

DoD Inkjet Printing of Weakly Elastic Polymer Solutions

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Abstract

Fluid assessment devices, such as high frequency rheometers and torsion resonators, filament stretching and thinning systems, and oscillating DoD drops, requiring small volumes and avoiding the need for jetting, are particularly useful in the design of functional fluids for inkjet printing applications. With the increasing use of complex (rather than Newtonian) fluids for manufacturing, single frequency fluid characterisation cannot reliably predict good jetting behaviour, owing to the range of shearing and extensional flow rates involved. However, the scope of inkjet fluid assessments (beyond achievement of a nominal viscosity within the print head design specification) is usually focused on the final application rather than the jetting processes. The experimental demonstration of the clear insufficiency of such approaches shows that fluid jetting can readily discriminate between fluids assessed as having similar LVE characterisation (within a factor of 2) for typical commercial rheometry measurements at shearing rates reaching 10^4 rad s^{-1} .

Jetting behaviour of weakly elastic dilute linear polystyrene solutions, for molecular weights of 110-488 kDa, recorded using high speed video was compared with recent results from numerical modelling and capillary thinning studies of the same solutions.

The jetting images show behaviour ranging from near-Newtonian to “beads-on-a-string”. The inkjet printing behaviour does not correlate simply with the measured extensional relaxation times or Zimm times, but may be consistent with non-linear extensibility L and the production of fully extended polymer molecules in the thinning jet ligament.

Fluid test methods allowing a more complete characterisation of NLVE parameters are needed to assess inkjet printing feasibility prior to directly jetting complex fluids. At the present time, directly jetting such fluids may prove to be the only alternative.

Introduction

Our previous work [1, 2] has explained how the molecular weight (M_w) variation of maximum concentration limits for DoD inkjet printing of weakly elastic polymer solutions arises from basic principles. The most significant barrier for DoD jetting of polymer solutions arises from the critical concentration c^* above which the molecule chains touch one another under no-flow conditions. For lower M_w , at concentrations c approaching c^* the solution viscosity increases rapidly and exceeds the DoD print-head drive capability to produce usable jetting and drop speeds. At higher M_w , unravelling of the molecular chains in the extensional flow tends to increase further the viscosity, thus limiting the maximum concentration that can be jetted to below the relevant c^* . Improvements to the original model account for the molecular pre-stretching within the DoD nozzle, predicting [2] the absolute

values of the maximum concentrations, the location of boundaries between the 3 regions of Newtonian, elastic and fully stretched molecules, and molecular scission (observed at certain M_w [3]), representing real progress for DoD inkjet printing applications.

For Zimm time λ_Z (taken by polymer molecular chains to relax back to equilibrium) and the jet extensional rate $\dot{\epsilon}$ (given by the ratio of the final jet speed U to the DoD nozzle diameter D), the Weissenberg number Wi is given by equation (1).

$$Wi = \lambda_Z \dot{\epsilon} = \lambda_Z U/D \quad (1)$$

At small strains, polymer molecules have linear viscoelastic (LVE) response, but at larger strains the finite non-linear viscoelasticity (NLVE) response enters the underlying picture for inkjet printing. The molecular chains (of finite extensibility L) may become fully stretched during jetting if $Wi > L$, are not stretched if $Wi < \frac{1}{2}$, and partly stretch otherwise. The values of the Zimm relaxation time λ_Z and finite extensibility L depend on the polymer and its molecular weight M_w , solvent viscosity and quality factor for the polymer; the elastic modulus G of a polymer solution depends linearly on concentration c and absolute temperature but inversely on M_w . [1].

Jetting predictions

Jetting $<1 \text{ wt}\%$ ($c \sim 10\% c^*$) solutions of 110-488 kg/mol polystyrene (PS) in diethyl phthalate (DEP) solvent, produces jet ligaments with partly stretched molecules at speeds of 1-4 m s^{-1} . So although such weakly elastic polymer solutions are predicted to behave rather like Newtonian fluids with viscosities slightly above that of the solvent, both LVE and NLVE effects might be present. The print-head drive voltages required to produce drops with a specific final speed have a threshold value which is increased by the polymer viscoelasticity (represented by viscous and elastic G moduli). Consistent linear variations of drop speed with DoD drive voltage have in fact been noted for dilute polymer fluids jetted by many workers [4]. The response of polymer solutions can also be measured by suitable rheometers, such as the piezo axial vibrator (PAV) devices operating at small amplitude, to provide high shear rate testing measurements of the G moduli up to 10^4 rad s^{-1} [5].

