

Jetting Complex Fluids containing Pigments and Resins

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Abstract

We have previously studied DoD jetting of complex model fluids based on dilute polymer solutions, resulting in the identification of a new regime of polymer jetting and some basic rules for predicting the limiting polymeric concentrations under real conditions such as print head nozzle diameter, jetting speed, solvent quality and polymer molecular weights [1, 2]. There has been no systematic experimental study of the effect of particles on DoD scale jetting, despite the ground-breaking work by Furbank and Morris [3] as reported in NIP17 for the effects of particles on dripping, although theoretical modelling for liquid bridges/filaments containing particles has been recently published [4] and could be relevant to local thinning of DoD ligaments.

A series of pigmented inks in the solvent dipropylene glycol methyl ether (DPM) has been used to help study effects of pigment particle size ($d_{90} = 3.6, 2.6, 1.6, 1.0, 0.8 \mu\text{m}$) on DoD jetting. These inks contained 35 wt% of the inorganic black pigment copper chromite and had a low shear-rate viscosity of $\sim 15 \text{ mPa s}$. Ink characterisation used a high frequency rheometer [5] and a novel fast (5 m/s) filament stretching device [6, 7], while the DoD jetting used MicroFab 80 μm diameter nozzles [8]. Jetting experiments were performed at 100 Hz to avoid nozzle clogging.

We report the first systematic experimental studies for DoD scale jets of characterized inks comprising (a) particles with no resin; (b) resin with no particles; and (c) combinations of particles and resins [9, 10]. These results will provide new insights into the jetting of pigmented inks and be important for new applications.

Introduction

Reliable inkjet printing of colloidal or particle suspensions, is desirable for modern manufacturing processes. Deposition of hard particles such as inorganic pigments is of increasing interest for larger scale decorative applications, but is currently restricted to relatively small particle ($d_{90} \sim 1 \mu\text{m}$) sizes. Dispersion agents based on added polymers can coat larger particles to avoid settling within ink reservoirs. The unwanted production of small satellite drops during inkjet printing, and perhaps triggered by or containing single particles as found in dripping studies [3, 4], might also be controlled by resins. Therefore the jetting of larger particle suspensions in DPM, a water-soluble carrier fluid, with added resins was the major driver for the current work [9]. Real particle loadings of up to 35 wt%, corresponding to volume fractions Φ between 10-30 vol%, below the maximum 64 vol% for spheres and “jamming thresholds” for particulate flow through nozzles [11].

We report the study of particle suspensions DoD jetted with resins [9, 10]. Newtonian solvent jets have been studied by many authors, e.g. Dong et al [12]. Furbank and Morris [3] explored

dripping scenarios for particle-laden fluids, while McLroy and Harlen [4] have recently modelled filament stretching and eventual break-up of such fluids. Estimates suggest that these modelling results might also apply to particle-laden ligament thinning under DoD jetting conditions, although the predicted effects on the break-off time may not be measurable at realistic particle loadings.

Jetting of polymeric solutions has also been reported by many authors, e.g. Basilevskii et al [13], de Gans et al [14], A-Alamry et al [15] and Hoath et al [16]. Weakly elastic polymer solutions in DEP, a relatively viscous solvent, were studied by Hoath et al [2], who found a new regime of polymer jetting and some 1-D modeling rules for predicting the limiting jetted polymeric concentrations under real conditions such as print head nozzle diameter, jetting speed, the solvent quality factor and polymer molecular weights, which were consistent with the existing data.

McIlroy et al [1] further improved the underlying assumptions and accuracy of these jetting predictions using 2-D modelling and also explained the particular range of molecular weights that ruptured during inkjet printing [15]. Some recent experiments [17] demonstrated that complex viscosity (linear viscoelasticity) need not determine the DoD jetting behavior for polymer solutions. This finding emphasizes the on-going need to fully characterize the (non-linear) properties of all inks intended for DoD inkjet printing.

