Links between fluid rheology and drop-on-demand jetting and printability

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Abstract

This paper links measurements of jetting performance in drop-on-demand printing with the high-frequency rheological properties of model viscoelastic fluids containing linear polymers with various molecular weights.

Jet formation and evolution were studied for solutions of polystyrene in diethyl phthalate. Ligament length, initial jet ejection speeds and ligament extension and retraction rates were determined by high-resolution imaging with high time resolution. For these fluids, the viscosity measured under low shear-rate conditions showed no correlation with their jetting performance. The jetting behavior was, however, well correlated with high frequency rheological properties measured at 5 kHz with a piezoelectric axial vibrator (PAV) rheometer.

This study shows that high frequency rheometry can provide useful predictive data about the jettability of fluids, and differentiate between inks that have similar low shear-rate viscosity yet show different jetting behavior.

Introduction

Previous research [1-5] has shown that useful information can be extracted from the detailed study of drop-on-demand inkjets and ligaments. The level of actuation required to achieve a certain speed (say 6 m/s) at a typical printing distance of ~1 mm from the nozzle can be used to characterize an important property of the fluid. Fluids with low values of low shear-rate viscosity require low actuation levels and the ligament extends almost linearly with time until it detaches; higher viscosity fluids need stronger actuation, and the jet decelerates more rapidly after emergence and detaches later. However, when the fluid exhibits viscoelastic behavior the value of low shear-rate viscosity may not fully reflect the resistance to flow through the nozzle or the deceleration of the ligament. This is one reason why the characterization of real inks for drop-on-demand printing is particularly challenging.

Filament-stretching rheometry of polymer solutions [6] can be used to explore their extensional rheology, and results from such experiments suggest that above a certain polymer concentration poor jetting behavior will occur; such fluids may not form jets, or jets which form may not detach from the nozzle.

An approximate reciprocal relation holds between the maximum concentration of polystyrene (PS) in a good solvent which will jet satisfactorily and the polymer molecular weight, for values between 20 kDa and 500 kDa [7, 8]. This has significant implications for the quality assurance of ink which incorporates polymers, since poor control over the molecular weight distribution may adversely affect the jetting performance [8, 9].

The rheological behavior of viscoelastic fluids is commonly represented in terms of complex viscosity $\eta^* (= \eta' - i\eta'') = G^*/i\omega$, where G^* $(= G' + iG'')$ is the complex modulus at angular frequency $\omega (= 2\pi f)$. G' represents the elastic (storage) component and G'' the viscous (loss) component. The magnitude of G^* is determined by $|G^*|^2 = G'^2 + G''^2$. At low frequency, the viscous modulus $G'' \approx \eta_o\omega$ while the elastic modulus $G' \approx 0$; laboratory measurements of viscosity are typically carried out at such low frequencies (<100 Hz) that they determine only G'' (see Figure 1). However, the timescales involved in the generation of jets and drops in drop-on-demand printing correspond to frequencies some 100 times greater [10] and for viscoelastic fluids the elastic effects may become highly significant.

The present work examines the correlation between jet production from a commercial inkjet head, described in terms of ligament length, initial jet ejection speeds and ligament extension and retraction rates, and rheological measurements made on the same fluids at 5 kHz with a piezoelectric axial vibrator (PAV) rheometer [11], for a range of model fluids containing polystyrene as a solute.

Experimental methods and materials

Model fluids

Model fluids were prepared with an effectively constant value of low shear-rate viscosity (η = 19±2 mPa s at 21±1°C) by dissolving mono-disperse polystyrene (PS) in diethyl phthalate (DEP, with a viscosity of 10 mPa s). Four different molecular weights of PS were used: 24 kDa (designated PS24), 75 kDa (PS75), 110 kDa (PS110) and 210 kDa (PS210). Two series of solutions were prepared: using PS110 (from 0 to 1 wt%) with added PS24 ($\leq$2.5 wt%) to achieve the target viscosity; and using PS210 (from 0 to 0.6 wt%) with added PS75 ($\leq$ 1.0 wt%).

