Jetting of complex fluids

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Abstract

Recent results from a number of UK academic inkjet research studies advance the understanding of complex fluid jetting behaviour and may be of interest to the wider digital fabrication community for the enhancement of inkjet printing applications.

Keywords

Inkjet, polymer, rheology, shear thinning fluids, colloids, satellites, holography

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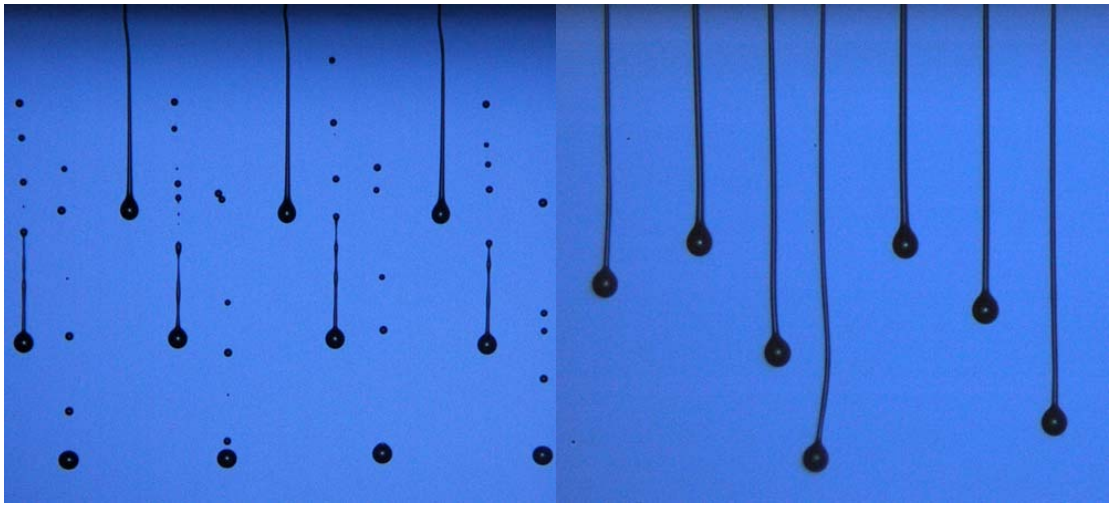
Introduction

Digital fabrication using inkjet printing techniques usually relies upon accurate delivery of fluid drops onto a substrate, when and where directed by the print head, with a controlled speed and a fixed gap maintained between the print head and the substrate. Inkjet print head arrays in machines are often assessed optically, nozzle by nozzle, for in-flight drop speed and (2-D) directionality. For digital fabrication rather than graphics printing, the drop speed, volume and directionality have to be known for every timed actuation of a nozzle, but failure to take account of complex fluid jetting behaviour can degrade performance and reduce product quality.

The viscosity η of jettable fluids can be within quite a wide range (1-50 mPa s); individual fluid viscosity depends on temperature and for complex (non-Newtonian) fluids on the instantaneous shear rate experienced and the shear rate history. Complex fluids may show viscoelasticity, shear-thinning and other complex aspects of rheology. The ranges of typical fluid density ρ (800-1200 kg/m^3) and surface tension σ (20-70 N m^{-1}) are far smaller, so the highest jet speeds produced by DoD print heads are usually limited by the extensional viscosity of the fluid within the neck of the nozzle (of diameter D). Lower speed limits may be needed in practice to help avoid satellite production (see below), aerodynamic effects and drop splashing on impact.

For complex fluids based on Newtonian solvents, additives reduce the jet speed at constant print head drive, in comparison with the Newtonian solvent; this reduction is often proportional to the concentration of the additive (often below 0.1 - 10 wt% or 20 vol%), and compensation to maintain jet speed requires raising the print head drive voltage (or choosing a shorter nozzle), which increases shear stresses in the fluid.



(a) (b)

Figure 1. Fluid with high polymer content may never break off from the nozzle but form very long thin ligaments. The jets in (a) have no added polymer but the jetted fluid in (b) contains high molecular weight polymer. The Xaar 126-200 print head used for this work has a 137 µm spacing of 50 µm diameter nozzles (just above the top of both images shown).

Inkjet printing is degraded by the presence of satellite drops (see Figure 1a) following break up of long ligaments produced when jetting at high jet speed U (which is often used to improve jet directionality. Techniques to reduce satellite formation in DoD printing include selection of nozzle geometry, the control of the waveform applied to the print head actuator and deliberate modification of the fluid behaviour. The focus of the present paper is on the fluid.

Higher ratios of viscosity to surface tension can help to limit satellite production: empirical approaches commonly used include polymer additives to increase fluid viscosity, surfactants to reduce surface tension, and shear thinning fluids which relax fast enough to restore the low shear-rate viscosity in the jet after it emerges from the nozzle. However, as Figure 1b vividly demonstrates, too much polymer can prevent jet break off from the nozzle and simply produce long continuous filaments of liquid. Achieving a balanced fluid formulation in order to produce drops of high speed without satellites is difficult and such “sweet spots” may not exist despite using

quality assessment and control (QA, QC). Some of the high frequency fluid assessment techniques developed for QA and exploited in earlier work[1-3] are discussed later in this paper. Other related work based on videos of the break-up of colliding mm-scale jets of dilute polymeric fluids, appears to correlate well with inkjet scale jetting behaviour and rheological assessments, as reported elsewhere.[4,5]

Fluid jets passing at speed U through short DoD nozzles (length/D ~ 1) experience high extension rates of ~ $8U/D$. At fluid speeds ~10 m/s for D ~50 μm, nozzle shear rates exceed ~ 10^6 s^{-1}. As such rates exceed the upper frequency limit for conventional rheology test methods (1 s^{-1} – 10^4 s^{-1}), more specialised methods are needed to determine fluid properties to contribute to improvements in both print head design, ink formulation and QC. Knowing the rheology at very high shear rates can provide input to models and simulations, particularly for jetting but also for impact and initial spreading phases in deposition.

The range of complex fluids used in manufacturing far exceeds that for graphics printing, and so the effects of complex fluid properties on jetting need to be further explored. Recent results from a number of our academic research studies are brought together in this paper to help inform the digital fabrication community of advances in understanding of the jetting of complex fluids in comparison with, and beyond, the simple Newtonian fluids. The paper discusses the jetting behaviour of complex fluids, experimental methods for shadowgraph imaging of jets and drops, dilute polymer solutions, colloidal dispersions and shear thinning fluids intended for functional material deposition, ligament break-up, validation and application of simulations, high frequency rheology and results from filament stretching and thinning equipment.

Behaviour of complex fluids in jetting

The rheology of complex fluids at high extension rates has a significant influence on jetting. In early work[4] on the high speed (6 m s^{-1}) jetting of high molecular weight (M_W ~110-488 kDa) dilute linear polystyrene (PS) in the viscous solvent DEP (diethyl phthalate) the maximum jettable concentration was linked to the measured elastic modulus G' of linear viscoelasticity (LVE) for PS solutions in DEP. This conclusion has been discussed in a recent study of Xanthan gum jetting,[6] where the non-linear finite extensibility involved in drop formation has been separated from the effects within the nozzle, although both effects act together to control the final drop speed.

