Sensors and Actuators A 236 (2015) 309–314

Contents lists available at ScienceDirect

Sensors and Actuators A: Physical

journal homepage: www.elsevier.com/locate/sna

Observation of viscoelastic solutions with ferromagnetic stirrers

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ARTICLE INFO

Article history:
Received 4 June 2015
Received in revised form 23 October 2015
Accepted 2 November 2015
Available online 10 November 2015

Keywords:
Viscoelastic behavior
Magnetic particles
CTAB/NaSal
Glycerol

ABSTRACT

Viscoelasticity in fluids is present in many common substances, from paints and glues to ketchup and mayonnaise. The rheological behavior of fluids can be accurately studied with laboratory equipment and encompasses an active area of research. However, instead of precisely analyzing the viscoelastic parameters, some applications simply require the detection of presence of viscoelastic behavior in fluid. This is desirable in online biofilm monitoring, for instance, where it is important to discern inorganic accumulation (shown as purely Newtonian behavior) from biofilms (viscoelastic behavior). Therefore, this study presents a simple method for potentially detecting the presence of viscoelastic behavior in a fluidic sample. Two sample solutions were compared: glycerol as the Newtonian fluid and a solution of cetyltrimethylammonium bromide (CTAB) and sodium salicylate (NaSal) as the viscoelastic fluid. They were compared by observing the rotational response of a magnetic particle in a rotating magnetic field, where the presence of underdamped oscillations was attributed to the viscoelasticity of the fluid. According to these preliminary results, the setup may be used to detect the presence of viscoelastic behavior in the fluid.

1. Introduction

Rheology, the quantitative study of material flow and reformation under stress, is a fundamental analysis for many viscoelastic materials including polymer melts, paints and adhesives. Viscoelastic measurement techniques share features with other mechanical testing protocols. The methods used rest on creating a force or torque that displaces the specimen (strain). The viscoelasticity of fluids can be measured with various rheometric techniques, such as capillary, rotational, cone and plate, linear shear or acoustic rheometers. However, the use of these techniques can be restricted due to the large size of the equipment, relatively high cost, limited measurement range and the lack of online measurement. Therefore, there is a need for compact sensors with a simple operating principle—especially in applications that only require to recognize characteristics of viscoelastic fluids.

In addition to commercial rheological apparatus, previous studies have investigated promising techniques for microrheological applications; for example in accessing the internal components of living organisms and influencing fluid properties at the nanoscale level. The techniques include particle and laser tracking, magnetic tweezers, diffusing wave spectroscopy, atomic force microscopy, microcantilevers, resonator devices and magnetoviscous phenomena in ferrofluids [1–4]. In addition, magnetic microparticles have been applied in many novel microrheological applications. Ziemann et al. used magnetic beads to evaluate their frequency dependency with storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ [5]. Rotational magnetic microrheology has been used to investigate the cell interior in terms of viscosity and relaxation time [6]. Hu et al. applied a 3D magnetic twisting device, suitable for studying the mechanical properties of cells [7]. Chevry et al. showed magnetic wire-based sensors were applicable for characterizing the microrheology of complex fluids [8].

Chevry et al. [8] studied the low inertial behavior of a magnetic bar in a microscale viscoelastic medium and found possibility to derive the following viscoelastic parameters from the medium's rotational response: the static viscosity of the fluid, η_0, elastic modulus, G_0, and as their quotient, τ_R, the relaxation time of the fluid. In our setup, a similar approach was chosen, but macroscopic particles were used to enable online measurement. In contrast to the nanoscale application, our approach introduced imperfections, such as non-uniform friction and the moment of inertia of the sensor. The results were compared with Chevry et al. results not only to distinguish micro- and macrorheology, but also to compare sim-

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http://dx.doi.org/10.1016/j.sna.2015.11.002
0924-4247/

ulations and actual measurements, which consider the moment of inertia of the particle.

Among the various magnetic particle applications, asynchronous magnetic bead rotation (AMBR) sensors have shown applicability as biosensors and are ideal for detecting bacterial cells and analytes [9–11]. AMBR sensors, based on straightforward principles, observe the critical rotational frequency of the particle in a rotating magnetic field [8,9,12–14]. In low-driving frequencies, the particle synchronously follows the external field until the driving frequency is increased to the critical frequency ω_c characteristic of the medium. Then the particle rotates slower forward due to the periodical backflips in the reverse direction, what is known as asynchronous mode. Thus, in the asynchronous mode particle's rotation frequency depends nonlinearly on the external frequency. In previous applications of AMBR sensors, viscosity was measured by the average rotational frequency. Instead, we show that details in the rotational pattern, i.e., underdamped oscillations, refer to the viscoelastic behavior of the fluid.

As a viscoelastic model fluid, CTAB/NaSal solutions were used. CTAB and NaSal were mixed together in water medium since this solution has been extensively studied in various fields of viscoelastic fluids [15–18]. In a suitable saline environment, CTAB forms longitudinal worm-like micelles that exhibit sensitively changing rheological properties. Thus, in this study, we compared the viscoelastic features of CTAB and NaSal solutions by magnetic stirrers with results for conventional rheometers and numeric simulations.

