The Effect of Inkjet Ink Composition on Rheology And Jetting Behaviour

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Abstract

This proceeding describes the development of two apparatus used to characterise ink-jet fluids. In term of Linear Viscoelasticity (LVE), the recently developed Piezo Axial Vibrator (PAV) was used to characterize the high frequency response of model ink-jet fluids. Two series of model ink-jet fluids were investigated. The first series was a mixture of diethyl phthalate and mono-disperse poly(styrene) and the second series examined the influence of dispersant and pigment on a commercial UV carrier fluid (varnish). Both the polymer and pigment loaded fluids showed a development of LVE with increasing concentration. A filament stretching apparatus, called the "Cambridge Trimaster" was used to characterize the fluids high speed stretching and break-up behaviour. Examples of the apparatus response for polymer solutions are given. Both apparatus provide valuable data in relation to the coupling of ink-jet rheology and jetting properties.

Introduction

Liquid droplet formation is relevant to several applications where the deposition of a controlled volume of fluid on a specific location is required. Inkjet printing [1], Organic Light Emitting Diode (OLED) [2] fabrication or Deoxyribonucleic Acid (DNA) [3] in situ synthesis are examples. Different techniques can be employed to form a droplet and piezo-type Drop-on-Demand is one of the most recent. This method consists in creating a pressure wave within a micro-capillary channel full of liquid with an orifice at one end with a typical diameter D_0 of 20 to 50 µm. Piezo-electric wall actuators generate a pressure wave which acts against the fluid viscosity and surface tension. A ligament of liquid is ejected from the orifice and subsequently breaks into droplets [4].

Droplet formation is influenced by the both the physical properties of the ejected fluid and the process itself. The fluid density ρ, viscosity η and surface tension σ are relevant and typically the viscosity is between 1 to 20 mPa.s at temperature between 25°C and 50°C and surface tension 20 to 40 mN/m for ink-jet applications. The amplitude of the pulse applied on the fluid also influences the jetting by modifying the fluid velocity U outside the printhead. From dimensional analysis, the Reynolds number, which represent the ratio of the inertia to viscous force, and the Weber number, which represent the ratio of the inertia to surface tension force, have been found to control the jetting process [5]. They are defined as following:

$$\mathrm{Re} = \frac{\rho D_0 U}{\eta} \quad (1)$$

$$\mathrm{We} = \frac{\rho D_0 U^2}{\sigma} \quad (2)$$

The Ohnesorge number, which represents the ratio of viscous to surface tension forces and which is independent of the droplet velocity, also plays an important role. It is defined as following

$$\mathrm{Oh} = \frac{\eta}{\sqrt{\rho D_0 \sigma}} \quad (3)$$

Fromm [5] predicted that stable droplet formation can occur for $Z > 2$ where Z is the inverse of the Ohnesorge number. Later, a computational and experimental study about the DOD drop formation by Reis and Derby [6] showed that a printable fluid should obey $1 < Z < 10$. The lowest value of Z is governed by the dissipation of the pressure wave by the viscosity of the fluid whereas the higher limit is determined by the fact that the fluid forms satellites droplet instead of a unique droplet. More recently, Jang *et al* [7] have also shown that jetting, at 3 m/s, of fluid with Z number between 1.43 to 17.32. They refined the previous interval to be between $4 < Z < 14$.

These past studies have only considered Newtonian fluids, however, it has been established that viscoelasticity can strongly influence ink-jet performance [8]. Ink-jet fluid linear viscosity can be represented in term of a Complex viscosity $\eta^* = (G' + iG'')/\omega$ where G' is the elastic modulus and G'' is the loss modulus. Previous work has shown that inkjet fluids can be characterised using G' and G'' data, however, the short relaxation times involved with ink jet fluids require special experimental techniques to be adopted [8, 9].

In the present work, the recently developed Piezo Axial Vibrator (PAV) [10] has been used to quantify the LVE of a series of model polymer fluid and commercial UV ink. In addition, a "Cambridge Trimaster" filament stretching apparatus was used to investigate the effect of polymer and particle loading on the filament thinning and break-up profiles. The "Cambridge Trimaster" was developed from work carried out using an MPR as a filament break-up device [8].

