Properties of PEDOT:PSS from Oscillating Drop Studies

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Abstract

PEDOT:PSS is commonly inkjet printed in aqueous solutions with surfactant additives for improved electrical properties in organic electronics applications. These shear thinning complex fluids have been found to DoD jet surprisingly well over a wide range of drive voltages and drop speeds, behaving rather like Newtonian fluids with far (ten times) lower viscosities than measured at low shear-rate. As ~ 1 wt% PEDOT:PSS solutions showed little evidence for satellite production even at high jet speeds this would suggest that the fluid has regained high viscosity levels, in order to slow the necking rate, on timescales << 100 μs and much faster than accessible to conventional mechanical testing means.

Experimental work on the break-up of Newtonian ligaments was recently extended to DoD-scale ligaments, and supports the interpretation that the PEDOT:PSS ligaments attain higher viscosity during flight than during the jet emergence from the print head nozzle, although such rapid recovery timescales for PEDOT:PSS were not predicted from its measured rheology.

Our recent work has focused on oscillating drop (OD) techniques for determination of properties of DoD (50 μm) scale aqueous PEDOT:PSS solutions (with and without surfactants) and on a larger (3mm) dispensing scale for more general shear thinning fluids. Imaging studies by one of us (SW) evaluated diffraction effects on OD analyses.

The small effects of weak elasticity on the drop oscillations, as assessed theoretically by Khismatullin and Nadim (2001), have been exploited to provide new limits to the recovery time for aqueous PEDOT:PSS based on the fluid viscosity deduced from measured rheology and OD decay rate. These limits are consistent with recent numerical simulations of shear thinning fluid jetting.

Introduction

Inkjet printing commonly involves complex fluids [1] in order to achieve the required properties for successful deposition on a substrate but also to maintain reliable jetting behavior. Aqueous PEDOT:PSS - poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) - is commonly used with surfactant additives to provide transparent conductive polymer layers [2] and more recently to provide resistive components with controlled resistance values [3]. One pragmatic reason why this particular fluid is chosen is that the functional fluid PEDOT:PSS with surfactants appears to jet extremely successfully using drop-on-demand (DoD) inkjets.

A recent paper [4] explored some reasons why this might be, in comparison with Newtonian fluids similarly jetted [5]. High resolution spark flash images of DoD jetting showed that aqueous PEDOT:PSS solutions delay satellite production at all jet speeds (~ 2-16 m/s) relative to Newtonian fluids found to require similar values of DoD inkjet print head drive voltage [4]. The control of satellite production and preferably the total elimination of satellites in inkjet printing are considered central goals for functional applications, so this finding is immediately significant for novel fluid formulations: understanding the origin of satellite control irrespective of jet speed will help creation of inkjet fluid by design.

Inkjet printing involves very high (> 10^5 s^{-1}) shear rates, far higher than accessible to the conventional rheometers that are used to assess inkjet fluids. Such high shear rates arise in the print-head nozzle, close to the nozzle wall, and also when the ligament necks to produce the jet break-off event and later to form the satellites. The surface age for fluids is often short (< 100 μs) during printing, and estimation of dynamic surface tensions on such timescales eludes conventional maximum bubble pressure equipment. This is significant for fluids containing surfactants, as these have to reach the jet surface from the bulk in order to reduce the fluid tension.

High frequency rheological measurements [4] showed that aqueous PEDOT:PSS fluid is highly shear thinning. The recovery time of shear thinning fluids is often much longer than 1 s (e.g. for synthetic materials such as gels for paint) and can be easily assessed mechanically. However, our results from the break-up of long Newtonian filaments and DoD ligaments [6] suggested that the observed delays to ligament break-up for the aqueous PEDOT:PSS solutions could be consistent with > 4-5 decades faster (<< 100 μs) recovery of high viscosity conditions within fluid outside the inkjet nozzle, rather than due to the presence of polymer elasticity or structural changes due to the 0.5 wt% surfactant additives used. However, further work was clearly needed to resolve such a large discrepancy in relaxation timescales.

Our experimental oscillating drop work [7] aimed to address concerns raised about the interpretations of DoD satellite reduction based on unmeasured fluid properties, such as very rapid recovery of high viscosity, while a companion study had focused on accurate measurements of the properties of shear thinning fluids in general [8]. We present our results [7] for the high frequency behaviour of drops of aqueous PEDOT:PSS fluids with and without (surfactant) additives. The dynamic surface tension and high frequency linear viscoelastic (LVE) viscosity measurement ranges are extended significantly by such oscillating drop studies.