So are such available LVE characterization methods sufficient for predicting all inkjet fluid behavior in DoD printing? The present work reports a deliberate experimental test of this question, and a resounding negative answer [6] which has significant implications for future work towards testing unknown inkjet fluids.

Model Fluids

Table 1 lists the characteristic parameters of the weakly elastic polymer solutions chosen to test whether the high frequency measurements of viscosity and elasticity [6] provide sufficient

information for prediction of the fluid DoD jetting behavior. Linear PS of mono-disperse M_w was dissolved in DEP to provide solutions within 35% of $c/c^* = 0.10$. (Such variations do not have a large effect on the effective molecular relaxation time relative to the Zimm time λ_z , according to Vadillo, Mathues and Clasen [7].) For each solution in Table 1, the measured complex viscosity η^* exceeds the viscosity η due to the presence of polymer elasticity, while added polymer has slightly increased the solution viscosity η above the 10 mPas solvent viscosity. Finite molecular extensibility L and λ_z are deduced from theoretical predictions for PS in DEP. Note that the model fluids differ significantly, beyond the similar values for the LVE modulus G , since both λ_z and L vary with M_w .

Table 1: Characteristic parameters on the jetted fluids [7].

M_w (kg/mol)	c (wt%)	c/c^* (-)	η^* (mPas)	η (mPas)	λ_z (μ s)	L (-)
110	0.5	0.134	13.2	12.4	7.8	14.8
210	0.4	0.143	13.0	12.5	20.0	21.3
306	0.2	0.080	12.0	11.6	32.9	25.2
488	0.1	0.065	11.7	11.0	83.8	31.0

Figure 1 plots results of PAV measurements [6] for the model PS fluids (labelled by M_w in kg/mol) for frequencies $f < 2000$ s⁻¹, where $\omega = 2\pi f$ and components G'' and G' of the complex modulus G^* link to viscosity and elasticity via the relations in equation (2).

$$\eta^* = G^*/\omega, \eta = G''/\omega \text{ and } |G^*|^2 = |G'|^2 + |G''|^2 \quad (2)$$

The units of G , G' and G'' are those of pressure (Pa). These characteristic plots were obtained using PAV devices [5]. Figure 1 also shows fitting curves for the elastic modulus G' that include the multiple (higher order) Zimm modes needed to describe this data at frequencies exceeding 2000 s⁻¹ [6].

Nevertheless, the model PS fluids appear similar at low frequency, equivalent to shear rates up to 10⁴ rad s⁻¹, which is at the limit of conventional rheometry as we have noted before [7].

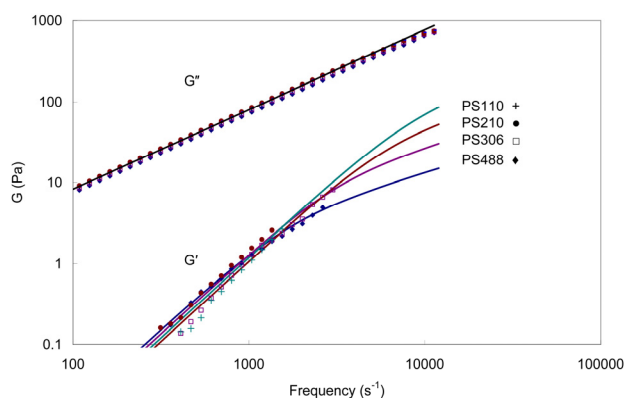


Figure 1. Measured components G' and G'' of the complex modulus G for the fluids of Table 1. Taken with permission from Vadillo, Mathues and Clasen [7].