Experiment; fluids and apparatus

Two series of test fluid have been investigated. The first was a series of mono-disperse poly(styrene) with a molecular weight of 110 kg/mol (PS110) at different concentrations (0, 0.1, 0.2, 0.5 and 1wt% respectively) dissolved in mixtures of diethyl phthalate (DEP) and diotyl phthalate (DEOP) in order to obtain a matched zero shear rate complex viscosity of 17 mPa.s at 25°C. The second series of fluids was a pigment paste of Phthalocyanine blue organic particle (average diameter ~100nm) and poly-disperse poly-acrylate (molecular weight 10 to 20 kg/mol) at different weight concentration (0, 2, 4 and 6wt%) diluted in mixtures of three Acrylate-monomers UV varnish with base viscosity of 10, 20s and 30 mPa.s respectively. These fluids have been provided by SunJet, the inkjet division of SunChemical®. A resulting matched

zero shear rate complex viscosity of 17mPa.s at 40°C was obtained for this series. The fluid physical properties are summarized in **Table 1.**

	Series I	Series II
Solvent	Diethyl Phtalate / Dioctyl Phtalate	Acrylate monomer
Viscoelastic enhancer	Polystyrene (110 kg/mol)	Phthalocyanine blue organic particle and poly-acrylate
Key variables	0 to 1wt%	0 to 6wt%
η_0 (mPa.s)	17 (at 25°C)	17 (at 40°C)
σ (mN/m)	37 / 15	32
ρ (kg/m3)	1120 / 950	1050

Table 1: Physical properties of polymer (series I) and pigment solutions (series II)

The high frequency linear viscoelasticity (LVE) of the fluids were investigated using a Piezo Axial Vibrator (PAV), which was developed by the Prof. Pechhold [10, 11].

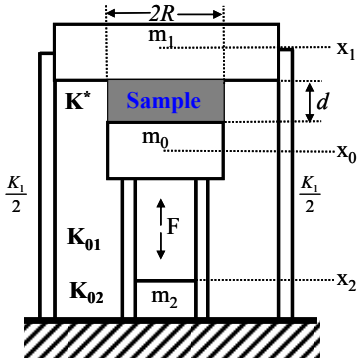

***Figure 1**: Mechanical Model of the PAV*

The apparatus, schematically presented in figure 1, consists of a thin cavity of liquid (d < 200μm) surrounded by solid surfaces. An oscillatory piezo-element activated squeeze flow is generated by the motion of a bottom plate with a very small amplitude of approximately 5nm over a range of frequency from 0.1Hz to 10000Hz. The complex spring constant K^* of the apparatus is first determined without the fluid being presented and then with the fluid present, the difference giving the response of the fluid on its own. The PAV gives the shear modulus, $G^* = G' + iG''$, and the complex viscosity $\eta^* = G^*/i\omega$ (where ω is in rad/s). The temperature is regulated in the PAV and a range between 5°C and 50°C can be investigated.

The second experimental set up is a filament stretching, extensional rheometer, the "Cambridge Trimaster" [12]. This apparatus performs filament stretching at a constant velocity for a fluid initially placed between two pistons of initial diameter 1.2mm. Both pistons, are attached on the opposite side of a belt, and move symmetrically apart for a given distance allowing the mid-filament to remain in a central position during the experiment.

The pistons can moved from a distance of 10μm to 10cm at a maximum relative velocity of 1m/s. When the pistons stop, the filament self-thins under the action of the capillary and viscous forces. The Bond number was calculated to be small ($Bo = \rho g D_0^2/4\sigma = 0.1$), confirming that gravitation effects were negligible in comparison to capillary forces. A high speed camera (Photron Fastcam 1024 PCI) was coupled with the "Cambridge Trimaster", allowing the transient profiles to be recorded at a frame rate as fast as 100000 frames per second at the reduced resolution of 32x32 pixels, and with a shutter time as low as 3μs. The continuous light is guided by fibre optics. The filament thinning measurement, as well as the filament break-up behaviour, was obtained using automatic image treatment specifically developed for, and included within, the "Cambridge Trimaster" software suite. This apparatus enables the measurement of the transient elongational viscosity and the observation of filament profiles. Both elements are relevant to inkjet droplet and satellite formation.

