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Flexibility of three differential constitutive models evaluated by large amplitude oscillatory shear and Fourier transform rheology

Radek Pivokonsky*, Petr Filip, Jana Zelenkova

Institute of Hydrodynamics, Acad. Sci. Czech Rep., Pod Patankou 5, 166 12, Prague 6, Czech Republic

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ABSTRACT

Using Fourier transform rheology the Giesekus, exponential Phan-Tien and Tanner, and modified eXtended Pom-Pom constitutive models were examined in the non-linear regime represented by large amplitude oscillatory shear (LAOS) measurements. For the experiments a 5 wt% solution of poly(ethylene oxide) (molecular weight 1000 kg/mol) solved in dimethyl sulfoxide was used. The minimal number of harmonics required for an adequate reconstruction of the original raw time-stress signal was shown. An emphasis was paid to simultaneous consideration of the normalised stress magnitudes and the phases of individual harmonics in the fitting procedure adjusting the non-linear parameters of the studied constitutive models.

1. Introduction

Large amplitude oscillatory shear (LAOS) measurements range to the non-linear viscoelastic tests. The advantages of the LAOS test consist in its relatively simple analysis and in the possibility to apply the same devices (rotational rheometers) as in the case of measuring linear viscoelastic characteristics. Starting from the 60s' [1–3] with an application of the Bowditch-Lissajous plots, the LAOS technique consecutively attracted attention [4–6]. Simultaneously with the development (and accuracy) of the measurement technique, the LAOS analysis was based on more sophisticated approach concerning not only the new techniques [7–11] but also processing the 'classical' Bowditch-Lissajous plots [12–14]. These advances are described e.g. in the review paper [15].

As the LAOS measurements deal with a non-linear viscoelastic region, it gives also a possibility to evaluate efficiency of empirical, differential and integral constitutive models for various materials in this broader region. The traditional empirical models such as power law, Bingham, Herschel-Bulkley were analysed e.g. in Refs. [13,16]. Among more advanced constitutive models the following three have attracted most attention: the pom-pom model [17–21], the Giesekus model [16,22–25], and the Phan-Tien and Tanner model [26,27]. Applicability of the individual constitutive models strongly subjects to the materials for which the LAOS measurements are put into effect.

Recently, the Giesekus [28], exponential Phan-Tien-Tanner [29] and modified eXtended Pom-Pom [30] models were applied and their efficiency was compared [30–32] for low- and high-density PE materials in steady and transient shear and uniaxial elongational flows. Applicability of the Giesekus and PTT models for polymer solutions using LAOS technique was tested e.g. in the above sited references [23–25,27]. The aim of this contribution is to evaluate the predictions of the three models in large amplitude oscillatory shear (LAOS) for which as a testing material was chosen a 5 wt% solution of poly(ethylene oxide) in dimethyl sulfoxide. In applying Fourier transform rheology the same emphasis was simultaneously put both to the normalised stress magnitudes and to the phases of the individual harmonics generated by the original

* Corresponding author.
E-mail address: pivokonsky@ih.cas.cz (R. Pivokonsky).

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raw time-stress signal.

2. Experimental section

2.1. Material and preparation of polymer solutions

The samples used for the experiments were prepared as a 5 wt% solution of poly(ethylene oxide) (PEO) in dimethyl sulfoxide (DMSO). The chosen PEO (Sigma Aldrich, USA) has the molecular weight 1000 kg/mol. Dimethyl sulfoxide (Penta, Czech Republic) was used as a solvent due to its good solubility of PEO and also for low evaporation (boiling point of DMSO attains 189 °C). The samples were stirred by magnetic stirrer (Heidolph MR Hei-Tec, Germany) with the help of a teflon-coated magnetic bar at 60 °C for 24 h.

2.2. Rheological characterization of polymer solutions and data processing

A rotational rheometer Physica MCR 501 (Anton Paar, Austria) equipped with the Peltier control system (C-PTD200) using a cone-plate geometrical arrangement to ensure a uniform strain field (a diameter 50 mm/1°) was applied for the measurement of the linear viscoelastic properties at three different temperatures (35, 45, and 55 °C).

The master curve was calculated for 35 °C, and the relaxation spectrum used for fitting the Maxwell model is depicted in Fig. 1.

The large amplitude oscillatory shear properties were measured at 35 °C under frequency 0.2 Hz for strain attaining 40. In principle, the rheometer MCR 501 ranges to the class of stress-controlled rheometers (combined motor transducer system). Hence, a strain controlled regime is imitated by permanent recalculation of a chosen strain value. In this case a maximal error between required and real values reached 2.8%, a mean error value attained approximately 1%. Application of stress-controlled rheometers for LAOS measurements is discussed in Refs. [33,34].

First, the raw data obtained from the measurements were trimmed to the full periods (time window) as a misinterpretation can occur for the Fourier transformation calculated from a non-periodic signal (resulting in incorrectly obtained amplitude and more dispersed signal; for an inverse reconstruction of the signal, accurateness of both magnitude and phase is substantial). Further, the Fourier transformation was calculated with the help of the Matlab software (The MathWorks, Inc., USA).

