

## SIMPLE SCALAR MODEL AND ANALYSIS FOR LARGE AMPLITUDE OSCILLATORY SHEAR

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### ABSTRACT:

This work presents a simple, scalar model for predicting a nonlinear shear stress response of a viscoelastic fluid in Large Amplitude Oscillatory Shear (LAOS) experiments. The model is constructed by replacing the viscosity in the well-known Maxwell model by a shear rate dependent viscosity function. By assuming the empirical Cox-Merz rule to be valid, this shear rate dependent viscosity function is specified based on the Maxwell expression for the complex viscosity. We thus construct a particular case of the White-Metzner constitutive equation. Numerical solutions as well as an asymptotic analytical solution of the model are presented. The results, analyzed for higher harmonic content by Fourier transform, are compared to experimental data of a viscoelastic solution of wormlike micelles based on cetyltrimethylammonium bromide. Good agreement is found for low frequencies, where viscous properties dominate.

### KEY WORDS:

Large Amplitude Oscillatory Shear (LAOS), constitutive modeling, Cox-Merz rule, Maxwell model, non-linear rheology, worm-like micelles

## 1 INTRODUCTION

Nonlinear viscoelasticity plays a crucial role for the mechanical behavior of complex fluids (e.g. polymer melts, polymer solutions, and dispersions) under many processing and application conditions. The use of Large Amplitude Oscillatory Shear (LAOS) experiments, where a sample is subjected to a sinusoidal shear deformation  $\gamma(t) = \gamma_0 \sin(\omega t)$  has become a common technique to probe nonlinear viscoelasticity of materials [1–6]. Its main advantage is the possibility to investigate the effect of both characteristic dynamic variables, the Deborah number  $De$  and the Weissenberg number  $Wi$  using the same test with the most common rheological equipment, a rotational rheometer. The Deborah number  $De = \lambda/\tau_d$  is defined as the ratio of a characteristic relaxation time of a material  $\lambda$  and a characteristic time of observation  $\tau_d$ , which for oscillatory flow is the inverse of the angular frequency  $\tau_d = 1/\omega$ . This  $De$  measures to which degree elastic effects influence the

overall mechanical response. The Weissenberg number  $Wi = \lambda/\tau_d$  is the ratio of  $\lambda$  and a characteristic time of the deformation  $\tau_d$ . For steady shear  $\tau_d$  is the inverse of the shear rate  $\tau_d = 1/\dot{\gamma}$  whereas for oscillatory shear  $\tau_d = 1/\dot{\gamma}_0 = 1/(\omega\gamma_0)$  [7], where  $\dot{\gamma}_0$  denotes the shear rate amplitude. The Weissenberg number can be interpreted as a dimensionless shear rate, indicating the influence of nonlinear behavior. Further advantages of using LAOS to probe nonlinear viscoelasticity include the omission of sudden signal jumps in the strain input, as in step experiments, and the ability to probe large strain rates without edge failure [8].

Recent efforts in constitutive modeling of LAOS behavior have led to approximate solutions that provide material functions for a couple of nonlinear models. Whereas some of these are truncated expansions in the shear rate amplitude (corotational Maxwell [9]), or in the shear strain amplitude (Giesekus [10] and Pom-Pom [11]). Others are asymptotic solutions, such as the molecular stress function model [12, 13] and a thixotropic

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Equation A.26 shows that the  $De$  dependence of  $Q_o$  is quadratic for small  $De$ , whereas the asymptotic limit for large  $De$  is a linear function of  $De$ :

$$\lim_{De \rightarrow 0} Q_o = \frac{(1-c)}{24} De \quad (\text{A.27})$$

Combining Equations A.26 and A.27 results in Equation A.28, which captures both limiting behaviors.

$$Q_{o,a} = \frac{(1-c)}{8} \frac{De^2}{(1+3De)} \quad (\text{A.28})$$

The approximate function  $Q_{o,a}$  has then the form of Equation 16 but is inexact in comparison to Equation A.26 around  $De = 1$ .

