001\%$, $C_2 = 2C_1$, $C_3 = 4C_1$ (for PA & NSF), respectively: $C_1 = 0.0005\%$, $C_2 = 2C_1$ and $C_3 = 3C_1$ (for PB & AF).

Oscillatory, stressing and creeping tests have been performed in order to characterise the rheology of the samples (i.e. dependences of viscosity and elasticity on the shear rate, respectively frequency) using MC 300 and MC 1 Physica rheometers. The geometry for the tests were cone and plate (oscillatory tests on MC 300), double Couette geometry, for creeping tests on MC 1, respectively.

In Fig. 1 and Fig. 2 are presented the experimental results for PA, and in Fig. 3 and Fig. 4 are shown the corresponding experimental data for PB.

Comparison the variation of elastic oscillatory modulus $G'(\omega)$ for PA and PB probes with polymer additives, Fig. 1 and Fig. 3, put in evidence the qualitative and quantitative differences between samples. Evident, in both experiments the emulsions discloses at low frequencies higher values of elasticity than the pure oils, see also [1, 5]. But, since for PA $G'$ is generally increasing with the polymer concentration, for PB presence of polymer decreases the magnitude of $G'$.

![Probe A at 5°C](image)

Figure 1. Dependence $G'(\omega)$ for pure oil A, PA and PA additivated with NSF polymer (constant strain amplitude - 0.1).
Figure 2. Comparison between shear and oscillatory (dynamic) viscosity functions for PA and PA additivated with NSF polymer.

In the case of PA, the presence of polymer in low concentrations (C1 and C2) increases elasticity of the sample, which is based on a viscous fluid (pure oil) additivated with solid particles (asphalt). At higher concentration (i.e. C3) elasticity at low frequency is decreasing at the initial level of emulsion due the decreasing of asphalt particle relative motion within the viscoelastic fluid. At high oscillatory frequencies, \( \omega > 10 \text{ s}^{-1} \), the answers of all additivated samples disclose same elastic modulus, due to the dominant role of the particles motion against the polymer concentration.

Figure 3. Dependence \( G'(\omega) \) for pure oil B, PB and PB additivated with AF polymer (constant strain amplitude - 0.1).

Rheology of PB is dominated by paraffine network structure within the oil. The presence of polymer in PB determines the decrease of emulsion elasticity due the decrease of paraffine network strength in the presence of polymer. The decrease of \( G' \) with increasing frequency put also in evidence the fragile character of the paraffine network structure within the initial emulsion.

Emulsions are viscoelastic fluids for which complex viscosity is higher than shear viscosity, see Fig. 2 and Fig. 4, also [1, 5]. Both samples disclose a shear thinning character, more relevant for PB due the fragility of paraffine bonds. In the case of additivated probes, viscosity reach a minimum at concentration C2 (the non-monotonous variation of viscosity with increasing polymer concentration is characteristic for polymers which play the role of surfactant for the based fluid, [6, 8]).

Figure 4. Comparison between shear and oscillatory (dynamic) viscosity functions for PB and PB additivated with AF polymer.

It is also remarkable the existence of a local maximum in the viscosity function of the pure PB, see Fig. 4. The non-monotonous dependence of flow curve, respectively of viscosity function \( \eta(\dot{\gamma}) \), is an indication that PB might disclose a more complex rheological character (we are referring to thixotropy).

3. MODELLING

Rheological models for viscoelastic fluids are represented by time differential or integral equations, where the unknown function is the local extra-stress tensor, [5]. The main material functions which characterize their rheological behavior, viscosity and elasticity, are in general strain rate dependent (shear thinning or shear thickening character). Complex viscoelastic fluids (i.e. non-homogeneous fluids, multiphase fluids or fluids with chemical evolution) disclose, beside relaxation and recovery, thixotropy.

Thixotropy is a rheological behavior determined by the irreversible change of molecular structure due shearing. Thixotropy is relevant if viscosity is function not only by the strain rate, but also by the sign of the time strain rate gradient. In Fig. 5 and Fig. 6 are shown the results of a thixotropic test applied to our samples:
shear rate is increasing from 1 s\(^{-1}\) to 1000 s\(^{-1}\) and decreasing back to 1 s\(^{-1}\) in 1000 s (100 measured points). One can be observed that viscosity of sample PA is not dependent on the time gradient of \(\dot{\gamma}\): up and down flow curves are identical.

This is not the case for PB; thixotropy is remarkable for this sample, respectively the “down” flow curve is below the “up” flow curve.

\[
\frac{\eta - \eta_\infty}{\eta_\infty - \eta_0} = \left[1 + (\dot{\gamma})^n\right]^{\frac{1}{a-1}}.
\]

The material constants obtained by the fitting of experimental data with (1) are presented in Tab. 1.

<table>
<thead>
<tr>
<th>Probe</th>
<th>(\eta_0) [Pas]</th>
<th>(\eta_\infty) [Pas]</th>
<th>(\dot{\lambda}) [s]</th>
<th>(n) [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA</td>
<td>1.6</td>
<td>1.1</td>
<td>0.01</td>
<td>0.7</td>
</tr>
<tr>
<td>PAC1</td>
<td>1.0</td>
<td>0.09</td>
<td>2.6</td>
<td>0.13</td>
</tr>
<tr>
<td>PAC2</td>
<td>0.5</td>
<td>0.04</td>
<td>1.8</td>
<td>0.4</td>
</tr>
<tr>
<td>PAC3</td>
<td>1.0</td>
<td>0.03</td>
<td>7.9</td>
<td>0.6</td>
</tr>
</tbody>
</table>

The data from Tab. 1 discloses the qualitative and quantitative influences of the added polymer. The presence of polymer decreases the level of viscosity coefficients and increases the characteristic time in parallel with the increasing of shear thinning character (given by the decreasing of index \(n\)).