Aqueous PEDOT:PSS rheology

Figure 1 shows the shear rheology of aqueous PEDOT:PSS fluids at various concentrations [4] as a function of shear rate up to frequencies of about 50 kHz measured using a Bohlin C-VOR 150 rheometer. The shear viscosity reduces with increasing shear rate by a factor of about 10 for the nominal 1.0 wt% PEDOT:PSS fluid. Figure 2 shows the elastic response for these fluids [4], on the same scale as Figure 1, measured up to frequencies of 5 kHz using a special piezo axial vibrator (PAV) device []. Elasticity is present at all frequencies, but nowhere dominates the viscous response.

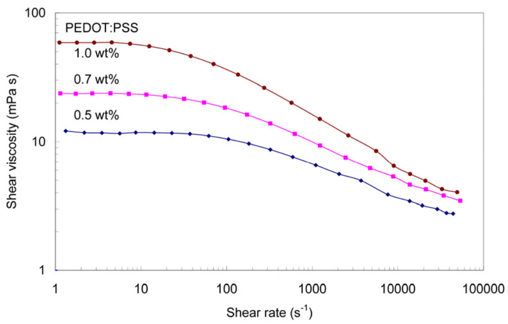

Figure 1. The measured [4] shear viscosity (mPa s) versus shear rate (s^{-1}) for PEDOT:PSS at nominal 1.0 wt%, 0.7 wt% and 0.5 wt% concentration in water.

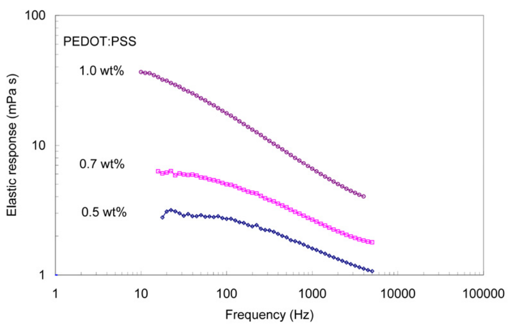

Figure 2. The measured [4] elastic response (mPa s) versus frequency (Hz) for the same fluids as in Figure 1.

Oscillating Newtonian drops

DoD print-heads jets of modest (few mPas) viscosity liquids readily produce single, slowly moving main drops of radius R that are suitable for (small amplitude < 0.1 R) oscillating drop studies. The recoil and coalescence of the ligament with the main drop after the jet break-off from the nozzle meniscus alters the shape of the drop, resulting in oscillations driven by the dynamic surface tension damped by non-zero viscosity, before the spherical drop shape is finally attained. Sufficiently high viscosity can result in drop shapes that do not even oscillate but decay exponentially towards spherical shape.

The drop shape oscillation frequency for low viscosity and elasticity depends on the liquid surface tension, density and drop size, and the oscillation mode. The higher order shape modes have higher frequency and dissipate faster than the lowest, (quadrupole) l=2 mode, so the shape tends to this single lowest mode. This l=2 mode is considered in this paper; full expressions are available [8].

For Newtonian drops the angular frequency Ω^* and decay time τ for the l=2 shape mode oscillations are related to the fluid parameters by equations (1)-(3), where frequency $\Omega^* = \Omega$ for inviscid ($\eta = 0$) fluids.

$$\Omega^{*2} = \Omega^2 - 1/\tau^2 \quad (1)$$

where

$$\Omega^2 = 8\sigma/\rho R^3 \quad (2)$$

and

$$1/\tau = 5\eta/\rho R^2 \quad (3)$$

with fluid surface tension σ, density ρ and viscosity η.

Newtonian liquids can also be characterized by the Ohnesorge number, Oh

$$Oh = \eta/\sqrt{(\rho\sigma R)} \quad (4)$$

Equation (1) suggests that drop shape oscillations cannot occur if $\Omega < 1/\tau$, corresponding to Ohnesorge number $Oh < 0.4\sqrt{2}$ and viscosity

$$\eta > 0.566\sqrt{(\rho\sigma R)} \quad (5)$$

Equation (5) limits the dynamic viscosity to ~ 20 mPa s for DoD scale oscillating drops, i.e. well above the (1 mPa s) viscosity of water and the high shear rate aqueous PEDOT:PSS fluids but below the low shear-rate aqueous viscosity (> 60 mPa s) of 1 wt% PEDOT:PSS. This permits an accessible experimental test of the fast recovery time for the dynamic viscosity of the aqueous PEDOT:PSS fluids, using typical DoD scale oscillating and non-oscillating deformed droplets and on the DoD jetting timescale. We present and discuss our findings for such tests [7] in this paper.

