Colloidal Suspension Rheology and Inkjet Printing

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Abstract

This work reports the first systematic survey of colloidal suspension jetting [1], as opposed to dripping liquids containing particles [2], and it complements a previous survey of the jetting of complex fluids [3]. Colloidal suspensions of stabilised polystyrene particles in water/ethylene glycol were formulated for maximum stable loadings (vol%) and low poly-dispersity index (PDI), for a range of spherical particle sizes (80 nm to 850 nm). Each preparation batch was characterised using squeeze mode rheometry [4] and filament stretching devices [5, 6] while being independently assessed using drop-on-demand (DoD) inkjet printing from MicroFab nozzles with either 30 µm or 80 µm diameter. Nozzle blocking was reduced for the jetting tests by maintaining a 100 Hz printing frequency throughout waiting periods. Additional experiments used a transparent containment chamber around the 30 µm nozzle exit to examine jetting behaviours that might be caused by the humidity level. Jetting for each batch (characterised by colloidal particle size, vol%, nozzle size, etc.) was considered successful if high speed videos used for measurements of drop speed and determination of the jet break-off time from nozzle meniscus were reliably and consistently achieved at several drive voltages. Jetted drop speeds for all the colloid suspensions tested showed a linear dependence on drive voltage above a threshold voltage as previously reported for Newtonian and weakly elastic drop speeds [7]. Mapping of successful DoD jetting as a function of colloidal particle size (nm) and vol% for 80 µm (30 µm) nozzle diameter reached 37 vol% (30 vol%) without any evidence for any spherical 80-850 nm (300-850 nm) particle size effect on jetting.

The rheology of these colloidal suspensions, obtained independently from jetting, exhibits rather Newtonian behaviour with a range of viscosities within a factor of 2. Likewise, the filament stretching experiments that are sensitive to non-linear effects such as relaxation time [5, 6] could not discriminate between solvent and suspensions. Beyond issues with blocking (and stability), colloidal suspensions were jetted easily, in line with expectations based on the measured rheology and low non-linear effects.

Introduction

Inkjet printing of complex fluids containing a variety of different materials, e.g. polymers and colloidal dispersions, still needs to be far better understood for reliable fabrication and additive (3D) manufacturing purposes. A first challenge for design of complex fluids intended for drop-on-demand (DoD) inkjet printing is rheological characterization at high frequencies.

The shear rates at the nozzle wall during DoD jetting can often reach 10^6 radians/sec, far beyond the reach of conventional mechanical testing. Extension rates within thinning jet ligaments also become high during DoD jetting with drop formation, so that the material response needs characterization at high frequencies.

Another challenge is DoD nozzle exit blocking, caused by drying and increased particle density on the surfaces of the nozzle plane and the liquid meniscus. For some of the studies reported here a special jetting chamber design, that raised local humidity around the nozzle, was introduced to reduce nozzle drying rates, but would not be feasible for practical applications. Nevertheless use of similar chambers have permitted some useful initial studies of the airflows around jets and drops above moving substrates [8], illustrating the value of studies which deliberately simplify issues.

Ethylene glycol water (EGW) mixtures were chosen to carry the colloid particles to reduce meniscus drying issues for DoD jetting studies, as our earlier work using more volatile formulations had suffered from nozzle blocking. However this ignores all the issues of unacceptably long droplet drying times on the substrate. Nevertheless, EGW carrier provides a basis for jetting comparisons of fluid preparations using specific (80 nm – 850 nm) colloid particle sizes at low poly-dispersity index (PDI) up to the maximum stable concentrations achieved in formulations.

The aim of the present work was to establish some experience in DoD jetting colloidal suspensions that might inform industrial applications. Can a fluid ink with the maximum colloidal particle concentration that can be stably formulated, actually jet? (It is well-known that the maximum concentrations of high molecular weight polymers in DoD jetting can be ppm rather than >10 vol%.) Are there other restrictions on the jetting of these colloidal fluids, perhaps related to humidity, the relative size of the colloidal particles and the DoD nozzle, or blocking? Can far larger particles be jetted, with or without added polymer? We report some of our findings to date. Further details and results of our related research programs are given in the literature [1, 9] or in recent conference talks, papers and posters [10].

