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High-frequency Rheology of a High Viscosity Silicone Oil Using Diffusing Wave Spectroscopy

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Abstract:
Measurements and modeling of rheological properties of a high viscosity silicone oil (polydimethylsiloxane, PDMS) at high frequency are reported. The linear viscoelastic properties are measured by small amplitude oscillation shear (SAOS) tests with a rotational rheometer. Furthermore, Diffusing Wave Spectroscopy (DWS) is used, which expands the angular frequency range of the measured loss and storage moduli up to 10^5 rad/s, in a temperature range of 20 - 70°C. Good agreement between both methods is found in the overlapping frequency region, especially at higher temperatures. The DWS data show that the elastic modulus stays dominant and increases with frequency, without a second cross-over point up till 10^8 rad/s. Flow curves, measured with rotational and with capillary rheometry up to a shear rate of $7.6 \cdot 10^4$ s^{-1}, show shear thinning behavior, which implies nonlinear viscoelasticity. Comparison of the dynamic and complex viscosity shows that the Cox-Merz rule is valid in a frequency range spanning six orders of magnitude. A multi-element White-Metzner model is proposed as a constitutive equation, which accurately describes the nonlinear viscoelastic properties, including the decrease of the loss and storage moduli during amplitude sweeps in oscillatory shear measurements.

Key words: high frequency microrheology, Diffusing Wave Spectroscopy, PDMS, Cox-Merz rule, White-Metzner model

1 INTRODUCTION

Silicone oils (polydimethylsiloxane, PDMS) have multiple application areas ranging from fundamental research and applied sciences to many branches of modern industry [1, 2]. In particular, PDMS is frequently used in polymer science and materials science for its interesting rheological properties, e.g. as matrix fluid in suspensions [3 – 6] and colloidal dispersions [7], or as a component of polymer blends [8, 9]. PDMS is also a popular test material for new rheological theories [10], and for novel measuring methods and devices [11]. Some rheometer manufacturers use PDMS also as calibration liquids [12]. To optimize the use of silicone oils for fundamental research or industrial applications, it is crucial to have a good description of their rheological properties over a large frequency range. However, for high viscosity silicone oils, reliable data at high frequencies is often lacking.

Previous works on the rheology of pure silicone oils study samples with zero-shear viscosities in the 10 – 50 Pas range or below [2, 13]. Only a few papers consider silicone oils with much higher viscosities [14, 15]. A detailed investigation of shear thinning [16] and a thorough analysis of the relaxation times [17] in high viscosity PDMS give valuable information about their rheological properties within the measurement range of conventional rotational rheometers. There are only few methods available to study rheological behavior beyond 100 Hz. For a recent review on high frequency mechanical and optical rheometry techniques [18]. Regarding high viscosity PDMS, an ultrasound-based technique was successfully applied to samples of 100 and 500 Pas zero shear viscosity, and a second crossover of the loss and storage moduli was found between $10^6 – 10^7$ Hz [19]. One of the few high frequency rheometry techniques is Diffusing Wave Spectroscopy (DWS) [20, 21]. For transparent materials such as PDMS, DWS

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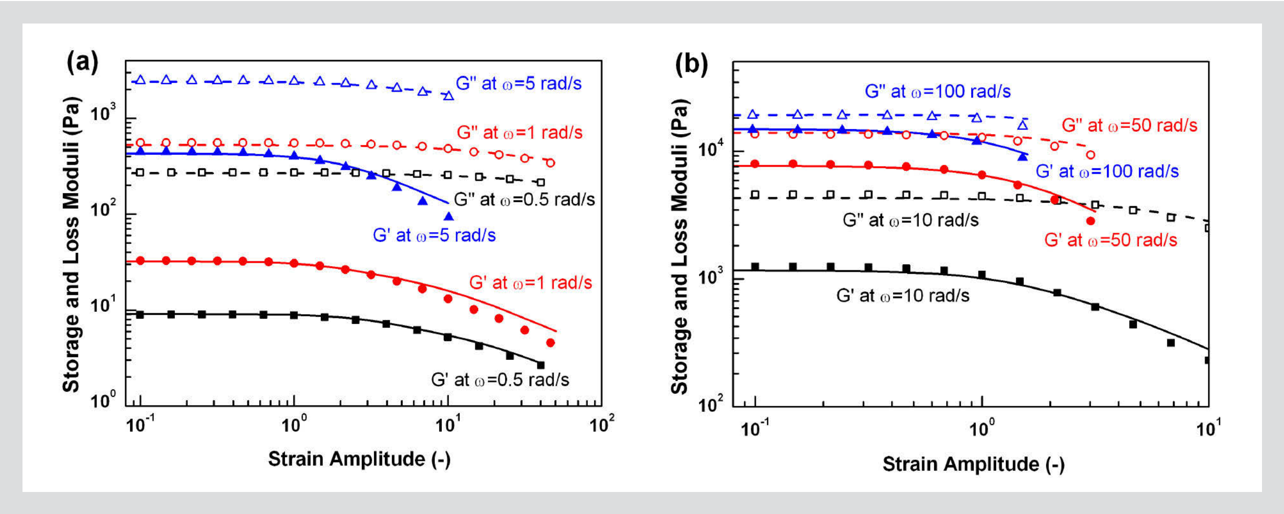