At concentrations below 0.01 wt% these PS solutions had Newtonian behaviour but, at somewhat higher concentrations (0.1 wt%), elasticity significantly restrained the jetting until a concentration level beyond which no jetting could be produced by the piezoelectric actuation of the Xaar XJ126-200 print head (50 μm nozzle diameter) at its maximum drive voltage. The experimental M_W (molecular weight) dependence of the maximum concentration agreed with results of the numerical simulations which had included viscoelasticity[7]. Both results disagreed with the predictions from FENE (finitely extensible non-linear elastic) models of long chain polymer molecules, which otherwise provide reasonably successful representations of linear polymer behaviour.

Other workers[8,9] jetted a range of dilute solutions of PS in less viscous solvents, but found no obvious correspondence of limiting PS concentration vs. M_W with the expected elastic response from polymer theory. Significant geometrical differences (long vs. short nozzle) between the print heads used in the different studies[4,8,9] also greatly complicated simple model predictions of dilute polymer fluid jetting. This is

because the time taken by molecules in passing through regions of high shear has to be compared with a typical relaxation time for a stretched molecule to coil up.

Experimentally, the extraction of relaxation times for dilute polymeric solutions has proved difficult, and until recently[10] had proved inaccessible for PS. From the Zimm "dumbbell" model for polymers, isolated molecular chains would be expected to show relaxation times ~ 7-80 μs for M_W = 110-488 kDa PS in DEP, which are rather short times for filament thinning. Effective relaxation times are known to be dramatically increased when the polymer concentration approaches the critical concentration c^* at which the chains overlap under static conditions. However in jetting the chains can become uncoiled and even fully stretched within the flows in the nozzle and/or the necking ligaments. For PS in DEP the critical concentration c^* is typically 1.0-0.2 wt% dependent on M_W, and relaxation time enhancements especially influence the lower molecular weights. For lower viscosity solvents[6] such effects may be smaller.

While the elastic modulus G' and viscous modulus G'' are linear viscoelastic (LVE) properties, the finite chain length L of a fully stretched chain is a contribution to the non-linear viscoelastic (NLVE) response of the polymer chain to the imposed fluid flow. Once the polymer chains are stretched, if the flow continues they behave like rigid rods and the fluid exhibits a fixed high viscosity[11]. Since constant viscosity is characteristic of Newtonian fluids, high speed flows produce a Newtonian-like behaviour in the fully stretched "dilute" polymer solution, albeit with a very much higher viscosity than for the same fluid under stationary conditions. By contrast only in the intermediate flow regime will dilute polymer fluids show an elastic response.

This is one key underlying reason why finding a "sweet spot" for polymer additives is difficult. The time required for polymer chains to become fully stretched is also very important, because the highest shear stresses only apply to the chains still within the nozzle.[12] The eventual reconciliation of all these issues and the implications for jetting of dilute polymers, applications and print heads are discussed below. This constitutes a major advance in the understanding of the jetting of complex fluids.

For many digital fabrication applications with aqueous formulations, the fluids contain surfactants intended to better promote drop spreading on the substrate. This spreading takes place on sub-second timescales[13-15], prior to drop drying or curing, that are accessible to measurements of dynamic surface tension (DST) using standard bubble tensiometers (>0.015 s bubble life). These may provide a rough guide to behaviour at the much shorter (~150 μs) timescales involved in DoD jetting, but leave some doubt as to the value of the surface tension applicable to the drop compared with the liquid which may have wetted the inkjet nozzle plate due to the jetting processes (or during nozzle plate cleaning).

As very short surface ages are easier to establish for continuous ink-jet (CIJ) jets and for free drops (in CIJ or DoD), rather than for pendant drops and bubbles, the DST at timescales relevant to DoD jetting can be determined for aqueous Newtonian fluids from CIJ jet oscillations[16] or from free drop oscillations[17,18]. Such methods can also be used to access dynamic viscosity, because free drops will tend to oscillate at a measurable frequency. Recently, free drops resulting from stretching of ~1 mm diameter filaments of complex fluids have been analysed to estimate both the DST and viscosity[18].

Other recent methods for assessing the surface tension of (Newtonian) fluids at short timescales are to measure free filament or DoD ligament retraction speeds[19] or the critical geometric length to width ratio for free ligaments that just avoid break-up[20,21]. While such methods have limitations they can easily discriminate between the high values of DST for pure aqueous solutions and the lower value EST (equilibrium surface tension) for fluid formulations containing surfactants. Some further data and explanations are provided below (experiments and modelling).

Suppression of satellite drops in DoD jetting might be assisted by dynamic non-Newtonian effects. Numerical simulations for the geometry of a particular print head (Length/D =1; D = 50 μm) at fixed actuation drive predict[7] that for the linear PS in DEP system a "sweet spot" without satellites exists at $M_W \sim$ 100 kDa (100 kg mol^{-1}). It is expected that the polymer elasticity at a particular concentration would permit single drop formation but later prevent ligament break-up. However, simulations based on a constant final drop speed of ~ 6 m s^{-1} rather than a constant drive voltage show no "sweet spot", so that the practical value of using polymer elasticity to prevent satellites is questionable. There may, however, be benefits for deposition from the higher viscosity of the polymer solutions, provided that the complex fluid behaviour is predominantly Newtonian-like. Lowered jetting viscosity at a given additive concentration within the DoD nozzle could permit even higher additive concentrations to be jetted, within the constraints of the print head drive voltage for a given actuation waveform. However this lower viscosity would normally be associated with earlier production of the satellite drops, unless the fluid viscosity η recovers rapidly in flight, to such a high value that the ligament necking speed gets

slowed down significantly. This fluid would then be classed as a shear thinning fluid. Highly shear thinning effects have been reported[22] for the complex fluid PEDOT:PSS commonly used in digital fabrication of organic electronics[23,24]. The shear thinning and recovery timescales eliminated satellite production within 0.8 mm of the print head at drop drive speeds between 2 and 15 m s^{-1}. Newtonian fluids with similar viscosity produced on average several satellites in the gap, and at a rate that increased as the drop speed was increased. Diluted aqueous PEDOT:PSS solution produced intermediate numbers of satellites, increasing with drop speed and dilution.

Experimental equipment and methods

High resolution, high speed imaging forms the basis for our detailed studies of jetting. Shadowgraph imaging with systems comprising High Speed Photo-Système nanolite spark flashes (20ns) with either Nikon D-series DSLR cameras, or Prosilica CCD cameras as shown schematically in Figure 2, or alternatively Adept Electronics long duration (2ms) flash lamps with 1 Mfps Shimadzu Hyper-Vision HPV-1 camera as shown schematically in Figure 3. Print head systems used include Xaar XJ126-200 with PCI+ control, MicroFab ABP with MicroJetIII control, Spectra Dimatix SX3 with Inca Digital controller, and Xaar XJ1001 with XUSB controller. Stanford Research Systems SR620 time interval counters and DG535 gate and delay generators were also used wherever sub-µs timing precision was required with flash imaging.