Rheology

Table 1 details the colloidal dispersions in EGW carrier fluid that were assessed and jetted in the present work. Mono-disperse (low PDI) polystyrene particles, with d_{50} ranging from 90nm to 850nm, were formulated at stable loadings up to about 37 vol%.

Each preparation batch of colloidal fluid was characterized by using squeeze mode PAV rheometers [4] and filament stretching devices [5, 6] to determine the complex viscosity η* to frequencies of 5 kHz and to compare with the filament thinning behavior of the Newtonian EGW carrier fluid, respectively. Such characterization revealed that these colloids behaved very like Newtonian fluids.

Table 1: Colloidal fluids tested in the present work [7]

Colloid Batch	Carrier Medium	Diameter d_{50} (nm)	PDI: size range	Solids (vol%)
HA09	EG77.5W	492.9	0.05	24.1
HA10-1	EG25W75	444.6	0.10	30.6
HA11-1	EG25W75	542.7	0.08	36.6
HA11-2	Water	615.8	0.03	44.1
C46	EG77.5W	794.9	0.08	18.1
CA09	EG77.5W	363.0	0.11	22.0
CA22	EG77.5W	858	0.22	23.0
CA26	EG77.5W	92	0.13	30.6
CRF01	EG77.5W	168	0.04	20.5
CRF03	EG77.5W	796	0.28	21.7
CRF04	EG77.5W	361	0.08	21.5

Figure 1 shows an "Einstein plot" for the measured complex viscosity η* at colloidal volume fraction Φ of some of the colloidal suspension batches shown in Table 1. The Einstein relation shown is linear in Φ for very low volume fractions, whereas the Bachelor relation is quadratic in Φ and gives a better account for all these colloidal suspensions except CA26 (the smallest colloid particles). Figure 2 shows filament stretching was similar for these batches.

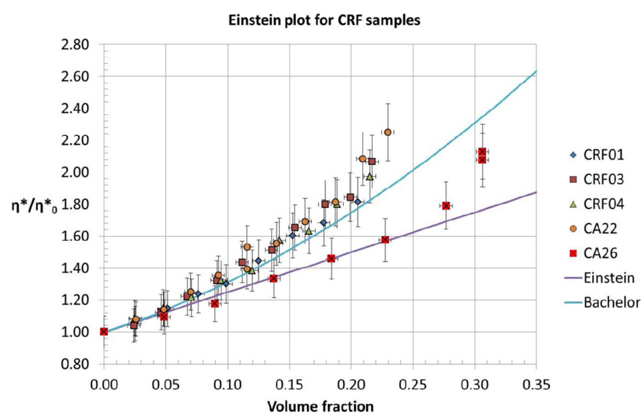

Figure 1. Einstein plot of complex viscosity increase with the volume fraction Φ, for some of the colloidal batches from Table 1. (See text)

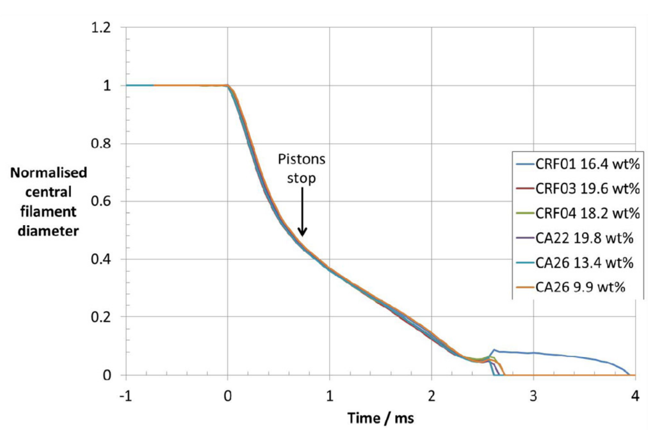

Figure 2. Filament thinning comparison between colloidal batches of Figure 1.