Criteria for jetting comparisons

The criteria adopted for comparisons of jetting behavior of all the fluids tested in these experiments are pragmatic, guided by earlier observations of liquid jets and drops in DoD inkjet printing. The main (leading) drops have speeds that appear to vary almost linearly with print head drive voltage (above a threshold value of drive voltage that depends on viscosity), principally as a result of inertia and the duration of the drive pulse needed to propel the liquid through the nozzle [18]. The DoD jetting threshold drive voltage is empirically determined by extrapolation from speeds measured at higher drive voltages (where viscosity is significant) rather than from lower drive voltages (where surface tension is significant). The speed-drive curve for the jetted solvent has a gradient that seems representative of weakly elastic polymer solutions, shear thinning fluids and colloidal suspensions. The gradient of the speed-drive curve also appears to be relatively insensitive to the fluid viscosity.

Increased particle loadings can disproportionately increase the required print head drive to jet the fluid. Suspension viscosity η increases non-linearly with increasing vol% Φ , well above Einstein's value $\eta = \eta_s [1 + (5/2) \Phi]$ for low concentrations of non-interacting spheres in a Newtonian solvent with viscosity η_s . The Einstein result predicts that suspension rheology will be Newtonian, i.e. independent of shear rate, and also independent of

the particle size. As DoD inkjet printing is known to involve extreme shear rates reaching 10^6 rad/s, so that jetting of particle-laden liquids could be significantly influenced by any deviation from Newtonian behaviour.

Some empirically useful criteria or benchmarks for comparison of results for jetting particle-laden (and resinous) liquids from the same DoD nozzle are (i) the break-off time, (ii) the threshold drive voltage, and (iii) the gradient of the speed-drive curve. These criteria were used in the present work to help judge whether particle size at 35 wt% loading, or ~ 1 wt% resin content, controls the observed jetting behaviour.

Experiments

All the particle suspensions were prepared at 35 wt% in the low viscosity ($\eta_s = 3.7$ mPa s) low (0.148 kDa) molecular weight solvent dipropylene glycol methyl ether (DPM). Hard particles were selected with 5 different d_{90} size grades (0.8 μm , 1.0 μm , 1.65 μm , 2.6 μm and 3.6 μm) after grinding the same batch of copper chromite black spinel pigment with 10 wt% of an active low molecular weight polymeric dispersant. The particle size distributions for these pigmented inks were fully characterized, with the results shown in Figure 1. These results show that the hard particle suspensions produced by grinding were far from mono-disperse, with the larger particles having significant admixtures of smaller particles of typically 200-300 nm size.

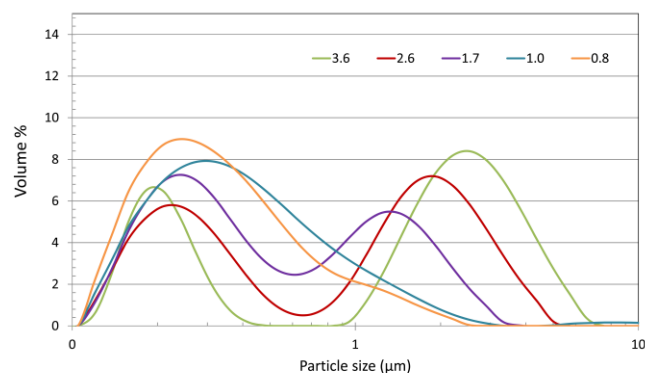


Figure 1. Particle size distributions measured for the 5 different size grades.

The 10 wt% dispersant in DPM had Newtonian behavior with a viscosity of 6 mPa s, while the 35 wt% pigmented inks had a low shear-rate viscosity of typically 15 mPa s.

Resins of different chemical structures and molecular weights (cellulose at 80 kDa and 370 kDa, acrylic at 30 kDa and 250 kDa) dissolved in DPM solvent, were prepared at various concentrations and jetted in combination with the particle-laden suspensions.

The solutions were manually agitated before decanting into small (3 mL) reservoirs for jetting from 80 μm diameter MicroFab AB print head nozzles. Specific print head drive waveform timings were maintained for all comparisons, with the drive voltage suitably adjusted for jetting. A continuous 100 Hz printing regime, with the exception of when manually triggered for video recording, was used to avoid unwanted nozzle clogging. DPM solvent purges

of the print head were used to eliminate any cross-contamination between the jetted fluids.

The 80 μm MicroFab print head has an exit diameter 20 times bigger than the largest particle d_{90} size and Figure 1 shows that the entire size distribution was always below 10% of the nozzle diameter, which is considered sufficient to avoid particle jamming and should not bias our jetting results towards smaller particles.