Image analysis software for extraction of jet and drop shapes included IrfanView and ImageJ, with additional Visual Basic, LabView and MatLab programs. Automated experiments used a LabView interface and a National Instruments DAQ card to trigger a MicroFab print head, provide controlled delays to the spark flash power supply and to handle CCD image capture, transfer to PC and file naming.

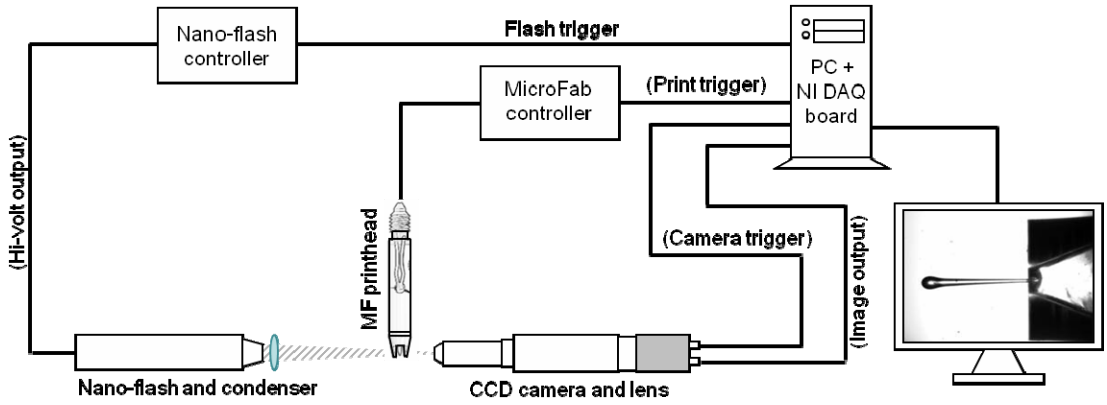


Figure 2. Schematic for complex fluid jetting studies using an automated shadowgraph imaging system[25].

Calibration of the spatial resolution (µm/pixel) in the recorded images was achieved by placing known calibration scales and wires in the image plane of the cameras at the same magnification setting as the experiments. Visible nozzle diameters and the known nozzle pitch spacing provided alternative calibrations and cross-checks. DoD drop speed measurement errors were < 0.1 m s^{-1} in our jetting work. The drop speed is normally assessed ~ 1.0 mm downstream (beneath) the nozzle exit, while displacement of the jet tip is always used for the determination of jetting speed. Holographic measurements of jetted drop sizes, 3-D position and velocities over large fields of view are described elsewhere[25].

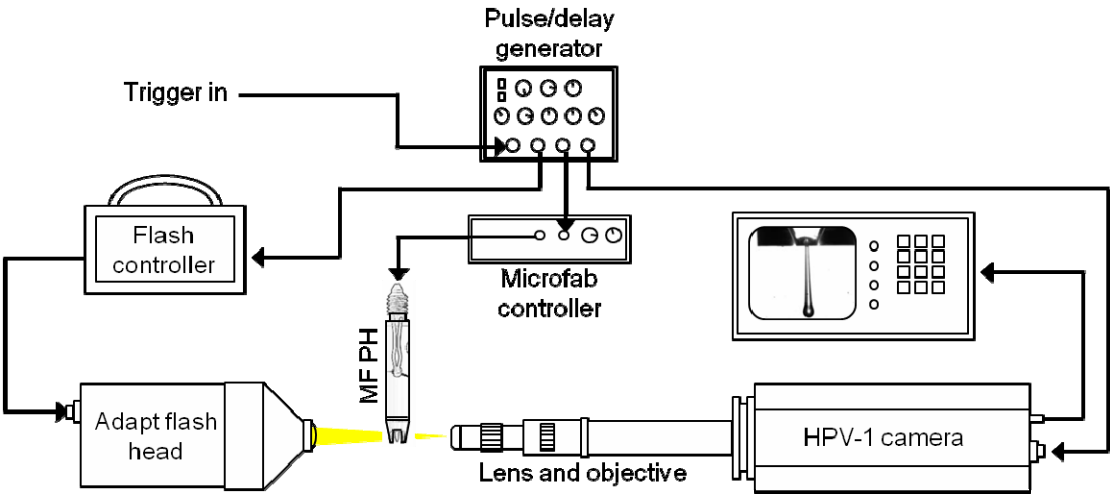


Figure 3. Schematic for shadowgraph imaging with Adept flash and 1 Mfps Shimadzu HPV-1 camera.[27]

Shadowgraph imaging of jets, ligaments, drops and satellites with variable light source intensity from image to image (e.g. due to flash variations) and within an image (e.g. due to shadowing by the print head nozzle plane) requires careful consideration of optical phenomena, such as fringing and image burn-out, that can affect the deduced drop size or shape. Small particles, satellites and thin filaments can easily have dimensions well below the optical resolution, but in comparisons between the successive images in a timed sequence they can be readily detectable by eye. Satellites can cause problems for the users of inkjet systems by reducing print quality, and small satellites (mist) can contaminate equipment causing failure. Empirical assessments of satellite production in jetting have classed visible DoD satellites as being either large or small, since they had appeared to fall into a cascade of scales.[28] The majority of inkjet mist production is from thin sub-micron diameter ligaments.

When DoD jets break off from the nozzle meniscus with a sizable fluid ligament, the recoil of this ligament into the main body of the fluid can cause free drop oscillations if the viscosity is not too high. As these drops are typically 20-50 μm diameter, drop oscillations occur at frequencies > 10 kHz. High speed images allow measurement of the frequency and determination of the surface tension at very short ($<10^{-4}$ s) time scales and the viscosity of the fluid if the drop size and the fluid density are known. Alternatively, the fluid properties can be deduced from oscillating drops remaining briefly between the separated pistons of filament stretching devices (e.g. TrimasterII)[3]. Our oscillating drop studies are discussed elsewhere[17,18].

Complex fluids were prepared on a small laboratory scale, with concentrations determined by weighing. Room temperature ultrasonic baths were used to mix

polymeric and colloidal fluids, and magnetic stirring for Laponite RD. All solvents were filtered to 0.45 μm prior to use and large debris were removed by 5 μm filtration before small (20-50 μm) diameter nozzles were used for jetting experiments. Fluids were assessed with a Malvern Instruments Bohlin C-VOR150 rheometer with parallel plates < 50 kHz, piezo axial vibrator (PAV) < 10 kHz and torsion resonators ~ 70 kHz that are sensitive to the linear viscoelastic response and a Trimaster II filament stretching device for the viscoelastic relaxation time τ. Spot checks of solution viscosity were made with a Hydramotion Viscolite 700 rheometer at 3.3 kHz, velocity of sound measurements used a Karl Deutch Echometer model 1071; DST was measured using a SITA pro-line T15 bubble tensiometer down to bubble lifetimes of 0.015 s. Material densities were determined from the literature or manufacturers specifications. Concentration limits and jetting speeds were determined as a function of print head drive voltages for polymer solutions and colloids go/no-go jetting tests. Fully analyzable and prolonged observations of free and DoD ligament recoil (or drop oscillations) always rely upon good repeatability and controlled forward speed, which often depended on successful avoidance of nozzle clogging and the break-off timing. In practice many observations had to be discarded in favour of "valid" events; even these had to be scrutinised for consistency with assumptions of the models for the fluid and process.