Experiments

An ultra-fast camera (Shimadzu HPV-1) with high power (500W) long duration (1 ms) flash lamp (Adept Electronics Ltd) was used to record 102 images at 500,000 frames per second, at a spatial resolution of 2.44 µm/pixel [3]. The visible path-length obtained with this system was almost 1 mm, the conventional distance corresponding to the stand-off and often used for specification of drop speed. For jetting studies using a 30 µm diameter MicroFab nozzle this path was contained within and imaged through the transparent (Perspex) walls of a chamber that was used to maintain humidity at raised levels above the ambient. As clogging by debris in the jetted fluids was encountered for the smaller nozzle, jetting studies with 80 µm diameter MicroFab nozzle were also made without this chamber, to better represent realistic inkjet conditions, and a continuous 100 Hz printing rate applied to avoid the occurrence of significant nozzle blocking [1].

Table 1 lists properties established for the various colloidal fluid batches at the maximum stable concentrations that could be formulated. Successful DoD jetting of these colloidal suspensions would show that the formulations for various particle sizes, and the rheology resulting from them, should not limit their application.

The HA09 colloid batch was jetted from a 30 µm diameter MicroFab print head nozzle at several dilutions (18%, 12%, and 6%) for comparison with EGW mixtures prepared with similar viscosity as the corresponding diluted colloidal fluid at low shear-rate. The video image data were also analyzed frame by frame to obtain large and small sized [11] satellite production rates as a function of main drop and jet ligament speeds, and also the differences in the timing of satellite drop formation from the thinning jet ligament occurring after the main drop pinch-off, relative to that observed for the Newtonian EGW carrier.

Results

Figure 3 maps the vol% and colloid particle (d_{50}) size for all the polystyrene colloidal suspensions in EGW carrier medium from Table 1 that were jetted from the 80 µm diameter MicroFab nozzles in the present work [1]. Little or no effect of the near mono-disperse colloid d_{50} size on maximum loadings for DoD jetting was observed for up to 37 vol% for the 80 µm diameter nozzles and up to 30 vol% for the 30 µm diameter nozzles (not shown).

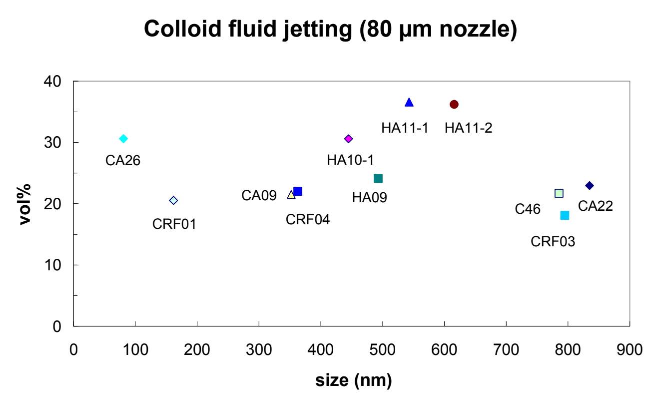

Figure 3. Colloidal suspensions formulated for the present work are mapped against vol% and nearly mono-disperse colloid (d_{50}) size (nm). Labelled solid symbols represent the successful fluid jetting from 80 µm MicroFab nozzles.

The influence of the bulk viscosity on DoD jet speed, for the HA09 colloidal suspension at several dilutions with EGW carrier fluid, is shown in Figure 4. The EGW carrier was jetted at ~9 m/s but the HA09 colloidal solution jetted somewhat slower than this, recovering the speed as it was reduced by successive dilutions.

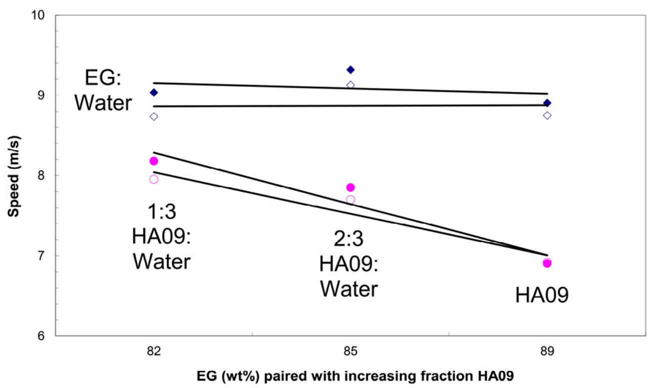

Figure 4. Main drop speeds of HA09 colloidal suspensions at several dilutions with EGW carrier as a function of EG wt% content of the EGW carrier solution.