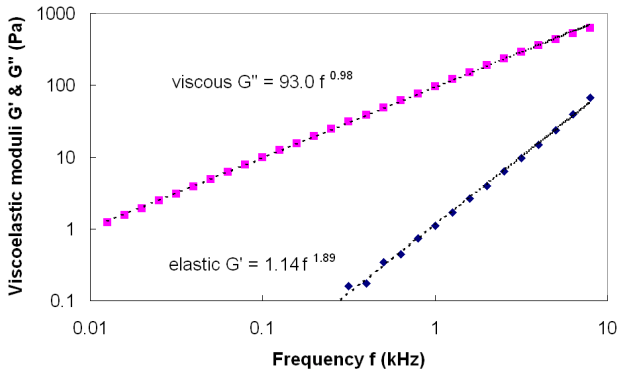

Figure1: Viscoelastic moduli G' and G" determined by PAV as a function of frequency for the 1 wt% PS110 solution.

Rheometry

The principles of PAV squeeze flow rheometry have been described elsewhere [11]. Figure 1 shows the typical variation of G′ and G″ with frequency for one of the fluid samples, as measured by the PAV method. The power law coefficients of 1.89 for elastic modulus G′ and 0.98 for viscous modulus G″ are close to the theoretical values of 2 and 1 respectively for linear viscoelastic fluids [8].

The ratio G′/|G*| evaluated at 5 kHz was used to characterize the model fluids used in the present work. The elasticity ratio G′/|G*| for the fluid containing 1 wt% PS110 in DEP is ~6 % at 5 kHz; as discussed below this particular fluid has sufficient elasticity to disrupt its jetting, although at this frequency the effect of G′ on the value of |G*| is still very small. Such weak elasticity would not be detectable by low frequency measurements.

Jetting and data analysis

The model fluids were jetted at room temperature with a Xaar XJ126-200 print head, using the same waveform timings throughout but adjusting the piezo drive level for each fluid to achieve a drop speed of ~6 m/s at 1 mm printing distance. The jets and drops were analyzed by high speed imaging, based on very rapid (~20 ns) single flash photography, as described earlier [1-3].

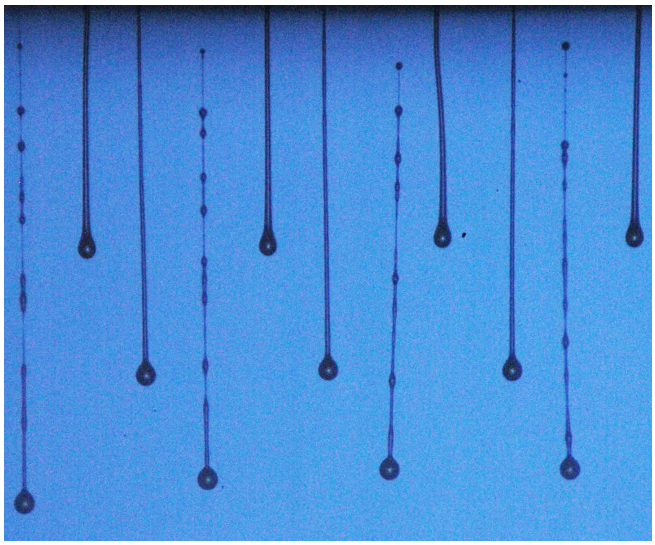

Figure 2: High speed flash image (field of view 1.2 mm × 1.4 mm) for a dilute polymer solution (0.25% PS210+PS75+DEP) near the limit for printability.