Of course, evolution of material coefficients from (1) is not monotonous. The fitting of experimental data with (1) and material coefficients from tab. 1 are represented in Fig. 7. The modeling of shear thinning character is found satisfactory, so we can approach the next step (much more difficult): representation of the elastic behavior making use of a differential constitutive relation. Due to the absence of thixotropy, the viscoelasticity of the sample is probably well described by an Oldroyd model with shear strain dependence of the material functions [1, 7]. A further near target of our work is to establish a complete rheological constitutive relation for PA; first results are expected to be obtained up to the end of 2004.

### 3.2. Rheological model for PB

The experiments disclose a more complex rheological behavior for PB, in comparison to PA.

The non-monotony of the flow curve and thixotropy, associated with the viscoelastic behavior, make from PB one of the most difficult fluid to be modeled. Actually, there are no constitutive relations able to model consistently all these macroscopic flow characteristics.

For a more general picture of PB sample, we have performed additional tests, some of them being presented in Fig. 8 and Fig. 9.

From Fig. 8 one can observe that increasing the polymer concentration, the thixotropic character is decreasing, simultaneous with the non-monotony of the flow curve.

In Fig. 9 is shown the influence of transitory regime on the non-monotony of the flow curve. There are represented four curves obtained at different test conditions, i.e. different slopes in time for the increasing
of the shear rate in the interval $[1, 1000]$ s$^{-1}$ (the experimental time for each measured point is different, from 1 s to 2000 s).

![Figure 7. Experimental and theoretical viscosity function for samples PA.](image)

Figure 7. Experimental and theoretical viscosity function for samples PA.

![Figure 8. Thixotropy test for PB and PB additivated with AF polymer. The thixotropy is decreasing with increasing the polymer concentration.](image)

Figure 8. Thixotropy test for PB and PB additivated with AF polymer. The thixotropy is decreasing with increasing the polymer concentration.

![Figure 9. Transitory and steady flow curve for PB](image)

Figure 9. Transitory and steady flow curve for PB

![Figure 10. Transitory and steady flow curve for PB (detail).](image)

Figure 10. Transitory and steady flow curve for PB (detail).

It is important to remark that the “time evolution” of flow curve has the tendency to reach assimptotically the “plateau” in the range $\dot{\gamma} \in (30,100)$ s$^{-1}$, see the detail from Fig. 10. This behavior suggests that PB might be described by a family of constitutive relation with non-monotonous flow curves, i.e. viscoelastic models which disclose intrinsic material instability, for details see [3, 4].

From our previous experience, the rheological modeling of samples which disclose thixotropy is a very complex problem and for a moment is not a goal for our research.

4. CONCLUSIONS

The paper presents an experimental investigation of the rheological behavior of emulsions in simple shear and oscillatory viscometric flows. The samples under investigation are water-in-oil emulsions based on two different Romanian oils. The samples are additivated with polymers to improve their flow
properties, respectively to decrease viscosity and elasticity, and consequently to limit the pressure loss during their transport in pipes.

The present study proposes an experimental procedure to test emulsions from rheological point of view.

The procedure implies the measurement of dynamic properties (elastic and viscous moduli) and shear viscosity dependence, not only on strain rate, but also on strain rate gradient in time.

The experimental investigations put in evidence similarities and differences between the two samples. Both samples disclose some general characteristics of emulsions: (i) relevant, but fragile, elasticity (see Fig. 1 and Fig. 3), (ii) shear thinning behavior, with differences between the dynamic viscosity and shear viscosity (see Fig. 2 and Fig. 4).

Probe PB has a strong thixotropic character, which offers important information about the internal network structure within the based oil (i.e. presence of paraffine).

The rheology of the samples are influenced by the presence of additives; using the test procedure for different polymer concentrations we are able to establish the amount of polymer necessary to be added for improving the transport properties of the oils.

One can conclude that the proposed experimental procedure has a wide range of applicability in optimization and control of rheological properties for different industrial fluids.

The experimental investigation on the samples rheology is just one aspect of our project. The aim of our work is to construct constitutive relations for the tested fluids, starting from experimental procedures based on viscometric and extensional motions. The data are then interpreted within the framework of constitutive relation theory and the final model is establish. An attempt in this direction was presented in §3 of the present paper.

One main target in our further study is to develop a special device and procedure to test emulsion in dominated extensional flows. Extensional rheological properties of viscoelastic fluids, especially emulsions, are of great interest for practical applications. Measuring and modelling extensional properties of viscoelastic fluids is a challenge for any research group working in rheology. It is also for us.

ACKNOWLEDGMENTS

The present work has been supported from the research contract “Politehnică” University of Bucharest – CCEPM no. 18/2003, beneficiary ICPT Câmpina. Experiments have been performed at REOROM Laboratory from “Politehnică” University of Bucharest and National Center for Engineering of Systems with Complex Fluids from “Politehnică” University of Timisoara.

REFERENCES

7. Macosko Ch. (1994) Rheology principles, measurements, and applications, VCH Publ. Inc., USA