As the satellite droplets formed from DoD polymer ligament break-up were found to follow a hierarchy of sizes [12], an analysis for the break-up of HA09 colloid fluid is of interest here. The average satellite count initially formed and after final merging are shown in Figure 5 as a function of the main drop speed.

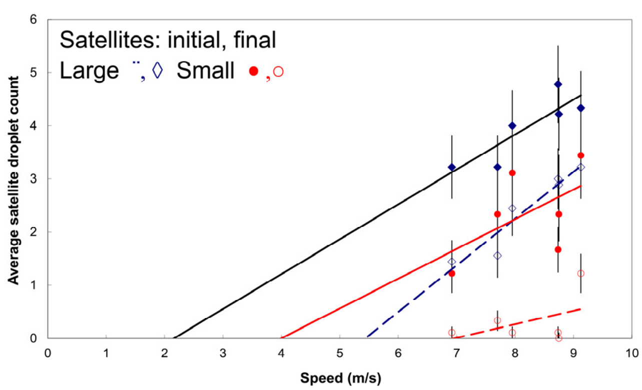

Figure 5.Production rates for HA09 fluid satellites as a function of main drop speed. Average satellite numbers created initially (filled symbols) and after final merging (open symbols) within the ~1 mm field of view: diamonds (large) and circles (small) satellites, following the analysis for polymer DoD satellites [12].

Figure 6 displays the observed satellite production rates for the HA09 colloidal and EGW mixtures during jetting was tracked (within the field of view) as a function of the elapsed time after jet break-off in order to observe any differences in jetting of colloid compared with carrier fluid. The main head pinch-off events, occurring well before several smaller satellites formed from the long trailing ligament, were similarly delayed for all fluid types. Rear-merging events, of fast satellites with the leading main drop, were readily identified, while slower satellites left the 1 mm field of view just within the ~200 µs video recording period at 500 kfps.

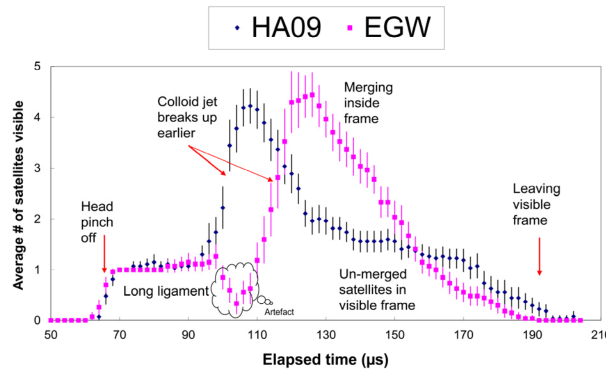

Figure 6. Average number of satellite drops visible within a ~1 mm field of view for HA09 and EGW jets that break-up after earlier formation of the main drop. Error bars reflect the statistics of the measurements over repeated jet events.

An image analysis artefact (later detected by eye) mis-identified thinnest ligaments for a small period of elapsed time, but otherwise did not disrupt evidence for differences of EGW from HA09 jets.

Interpretation

Previous experimental work on dripping of suspensions by Furbank and Morris [2] and numerical models for the thinning of particle-laden liquid bridges by McIlroy & Harlen [13] had showed sensitivity to colloid size (relative to nozzle) and vol %. In contrast, the jetting drop speed and break-off time for the colloidal suspensions mapped in the present work are not sensitive to these for 80 µm diameter MicroFab print-head nozzles, up to loadings of 37 vol%, although for 30 µm diameter nozzles the maximum jetted concentration was lower at about 30 vol%.

