PhD THESES

# Measurements and modeling of the nonlinear viscoelastic properties of a silicone oil

Author:
**Zoltán Kőkuti**

Supervisor:
**Dr. Attila Czirják**

Doctoral School of Physics

Institute of Engineering and Materials Science

University of Szeged
Faculty of Science and Informatics

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## Introduction

Rheology is the science of the flow and deformation of matter (gas, liquid or “soft” solid) under the effect of an applied force. The basic concepts of rheology are the temperature and shear rate dependent viscosity and the viscoelastic or plastic behavior. Rheology generally accounts for the behavior of complex fluids (show complex flow behaviors). These complex behaviors depend on the material structure, therefore rheometry, which is the experimental characterization of a material's rheological behavior, is considered as a major material test method. Today rheology and rheometry are used especially to characterize the complex fluids appearing in the technical, material, and life sciences. Furthermore the development of the food, construction, pharmaceutical, chemical, automobile industry increasingly requires the precise continuum mechanical description of the products and system fluids.

In rheology the viscoelastic fluids are one of the most studied materials, which exhibit both viscous and elastic characteristics during deformation. The elastic properties of such fluids are generally provided by the long-chain molecules, therefore the typical viscoelastic fluids are polymer melts or solutions. If the applied shear is high enough to a viscoelastic liquid, it usually results in a nonlinear material response. The measuring and modeling of the nonlinear viscoelastic material properties belong to the most complex problems of modern rheology.

Silicone oils (polydimethylsiloxane, PDMS) have many application areas ranging from fundamental research and applied sciences to several branches of modern industry. In particular, PDMS is frequently used in polymer and materials science because of its peculiar rheological properties. PDMS is also a popular test material for new rheological theories and for elaborating novel measuring methods and devices. The automotive industry mainly uses the silicon oils for the controlled reduction of vibrations and oscillations. Its special application area is in the torsional viscous dampers, which are located at the free end of the piston engine crankshaft, where the necessary high viscosity is provided by the silicone oil. 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 both in the linear and nonlinear viscoelastic range.

In this PhD thesis a detailed experimental investigation on the rheological properties of a high viscosity silicone oil and its modeling based on the measured data (polydimethylsiloxane, PDMS) are reported. The particular substance is a good representative of this important material class. The motivation of this research is the above-mentioned automotive industry application. Only a few papers consider the rheological behavior of silicone oils with high viscosities, the reason for this is that these materials are difficult to measure with the conventional measuring instrumentations. During my measurements I used the most modern measuring devices, whereby I made important relationships with national and foreign research centers, industrial partners. I tried to build mathematical models, which besides the accurate material description, have a physical meaningful content as well. For the numerical solution of these equations I used software regarded standard in their field.

# Objectives

My first goal was to measure accurately the fundamental rheological properties of the selected representative silicon oil in the widest possible temperature and shear rate and frequency range with the available rotational rheometer at the University of Szeged. Even at this time I have found out that this silicone oil is a nonlinear viscoelastic material. The sample presumably fulfills some important rheological rules, which allows to develop a relatively simple, physically meaningful, lumped parameter rheological model.

Based on the above-mentioned, my objective was to extend the rheometric measurements in several directions. Regarding the applications of the silicon oil, my main objective was to determine the storage and loss moduli, and other linear viscoelastic parameters in the widest possible frequency range. For this task the Diffusing Wave Spectroscopy method was proved to be the best.

Since the met of the so-called Cox-Merz rule played an important role in the nonlinear viscoelastic model I developed, it was a major objective to accurately check the met of this rule at the widest possible shear rate range. For this we needed to accurately measure the dynamic viscosity of the silicon oil with capillary rheometer at the fixed temperature range.

The best way to measure the nonlinear viscoelastic properties from the rheometry point of view is to use large amplitude oscillatory shear (LAOS) tests. In addition, these LAOS tests are providing major data for the vehicle industry cooperation, which is my initial motivation. Thus it was an important objective: to map the nonlinear viscoelastic behavior of the representative silicon oil using such experimentally tests. As well as to further develop the lumped parameter nonlinear rheological model so that it can simulate the results of the LAOS tests.

The most important lumped parameter rheological models have different types of space dependent generalizations where the time derivate is replaced by a suitably chosen differential operator. My objectives were to develop such a space-dependent generalization, and to run simulation tests on it. For this, the simulation of shear processes taking place in the rheometer gave a very good opportunity. Some nonlinear viscoelastic effects such as the Weissenberg effect influences the rheological measurements at an unclear extent. Because of complex partial differential equations of the space dependent models I planned to solve the simulation with a finite element software.