Models - dilute polymer solution jetting

We have shown elsewhere[28] that based on a simple model[29] dilute polymer jetting behaviour should be predictable from the DoD hardware nozzle size and jetting speed and solvent choice for various dilute linear polymer solutions.[30] This simple model approach has been greatly improved[12] by incorporating the proper treatment of

polymer chain pre-stretch within the nozzle flows and using measured effective relaxation times in extensional flow and not the Zimm predictions[10].

Results – dilute polymer solution jetting

McIlroy *et al*[12] showed that pre-stretching of molecular chains within a nozzle tends to blur the transition between partly stretched (elastic) and fully stretched (rigid rod) behaviour at the high jet speed (6 m/s) used in an earlier study by Hoath *et al*[29]. The lower M_W regime is also influenced by the effective polymer relaxation times[10] that can depend strongly on the ratio c/c^*. [32,33] The predictions of ×10 lower maximum concentrations now agree[12] far better with the 6 m s^{-1} jetting results for viscous solvents[29] than the original predictions from the simple 1-D model. Polymer jetting results at slower speeds, by other groups[8,34] who used lower viscosity solvents, remain well described. As a result, the effects of the hardware on polymer jetting are now well understood, with a successful[12] prediction of polymer chain breaking results[34] originating within print head nozzles.

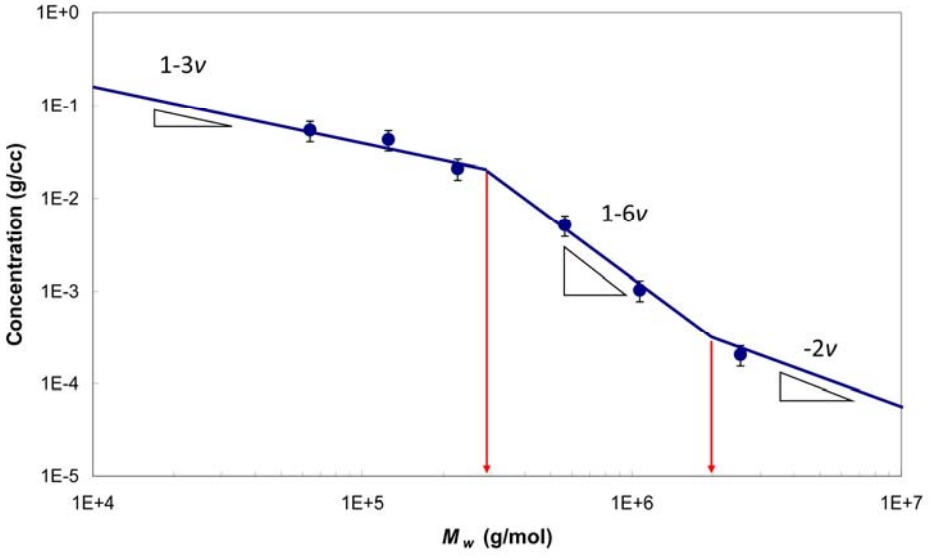


Figure 4. Data for maximum concentrations for jetting PS taken from de Gans et al[8] compared with the power law slope predictions in the 3 regimes of the simple jetting model of Hoath et al[29]. Calculations of McIlroy et al[12] show very similar results for the low jet speed, wide and long tapered nozzle geometry and low viscosity solvent used by de Gans et al[8].

Models – ligament break up

Following detachment, a jet from a DoD print head typically forms a massive head and one or more ligaments. A simple model[19] treats these ligaments as cylindrical lengths of radius R which then contract under surface tension towards a central point. An important question asked recently by Castrejón-Pita *et al*[20] about free flying liquid ligaments is whether they will subsequently contract into a single drop or break up into two or more drops. Evidence for the break up of free fluid ligaments from large scale experiments showed that there appears to be a geometrical criterion for ligament break-up determined by $Oh = \eta/\sqrt{(\rho\sigma R)}$, the dimensionless Ohnesorge number, such that more viscous fluids tend to support longer filaments without break-up. Experiments conducted on the scale of DoD inkjets[21] showed that the same criterion applied to free ligaments and furthermore that the same criterion could be interpreted geometrically for Newtonian DoD ligaments attached to massive heads. The geometrical criterion is linear in Ohnesorge number for this simple model[21]. The physical origin of this limiting geometric ratio apparently arises from the independent competition between the times taken for ligament shortening at Taylor's speed (due to the surface tension) and for radial necking of fluid (which depends on the ratio η/σ).

Results – ligament break up

Figure 5 maps results from HPV-1 video records for a jetted Newtonian solution at various temperatures from a MicroFab single nozzle print head. The temperature controlled the viscosity value for the Newtonian solution and hence the Oh number. The solid line represents the simple criterion established[21] from both large scale video data[20] and DoD scale spark flash data[21].

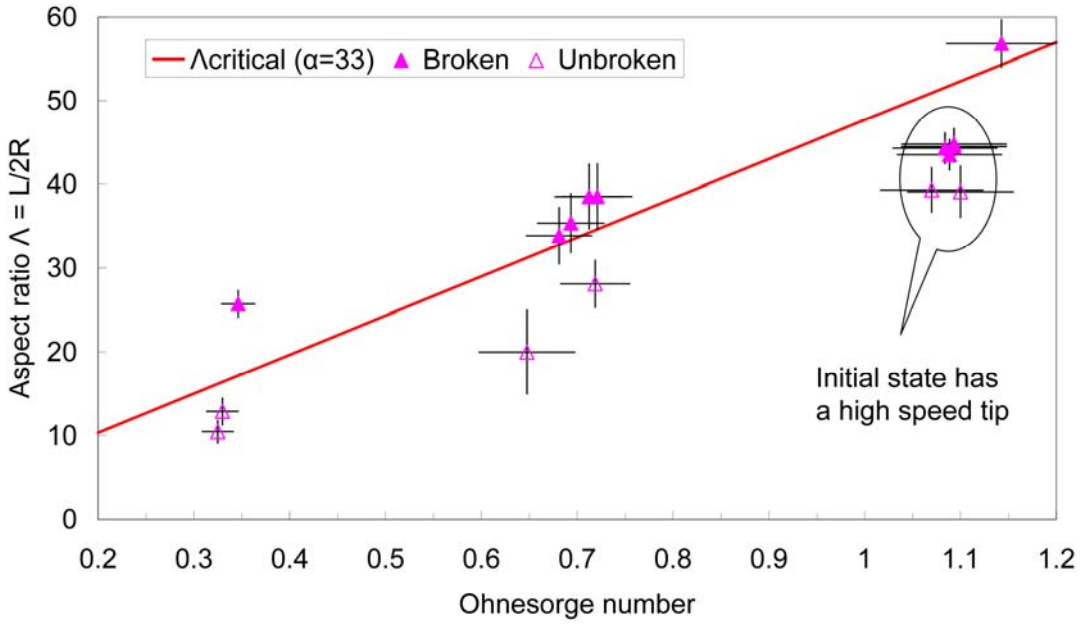


Figure 5: The measured geometrical aspect ratio Λ = L/2R for DoD ligaments vs. Ohnesorge number for Newtonian fluids has a predictable[21] critical value (red line). Filled symbols (generally above the line) record ligament break up events and unfilled symbols (below the line) represent long DoD ligaments that have coalesced without satellite formation. Deviations below the critical predictions at high Ohnesorge number are attributed to jet stretching due to excessive high speeds.