Results

At 5-20 wt% concentrations of the high molecular weight resins in DPM, the liquid jets did not emerge from the nozzle exit. At lower concentrations (e.g. 1 wt% 370 kDa cellulose in DPM, and 4 wt% 250 kDa acrylic in DPM), the resin jets emerged but did not break-off from the body of liquid but retracted back into the nozzle after the end of the DoD actuation waveform. Such typical behaviour¹¹ shows that the addition (or unwanted presence) of sufficient high (100's kDa) molecular weight polymer to most liquids can significantly limit DoD jet speed. Lower concentrations of resin (0.5 wt% 370 kDa cellulose and 2 wt% 250 kDa acrylic) was jetted successfully when mixed with 31.5 wt% pigmented ink.

Figure 2 shows the drop speed measured as a function of drive voltage for the pigmented inks and the DPM solvent. Under DoD jetting conditions these (opaque) pigmented inks behave with similar viscosities to the (clear) 3.7 mPa s solvent although at low shear-rate ink viscosities were several times higher than this value.

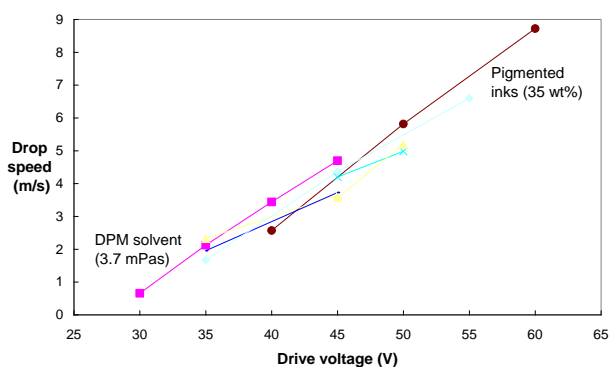


Figure 2. Drop speeds for the DPM solvent and the 35 wt% pigmented inks in DPM solvent as a function of the 80 μm MicroFab AB print-head drive voltage. Measurements at different drive voltage for a given fluid are shown connected.

Figure 3 shows the break-off times for the jetted pigmented inks and the DPM solvent, as a function of the print-head drive voltage. The small differences between jet break-off times across the drive voltage range (hence main drop speeds) or pigment size again suggests that at 35 wt% particle loading the fluid viscosity in jetting must be similar to that for the 10 wt% particle dispersant. This apparent independence of break-off time on drive voltage has reported previously [19] and has been exploited below in order to increase the statistics available for comparisons with added resin.

Our findings for jetting resins only are not reported here, but will be shown later in a paper dealing with the jetting of colloids. Earlier work on jetting polymers is already published [1, 2].

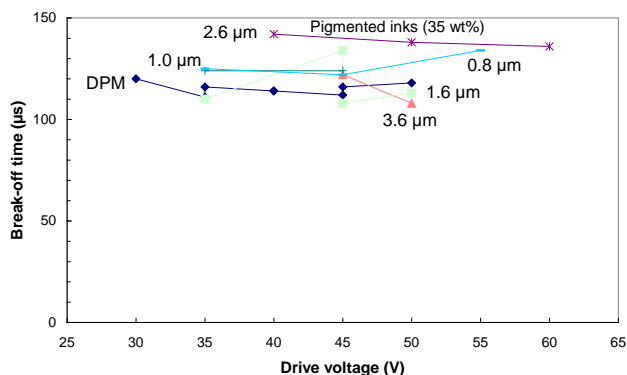


Figure 3. Break-off times for jets of the pigmented inks as a function of the drive voltage. Results at different drive voltage for a given fluid are shown connected, with the d_{90} particle size labelling each pigmented ink series.

Figure 4 shows the DoD jet break-off times observed for the “Particles-only” series shown in Figure 2 and the 9:1 combination by weight of the pigmented inks mixed with a high molecular weight resin to keep the particulate concentration reasonably high (at 31.5 wt%). The additives, either 0.5 wt% (370 kDa cellulose) or 2 wt% (250 kDa acrylic) in DPM, had sufficiently low viscosity for successful jetting by the 80 μm Micro-Fab print-head. These break-off times are based on averages over drive voltage, and are shown with error-bars that represent the variation over drive voltage and the statistics available for each of the jetted inks. The straight lines represent these times averaged over particle size.