3. Results

The raw data (trimmed to the full periods) obtained by large amplitude oscillatory shear measurements were processed by the Fourier transformation (determination of the magnitudes and phases for the individual harmonics). Consequently, the first 29 harmonics (i.e. up to 15th odd harmonic) were identified (presence of noise was negligible). Fig. 2 documents a reconstruction of the original raw signal (a thick line). The odd harmonics were successively added to the first approximation represented by first three harmonics (in fact, by the first and third harmonics as the even harmonics are completely negligible). It is apparent that a partial summation up to the 13th harmonic still exhibit a wavy character, and it is necessary to consider at least the first 15 harmonics for a corresponding sound approximation of the initial raw signal.

Efficiency of the individual harmonics or their sum does not subject to mere correspondence between the experimental and theoretical values ('zero-th' derivative) but especially to the courses of first and second derivatives, in other words, to compliance with increase and decrease, convexity and concavity of the experimental data. These tendencies were taken into account in evaluating a number of harmonics which sum satisfactorily characterizes a course of full raw signal. An algorithm of least mean squares was applied to 2000 points equally distributed within one period (5 s). This selected sample seems to be a good representative of the overall number 150,000 of measured points per one period. A limit 10^{-5} was taken as satisfactory for a relation Sum[($\tau_{\text{raw signal}}-\tau_{\text{appr}}$)^2]/2000 representing a mean of summation of square deviations of the normalised stresses of raw signal from summation of first two, three, etc. odd harmonics over the whole sample of 2000 points. The mean square deviations for first two odd harmonics (1–3), first three odd harmonics (1–5), (1–7), (1–9), (1–11), (1–13), and first eight odd harmonics (1–15) consecutively attained the values 7.6×10^{-3}, 2.2×10^{-3}, 7.5×10^{-4}, 1.8×10^{-4}, 7.7×10^{-5}, 2.3×10^{-5}, and 5.7×10^{-6}. At this step ($<10^{-5}$) the process was stopped.

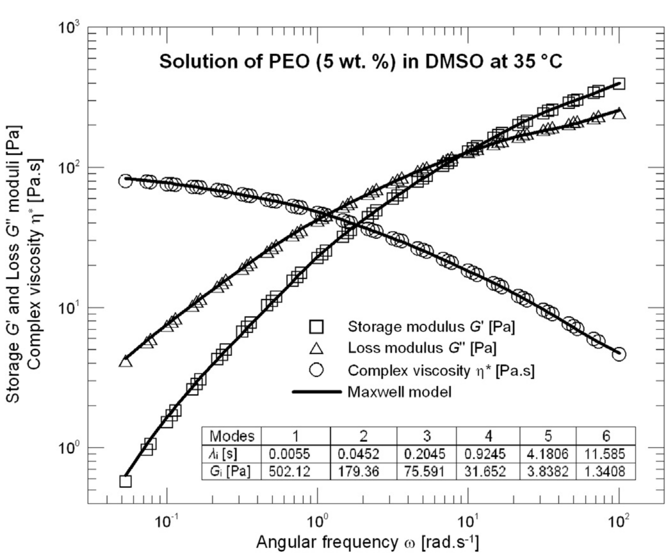

Fig. 1. Comparison between the Maxwell model fits and measured complex viscosity η^*, storage G' and loss G'' moduli.

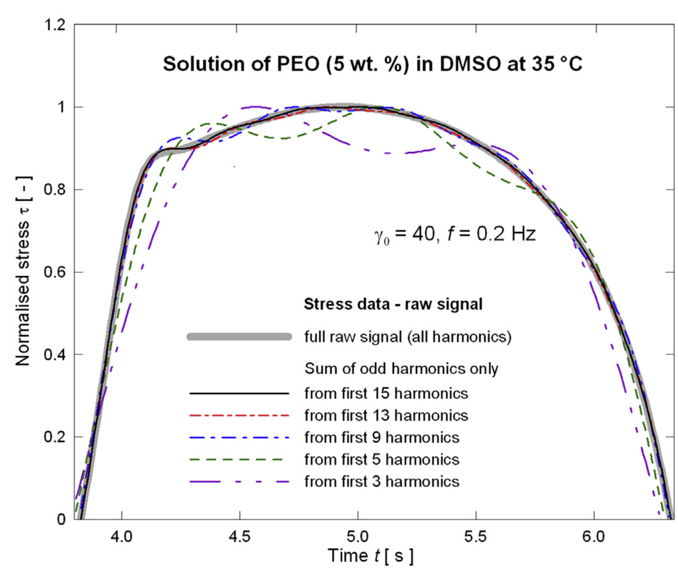

Fig. 2. A comparison between the normalised raw stress signal and the approximations represented by successive summation of the harmonics.

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