The simple criterion is reasonably accurate if it is applied to Newtonian liquid ligaments which immediately start to contract, as the observed trends at higher *Oh* show that jets do break up if they are stretching too fast. For applications to jets and ligaments the simple Ohnesorge number-based criterion[21] appears very effective.

Jetting of shear thinning fluids

A complex fluid commonly jetted for functional electronics applications is aqueous poly(3,4-ethylenedioxythiophene):(polystyrene-sulphonate) (PEDOT:PSS) plus surfactants to enhance electrical conductivity in the final transparent film or track. Despite having such a high viscosity at low shear rates that it would not normally be jetted from industrial DoD print heads, this fluid actually jets well, helped by a shear thinning fluid behaviour unlike the viscoelastic response seen for PS in DEP. There are significant delays in the creation of satellites from long ligaments trailing behind fast moving heads, proportional to the PEDOT:PSS concentration.[22] The long

PEDOT:PSS tails behaved as if they had very rapidly regained the high viscosity normally associated with low shear rate conditions, thereby raising the effective Ohnesorge number and delaying the ligament break up. Figure 6 shows the effect of PEDOT:PSS content on the average production rates of satellites within 800 µm of a 40 µm diameter DoD nozzle, and data for two Newtonian liquids for comparison. The effective viscosity for these PEDOT:PSS solutions in the nozzle was 3-10 mPa s.

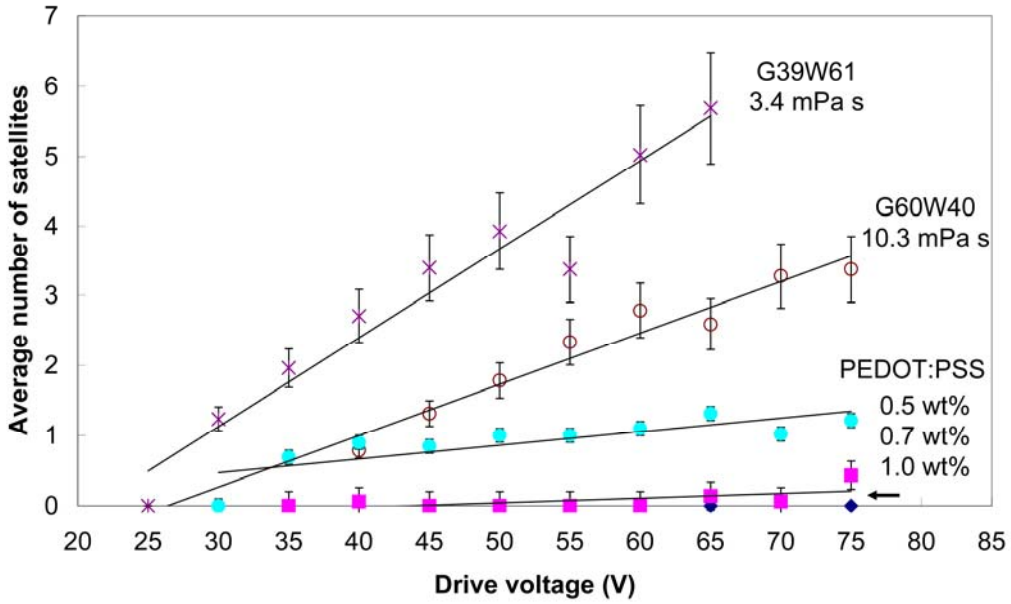


Figure 6. Average number of satellites visible within 0.8mm of the nozzle as a function of drive voltage (∝ jet speed) for Newtonian G (glycerol) W (water) mixtures and aqueous PEDOT:PSS solutions showing systematic effects due to complex fluid behaviour.[22] Newtonian mixtures are labeled with wt% and viscosity while PEDOT:PSS by nominal solid wt%.

Validation and application of simulations

Inkjet technologies often make progress through empirical tests, with computer simulations playing a less significant role in the development of a product. Although several numerical methods exists that aim to simulate drop formation, in practice only a few have been experimentally validated. In addition to this complication, the limitations of most commercially available software are often not clearly specified and most droplet-based systems operate at printing frequencies and spatial scales that are difficult to study experimentally. A recent exception has been presented[35]. In this

work, a large scale droplet generator was used to produce, in a fully characterized environment, drops on demand. The system utilizes nozzle diameters of ~ 2 mm and can operate under DoD and CIJ modes[36]. In brief, in DoD mode, the system uses an electromagnetic transducer to produce the single pressure pulse that jets the liquid. Most of the components of the systems are optically transparent and compatible with techniques such as laser Doppler anemometry (LDA) which can extract local fluid velocities inside the print head. The system also contains a pressure transducer, and thus the jetting pressure is also readily measured. Being on the millimetre scale, the nozzle characteristics can be studied by conventional microscopy and the jetting recorded by conventional shadowgraph photography. In the study, all the fluid characteristics, the nozzle geometry and the driving waveforms were input to a Lagrangian model with adaptive mesh nodes. Experimental and simulation results are shown in Figure 7. Qualitative shape and quantitative speed comparisons demonstrate that Lagrangian code simulations can accurately replicate the creation of Newtonian droplets. We have successfully simulated non-Newtonian DoD jetting for solutions of dilute polymers[7] and shear thinning fluids, and modelled particulate jets.