Figure 2 shows an example of a typical image for a fluid close to the limit of printability. The systematic timing difference between adjacent nozzles assists the visualization of the progression between jetting and the formation of beads on the long ligaments, which are <3 μm in diameter at the top in the cases where they have detached from the nozzles. These ligaments still connect all the ejected fluid. Images obtained with increased delays can track the final fate of the ligaments to determine whether they collapse to form a single drop or break up into multiple satellites, or for higher polymer concentrations, whether the ligaments ever detach from the nozzle plane. Long ligaments that do not detach can later fully retract back inside the nozzle, while at even worse printability levels the fluid may barely emerge from the nozzle.

Results

Rheometry

Although the low shear-rate viscosities of the fluids lay within a narrow range (17.5 to 20.7 mPa s at ~21°C), the ratio G′/|G*| at 5 kHz determined by the PAV method (at ~25°C) rose linearly with the concentration of the higher molecular weight polymer for both series of model fluids, as shown in Fig. 3.

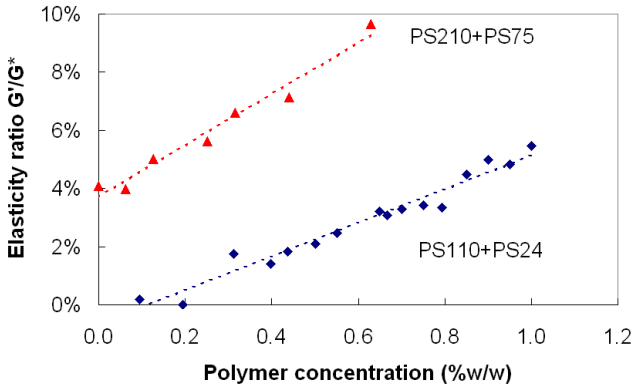

Figure 3: Elasticity ratio G′/|G| measured at 5 kHz for both fluid series. All fluids had essentially the same low shear-rate viscosity but the content of the higher molecular weight polymer (shown on the x-axis) was varied. The upper curve is for the PS210+PS75 fluid set and the lower curve is for the PS110+PS24 fluid set.*

Jetting behavior and ligament length

The overall ligament length was measured from the high speed images and is plotted in Figure 4 against time after initial ejection for the fluids containing PS210+PS75. For the higher concentrations of PS210, more actuation is needed to achieve the target velocity of ~6 m/s at 1 mm, deceleration of the ligament before it detaches becomes greater, and the detachment time becomes later. The final drop diameter was however found to be independent of the polymer concentration, but for higher polymer concentrations the total volume of fluid in the drops and ligament was greater. Similar results were obtained with the other fluid series (PS110+PS24).

Figure 5a shows the overall ligament lengths after the jet had detached from the nozzle plane for the fluid series of Figure 4 (PS210+PS75), but now plotted as a function of the distance travelled by the tip of the jet. Figure 5b shows a similar plot for the PS110+PS24 series.

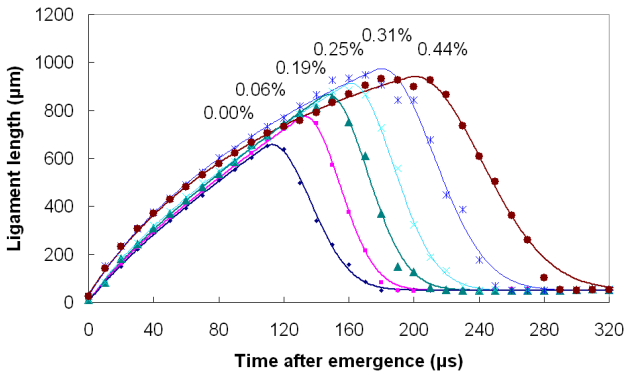

Figure 4: Ligament length vs. time after emergence for the set of PS210+PS75 fluids with main drop speed ~6 m/s at 1 mm. The curves are labeled with the concentration of PS210 in the solution (wt%).