2. Materials and methods

2.1. Materials

For measuring the viscoelastic medium, 13.7 mM and 20.6 mM CTAB (Sigma–Aldrich, Finland) solutions were prepared from 10% (w/v) stock solution containing 0.5 M NaCl to enhance the solubility. In addition, NaSal (Sigma–Aldrich) was diluted in 10% (w/v) stock solution and mixed together with CTAB in 0.73 molar-based ratio. The final solutions remained at a 0.5 M NaCl brine concentration.

For the comparison with viscoelastic fluids, the Newtonian fluid was prepared by diluting glycerol (Sigma–Aldrich SZBD164CV) to 85% (w/w) with ultrapure water. The viscosity of the solution was 90.9 cP ± 0.4 cP calculated by interpolating the 85% (w/w) glycerol data at the measurement temperature 22.3 °C. The viscosity was determined from the sixth powered equation fitted on data for aqueous glycerin solutions depending on the temperature and glycerol mass percentage [19,20].

To detect viscoelastic behavior with the magnetic stir bar sensor, the sensor was applied toward two model fluids with similar viscosity: glycerol and CTAB NaSal solution. Thus, the 20.6 mM CTAB NaSal solution was characterized with a rheometer (Anton Paar MCR 502, Switzerland) by using a spindle (d = 50 mm) and a 2° angle. The solution showed characteristically viscoelastic behavior as shown in Fig. 1.

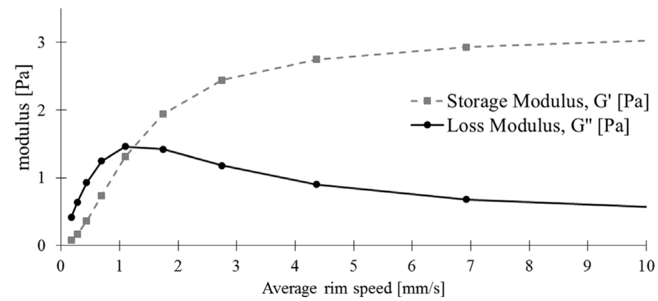

Fig. 1. Storage modulus G' and loss modulus G" of the 20.6 mM CTAB/NaSal/NaCl matrix showing viscoelastic behavior. The solution was measured with a conventional rheometer. For the Newtonian fluid, such as the water-glycerol solution, the storage modulus G' equals zero, and the loss modulus G" equals $\eta\omega$, thus equal to a linear function of viscosity (η) and angular speed (ω) [15].

2.2. Equipment and data processing

Measurements with magnetic stir bars were performed in 150 μl samples pipetted into separate wells in a standard 96-well plate (Thermo Fisher Scientific, #469264, Denmark). The round stir bar (Semadeni, #2174, Strong Epoxy Pro, Ø 3 mm) contains a PTFE coated permanent Alnico V magnet (Ø1.5 mm × 1.5 mm). These magnets are generally used as stir bars, and are not designed to be used as sensors. The magnetic stir bar was flattened on one side (see Fig. 2) to limit the rotational freedom to a single axis (z-axis). Additionally, a round-bottomed well reduced the lateral movement of the particle and reduced the interaction errors between the particle and the well walls.

The setup for the magnetic sensor, presented in Fig. 2, consisted of four laminated steel core coils (ELC54-19-10000, ERSE Audio) placed in pairs to surround the permanent magnet. The coils were driven by sinusoidal waves (90° phase difference) to generate an oscillating magnetic field. The wave signals were generated with an NI DAQ card (NI USB-6341, National Instruments) and amplified with the Ampaq-L2 current amplifier (Quanser, Canada). The driving magnetic field amplitude was set to 8.0 V, which translates to a magnetic field of 1 mT. The rotation was tracked using a digital camera (mvBlueCOUGAR-XD) mounted above the sample, which can record data above 1000 fps when the area being tracked is small (less than 100 × 100). The pattern tracking was video recorded, and the images were processed with LabVIEW™ 2013 (National Instruments).

To evaluate the viscoelastic performance of the solution, the particle rotation frequency was calibrated by steadily increasing the field frequency, which is known as the external driving frequency. The average particle frequency was determined by visually counting the forward revolutions of the sensor (Figs. Fig. 3a, and 6a/d). An average of five sequential laps was chosen to sufficiently represent the average rotation frequency without requiring a long calibration period. In addition to the calibrations, recorded data was applied to study the particle angle as a characteristic sinusoidal wave at different points of the calibration curve. The instantaneous angle of the magnet was monitored with LabVIEW pattern tracking software.

3. Results and discussion

3.1. Magnetic stir bar actuation and observation

The magnetic field setup and tracking were initially tested with Newtonian fluids, water and glycerol. In the pure water solutions, the magnetic rotation of the sensor particle was synchronous due to the low viscosity. Therefore, 85% glycerol solution was used as the initial testing fluid. The average rotational speed of the sensor as a function of driving frequency, and the instantaneous rotational behavior of the magnetic stir bars (Fig 3(a)) are similar to the results presented in the literature [8,14]. Fig. 3(b) shows an oscillating rotation of the sensor particle in the asynchronous area in Newtonian fluid.

In the ideal case of zero friction, the asynchronous forward rotation of the particle decreases indefinitely with increasing driving frequency. With the magnetic stir bars used here, there is a maximum driving frequency where the net forward rotation goes to zero (roughly at 1.6 Hz in Fig. 3a). This is most likely due to the angle dependent friction present in the system (Fig. 4(a)). To eval-