## REFERENCES

- [1] Dodge JS, Krieger IM: Oscillatory shear of nonlinear fluids I. Preliminary investigation, *Trans. Soc. Rheol.* 15 (1971) 589–601.
- [2] Pearson DS, Rochefort WE: Behavior of concentrated polystyrene solutions in large amplitude oscillating shear fields, *J. Polym. Sci., Part B: Polym. Phys.* 20 (1982) 83–98.
- [3] Giacomin AJ, Jeyaseelan RS: A constitutive theory for polyolefins in large amplitude oscillatory shear, *Polym. Eng. Sci.* 35 (1995) 768–777.
- [4] Giacomin AJ, Dealy JM: Using large-amplitude oscillatory shear, in *Rheological Measurement*, Kluwer Academic Publishers, Dordrecht, Netherlands (1998).
- [5] Wilhelm M: Fourier-transform rheology, *Macromol. Mater. Eng.* 287 (2002) 83–105.
- [6] Hyun K, Wilhelm M, Klein CO, Cho KS, Nam JG, Ahn KH, Lee SJ, Ewoldt RH, McKinley GH: A review of nonlinear oscillatory shear tests: Analysis and application of large amplitude oscillatory shear (LAOS), *Prog. Polym. Sci.* 36 (2011) 1697–1753.
- [7] Dealy JM: Weissenberg and Deborah numbers - Their definition and use, *Rheol. Bull.* 79 (2010) 14–18.
- [8] Blackwell BC, Ewoldt RH: A simple thixotropic-viscoelastic constitutive model produces unique signatures in large-amplitude oscillatory shear (LAOS), *J. Non-Newton. Fluid. Mech.* 208–209 (2014) 27–41.
- [9] Giacomin AJ, Bird RB, Johnson LM, Mix AW: Large-amplitude oscillatory shear flow from the corotational Maxwell model, *J. Non-Newton. Fluid. Mech.* 166 (2011) 1081–1099.
- [10] Gurnon KA, Wagner NJ: Large amplitude oscillatory shear (LAOS) measurements to obtain constitutive equation model parameters: Giesekus model of banding and nonbanding wormlike micelles, *J. Rheol.* 56 (2012) 333–351.
- [11] Hoyle DM, Auhl D, Harlen OG, Barroso VC, Wilhelm M, McLeish TCB: Large amplitude oscillatory shear and Fourier transform rheology analysis of branched polymer melts, *J. Rheol.* 58 (2014) 969–997.
- [12] Wagner M, Rolón-Garrido VH, Hyun K, Wilhelm M: Analysis of medium amplitude oscillatory shear data of entangled linear and model comb polymers, *J. Rheol.* 55 (2011) 495–516.
- [13] Abbasi M, Ebrahimi NG, Wilhelm M: Investigation of the rheological behavior of industrial tubular and autoclave LDPEs under SAOS, LAOS, transient shear, and elongational flows compared with predictions from the MSF theory, *J. Rheol.* 57 (2013) 1693–1714.
- [14] Saengow C, Giacomin AJ, Kolitawong C: Exact Analytical solution for large-amplitude oscillatory shear flow, *Macromol. Theory Simul.* 24 (2015) 352–392.
- [15] Boisly M, Kästner M, Brummund J, Ulbricht V: Large amplitude oscillatory shear of the Prandtl element analysed by Fourier transform rheology, *Appl. Rheol.* 24 (2014) 35478.
- [16] Hyun K, Wilhelm M: Establishing a new mechanical nonlinear coefficient  $Q$  from FT Rheology: First investigation of entangled linear and comb polymer model systems, *Macromolecules* 42 (2009) 411–422.
- [17] Reinheimer K, Gross M, Hetzel F, Kübel J, Wilhelm M: Fourier transform rheology as an innovative morphological characterization technique for the emulsion volume average radius and its distribution, *J. Colloid Interface Sci.* 380 (2012) 201–212.
- [18] Giacomin AJ, Bird RB, Johnson LM, Mix AW: Corrigenda: Large-amplitude oscillatory shear flow from the corotational Maxwell model [J. Non-Newtonian Fluid Mech. 166, 1081–1099 (2011)], *J. Non-Newton. Fluid. Mech.* 187–188 (2012) 48–48.
- [19] Ewoldt RH: Defining nonlinear rheological material functions for oscillatory shear, *J. Rheol.* 57 (2013) 177–195.
- [20] Bharadwaj NA, Ewoldt RH: Constitutive model fingerprints in medium-amplitude oscillatory shear, *J. Rheol.* 59 (2015) 557–592.
- [21] Ewoldt RH, Hosoi AE, McKinley GH: New measures for characterizing nonlinear viscoelasticity in large amplitude oscillatory shear, *J. Rheol.* 52 (2008) 1427–1458.
- [22] Rogers SA, Erwin BM, Vlassopoulos D, Cloitre M: A sequence of physical processes determined and quantified in LAOS: application to a yield stress fluid, *J. Rheol.* 55 (2011) 435–458.
- [23] Giacomin AJ: A sliding plate melt rheometer incorporating a shear stress transducer, Ph.D. thesis, McGill University (1987).
- [24] White JL, Metzner AB: Development of constitutive equations for polymeric melts and solutions, *J. Appl. Polym. Sci.* 7 (1963) 1867–1889.
- [25] Dealy JM, Larson RG: Structure and rheology of molten polymers, Hanser, Munich (2006).
- [26] Morrison FA: Understanding rheology, Oxford University Press, New York (2001).
- [27] Malkin A: Non-Newtonian viscosity in steady-state shear flows, *J. Non-Newton. Fluid.* 192 (2013) 48–65.
- [28] Zacharatos A, Kontou E: Nonlinear viscoelastic modeling of soft polymers, *J. Appl. Polym. Sci.* 132 (2015) 42141.
- [29] Bird RB, Armstrong RC, Hassager O: Dynamics of polymeric liquids, John Wiley & Sons, New York (1987).
- [30] Monsia MD: A simplified nonlinear generalized Maxwell model for predicting the time dependent behavior of viscoelastic materials, *World J. Mech.* 1 (2011) 158–167.