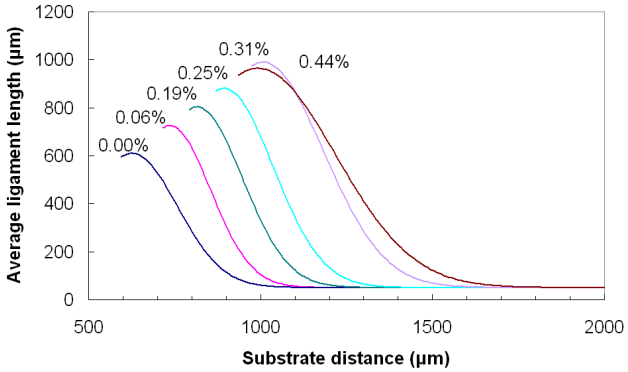

Figure 5a: Overall ligament length after detachment from the nozzle plotted against distance travelled by the jet tip for the PS210+PS75 fluids, with the concentrations of PS210 shown.

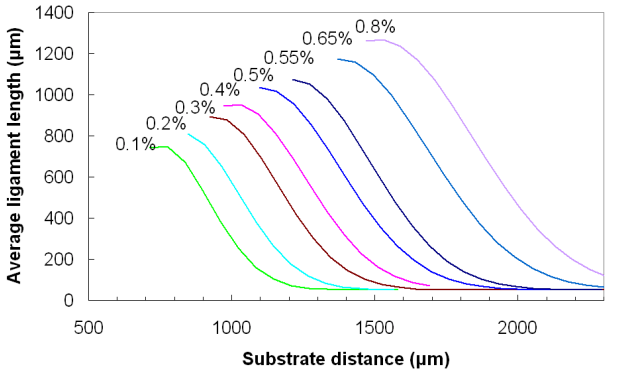

Figure 5b: Overall ligament length after detachment from the nozzle plotted against distance travelled by the jet tip for PS110+PS24 fluids, with the concentrations of PS110 shown.

Elasticity and jet detachment time

For the fluids in both series, correlations were found between the elasticity ratio G′/|G*| and the time at which the ligament detached from the nozzle (the break-off time), the emerging speed with which the fluid leaves the nozzle to achieve a final speed of 6 m/s after 1 mm travel, the mean deceleration of the tip of the jet, and the characteristic timescale of the ligament recoil process. These are plotted in Figures 6a and 6b and show similar trends for both sets of fluids. While the break-off time and the emerging jet speed increased roughly linearly with G′/|G*|, suggesting that they are linked with the fluid elasticity, the ligament recoil timescale (Tau) and the deceleration of the jet before break-off show non-linear relationships which differ for the polymers with different molecular weights.

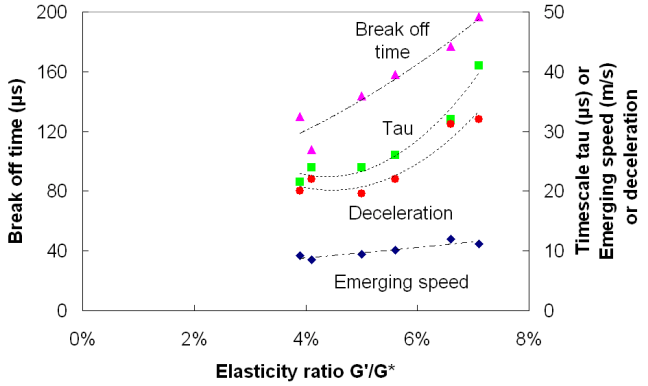

Figure 6a: Jet break-off time and other parameters describing fluid ligament length variations over time for PS210+PS75.

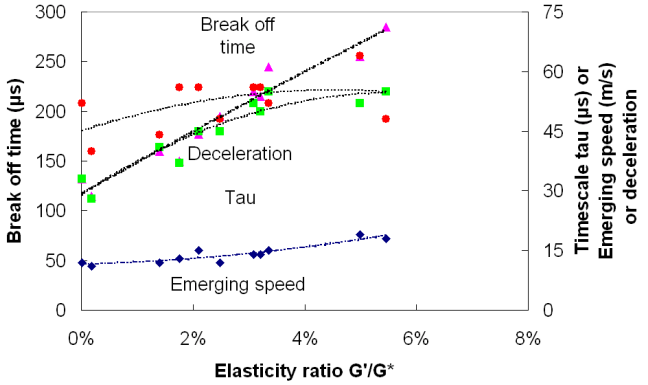

Figure 6b: Jet break-off time and other parameters describing fluid ligament length variations over time for PS110+PS24.