Oscillating viscoelastic drops

Elasticity (if present) tends to oppose viscous damping and slightly raises the shape frequency while, as shown by equations (1)-(3), increasing viscosity can lower the frequency towards zero. Models for viscoelastic fluid drops can combine these responses as a series combination of a viscous dashpot with a parallel combination of an elastic spring and a viscous (solvent) dashpot. Jeffreys' model has 2 time constants [9], each proportional to the relevant dashpot viscosity normalized by the elastic spring constant, τ_1 accounting for the liquid and τ_2 (shorter) for the solvent. The known ratio of solvent and solution viscosities equals the ratio of these time constants, so leaving 1 independent variable.

Khismatullin and Nadim [9] consider that in the asymptotic limit of low Deborah number $De_n = \Omega\,\tau_n$ the Jeffreys' formalism will produce the viscous Newtonian result for the oscillation frequency Ω given by equation (2) and the ratio of viscosities equals the ratio De_1/De_2. The viscosity in equation (3) has to be replaced by $\eta'(\Omega)$, the real part of the complex viscosity at the l=2 mode frequency Ω, while the frequency Ω is raised to Ω' due to the elastic spring [7]:

$$\eta' = \eta\,(1+De_1 De_2)/(1+De_1^2) \quad (6)$$

$$\Omega'^2 = \Omega^2 + 5\eta''/\rho R^2 \quad (7)$$

$$\eta'' = \eta\,(De_1 - De_2)/(1+De_1^2) \quad (8)$$

Using experimental values for viscosity ratio, equations (6)-(8) can be used to determine the variation of shape frequency and viscosity with relaxation time. Conversely by observing the viscosity for the oscillating drop and comparing this with the extrapolated value from the fluid rheology, as equations (7) and (8) give small effects, we can extract limits on relaxation time τ using equation (6) alone.

Figure 3 shows a prediction of the decay rate and frequency variations with De_1 based on equations (6)-(8) assuming the ratio of viscosities for water and the polymeric fluid $=De_2/De_1 = 0.36$. These curves show that the decay factor (normalized to 1 at viscosity η) decreases monotonically with De_1 and emphasizes the small effect of elasticity on drop oscillation frequency (normalized to 1 at frequency Ω). The ratio of $\eta'(\Omega)$ from the OD decay curve to $\eta'(\Omega)$ from the (extrapolated) elastic response curve determines the normalized decay factor, and the dashed green lines then show how the relaxation time τ_1 can be inferred from De_1 by $\tau_1=De_1/\Omega$.

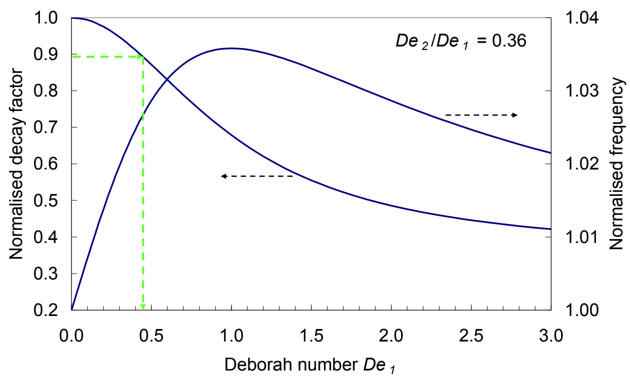

Figure 3. Normalized decay factor and drop oscillation frequency for small Deborah number De_1 in 53 µm diameter drops of viscosity 2.8 mPa s, density 1000 kg/m³ and surface tension 75 mN/m. (Normalization is described in text.).

Experiments

Details of the inkjet print head and visualization systems used for the OD measurements are fully described elsewhere [7, 8]. Calibration of the absolute radial size scale, accounting for higher-order shape oscillations [8] of Newtonian liquid water droplets of known properties, were checked using experimental and mathematical studies of optical diffraction by spheres and straight edges [10]. Absolute size corrections of ~ 3% to a standard image threshold method proved critical to consistently explain the extracted surface tension and viscosity for water drops. Fluid parameters deduced from OD l=2 mode studies of aqueous PEDOT:PSS, assuming known density and absolute radius, have uncertainties of about 10% in surface tension and 20% in viscosity. This precision is sufficient for discriminating high and low values for fluid viscosity, and setting upper limits on relaxation times [7].