Experiments

The model fluids and a Newtonian solvent mixture were jetted from a 30 μ m diameter MicroFab print-head nozzle using a range of bipolar drive voltages at a fixed waveform timing (2 μ s rise and fall times, 10 μ s “pull” times, 20 μ s “push” times, as described for DoD by Wijshoff [8]). High speed shadowgraph recordings of the jetting behavior were made using a Shimadzu HPV-1 camera at 500,000 frames s⁻¹ with 0.5 μ s exposure times for 102 frames of 312 \times 260 pixels and an Adept Electronics 500W flash light source of \sim 2 ms duration, with appropriate triggering of the MicroFab print-head drive, flash lamp and camera [9]. The optics was calibrated at 4.26 μ m/pixel and viewed a flight path of \sim 0.92 mm below the nozzle exit (1 mm is a typical “stand-off” distance for DoD inkjet printing). The nozzle was also purged with pure DEP between jetting the model fluids to avoid cross-contamination. The video sequences recorded for the model fluids at MicroFab print-head drive voltages of 32V and 35V, with systematic checks at other drive voltages, were used for comparison of jetting behaviors at speeds of 1-4 m s⁻¹ [6].

Results

Figures 2 and 3 compare the evolution of the jetted DEP, PS110, PS210, PS306 and PS488 solutions after their emergence from the 30 μ m diameter MicroFab print-head nozzle exit for drive voltages of 32V and 35V, respectively. Each fluid jet is shown at intervals of 10 μ s (with the background masked out by gray areas). The rightmost panel (jetted PS488 solution) is delayed by 175 μ s relative to the others in order to display the “beads-on-a-string” behavior observed for the polymeric ligament with the highest M_w . The complete set of jet sequences is available on open access [6].

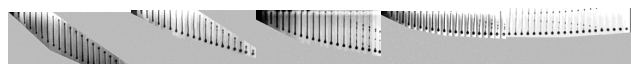


Figure 2. Solvent, PS110, PS210, PS306 and PS488 fluid jets at 32V drive.

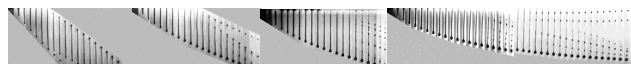


Figure 3. Solvent, PS110, PS210, PS306 and PS488 fluid jets at 35V drive.

Comments

While the Newtonian solvent jetted fastest and jetting at higher drive voltages raises the final drop speed, as expected, the weakly elastic polymer solutions also jetted differently from each other, with the PS110 fastest and the PS488 slowest. At 32V the final PS488 drop moves backwards (against gravity and towards the nozzle exit). The jets tended to collapse towards a single drop at 32V drive for the solvent and PS110, while at 35V the solvent jet sheds its trailing ligament early and consequently has a high speed main drop but the PS110 sheds a slow satellite later. Jet ligament break-off from fluid in the nozzle exit is noticeably and progressively later for PS210-PS488, while the bead formation has more time to develop before the final jet break-off from the nozzle.

Figure 4a plots deduced drop speeds, and Figure 4b observed break-off and bead formation times, against M_w , thereby providing a visual comparison of the jetting results at 32V and 35V drive [6].