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<http://www.appliedrheology.org>

- [31] Herrchen M, Öttinger HC: A detailed comparison of various FENE dumbbell models, *J. Non-Newton. Fluid.* 68 (1997) 17–42.
- [32] Kökut Z, Völker-Pop L, Brandstätter M, Kokavec J, Ailer P, Palkovics L, Szabó G, Czirák A: Exploring the nonlinear viscoelasticity of a high viscosity silicone oil with LAOS, *Appl. Rheol.* 26 (2016) 14289.
- [33] Yasuda K, Armstrong R, Cohen R: Shear flow properties of concentrated solutions of linear and star branched polystyrenes, *Rheol. Acta* 20 (1981) 163–178.
- [34] Cross MM: Polymer systems: Deformation and flow, Macmillan (1968).
- [35] Cox WP, Merz EH: Correlation of dynamic and steady flow viscosities, *J. Polym. Sci.* 28 (1958) 619–622.
- [36] Snijkers F, Vlassopoulos D: Appraisal of the Cox-Merz rule for well-characterized entangled linear and branched polymers, *Rheol. Acta* 53 (2014) 935–946.
- [37] Merger D: Large amplitude oscillatory shear investigations of colloidal systems: experiments and constitutive model predictions, Ph.D. thesis, Karlsruhe Institute of Technology (2015).
- [38] Khatory A, Lequeux F, Kern F, Candau SJ: Linear and nonlinear viscoelasticity of semidilute solutions of wormlike micelles at high salt content, *Langmuir* 9 (1993) 1456–1464.
- [39] Rehage H, Hoffmann H: Viscoelastic surfactant solutions: Model systems for rheological research, *Mol. Phys.* 74 (1991) 933–973.
- [40] Mair RW, Callaghan PT: Observation of shear banding in worm-like micelles by NMR velocity imaging, *Europhys. Lett.* 36 (1996) 719–724.
- [41] Britton MM, Callaghan PT: Two-phase shear band structures at uniform stress, *Phys. Rev. Lett.* 78 (1997) 4930–4933.
- [42] Salmon JB, Colin A, Manneville S: Velocity profiles in shear-banding wormlike micelles, *Phys. Rev. Lett.* 90 (2003) 228303.
- [43] Berret JF: Rheology of wormlike micelles: Equilibrium properties and shear banding transitions, in Molecular gels, Springer (2006).
- [44] Helgeson ME, Reichert MD, Hu YT, Wagner NJ: Relating shear banding, structure, and phase behavior in worm-like micellar solutions, *Soft Matter* 5 (2009) 3858–3869.
- [45] Helgeson ME, Vasquez PA, Wagner NJ: Rheology and spatially resolved structure of cetyltrimethylammonium bromide wormlike micelles through the shear banding transition, *J. Rheol.* 53 (2009) 727–756.
- [46] Ewoldt RH, Winter P, Maxey J, McKinley GH: Large amplitude oscillatory shear of pseudoplastic and elastoviscoplastic materials, *Rheol. Acta* 49 (2010) 191–212.
- [47] Giacomin AJ, Bird RB, Aumate C, Mertz AM, Schmalzer AM, Mix AW: Viscous heating in large-amplitude oscillatory shear flow, *Phys. Fluids* 24 (2012) 103101.
- [48] Dealy JM, Petersen JF, Tee, TT: A concentric-cylinder rheometer for polymer melts, *Rheol. Acta* 12 (1973) 550–558.
- [49] Tee TT, Dealy JM: Nonlinear viscoelasticity of polymer melts, *Trans. Soc. Rheol.* 19 (1975) 595–615.
- [50] Rouyer F, Cohen-Addad S, Höhler R, Sollich P, Fielding SM: The large amplitude oscillatory strain response of aqueous foam: Strain localization and full stress Fourier spectrum, *Eur. Phys. J. E* 27 (2008) 309–321.