Other measures of DoD jetting differences with colloidal particle size and concentration, such as the production rates for satellite droplets during jetting, are thought to be dominated by the speed for a given waveform rather than by the colloid particles. Figure 4 provides a means to compare the satellite formation from colloidal and Newtonian jets with similar speed and low shear-rate viscosity. After near-identical head pinch off times, the remaining long ligaments fragmentation behavior was somewhat different, with satellites produced about 15 µs (15%) earlier by the colloidal jet than by the EGW jet and yet persisting for longer within view, because they were slower and unable to rear-merge with the head.

Discussion

Figure 1 and Figure 2 summarize the colloid batch rheology as determined by techniques reported elsewhere [4-6]. The colloidal filament thinning plots in Figure 2 are consistent with Newtonian behavior without any evidence for the long-lived filaments often associated with high (> 100 kDa) molecular weight polymers. This is unsurprising for these batches because the polystyrene colloidal particle stabilizer used in the formulations was PEG 2080 (2 kDa polyethylene glycol). Nevertheless the filament stretching device was operated at 2 m/s separation speed, an order of magnitude faster than previously available [14]. Figure

3 shows little influence of the d_{50} size (for 90-850 nm) on the colloidal polystyrene concentration in ethylene glycol water carrier medium that can be DoD jetted through 80 µm nozzles. A similar result was obtained with 30 µm nozzles, although the maximum concentration was about 30 vol% instead of 37 vol%. Debris in solution that was observed within the (transparent) 30 µm MicroFab nozzle was sufficient to lower the overall speeds of several jetted undiluted batches from Table 1, which tends to limit the maximum concentration for a fixed jet speed or drive [3]. Figure 4 shows that the HA09 batch had higher measured drop and jet ligament speeds from a 30 µm MicroFab nozzle at fixed drive voltage than when more highly diluted with EGW carrier. This was entirely expected behavior, roughly consistent with loss of drop and ligament speeds that is proportional to the actual colloid vol%.

Figure 5 shows the measured satellite speed. More satellites are produced for faster jets, as has been observed for Newtonian solvents and for weakly elastic polymer fluids [3, 12].

Figure 6 shows that satellite production for HA09 (with d_{50} ~500 nm) colloidal suspension jetted from a 30 µm MicroFab print-head, following main drop head pinch-off, occurred on average about 15% earlier than for EGW. This is reasonably consistent with the results of a filament thinning model by McIlroy and Harlen [13] for colloid bridges having particle volume fraction $\Phi = 0.20$.

For all the colloidal particles sizes DoD jetted in the present work Brownian motion can be ignored and the Peclet number remains high enough for the model [13] to apply to DoD ligament. The thinning ligament exhibits viscosity nearer to that of the carrier fluid viscosity if particles are absent from neck regions, but otherwise flow with higher viscosity associated with the bulk fluid. Necking proceeds at a rate determined by surface tension/viscosity, as was shown for Newtonian jets and DoD ligament break-up [13].

The spatial resolution available over 1mm flight path when using the high speed video camera was insufficient to resolve the presence of individual colloid particles within the satellite drops. In principle large particles, shorter flight paths or use of imaging markers could be introduced to help test colloidal jetting models.

Conclusions

The colloidal batches do not have major differences in their rheology, and have little or no detectable effect filament thinning. The Newtonian carrier viscosity is enhanced by the added colloid vol% to an extent that is consistent with the existing models.

DoD inkjet printing of colloidal suspensions does not appear to be limited by the colloidal particle size (90-850nm), but for the smaller 30 µm nozzle, by nozzle clogging and nozzle drying issues. Jetting colloidal suspensions from 50 µm print head nozzles in the present work did not require any special methods when the DoD print-head nozzles were continually actuated at 100 Hz.

Evidence for differences between jetting colloidal rather than Newtonian fluids was provided by high speed videos at 500 kfps, for jetting speeds appropriately matched to a 1 mm field of view. Earlier production of satellites by colloidal jet ligament break-up is anticipated from the dripping studies of Furbank and Morris [2], and appears consistent with a model by McIlroy and Harlen [13].

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