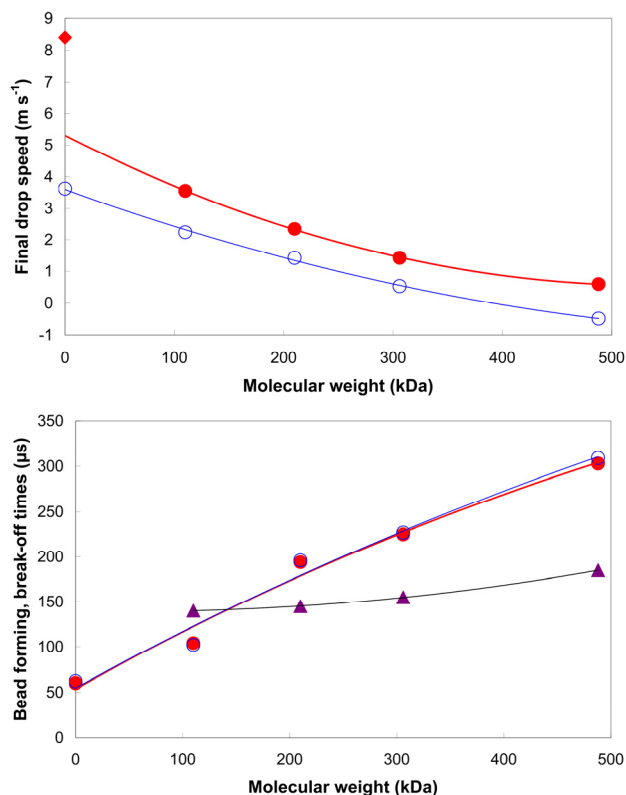


Figure 4. Jets at 35V (●) and 32V (○) drive voltage had, at each M_w , (a) final drop speeds and (b) average times for beads formation (▲) and jet break-off times. Newtonian solvent values shown at 0 kDa and the Newtonian 35V final drop speed (◆) is shown separately. Quadratic fits merely link series. (See text.)

Discussion

Although the quadratic fits shown in Figure 4a merely guide the eye, the final Newtonian solvent drop speed at 35V drive corresponds to the earlier break-off of the main solvent drop for this sole circumstance in Figure 3. The other fluid jets do not break-off at the head end but elsewhere: at the tail end for the lower M_w polymer jets and nearer the middle of the thinning ligament for slow head speed and the “beads-on-a-string” [10] behaviour akin to that observed with thinning polymeric filaments.

Figure 4b clearly shows that the polymer jet break-off times increase monotonically by $200 \mu\text{s}$ from PS110-PS488 irrespective of the drive voltage, while the average bead formation times are relatively insensitive to polymer M_w , and remarkably for PS110 beads appear after jet break-off. As discussed elsewhere [6] bead formation on viscoelastic threads starts after the stress has relaxed.

These fluids do behave rather differently despite the attempts to produce fluids with quite similar characteristics based on measurements of rheology up to 2000 s^{-1} . This immediately implies that further fluid characterization methods will be necessary in order to discriminate between or select suitable (polymeric) inkjet fluids before actually jetting them. Table 1 reveals that the jetted “similar” model fluids differed in their relaxation time λ_z and extensibility L values, so that we should consider whether these LVE and NLVE parameters can be measured and used to discriminate the inks without jetting.

In addition, from the recent work of Vadillo, Mathues and Clasen [7], whether the measured extensional relaxation times for PS110-488 ligament thinning correlate with fluid jetting behavior. Figure 5 compares the non-monotonic variation in the extensional relaxation time for these PS solutions with the smoothly increasing Zimm times for the same fluids. It would appear that the break-off time is not simply correlated with the measured extensional relaxation times (except where these are close to the Zimm times).

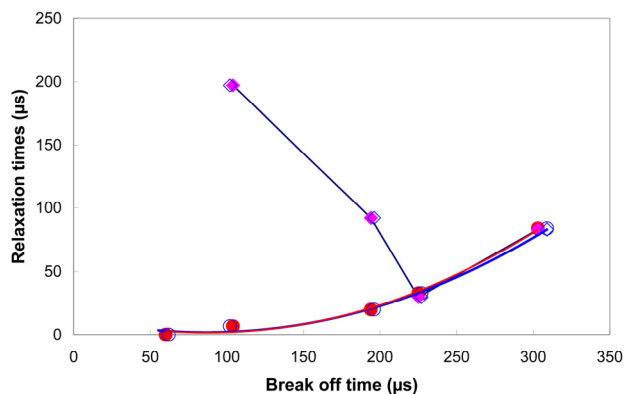


Figure 5. PS110-488 Zimm time (●) and extensional relaxation times (◆) from Vadillo, Mathues and Clasen [7] to the Newtonian and PS break-off times found at 35V drive voltage, with 32V break-off times shown by open symbols.