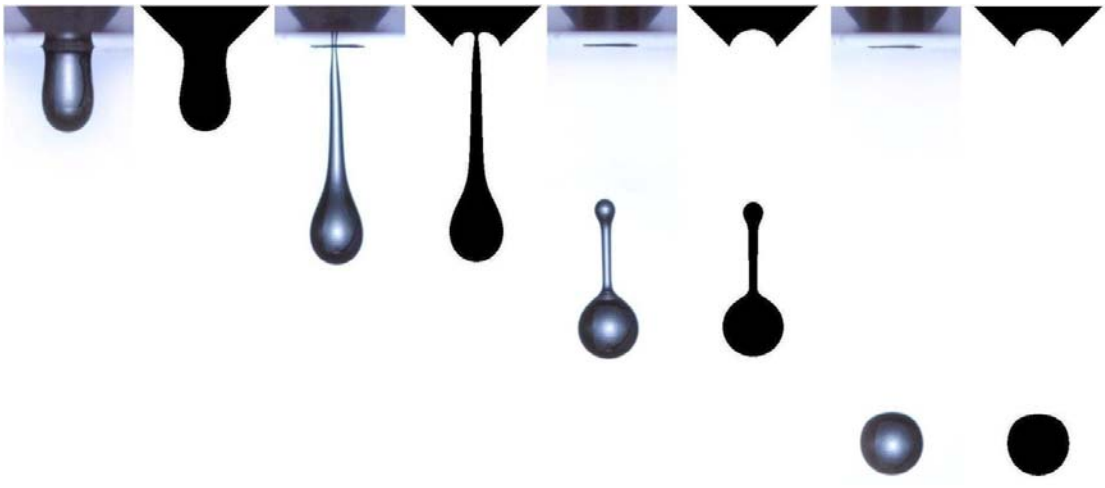


Figure 7: Comparison of numerical and experimental results of a drop jetted on demand. Experimental conditions, including the geometry of the nozzle and the velocity driving waveform, were introduced to the model. Reprinted with permission[35].

Summarizing the findings published previously[7,37], (i) simulations with FENE-CR find the same family of behaviour as experiments (e.g. by Bazilevskii *et al*[30]), (ii) using parameters extracted from LVE rheometry, good quantitative agreement between simulations and experiments was established for solutions of PS in DEP jetted through a DoD print head at fixed drop speed, and (iii) shear-thinning (or rather deformation thinning) fluids reduce production of satellites in the simulations as well as in experiments[22].

Rheological measurements

A piezo axial vibrator (PAV) technique[2,38] was used to study the linear viscoelasticity (LVE) of fluid films, which are typically less than 50 µm thick, over a range of frequencies. (The films are squeezed by less than 20 nm during the PAV testing.) Results are shown in Figure 8 for the "matched" polystyrene in DEP fluids of Table 1.

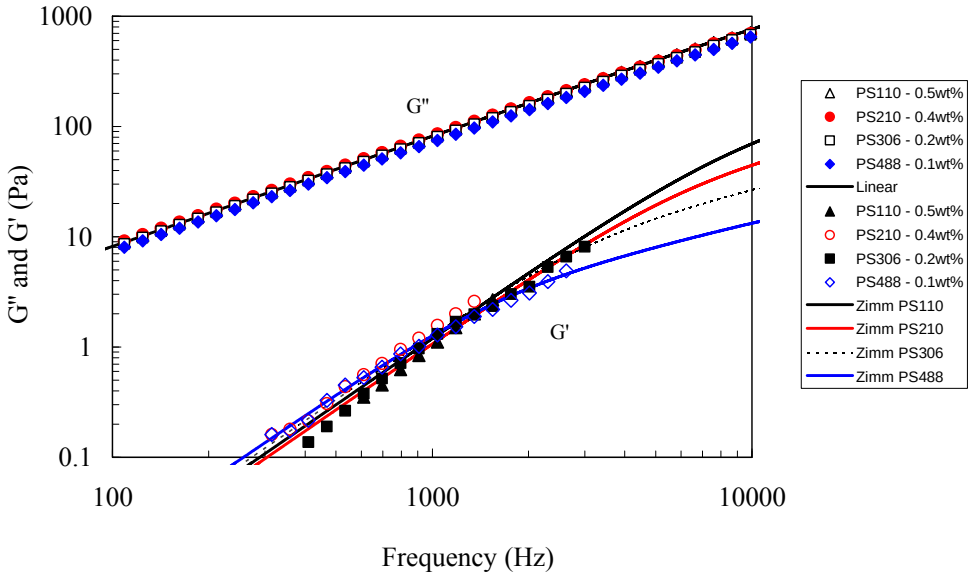


Figure 8. PAV results for the polystyrene in diethyl phthalate solutions of Table 1 showing "matched" linear viscoelasticity. Complex modulus $G^*=\sqrt{(G'^2+G''^2)}= 2\pi \times$ frequency $\times \eta^*$. Symbols in the legend above Linear represent G" and those below G'. Linear represents the fit to the G" modulus for PS110. The lines shown with the G' data are multi-mode Zimm model fits.[10,34]

Fluid	M_w (kg/kmol)	c (w/w)	c* (g/ml)	η_0 (mPa.s)
PS110	110000	0.5	2.56	16.3
PS210	210000	0.4	2.24	16.5
PS306	306000	0.2	1.9	15.5
PS488	488000	0.1	1.15	14.8

Table 1: Polystyrene in diethyl phthalate solutions with "matched" rheological results for linear viscoelasticity in Figure 8.

The overlapping sets of G'' (viscous modulus) and G' (elastic modulus) of Figure 8 show that the complex fluids of Table 2 had "matched" LVE behaviour below 2kHz.

Figure 9 shows that this low frequency "matching" was insufficient to predict jetting behaviour of Table 1 fluids from a 30 μm diameter MicroFab nozzle operated at fixed (±35 V) drive voltage. The image strips shown in Figure 9 correspond (left to right), to the pure DEP solvent and PS110 after 145 μs, and PS306 and PS488 after 200 μs. These striking differences can be ascribed to non-linear viscoelastic effects.[39]

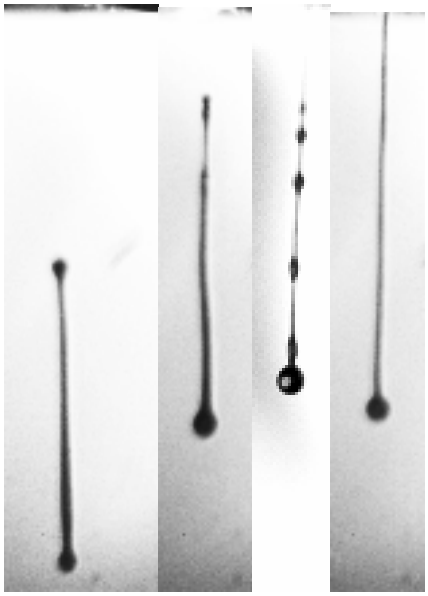


Figure 9. Jetting of viscous solvent and 3 fluids of Table 1 with matched LVE properties from the same MicroFab nozzle.[2,39] Delays: 145 μs for first 2 strips and 200 μs for the last 2 strips. These differences arise from NLVE behaviour of these fluids.

The NLVE behaviour determined from measurements in a "Trimaster" filament stretching rheometer[3] shows that polymeric fluids with matched LVE jetted very differently because of the very strong dependence[10] of the relaxation time τ on the "reduced" concentration c/c^*. Jetting produces extensional flow that increases the

effective relaxation time τ above the low shear-rate Zimm values by a factor of 20 for 0.5 wt% PS110 (Fig 9(b)) but by almost nothing for 0.1 wt% PS488 (Fig 9(d)). Stretching of molecular chains in highly extensional flow gives other non-linear effects as already shown above, which eventually limit the maximum jettable concentrations. A more complete description of these dilute polymer solution jetting experiments and their interpretation is provided elsewhere[39].