# Applied materials and methods

## Silicone oil

The investigated material is one of the most widely used silicon-based organic polymer, the polydimethylsiloxane (PDMS). The chemical formula for PDMS is $CH_3[Si(CH_3)_2O]_nSi(CH_3)_3$, where *n* is the number of repeating monomer units. The higher the sample molecular weight (higher *n*) is, the higher the sample kinematic viscosity becomes.

In this PhD thesis a detailed experimental investigation of the rheological properties of the AK1.000.000. (Wacker Chemie) type silicon oil and the modeling of the material based on the measured data (polydimethylsiloxane, PDMS) are reported. The viscosity of the sample is really high, approximately 1000 Pas at 25 °C. This material well represents the silicon oils, with viscosities between 200 and 2000 Pas, all of which is nonlinear viscoelastic material.

## Measurements with rotational rheometer

The rotational and oscillatory tests were performed with an Anton Paar Physica MCR 101 rheometer. This is a modern, computer-controlled device, which contains air bearing to reduce the friction of the rotating measuring head, thus allowing accurate measurements during the rotational and oscillatory tests. The frequency range of the rheometer is from 0.01 Hz to 100 Hz rad/s, while the temperature range is from 0 °C to 120 °C.

To describe the pure viscous properties of the PDMS simple shear tests were applied, where the increasing shear rate was set, and the shear stress was measured. To determine the linear and nonlinear viscoelastic range we used amplitude sweep tests. The essence of the amplitude sweep test is to measure the storage and loss moduli, while the input sinusoidal strain amplitude is continuously increased. In order to explore the linear viscoelastic properties of the silicone oil we performed small amplitude oscillatory shear (SAOS) frequency sweep tests, so the frequency of the input sinusoidal strain amplitude was increased, while the storage and loss moduli were measured.

To have a better insight into the nonlinear properties of the material we performed true LAOS (Large Amplitude Oscillatory Shear) test. Using the older conventional rheometers the measured raw shear stress signal was not available, so our measurements were done with an Anton Paar MCR702 rheometer. This is the latest model of the company, with increased precision and twin motor setup. The software provides both the raw shear strain and shear stress data signal both the FT-rheological and Ewoldt parameters.

For these measurements, mostly the concentric cylinder measuring geometry was applied with 10 mm inner gap (CC10), and in certain cases, the cone and plate measuring geometry with 25 mm diameter (CP25) was also used.

**Measurements with capillary rheometer**

Capillary measurements were performed in order to describe the viscous properties of the material at high shear rates. The measurement principle is simple: the fluid is pushed through a thin capillary with constant velocity, while the pressure gradient, which is needed to maintain the flow, is measured. From these measured data using mathematical calculations the shear rate, shear stress and the viscosity can be obtained. The flow pattern in the capillary rheometer is nonhomogeneous so several corrections need to be done before the measured (apparent) data can become analyzable.

A Göttfert Rheograph 25 capillary rheometer was the instrument to measure the viscosity of the silicon oil at high shear rates ($10^5$ 1/s). The device presses the material through two different capillaries at the same time, thus, the increase in the accuracy of the measurement was significant.

## Measurements with DWS method

Diffusing Wave Spectroscopy is a well-developed method to probe the viscoelastic properties of the silicone oil at higher frequencies. DWS is a passive microrheological technique, which probes the decorrelation of multiply scattered light due to the thermal motion of scattering objects in the sample. The sample is illuminated by a laser beam. The incoming light is scattered many times by the sample and the resulting intensity fluctuations are detected. The mean square displacement of the scattering particles is obtained from intensity correlation function. From the displacement using microrheological calculations the storage (G') and loss (G") moduli can be determined

For transparent materials, such as PDMS, the light scattering should be triggered artificially, typically by dispersing tracer particles in the material. To trigger the light scattering of the silicone oil titanium-dioxide tracer particles were added to the substance.

On the sample containing the well dispersed, having well-defined average hydrodynamic radius tracer particle we could perform the DWS measurements. The silicone oil was characterized in transmission mode with a DWS ResearchLab (LS Instruments) device, which includes a software package to perform the microrheological calculations.

## Mathematical and numerical simulations software

The developed constitutive equations, which were based to the measured data and later determined by many considerations, were solved in several computing environment.

The simulations, which contained lumped parameter models, were solved with the Wolfram Mathematica and the Matlab software. The defined constitutive equations were ordinary differential equations that could only be solved numerically. Therefor we produced a program code, which works as follows: we set the required shear rate signal, the program solves the constitutive equation and calculates the shear stress signal. From the input shear rate and output shear stress signal the program also calculates the appropriate linear and nonlinear viscoelastic properties. That is why this program could be regarded as a ‘virtual rheometer’.

The space dependent partial differential equations, which are the generalization of the lumped parameter model, were solved by numerical methods because of their complexities. The finite element method (FEM) are useful for these problems, therefore, the Comsol software was used. This is a modular, extremely widely used finite element simulation software, which also allows to supplement the equations of the described normal physical processes with further differential equations, for example: with space dependent constitutive equations.