Figure 6 shows the variation of the measured break-off times for PS110-488 with the finite extensibility L . The power law fits shown for the 32V and 35V drive voltages (with exponents of 1.63-1.69) are close to what might be expected (exponent = 1.5) from the simple jetting model [1], but perhaps rather fortuitously since the extensibility curve should not extrapolate towards 0 break-off time for $L < 10$ since the Newtonian ($L=0$) solvent break-off time was $61 \pm 1 \mu\text{s}$ [6]. Nevertheless this suggests that in these small diameter jets, where capillary thinning is extremely rapid, the molecular weight dependence arises from increases in the polymer extensibility rather than changes in the relaxation time. The final drop speeds plotted versus M_w in Figure 4a are independent of drive voltage and also roughly linear with extensibility, providing the polymer molecules are becoming fully stretched [6].

Measurement of short ($> 30 \mu\text{s}$) relaxation times in filament stretching and thinning has been reported by several groups [7, 12-15], approaching Zimm values for PS+DEP fluids. A key objection to such studies has been the far slower initial extensional rate of filament stretching methods compared with those encountered at DoD inkjet speeds. A recent progress report [14] on fast filament stretching, thinning and break-up has removed this objection. However the relatively low M_w and concentration regime chosen for the present study has depressed the role of the Zimm relaxation time because the polymer chains are short and can unravel before an elasto-capillary balance, more typical with higher M_w polymers, can be achieved during the jetting process [6]. As a result the extensibility rather than Zimm time has tended to dominate the DoD jetting behavior of these particular fluids and precludes any useful discussion of possible correlations between jetting behavior and Zimm time in this paper.

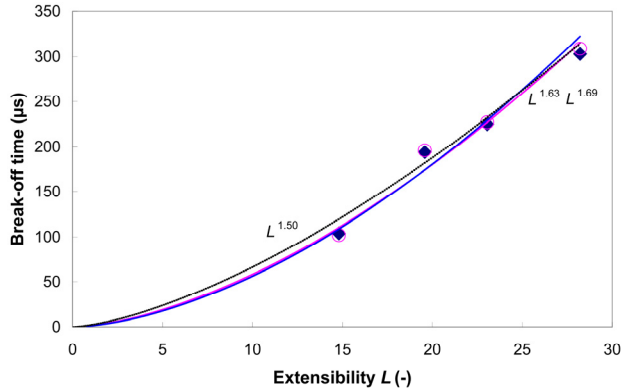


Figure 6. Break-off time versus extensibility L for the PS110-488 solutions at 32V and 35V. The power law exponents shown are discussed in the text above.

Recent theoretical work has examined the final stages of the thinning of viscoelastic filaments under tension leading to the formation of periodic “blisters” separating polymer density-enriched threads [16]. This may account for the observation of nanofibres left by the filament thinning process [17]. However, in our jetting work with dilute polymer solutions the unraveled molecular chains are quite short and less likely to be entangled, which was a condition for the analysis of blistering by Eggers [16]. Furthermore, the beads spacing of the “beads-on-a-string” in our jetting work is not sinusoidal but more reminiscent of the earlier stages of filament stretching and break-up that resulting in central drops between pistons [12], repeated iteratively in Figure 3 above.

Conclusions

Weakly elastic PS in DEP fluids, having similar low frequency LVE properties but prepared with different monodisperse molecular weights, require a more complete rheological characterization in relation to their feasibility for use in inkjet printing. In particular, measured extensional relaxation times for these fluids do not appear to account for observed jetting behavior. Rather, the predicted slowing of the main drop and delay in break-off time are most probably caused by polymer molecules becoming fully stretched in the thinning ligaments, producing an enhanced extensional viscosity whose molecular weight dependence can be predicted from molecular theory [6].

This conclusion is a consequence of the high jet speeds and small nozzle diameters in combination with the relatively high viscosity solvent and modest molecular weights of the polystyrene, resulting in high Weissenberg numbers and moderate extensibility. Experiments operating in other fluid jetting regimes, such as those of de Gans et al [11], where full extension does not occur, will have viscoelastic behaviour controlled by the relaxation time.

Consequently inkjet fluid assessment methods need to provide a full characterization including both linear and non-linear viscoelastic properties. This suggests fluid testing might require the use of sets of DoD print heads with different sensitivities to all the various VE parameters, rather than reliance on testing without jetting [9]. Such a “map of misery” [18] may be inevitable but may provide the way forward for future R&D strategies towards testing.

Acknowledgements

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