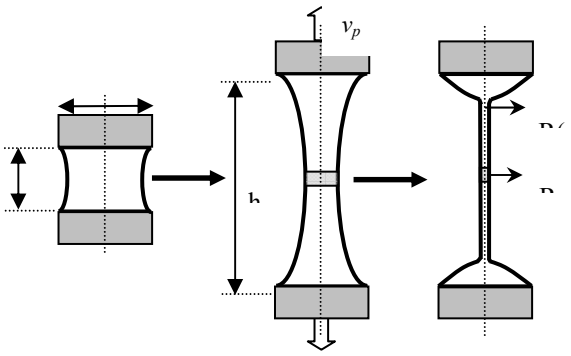

***Figure 2**: Schematic of the "Trimaster" filament stetching and breakup apparatus*

Results and discussion

PAV: Linear viscoelasticity.

Many weakly viscoelastic fluids can be described by a pure viscous component combined with a Maxwell spring and dashpot model as described by equation 4. In the low frequency limit it can be seen that G'' increases linearly with frequency and G' increases with the square of frequency. In equation 4, g is the elastic modulus of the Maxwell element and τ the relaxation time of the Maxwell element.

$$G'' = \eta_s\omega + \frac{g\omega\tau}{1+(\omega\tau)^2} \approx \omega(\eta_s + g\tau)$$

$$G' = \frac{g(\omega\tau)^2}{1+(\omega\tau)^2} \approx g(\omega\tau)^2 \qquad (4)$$

$$\eta^* = \frac{\sqrt{G'^2 + G''^2}}{\omega}$$

The G'' response as function of excitation frequency for the polymer solution series is shown in figure 4 and this data shows a linear frequency response for all the samples which is consistent with the low frequency limit of t v_p xwell model from equation 4. In addition, because the fluids had been viscosity matched, all of the curves overlap.

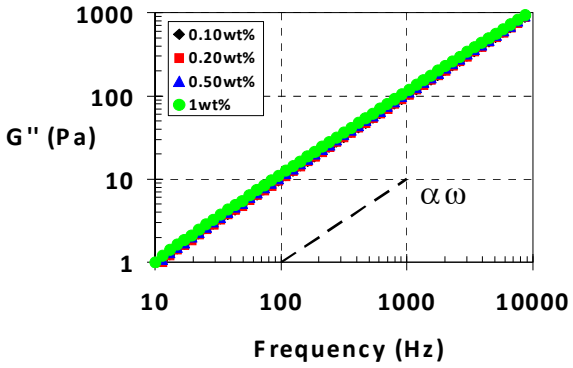

Figure 3: *Loss modulus G" of the solution of DEP-PS at different weight concentration, η^* = 17mPa.s at 25°C. The dash line is a guide and represents a linear evolution with the frequency.*

The G' response for the polymer solution series is shown in figure 4 and here it can be seen that as the polymer concentration increases, a G' response develops. In addition, the slope of the G' curves as a function of frequency is closer to a gradient of two, rather than one. Again, this is consistent with the low frequency limit model of equation 4 and it can be safely assumed that the origin of the LVE G' in this case is due to the presence of the entropically coiled polymer chains within the quiescent solution.

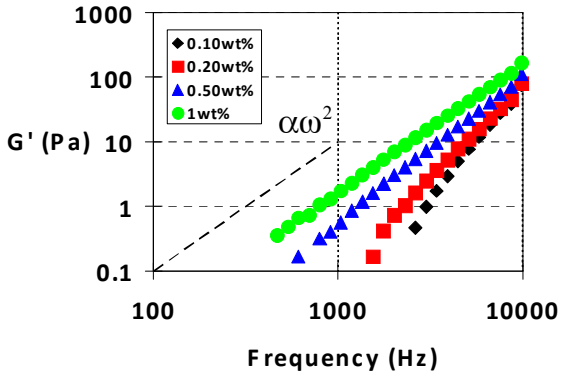

Figure 4: *Elastic modulus G" of the solution of DEP-PS at different weight concentration. The dash line is a guide and represents a power law evolution with index 2 with frequency.*

The G' response of the particle laden series of fluids is shown in figure 5. As with the polymer series, there is a development of G' with loading however in this case the slope of the G' curve is closer to one, rather than two as with the polymer solution. In the case of the particle loading series we believe the origin of the G' is due to particle interaction rather than entropy.

