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Review

Determination of the non-linear parameter (mobility factor) of the Giesekus constitutive model using LAOS procedure

Andreea Calin [a], Manfred Wilhelm [b], Corneliu Balan [c,*]

[a] Procter and Gamble, Brussels Innovation Center, Temselaan 100, 1853 Brussels, Belgium
[b] Institut für Technische und Polymerchemie, Karlsruhe Institute of Technology, 76128 Karlsruhe, Germany
[c] Reorom Laboratory, Hydraulics Department, "Politehnica" University of Bucharest, Splaiul Independentei 313, 060042 Bucharest, Romania

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ABSTRACT

The paper introduces a novel procedure to determine the non-linear parameter of the Giesekus model, in relation to the characterization of the non-linear oscillatory shear regime of viscoelastic polymer solutions based on polyacrylamide. Instead of using the shear-thinning viscosity as the representative non-linear effect, the third harmonic in the Fourier spectrum of the shear stress response signal is considered for computing the mobility factor. The fluid is subjected to large amplitude oscillatory shear (LAOS) and its response is recorded. Deviations of this signal from the sinusoidal form are specific to each material and gives both qualitative and quantitative measures of the non-linearity. By fitting the material response with the corresponding numerical solutions of the n-modes Giesekus constitutive relation, one can extract the values of the non-linear α_i-parameters that describe the fluid rheology. It is demonstrated that this procedure, which can be successfully applied to semi-concentrated polymer solutions, provides better results than the classical viscosity-fit method.

Contents

1. Introduction

The last decade brings a real progress in developing new measuring and material characterization procedures of complex fluids beyond the linear rheological behavior, through the corroboration of LAOS techniques with advanced data analysis, e.g. the application of the Fourier transformation in rheology.

The natural extension of oscillatory shear rheology in the linear regime is large amplitude oscillatory shear (LAOS). In LAOS experiments the fluids are subjected to large and finite oscillatory deformations, in which the response (oscillatory shear stress) is losing its pure single sinusoidal character (i.e. linearity) [1,2]. Oscillatory tests with large amplitude have been used for a long time as a technique to investigate the non-linearity in shear rheology [3,4], the earlier studies being mainly focused to the investigation of wall slip phenomena and the presence of possible yield stress with the material [5,6].

The straightforward application of the Fourier transformation in rheology is the characterization of complex fluids using the large oscillations measurements [7–9]. On the base FT-rheology, the post-process analysis and interpretation of the fundamental harmonics recorded in LAOS might be used as criteria for classifi-

* Corresponding author.
E-mail address: balan@daad-alumni.de (C. Balan).

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Table 1
Polyacrylamide – name, molecular weight, supplier, concentrations.

Name	Molecular weight (g/mol)	Producer	Concentrations (ppm weight)	Molecular weight distribution
0.01 M	10,000	Polysciences	50,000/100,000/250,000	Narrow
5 M	5,000,000	Polysciences	1000/5000/10,000	Narrow
9 M	9–11,000,000	BASF	500/1500/2500/5000/10,000/15,000	Broad
12 M	10–12,000,000	Roth	500/1500/2500/5000/10,000/15,000	Broad
18 M	18,000,000	Polysciences	250/500/750/1000/2000/3000/4000/5000/10,000/15,000	Narrow

cation of different behaviors in non-linear regime [10], respectively as method to distinguish the non-linear elasticity effects from dissipation associated to a given rheological state [11–13].

The relevance of the third harmonic (I_3) relative to the fundamental one (I_1), $I_{3/1} := I_3/I_1$, received a special attention [14], even though the elastic and viscous non-linearities cannot be unique separated exclusively from its intensity. For that reason a new non-linear coefficient has been introduced, $Q = I_{3/1}/{\gamma_0}^2$, which is more suitable to offer a base for a quantitative comparisons between experiments and simulations under non-linear oscillatory shear [15] (here γ_0 is the imposed strain amplitude).

LAOS procedure has the potential to disclose material properties associated to non-linear phenomena and/or structural characteristics of complex fluids, which are not accessible using classical rheometry. The application of LAOS has been useful for materials that exhibit strong non-linearities, e.g. dynamics of polymer solutions [15–17], flow of concentrated and diluted suspensions [18–21], biofluids characterization [22], non-linear soft materials [23], presence of yield stress within the viscoelastic behavior [24].