## New scientific results

**1.** The viscoelastic properties of the representative high viscosity silicone oil (Wacker AK1.000.000) were measured at different frequencies and temperatures with the conventional rheometer. The viscosity of the material at much higher shear rates that can be obtained with a rotational rheometer were measured on a capillary rheometer. From the analysis of the measured data, it was found that the silicon oil was a nonlinear viscoelastic material having a shear-thinning behavior, and obeying the so-called Cox-Merz rule as well as the so-called TTS (Time Temperature Superposition). The parameters of the above-mentioned properties were also determined.

Based on these measurements, a constant-weighed five-element White-Metzner type lumped parameter constitutive equation was developed, which described all the above-mentioned linear and nonlinear viscoelastic properties very well. The shear rate dependent viscosity was defined according to the Cox-Merz rule, and the weighing between the elements were done according to the rates which were valid in the linear regime.

[T1, T2, T3]

**2.** On the basis of DWS (Diffusing Wave Spectroscopy) measurements, which expand the measured loss and storage moduli to the high frequency range, it was found that in a temperature range of 20 – 70 °C, the DWS data fits well to the SAOS data in the overlapping frequency region, especially at the higher temperature end. From the analysis of the measured DWS data, it became clear that the elastic modulus stays dominant and increases with frequency without a second cross-over point up to $10^8$ rad/s.

It was pointed out that the investigated silicon oil obeyed the Cox-Merz rule in a much broader frequency range than was found from measurements on the conventional rheometer up to 16 kHz, at least.

It was verified that TTS rule was still valid for the predominant modulus in the high-frequency range. A joined master curve was created from the data sets measured by SAOS and by DWS, and the selected 60 °C being the reference temperature. This joined master curve is valid for almost six orders of magnitude frequency range. A six-element Maxwell model was fitted to the joined master curve, accurately describing the linear viscoelastic properties of the silicone oil.

[T3]

**3.** During the analysis of the measured large amplitude oscillatory shear (LAOS) tests of the silicone oil, it was found that typically, the non-linear viscoelastic behavior became significant above 100% shear amplitude, and the higher the angular frequency and the shear amplitude of the oscillation were, the stronger the nonlinearity was.

From the plot of the shear stress on elastic and viscous Lissajous-Bodwitch curves, it was observed that the silicon oil in the nonlinear regime displayed intracycle strain stiffening and intracycle shear thinning behavior. During the analysis of these process, it was found that the secondary loops in the viscous stress curves occurred because the rheometer controlled input shear rate signal was not a pure sinusoidal any more.

On the basis of the DWS and SAOS data, a modified, six-element, varying weighed White-Metzner type lumped parameter constitutive equation was developed. Compared to the constant-weighed five-element White-Metzner model (described earlier), this constitutive equation could describe well even the results of the amplitude sweep and LAOS measurements. The simulated results fit very well both to the raw shear stress signal and the elastic and viscous Lissajous-Bodwitch curves.

Based on the simulation complemented measured data, two nonlinear properties were compared with the help of Pipkin diagrams, both for the elastic and the viscous part. It was observed that the nonlinearity increases the weight of the higher harmonics in the shear stress signal decisively. Two particular phenomena were identified from the Pipkin diagrams. First, the viscous nonlinearity has a maximum around $\omega$=50 rad/s angular frequency, thus, the material becomes more and more linear from the viscous side above and below this frequency. Second, above $\omega$=30 rad/s angular frequency, the elastic nonlinearity becomes nearly independent from the angular frequency.

[T3, T4]

**4.** The lumped parameter varying weighed White-Metzner model was generalized to a space-dependent constitutive equation, where the upper convected derivate, which is valid even for high shear stress field, substitutes the normal time derivate from the lumped parameter model. Two rheometry measurements were modeled with this space-dependent constitutive equation using finite element simulations.

The shear rate dependent normal force of the silicon oil was calculated using finite element simulations for the cone and plate (CP) measuring geometry. This force is due to the shear perpendicular to the shear stress tensor components causing the Weissenberg effect. A comparison of the measured and the calculated data revealed that the space-dependent constitutive equation described this complex nonlinear viscoelastic behavior well.

For the simulation of the concentric cylinder (CC) measuring geometry, the finite element model was developed, which was used to simulate the CP measuring geometry, therefore, it could describe the time-dependent dynamics of the silicon–air interface. The CC simulations reproduced the interface deformations observed during measurements. From the analysis of the simulation results, it was shown that the Weissenberg effect did not substantially affect the precision of the simple shear tests for the CC10 measuring geometry.