Figure 9: Amplitude sweep data compared to their simulations with White-Metzner model (Equations 9 and 10) at lower and at higher angular frequencies.

stress, τ_i is the shear stress of the *i*-th element. This 6-element White-Metzner model is able to accurately describe the measured nonlinear viscoelastic properties of the silicone oil in the full frequency and shear rate range. In the low shear rate limit, the model equations go over into the linear Maxwell model, and give SAOS loss and storage moduli corresponding to Figure 7. The dependence of the shear flow viscosity on the shear rate was also simulated. As shown by the dashed black line in Figure 8, the model accurately accounts for the shear thinning, i.e. also for the Cox-Merz rule, in the entire measured range.

We performed a further independent test of our 6-element nonlinear White-Metzner model using amplitude sweeps in oscillatory shear measurements with the rotational rheometer. Both the loss and the storage moduli decreased with increasing shear amplitude, while the onset of this nonlinear effect shifted to lower amplitudes with increasing oscillation frequency. The calculated and measured moduli versus the shear amplitude are shown in Figure 9.a at lower and in Figure 9.b at higher frequencies. We find excellent agreement between the computer simulated storage and loss moduli and the experimental data.

7 CONCLUSIONS

We investigated the rheological properties of a high viscosity silicone oil with a zero-shear viscosity of approximately 1000 Pas at 25 °C. Diffusing Wave Spectroscopy can consistently extend the frequency range of loss and storage moduli of SAOS measurements obtained with a rotational rheometer, without any fitting, up to 10^5 rad/s. The high frequency behavior exhibits strong elastic dominance with a smooth frequency dependence in the investigated temperature range. Shear flow tests by the rotational rheometer were extended by capillary rheometry up to a shear rate of $7.6 \cdot 10^4$ s^{-1}, revealing shear thinning behavior and demonstrating the validity of the Cox-Merz rule. Based on this behavior, we defined a White-Metzner type constitutive equation, which fully accounts for the nonlinear viscoelastic properties of the silicone oil, including shear thinning and the decrease of both moduli with increasing strain amplitude in amplitude sweep tests.

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REFERENCES

[1] Jerschow P: Silicone Elastomers, Smithers Rapra Technology (2002)

[2] Ghannam MT, Esmail MN: Rheological Properties of Poly(dimethylsiloxane), Ind. Eng. Chem. Res. 37 (1998) 1335–1340.

[3] Hadjistamov D: Viscoelastic Properties of Filled Silicone Fluids, Appl. Rheol. 3 (1993) 113–119.

[4] Pavlinek V, Saha P, Kitano T, Tanegashima T: Influence of the Electric Field on the Electrorheological Behaviour of Cellulose Suspensions in Silicone Oils, Appl. Rheol. 9 (1999) 64–68.

[5] Mall-Gleissle SE, Gleissle W, McKinley GH, Buggisch H: The normal stress behaviour of suspensions with viscoelastic matrix fluids, Rheol. Acta 41 (2002) 61–76.

[6] Hadjistamov D: Viscoelastic Behavior of Disperse Systems with Silicone Oil and Different Fillers, Appl. Rheol. 12 (2002) 297–302.

[7] Ziegelbaur RS, Caruthers JM: Rheological properties of poly(dimethylsiloxane) filled with fumed silica: I. Hysteresis behaviour, J. Non-Newton Fluid Mech. 17 (1985) 45–68.

[8] Velankar S, Van Puyvelde P, Mewis J, Moldenaers P: Steady-shear rheological properties of model compati-

bilized blends, J. Rheol. 48 (2004) 725 – 744.