Discussion

The fluids used in this study all had very similar values of shear viscosity measured at low shear-rates, but a wide range of elastic behavior as determined by PAV at 5 kHz and shown in Figure 3. These differences in elastic properties had a strong effect on the jetting behavior of these fluids in a drop-on-demand printhead. The elasticity of the PS210 set was greater than that for the PS110 set, as shown in Figure 3, and a comparison of the vertical scales of Figures 6a and 6b shows that for the PS210 fluid

set the typical timescales and jet decelerations were about two thirds of the values for the PS110 fluids at similar polymer weight concentrations.

The curves in Figure 5 show that while the final main drop size may be independent of the polymer concentration, the overall length of the ligament increased markedly with the elasticity of the fluid. In order to achieve the same jet tip or drop velocity at a stand-off distance of 1 mm, greater actuation was needed for the more elastic fluids, which resulted in the ejection of a greater volume of fluid. Plots such as Figure 5 can be used to determine the maximum polymer concentration which is compatible with acceptable print quality for a certain nozzle-substrate separation, by determining the overall ligament length at the point when the jet tip strikes the substrate. It is evident that the 'printability' can in principle be improved by choosing a greater separation, so that the ligament length at impact is reduced, but at the expense of a lower final velocity.

A characteristic timescale associated with the ejection of a fluid jet can be estimated from the nozzle diameter divided by the fluid ejection speed; for the present conditions this is approximately 50 μm ÷ 10 m/s = 5 μs. The timescale for detachment of the ligament and its collapse is in contrast ~100 μs (see Figure 6). It is thus clear that although rheological measurements at 5 kHz (corresponding to a timescale of ~200 μs) should relate to the evolution of the jet outside the nozzle, they are unlikely to provide accurate information about the fluid properties most relevant to its ejection. Measurements at still higher frequencies are of major interest for this purpose [12].

Conclusions

For fluids which show viscoelastic behavior, properties measured by low-shear rate viscometers are insufficient to characterize their rheology for inkjet printing which typically involves much shorter timescales. Rheological data for the series of model fluids containing PS in DEP obtained by PAV at 5 kHz correlated well with measurements of ligament length and distinguished between fluids which had the same low shear-rate viscosity. Measurements at even higher frequencies may also be useful.

Plots of overall ligament length against jet tip position can be used to optimize printing conditions and compare the printability of different inks [12].

The ratio of elastic to total modulus $G'/|G^*|$ may be used to characterize a fluid; a linear correlation was found between this elasticity ratio and the time at which the ligament detached from the nozzle. High values of this elasticity ratio are associated with higher polymer molecular weight or higher concentration, giving fluids which either will not jet or cannot be printed due to the presence of extremely long ligaments.

Although the present work has utilized relatively dilute polymer solutions, for which the molecular chains do not overlap, it shows strong evidence for rheological effects in jetting. At higher polymer concentrations, even more pronounced effects are seen, for example for cellulose esters in good solvents [13], although in that investigation the relevant viscoelastic moduli were not independently measured. The results presented here represent the first quantitative link between high frequency rheology and jetting performance.

Acknowledgements

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Author Biography

Stephen Hoath received his B.A. in physics (1972) and his D.Phil. in nuclear physics from the University of Oxford (1977). He has since taught and worked in research and development in academia and industry. His research work has recently focused on the fundamentals of inkjet printing at the Inkjet Research Centre at the University of Cambridge, UK. He is a member of IOP and is a Chartered Physicist, Engineer and Scientist.