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Inkjet printing of weakly elastic polymer solutions ☆

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ABSTRACT

Fluid assessment methods, 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 rheometer 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.

1. Introduction

Inkjet printing involves jetting some liquid material through a nozzle opening to form drops with enough forward speed to reach a substrate at ~1 mm “stand-off” distance. Drop production can be tailored to liquid properties using piezo print head actuation timing, but optimum conditions are very often determined by empirical trial and error.

Newtonian fluids that can be usefully jetted from a given print head have a rather narrow range of properties, certainly within factors of 10, usually within factors of 2. In practice, print heads may be operated at a raised temperature to attain the optimum values of fluid properties (e.g. viscosity) that lie outside the jetting range at ambient.

With the projected interest in using complex (rather than Newtonian) inkjet fluids for manufacturing [1], such as functional fluids for flexible electronics and solar cells, effective fluid assessment techniques are of great interest. Demonstrations of links between rheology, drop formation and inkjet printing for linear polymers in solution have already shown [2] that single characterisation parameters such as the low shear rate viscosity do not provide sufficient indicators to assess good jetting behaviour.

Abbreviations: LVE, linear viscoelastic; NLVE, non-linear viscoelastic.

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This finding might seem unsurprising to fluid mechanics specialists in that jetting is an inherently non-linear process, but many empirical outcomes for drop-on-demand (DoD) inkjets appear straightforward and linearly predictable. Perhaps, because of this deceptive simplicity, the majority of fluid assessments prior to attempting inkjet printing are usually focused on the final application rather than on jetting processes.

Typical deformations of the piezo producing the jet are small compared to the nozzle width (20 nm against 30 μm), so the linear viscoelastic (LVE) response of the fluid might well have an effect; fluids of similar LVE may reveal non-linear jetting effects.

So, provided nominal properties can be achieved lying within the print head design specification, application and ink formulation engineers concentrate on deposition. Those more concerned with the jetting issues have pursued inkjet fluid assessments via rheological measurement. Our previous paper on links between rheology, DoD drop formation and inkjet printing [2] provides guidance on optimising jetting performance, based on measurements of LVE moduli and complex viscosity. Attempts have also been made to understand limits to jetting of dilute solutions of polystyrene observed in our experiments [3] and those of de Gans et al. [4], which led to consideration of non-linear viscoelastic (NLVE) effects in the DoD jetting process.

The interplay between the extensional rate *U*/*D* for jet speed *U* and nozzle diameter *D*, the longest Zimm relaxation time λ_Z and the finite extensibility *L* for the polymer weight M_W in the solvent viscosity η_s and the corresponding solvent quality factor *v*, appear to be key factors determining the jetting behaviour of high (100–1000 kDa) molecular weight polymer solutions, as discussed by Hoath, Harlen and Hutchings (HHH) [3], who developed a simple DoD model prompted by Bazilevskii et al. [5]. HHH provides estimates of the jet head slowing down in three regimes of jetting behaviour for polymer molecules, corresponding to the Newtonian low shear-rate viscosity in which the polymers remain close to their equilibrium conformation, a viscoelastic liquid in which the polymers become extended but then subsequently relax, or a liquid in which the polymers become fully extended resulting in an extensional viscosity $\sim L^2$ greater than the Newtonian low shear-rate viscosity. The filament thinning action before main drop detachment ("break-off") from the nozzle meniscus reduces the effects of the high extensional viscosity on the final drop speed by a factor of *L*. This "fully-stretched" regime predicts that higher polymer concentrations can be DoD jetted than predicted on the basis of a viscoelastic response with relaxation, which was unexpected and unreported prior to HHH.

McIlroy et al. [6] relaxed several assumptions in the HHH model and enlarged the predictions for polymer jetting to explain the observations, by A-Alamry et al. [7], of polymer molecule scission in DoD jetting. Partial unraveling of polymer molecules ("pre-stress") within the jetting DoD nozzle was identified as a key aspect explaining experimental results in HHH. These papers have provided an improved level of confidence in the interpretation of DoD jetting results and experiments obtained with a variety of print heads, polymer fluids and solvents, for example those described de Gans et al. [4] and A-Alamry et al. [7]. Interestingly here, the improved modelling [6] showed that the intermediate viscoelastic regime is masked, suggesting that extensional properties might prove useful indicators of the DoD jetting behaviour.