[T3]

## Publications

### Publications related to the thesis:

[T1] **Kőkuti Zoltán**, Kokavecz János, Holczer István, Danyi Antal, Gábor Zoltán, Czirják Attila, Szabó Gábor, Ailer Piroska, Pézsa Nikolett, Németh Huba, Palkovics László:
*„Torziós lengéscsillapítóban alkalmazott viszkózus folyadék modellezése”*,
A Jövő Jáműve, 2009/3-4 (2009) pp. 61-65

[T2] **Z. Kőkuti**, J. Kokavecz, A. Czirják, I. Holczer, A. Danyi, Z. Gábor, G. Szabó, N. Pézsa, P. Ailer, L. Palkovics:
*„Nonlinear viscoelasticity and thixotropy of a silicone fluid”,*
In: Ferencz Árpád, Klebniczki József, Lipócziné Csabai Sarolta, Borsné Pető Judit, Fábián Csaba (szerk.) Proceedings of the 2nd International Scientific and Expert Conference: TEAM 2010 : AGTEDU 2010 (ISBN:978-963-7294-85-3): (2010) pp. 577-583.

[T3] **Z. Kőkuti**, K. van Gruijthuijsen, M. Jenei, G. Tóth-Molnár, A. Czirják, J. Kokavecz, P. Ailer, L. Palkovics, A.C. Völker, G. Szabó:
*„High-frequency rheology of a high viscosity silicone oil using diffusing wave spectroscopy”*,
Applied Rheology **24**:6 (2014) 63984 (7 pages). IF:1.078

[T4] **Z. Kőkuti**, L. Völker-Pop, M. Brandstätter, A. Czirják, J. Kokavecz, P. Ailer, L. Palkovics, G. Szabó:
*„Exploring the nonlinear viscoelasticity of a high viscosity silicone oil with LAOS”*,
Applied Rheology, submitted, 2015

### Other publications

[1] **Z. Kőkuti**, J. Kokavecz, A. Czirják, I. Holczer, A. Danyi, Z. Gábor, G. Szabó, N. Pézsa, P. Ailer, H. Németh, L. Palkovics:
*„Nonlinear viscoelasticity of silicone fluids”*,
poster at the „Annual European Rheology Conference 2010, Göteborg”

[2] **Z. Kőkuti**, J. Kokavecz, A. Czirják, I. Holczer, Cs. Vass, A. Danyi, Z. Gábor, G. Szabó, N. Pézsa, P. Ailer, H. Németh, L. Palkovics: *„Nonlinear viscoelasticity and thixotropy of silicone fluids”,* poster at the „European Seminar on Coupled Problems 2010, Pilsen”

[3] **Z. Kőkuti**, J. Kokavecz, A. Czirják, I. Holczer, A. Danyi, Z. Gábor, G. Szabó, N. Pézsa, P. Ailer, L. Palkovics: *„Nonlinear viscoelasticity and thixotropy of a silicone fluid”*, presentation at the „TEAM 2010 / AGTEDU 2010”, Kecskemét, 2010. november 4–5.

[4] **Z. Kőkuti**, J. Kokavecz, A. Czirják, I. Holczer, A. Danyi, Z. Gábor, G. Szabó, N. Pézsa, P. Ailer, L. Palkovics: *„Nonlinear viscoelasticity and thixotropy of a silicone fluid”*, A Jövő Jáműve, 2011/1-2, pp. 134-136

[5] **Z. Kőkuti**, J. Kokavecz, A. Czirják, I. Holczer, A. Danyi, Z. Gábor, G. Szabó, N. Pézsa, P. Ailer, L. Palkovics: *„Nonlinear viscoelasticity and thixotropy of a silicone fluid”*, Annals Of Faculty Engineering Hunedoara – International Journal Of Engineering, 2011/2, pp. 177-180

[6] **Z. Kőkuti**, K. van Gruijthuijsen, M. Jenei, A. Czirják, J. Kokavecz, A. Danyi, P. Ailer, L. Palkovics, A. C. Völker, G. Szabó: *„High-frequency rheology of nonlinear silicone fluids”*, poster at the “International Congress on Rheology 2012, Lisbon”

[7] **Kőkúti Z.**, K. van Gruijthuijsen, Jenei M., Tóth-Molnár G., Czirják A., Kokavecz J., Szabó G., Ailer P., Palkovics L.: *Szilikonolajok nagyfrekvenciás reológiai tulajdonságai* A Jövő Jáműve: Járműipari Innováció (1-2) pp. 38-41. (2013)

[8] A. Czirják, **Z. Kőkuti**, G. Tóth-Molnár, P. Ailer, L. Palkovics, G. Szabó: *Simulated Rheometry of a Nonlinear Viscoelastic Fluid”* COMSOL Conference 2013, Rotterdam, contributed talk