Results for water OD

Figure 4 shows the l=2 mode amplitude oscillations deduced by image data analysis [8] for a 31 µm diameter satellite droplet formed during the break-up of a water jet DoD printed from a 40 µm diameter MicroFab print-head. The extracted values at f = 63 kHz: σ = 75±5 mN/m and η = 1.0±0.2 mPa s, which are as expected very close to the well-known characteristics for water [7].

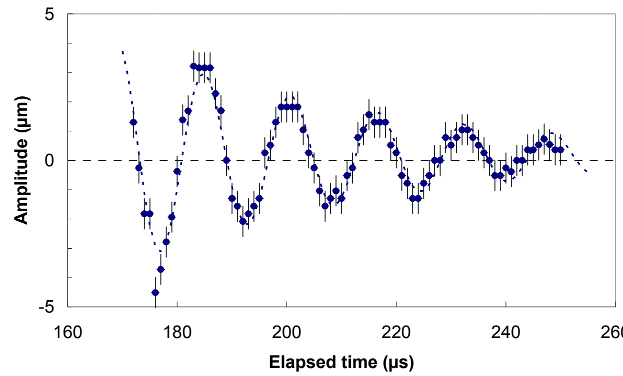

Figure 4. Oscillations observed at 63 kHz for a 31 µm diameter water drop. The l=2 mode amplitude shown dominates the oscillation at longer times.

Results for DST at low surface age

Figure 5 shows that the extracted dynamics surface tension (DST) values for aqueous 0.7 wt% PEDOT:PSS with Dynol and IPA additives obtained from OD studies are at least 2 decades below the lowest surface age accessible to usual maximum bubble pressure methods. In addition the calibration of these MBP surface tension devices may also depend on viscosity, whereas the OD studies provide a consistency check on DST and viscosity through direct determination of the OD frequency and the damping rate.

Dynol 607 is a surfactant and IPA (isopropyl alcohol) is a solvent. The OD values for the DST clearly lie above the MBP values but may also follow the DST trends, which approach similar values of the equilibrium surface tension (by design) [7].

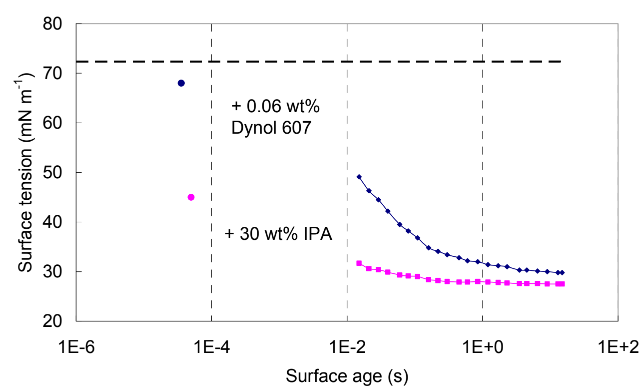

Figure 5. Comparison of OD and MBP results for 0.7 wt% PEDOT:PSS in water with either 0.06 wt% Dynol 607 surfactant or 30 wt% IPA solvent. The OD results were found for surface ages < 10^{-4} s and the MBP at ages > 10^{-2} s. The dashed line corresponds to the known surface tension for pure water [7].

Results for viscosity at high frequency

Figure 6 shows two successive (damped) OD sequences following the ligament recoils of 1 wt% aqueous PEDOT:PSS fluid printed by the same trigger (using a DoD waveform allowing, not suppressing, secondary jets). The amplitude, which roughly corresponds to the ratio of length to drop width, decreases linearly with time during the ligament recoil, as shown by the dashed lines.

The drop diameters (44 and 47 µm) and oscillation frequencies (29 and 26 kHz) both correspond to values of DST ~ 44±4 mN m^{-1} and viscosity ~ 3.5±0.7 mPa s. All such oscillating 1 wt% PEDOT:PSS drops show viscosity ~ 3.5 mPa s under high shear-rate and not the low shear-rate value > 60 mPa s of Figure 1. Therefore the very production of OD must involve shear thinning; in fact there would be no OD if the whole drop had η = 60 mPa s.