The present work reports the DoD jetting behaviour of the series of weakly elastic linear polystyrene (PS) in diethyl phthalate (DEP) solutions that were recently assessed using filament thinning techniques by Vadillo, Mathues and Clasen (VMC) [8], with a view to investigating the role of NLVE parameters in DoD inkjet printing. A brief summary of recent results reported by VMC and others closes this section.

Polymers introduce startlingly new physics [5,9–13] into purely Newtonian fluid flow behaviour. Attempts to provide a simple method for evaluating fluids intended for DoD inkjet printing have already shown [2,14] that simple low (<10^2 s^{-1}) shear-rate viscosity measurements are insufficient to characterise jetting performance. The LVE (moduli G'' and G') determined at high frequencies (>10^3 s^{-1}) are relevant to the DoD jetting performance as the repetition frequency of the piezoelectric drive pulses is typically 10^4 s^{-1} [15].

For mono-disperse PS solutions in DEP the relaxation times obtained from LVE, λ_0, are found to approach the Zimm time λ_Z in the dilute limit, with the ratio λ_0/λ_Z increasing as the concentration approaches c^* (the critical concentration) as a function of the reduced concentration c/c^* independent of molecular weight [12]. However the extensional relaxation times λ_E obtained from filament thinning [16] were found by VMC to have a much stringer concentration dependence. They reported values of λ_E for low molecular weight M_W < 220 kg mol^{-1} that were much longer than the Zimm times <20 μs. Hence even at concentrations $c/c^* < 0.1$ polymeric additives would be expected to lengthen filament thinning times during drop break-off in inkjet printing. Consequently the extensional relaxation time is an important determinant for inkjet performance.

Capillary thinning and related approaches might be considered as providing necessary assessment tools for characterising inkjet printing fluids, but their sufficiency has not yet been quantitatively demonstrated by inkjet experiments, despite the success enjoyed by some recent numerical simulations of polymeric fluid jets [17]. Mechanical stretching has slower timescales (by factors of 10–100) and larger linear size (by similar factors) than for DoD jetting. To test for correlations between thinning and jetting the present experimental work compares jetting behaviour of weakly elastic polymer solutions of mono-disperse PS in DEP with similar (within a factor of 2) low frequency properties shown in Fig. 1 [10]. PS solutions are indicated herein by their molecular weight (M_W) in kg mol^{-1} (e.g. PS110).

Fig. 1 shows these VMC fluids ($c/c^* \sim 0.1$) have similar zero shear viscosity η_0 and LVE response in the range 10^2–10^4 rad s^{-1} where it can be measured using a piezo axial vibrator (PAV) [18,19]. At low frequency, $G'' \sim \eta_0\omega$ while $G' \sim G\lambda^2\omega^2$, so the VMC fluids were chosen such that $G\lambda^2 \sim$ constant. This was a compromise between keeping c/c^* roughly constant so that values of η_0 and G'' are the same, but in practice this decreases by a factor of 2 as M_W increases between 110–488 kg mol^{-1} – and fixing $G\lambda^2$ – which increases by a factor of 1.5 as M_W increases from 210 –488 kg mol^{-1}. In addition, fitting a multi-mode Zimm model [8]

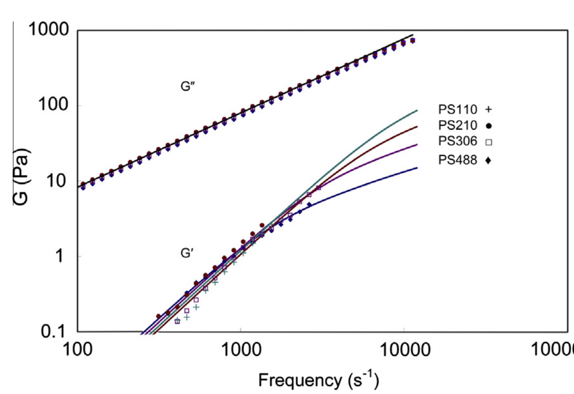

Fig. 1. Elastic G' and storage G'' moduli (measured using PAV) for the PS in DEP solutions of Vadillo, Mathues and Clasen that were jetted in the present work. Fits to the G'' data for PS110 and predictions of multi-mode Zimm models for G' data are shown [8].