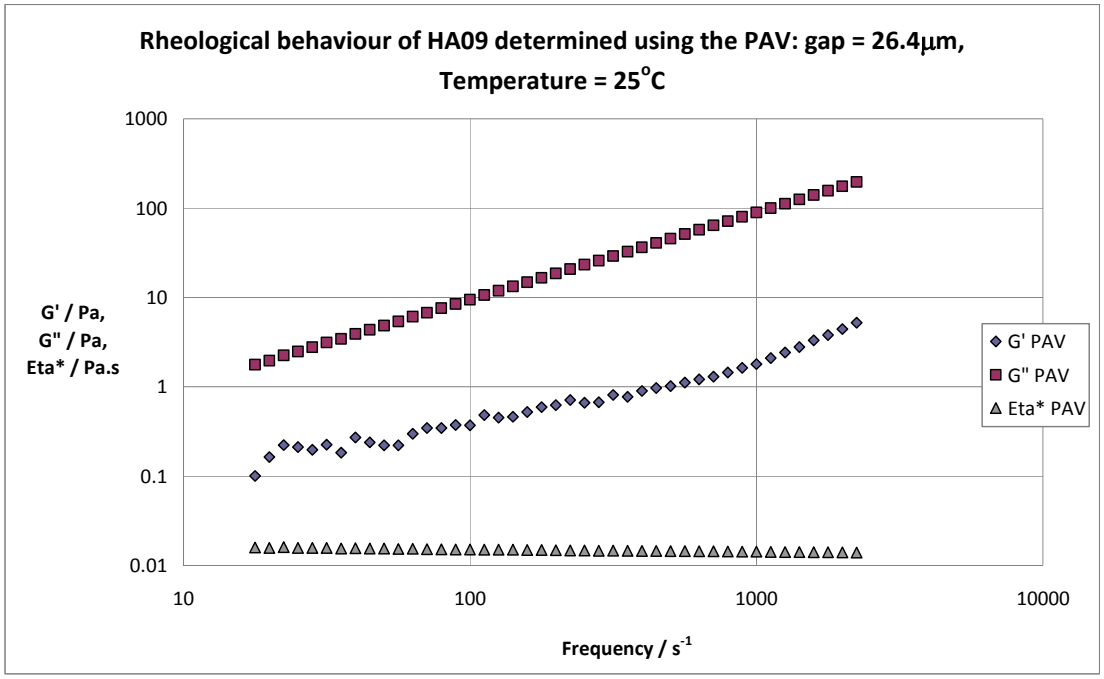


Figure 10. LVE moduli are both approximately linear in frequency giving a near-Newtonian complex viscosity Eta*. This polystyrene colloidal dispersion easily jetted from a 30μm diameter DoD print head.

It was noted[2] that the elastic modulus G' of pigmented inks has almost linear frequency dependence, quite different from the quadratic frequency dependence of G' for linear polymer solutions[38]. Thus pigmented inks show nearly Newtonian behaviour. Similarly, Figure 10 for the LVE rheology of mono-disperse stabilized polystyrene colloidal dispersion HA09 at 18 wt% solids in ethylene glycol / water has a complex viscosity (*Eta**) that is almost constant.

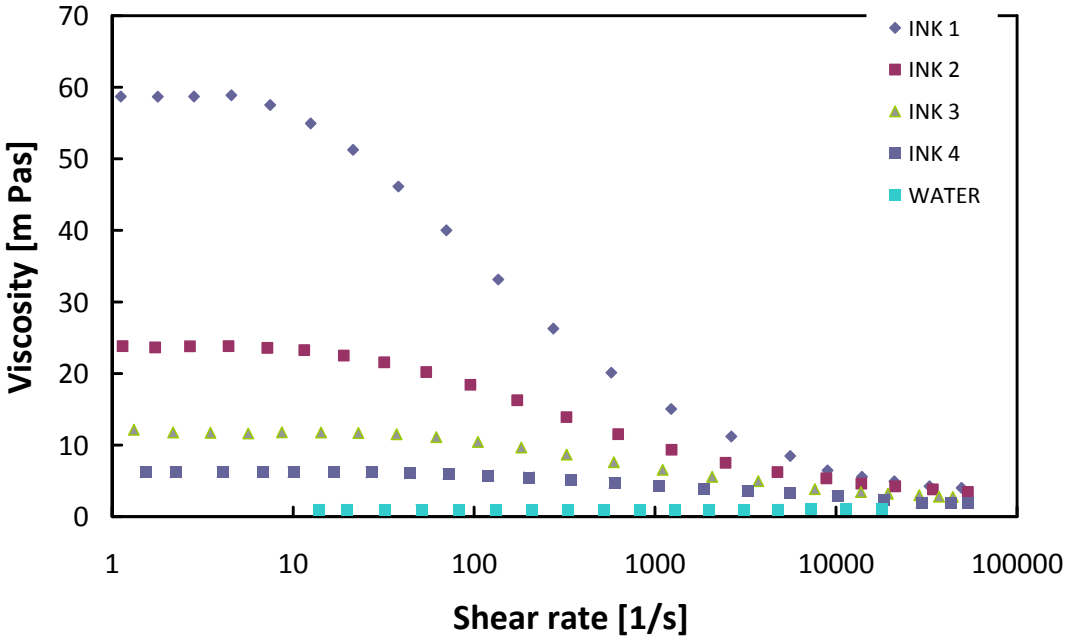


Figure 11. Viscosity data between 0.1 and 10,000 s^{-1} measured for various aqueous shear thinning solutions of Table 2.

Fig. 18	wt% PEDOT:PSS (*)	wt% Water	wt% Dynol 607	wt% Zonyl FSO-100
INK1	99.5	0	0.23	0.27
INK2	69.5	30	0.23	0.27
INK3	49.5	50	0.23	0.27
INK4	29.5	70	0.23	0.27
WATER	0	100	0	0

*Table 2. Aqueous PEDOT:PSS solutions with surfactants[22] corresponding to the comparison of rheology shown in Figure 11. * 100 wt% contains ~ 1.1 wt% solids in water, with d_{50} ~ 25 nm; Clevios PH 1000 from Heraeus Conductive Polymer Division.*

Shear thinning fluids such as aqueous PEDOT:PSS can show a far more marked change of viscosity with frequency. For example, PEDOT:PSS shear thins by an order of magnitude between zero shear rate and DoD jetting and drop oscillation shear rates. Table 2 shows the composition of the aqueous fluids that are compared in Figure 11.

Measurements using various techniques show aqueous Laponite RD fluids at 1-3 wt% loadings can have markedly different shear thinning capability. Figure 12 implies the fluids should be easily jetted for shear rates > 10^4 s^{-1}, very typical for DoD nozzles.