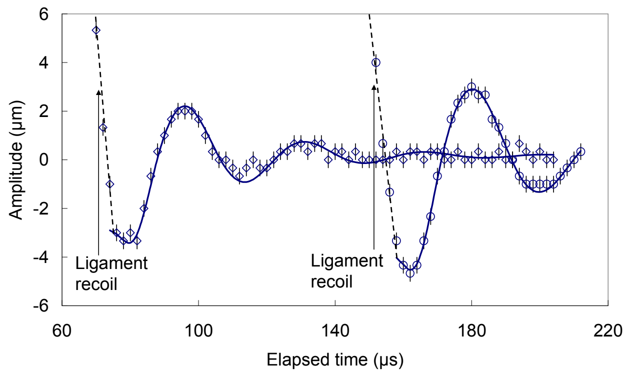

Figure 6. Aqueous ~ 1 wt% PEDOT:PSS drops of 46 µm and 49 µm diameter driven into the l=2 mode shape oscillations at 29 and 26 kHz following ligament recoil. Deduced DST and viscosity values are consistent with drop oscillations of low viscosity fluid as discussed in the text [7].

Interpretation for elastic fluids

Further analysis of the apparent surface tension and viscosity as deduced from OD studies can also proceed using the theory of Khismatullin and Nadim [9] elastic fluid drops as discussed above. Calculations for each drop size R and solvent/fluid viscosity ratio = De_2/De_1 at the l=2 mode frequency Ω provide appropriate versions of Figure 3 for application applied to the observed aqueous 1 wt% PEDOT:PSS drops. For each drop, the ratio of apparent fluid viscosity from OD with extrapolated viscosity (based on an assumed Carreau model frequency variation [11]) from high frequency rheometry determines the normalized decay factor. This allowed De_1 to be read from the graph and limited the elastic relaxation time τ_1 < 10 µs for all drops. This very rapid timescale appears consistent with numerical simulations of DoD jetting of generalized Newtonian fluid, where elasticity is NOT present, but not with a conventional interpretation of the viscoelastic rheology.

Discussion

We have not shown raw images of the aqueous PEDOT:PSS drop oscillations simply because the decaying amplitudes < 2µm (see Figure 6) have drop shape changes that are difficult to discern.

PEDOT:PSS jetting appears consistent with rapid recovery to high viscosity values, requiring elastic relaxation times << 100 µs. The observations of OD for 1 wt% PEDOT:PSS with very low viscosity values close to those extrapolated from high shear-rate rheology is in this respect puzzling, but small amplitude behavior for OD may be dominated by drop viscosity within an outer skin of thickness typically given by the l=2 mode amplitude. Thus DoD jetting of aqueous PEDOT:PSS may reduce satellites because the elastic ligament core recovers fast or is never sheared to the same extent as the outer regions that were ejected closer to nozzle walls.

A recent analysis of viscoelastic drops by Brenn and Teichtmeister [12] takes a difference stance on the extraction of the polymeric timescales from that in our paper [7]. Whereas Khismatullin and Nadim [9] assume the ratio De_2/De_1 = 0 while we used solvent/fluid viscosity ratio = De_2/De_1 =0.36, Brenn and Teichtmeister assumed knowledge of elastic relaxation time τ_1 from rheology to infer "deformation" time τ_2 from $De_2/De_1 = \tau_2/\tau_1$. Our results would then have implied a time τ_2 < 4 µs on this basis.

Conclusions

Irrespective of the continuing discussions on the origin of the observed satellite suppression mechanism, the present OD studies provide several significant improvements in fluid characterization: the dynamic surface tension can be measured for surface ages at least 2 decades shorter than by maximum bubble pressure method; the viscous component η' (Ω) of complex viscosity can be assessed (to ~ 20%) at frequencies Ω a decade higher than usual rheometry; the upper limits placed on the fluid elastic relaxation timescales are > 5 decades shorter than accessible to mechanical rheometry.

The large discrepancies, between steady state shear-rheology and dynamic processes such as DoD jetting and oscillating drops, that have been deduced for the aqueous PEDOT:PSS relaxation timescale may arise because different regions of fluid are accessed: bulk fluid for rheometry and the "outer skin" for OD and jetting. Further work on simulations to help clarify this is in progress [11].

Acknowledgements

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Author Biography

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