[9] Ndong RS, Russel WB: Rheology of surface-modified titania nanoparticles dispersed in PDMS melts: The significance of the power law, J. Rheol. 56 (2012) 27 – 43.

[10] Rolón-Garrido VH, Wagner MH: The damping function in rheology, Rheol. Acta 48 (2009) 245 – 284.

[11] Raimbault V, Rebière D, Dejous C, Guirardel M, Pistré J, Lachaud JL: High frequency microrheological measurements of PDMS fluids using saw microfluidic system, Sensors and Actuators B 144 (2010) 467 – 471.

[12] Brandstaetter M: MCR Series: Correct Adjustment of the Rheometer and Measurement of Standard Samples using RheoPlus, Anton Paar Application Report C92IA005EN-A (2013)

[13] Kataoka T, Ueda S: Viscosity-Molecular Weight Relationship for Polydimethylsiloxane, Polymer Letters 4 (1966) 317 – 322.

[14] Kissi NE, Piau JM, Attané P, Turrel G: Shear rheometry of polydimethylsiloxanes. Master curves and testing of Gleissle and Yamamoto relations, Rheol. Acta 32 (1993) 293 – 310.

[15] Hadjistamov D: Dependance of the First Normal Stress Difference of Silicone Oils on Zero-Shear Viscosity and Molecular Weight, Appl. Rheol. 6 (1996) 203 – 208.

[16] Hadjistamov D: Determination of the Onset of Shear Thinning of Polydimethylsiloxane, J. Applied Polymer Sci. 108, (2008) 2356 – 2364.

[17] Fan Y, Liao H: Experimental Studies on the Relaxation Behavior of Commercial Polymer Melts, J. Applied Polymer Sci. 110, (2008) 1520 – 1530.

[18] Willenbacher N, Oelschlaeger C: Dynamics and structure of complex fluids from high frequency mechanical and optical rheometry, Current Opin. Colloid & Interf. Sci. 12 (2007) 43 – 49.

[19] Longin PY, Verdier C, Piau M: Dynamic shear rheology of high molecular weight polydimethylsiloxanes: comparison of rheometry and ultrasound, J. Non-Newton Fluid Mech. 76 (1998) 213 – 232.

[20] Pine DJ, Weitz DA, Chaikin PM, Herbolzheimer E: Diffusing wave spectroscopy, Phys. Rev. Lett. 60 (1988) 1134 – 1137.

[21] Maret G: Diffusing-wave spectroscopy, Current Opin. Colloid Interf. Sci. 2 (1997) 251 – 257.

[22] Bird RB, Armstrong RC, Hassager O: Dynamics of Polymeric Liquids Volume 1 Wiley, New York (1987).

[23] Larson RG: Constitutive Equations for Polymer Melts and Solutions. Butterworth-Heinemann (1988)

[24] Ferry JD: Viscoelastic Properties of Polymers, Wiley, New York (1980).

[25] Morrison FA: Understanding Rheology, Oxford University Press, New York (2001).

[26] Mezger TG: The Rheology Handbook, Vincentz, Hannover (2011).

[27] Wacker Siliconöle AK, Wacker-Chemie GmbH, München (2001)

[28] Squires TM, Mason TG.: Fluid Mechanics of Microrheology, Ann. Rev. Fluid Mech. 42 (2010) 413 – 438.

[29] Mason TG, Gang H, Weitz DA: Diffusing-wave-spectroscopy measurements of viscoelasticity of complex fluids, J. Opt. Soc. Am. A 14 (1997) 139 – 149.

[30] Mason TG: Estimating the viscoelastic moduli of complex fluids using the generalized Stokes-Einstein equation, Rheol. Acta 39 (2000) 371 – 389.

[31] Zakharov P, Cardinaux F, Scheffold F: Multispeckle diffusing-wave spectroscopy with a single-mode detection scheme, Phys. Rev. E 73 (2006) 011413.

[32] Freeman SM, Weissenberg K: Conf. British Rheologist's Club 36 (1946).

[33] Cox WP, Merz EH: Correlation of dynamic and steady flow viscosities, J. Polymer Sci. 28 (1958) 619 – 622.

[34] White JL, Metzner AB: Development of constitutive equations for polymeric melt and solutions, J. Appl. Polymer Sci. 7 (1963) 1867 – 1889.