- [51] Ewoldt RH, Bharadwaj NA: Low-dimensional intrinsic material functions for nonlinear viscoelasticity, *Rheol. Acta* 52 (2013) 201–219.
- [52] Klein C, Spiess HW, Calin A, Balan C, Wilhelm M: Separation of the nonlinear oscillatory response into a superposition of linear, strain hardening, strain softening, and wall slip response, *Macromolecules* 40 (2007) 4250–4259.
- [53] Wilhelm M, Maring D, Spiess HW: Fourier-transform rheology, *Rheol. Acta* 37 (1998) 399–405.
- [54] Giacomin AJ, Gilbert PH, Merger D, Wilhelm M: Large-amplitude oscillatory shear: comparing parallel-disk with cone-plate flow, *Rheol. Acta* 54 (2015) 263–285.
- [55] Leblanc JL: Filled Polymers – Science and industrial applications, CRC Press, Boca Raton (2010).
- [56] Brader JM, Siebenbürger M, Ballauff M, Reinheimer K, Wilhelm M, Frey SJ, Weysser F, Fuchs M: Nonlinear response of dense colloidal suspensions under oscillatory shear: Mode-coupling theory and Fourier transform rheology experiments, *Phys. Rev. E* 82 (2010) 061401.
- [57] Kim J, Merger D, Wilhelm M, Helgeson ME: Microstructure and nonlinear signatures of yielding in a heterogeneous colloidal gel under large amplitude oscillatory shear, *J. Rheol.* 58 (2014) 1359–1390.
- [58] Payne AR: The dynamic properties of carbon black-loaded natural rubber vulcanizates, *J. Appl. Polym. Sci.* VI (1962) 57–63.
- [59] Allegra G, Raos G, Vacatello M: Theories and simulations of polymer-based nanocomposites: From chain statistics to reinforcement, *Prog. Polym. Sci.* 33 (2008) 683–731.
- [60] Pipkin AC: Lectures in viscoelastic theory, Springer (1972).
- [61] Hyun K, Kim W, Park SJ, Wilhelm M: Numerical simulation results of the nonlinear coefficient Q from FT-Rheology using a single mode pom-pom model, *J. Rheol.* 57 (2013) 1–25.
- [62] Bharadwaj NA, Ewoldt RH: The general low-frequency prediction for asymptotically nonlinear material functions in oscillatory shear, *J. Rheol.* 58 (2014) 891–910.
- [63] Bird RB, Giacomin AJ, Schmalzer AM, Aumate C: Dilute rigid dumbbell suspensions in large-amplitude oscillatory shear flow: Shear stress response, *J. Chem. Phys.* 140 (2014) 074904.
- [64] Czep MA, Abbasi M, Heck M, Wilhelm M: Effect of molecular weight, polydispersity and monomer of linear homopolymer melts on the intrinsic mechanical nonlinearity  ${}^3Q_0(\omega)$  in MAOS, *Macromolecules* 49 (2016) 3566–3579.
- [65] Nam JG, Ahn KH, Lee SJ, Hyun K: First normal stress difference of entangled polymer solutions in large amplitude oscillatory shear flow, *J. Rheol.* 54 (2010) 1243–1266.
- [66] Yesilata B, Clasen C, McKinley GH: Nonlinear shear and extensional flow dynamics of wormlike surfactant solutions, *J. Non-Newtonian Fluid Mech.* 133 (2006) 73–90.
- [67] Buchanan M, Atakhorrami M, Palierne JF, MacKintosh FC, Schmidt CF: High-frequency microrheology of worm-like micelles, *Phys. Rev. E* 72 (2005) 011504.
- [68] Cates ME, Candau SJ: Statics and dynamics of worm-like surfactant micelles, *J. Phys.: Condens. Matter* 2 (1990) 6869–6892.



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