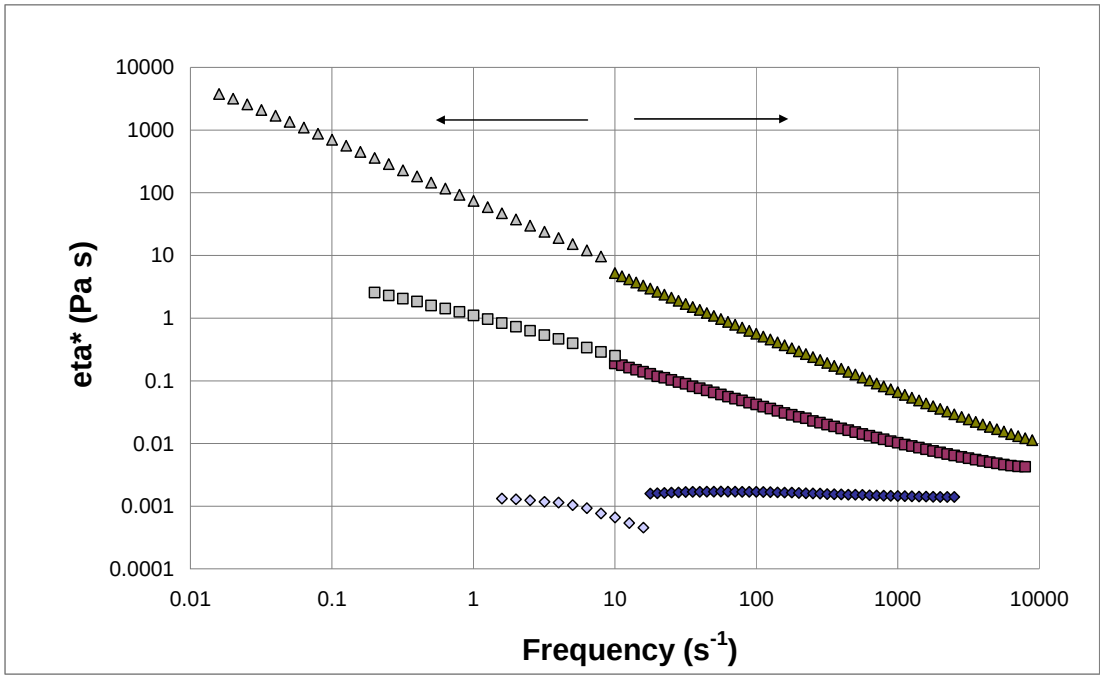


Figure 12. Complex viscosity data between 0.01 and 10,000 s^{-1} measured for aqueous Laponite RD samples at 1, 2 & 3 wt%.

Aqueous Laponite RD at 2 wt% loading has a shear viscosity variation by a factor of ~ 3 decades between low and high frequency shear conditions, which is ~ 2 orders greater than for the aqueous PEDOT:PSS at ~ 0.7 wt% loading. Our measurements demonstrate that both fluids, despite their high viscosity under low shear conditions, can indeed be jetted from a DoD printhead.

Discussion

Manufacturing techniques with inkjet processes have been made more resilient against drop placement errors in special cases (e.g. organic transistors[23]) by using surface treatments and self assembly processes; however these and other deposition-related digital fabrication topics (such as those[9] that involve jetting PS solutions) lie well beyond the scope of the present work based on high speed jets[40].

Jetting of polymers has been reported elsewhere (e.g. dilute linear and star polymers by the de Gans and Schubert group, poly-disperse mixtures of PEO by Carr and Dong, dilute and semi-dilute polymers by Yeates *et al*[41]), following early ground-breaking polymer jetting work of Basilevskii *et al*[27]. Our previous work on novel fluid assessment methods using large scale equipment[5] also correlated well with DoD jetting and PAV rheological assessments[4].

We have indicated how dilute polymer jetting studies help explain differences between jetting results obtained with a range of print head types and fluid conditions including solvent viscosity and quality, over a range of high molecular weights. This has allowed a wider picture of the observable maximum concentration limits to be established, together with predictions of polymer chain rupture within DoD nozzles. It also emphasises the need for QA of polymer additives used in ink-jet formulations, as high molecular weight components can produce deleterious effects on DoD jetting. Low viscosity solvents will be advantageous for jetting of higher concentration fluids, most especially if high drop speeds and higher molecular weight polymers are used.

The simple geometrical criterion found for Newtonian fluid ligament stability also provides an empirical upper limit for satellite free jetting of particle loaded fluid; the rupture of the jet filament will occur earlier as the ligament radius reduces towards the finite dimensions of the particles as is found in dripping and jetting experiments, though capture of particles in the thinning ligament provides other break up modes. It is also found that high concentrations suppress the average numbers of satellites but also prompt the production of much larger satellites than for Newtonian solvents.

For satellite-free jetting of polymeric fluids, trailing ligaments remain long and thin during the flight due to the relatively long polymer relaxation time, or ligaments rapidly recoil forwards into the main drop due to their elasticity; in both these cases our Newtonian criterion is not directly applicable.

Others, in particular the groups of McKinley & Clasen, use NLVE filament stretching for the extraction of polymer relaxation times for high molecular weight polymers. The typical stretching speeds attained with Trimaster II pistons of 1.2 mm diameter were ≤ 0.2 m s^{-1} providing access to ~ 100 μs relaxation times. Vadillo *et al*[10] showed that values down to ~ 30 μs can be determined for low viscosity polymer solutions.

Efficient and trustworthy simulations for jetting complex fluids are certainly needed. Recent examples for NanoCopper and NanoSilver Inks are provided by Lim *et al*[42]. At the present time the jetting of complex fluids from a range of DoD print heads often provides the most effective route to reliable fluid performance in applications.

Conclusions

Several results from the fundamental studies of jetting of complex fluids now impact on future applications of digital fabrication: (i) dilute polymeric additives can stretch and split into two pieces[34,12] within short (length/D ~ 1) industrial DoD nozzles working at high shear rates (~8U/D), (ii) polymer chains can be fully stretched outside the nozzle in the thinning ligaments[29], raising the ligament shear viscosity by >> 10× low shear solution viscosity and also allowing higher maximum concentrations of high molecular weight polymer fluids to be jetted faster than would be predicted from lower molecular weight fluids with elastic response; (iii) DoD jetting speeds are linear in drive voltage for Newtonian solvents and many dilute complex fluids, providing a

straightforward application to jetting speed control for industrial system integration[25]; (iv) satellite control by fluid modification still gives a maximum jet speed giving no satellites but this is greatly enhanced by shear thinning behaviour, as shown[22] for fluids such as aqueous PEDOT:PSS, and even for gels such as Laponite RD; (v) a simple physical criterion for break-up of Newtonian fluid filaments[21] may be applied to predict the likelihood of satellite free DoD jetting for dilute complex fluids; (vi) high frequency measurement techniques now available[38] have proved very valuable for accurate assessment of fluid suitability for DoD printing[2]; and (vii) existing simulations[7] and modelling[12] can predict the printability of complex fluids with improving relevance to industrial inkjet printing and digital fabrication.

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