One main goal of the research in this area of rheology is to establish a consistent procedure to quantify and interpret the non-linearity observed in LAOS experiment. One attempt is based on the superposition of some well defined characteristic response functions of typical non-linear rheological effects, which are associated to the material response recorded during the particular LAOS experiments [25].

A different frameworks to interpret the LAOS measurements is proposed in [23], where the Chebyshev polynomials of the first kind are used as orthonormal basis functions to quantify elastic and viscous non-linearities. In this interpretation the third-order Chebyshev coefficients (instead of the $I_{3/1}$, as in FT-rheology) are used as "fingerprint" of the deviation from linear viscoelasticity, in association with the two-dimensional Pipkin diagrams.

The rheological response of different constitutive relations towards controlled LAOS deformations has been also explored, see for example [23,25]. Specifically, the simulations were directed to the modeling of the third harmonic (for fixed material parameters) and its dependence on the applied frequency and strain amplitude.

The present work is focused on the analysis of the Giesekus model [26–28] in LAOS experiments. The main goal is to establish a procedure to calculate the spectrum of the non-linear α_i-parameters (so-called mobility factors) from the experimentally measured $I_{3/1}$ harmonic, using as samples the polymer solutions [29].

The Giesekus model (defined by three material parameters plus the Newtonian viscosity) is one of the most versatile and used differential constitutive relation to model the non-linear viscoelastic behavior, both in shear and extension [27,28]. In the linear regime the answer of Giesekus is reduced to Jeffreys model (analogue representation as a Maxwell fluid in parallel with a Newtonian one), but it yields fair predictions of non-linearities as shear-thinning viscosity and extensional thickening when $\alpha > 0$ [30]. Of course, as any other models, the Giesekus differential constitutive relation has its limits, but is still considered one in the first choices for describing the rheology of polymer solutions. The Giesekus constitutive equation (or its n-modes extension) was also previously used as "test equation" to represent the LAOS tests [23,31], to model the behavior of complex fluids under imposed high oscillatory deformations [9,32], respectively for comparison with the other models [33,34].

The next chapter of the paper presents briefly the experiments performed on aqueous polyacrylamide solutions, the samples used in our work. Results from the dynamic measurements (linear and non-linear regimes) are presented. The corresponding relaxation spectra are computed and the analysis of LAOS data is presented in the framework of FT-rheology. The third chapter is dedicated to the analysis of Giesekus model in LAOS and to the presentation of the numerical procedure to determine the non-linear parameters of the n-mode Giesekus model, the calculations being performed using data from chapter 2. The results are discussed and analyzed in the concluding section.

2. Experimental

2.1. Samples and setup

The samples used in this study are aqueous polyacrylamide solutions (prepared with distilled water). Depending on the polymer molecular weight and concentration, the viscosity and elasticity of the solutions vary over a broad range. This variation is the reason for choosing polyacrylamide solutions specifically as test fluids in this work, since they provide ample possibilities for experimental investigations. Five molecular weights were used, three with narrow molecular weight distribution and two with broad molecular weight distribution, see Table 1. All measurements were performed at 21 °C. Various concentrations were investigated to characterize the influence of concentration on the overall rheology of the polymer solutions, from weakly elastic viscous liquids to highly viscoelastic fluids. The rheology of the samples have been completely characterized in shear and extensional flows using rotational and capillary rheometers, respectively the CaBER extensional rheometer, for details see [29,35].

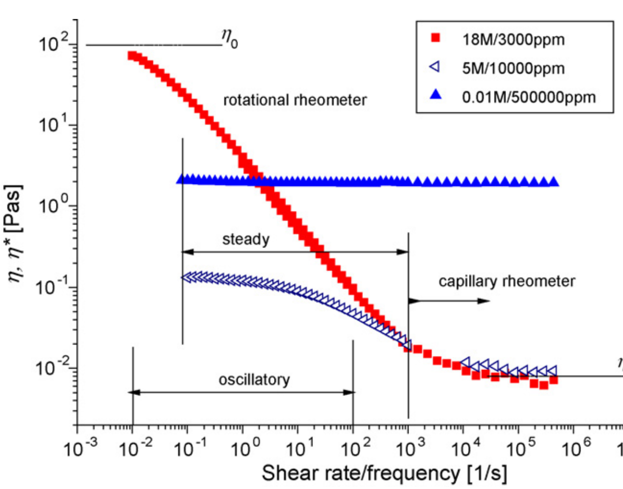

Fig. 1. Shear and complex viscosities of different polyacrylamide samples.