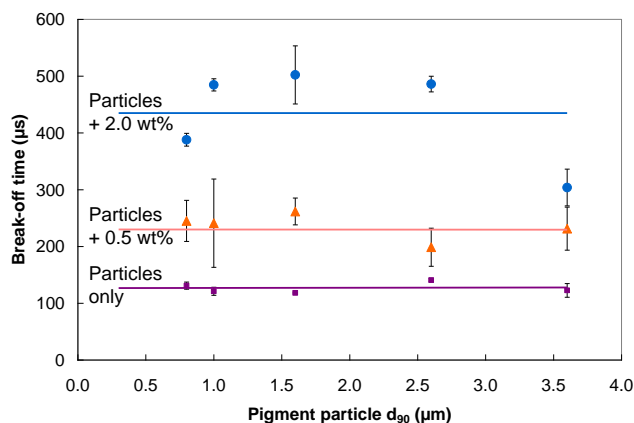


Figure 4. The break-off time measured for each particle size and added resin (either 0.5 wt% 370 kDa cellulose or 2 wt% 250 kDa acrylic). These break-off times are based on averages over drive voltage and shown with error-bars.

Discussion

Figure 1 shows that the hard particle size distributions were not mono-dispersed. There are however significant differences as the particle d_{90} size was reduced by grinding towards smaller size. At the loadings used, size has rather small effect on the jet speeds.

The pigmented ink break-off times shown in Figure 3 have typical uncertainties of $\sim 10 \mu\text{s}$ i.e. $< 10\%$ of the break-off time.

The jetted DPM has an uncertainty that is significantly lower than this, so that the critical differences between jetting particulate inks and the solvent carrier fluid may be in this greater uncertainty (due to the presence or absence of particles within the thinning regions of the jetted suspension) rather than in the absolute break-off time. This links well with the approach taken by McIlroy and Harlen [4] to model the thinning of particle-laden liquid bridges towards the break-off, but testing this also required far larger numbers of jetting events than were necessary to report the present work [10].

Figure 4 suggests that there is very little effect of particle size (for $d_{90} \sim 0.8\text{-}3.6 \mu\text{m}$) on the 80 μm DoD jet break-off time for the ~ 31.5 wt% hard particle suspensions in DPM with added 0.5 wt% (370 kDa) cellulose or 2.0 wt% (250 kDa) acrylic high molecular weight polymers. Either resin additive controls the break-off time. Taking into account the different polymer molecular weights and concentrations used in Figure 4, the increase in break-off time should scale linearly with concentration of a given polymer weight, and no chemistry need be invoked to explain the difference results.

No attempt to optimize the DoD waveform (to minimize the drop volume or jet break-off time) was made in the present work, as would be done for applications. It appears that the particle-only suspensions shear thin under DoD jetting conditions, which would tend to allow them to be jetted more easily than anticipated from their measured low shear-rate rheology. For the same drive voltage this would produce faster jets, and these could produce satellites. The addition of high molecular weight polymers can greatly delay DoD jet break-off at all drive voltages, while reducing the production of satellites if something akin to a polymeric jetting “sweet spot” [20] can be found for such complex pigmented inks.

Conclusions

Hard particle sizes ($d_{90} \sim 0.8\text{-}3.6 \mu\text{m}$) had negligible effect on DoD drop speed and jet break-off time for ~ 35 wt% (moderately loaded) suspensions. As the jet break-off time normally limits the printing frequency, remaining key factors are nozzle jamming or blocking and production of satellites. Inkjet fluid pigment sizes might be increased up to $1/20^{\text{th}}$ of the DoD nozzle diameter without jamming or any significant impact on drop speeds exceeding 2 m/s or on jet break-off time at a given drive voltage. Increasing the pigment sizes by a factor of 2 (to $\sim 2 \mu\text{m}$), bringing big benefits to some inkjet applications, appear to be quite feasible. Addition of < 2 wt% high (~ 250 kDa) molecular weight polymers can significantly delay the jet break-off, but it appears that using somewhat lower concentrations should reduce such delays while perhaps offering a satellite control independent of the particle size. Any influence on break-off delays arising from the chemical nature of the resin (cellulose or acrylic) used were dominated by the viscosity changes due to the ~ 1 wt% concentration of the additive. Again, such results will encourage further studies and applications.

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