For both polymer and particle loading, the development of G' can only be detected in a high frequency range, in this case, above 1000 Hz, which is beyond the range of normal mechanical rheometers. Thus, devices such as the PAV need to be used. Further details on PAV rheology applied to ink jet fluids can be obtained from [13].

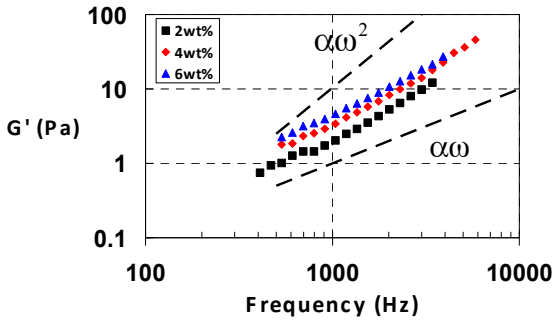

Figure 5: *Elastic modulus G" of the model inks with different weight pigment concentration, η^* = 17mPa.s at 40°C. The dash lines are guide and represent linear evolution and power law evolution with index 2 with frequency.*

Trimaster: Filament breakup

As an example of the way different fluid and particle loading can influence processing behaviour a series of Trimaster filament breakup situations are shown in figure 6.

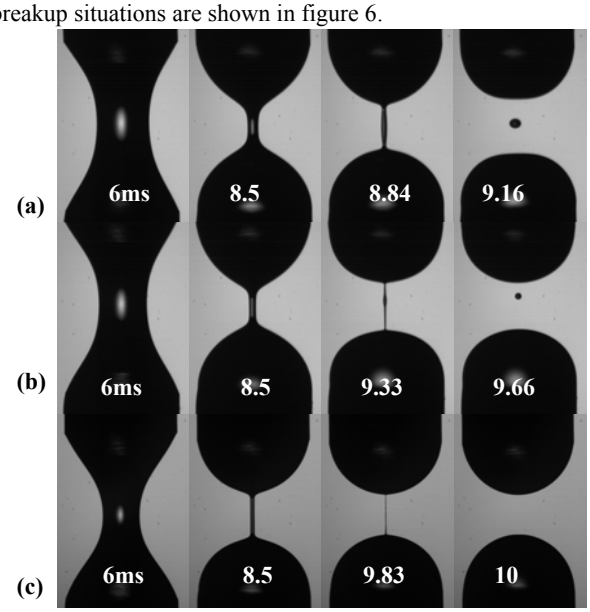

Figure 6: *Photograph of the filament break up captured with the Trimaster in the extensional viscometer mode of (a) DEP, (b) DEP + 0.2% PS110, (c) DEP + 0.5% PS110. Initial gap size: 0.6mm, stretching distance: 0.8mm, stretching velocity: 150mm/s*

Figure 6 shows that even with viscosity matched solutions the break-up behaviour can be different for different polymer loadings. In the pictures shown, filament stretching terminated at 6ms and subsequent breakup behaviour is followed. In the case of the pure solvent, end pinching is observed and a single central satellite drop is formed. As polymer is added, filament thinning occurs and no satellite drop is formed. The addition of additives into a fluid can effect both the form of the breakup and the timescale over which breakup occurs. Both are important in relation to ink jet printing. Further details on ink jet fluid breakup can be obtained from [8, 12].

Conclusions

Two different experimental apparatus have been presented and used to distinguish ink-jet fluids with similar base viscosity. The PAV gave the high frequency rheological characterization of weakly viscoelastic fluids and the second apparatus investigated filament breakup behaviour. The paper has demonstrated high frequency linear viscoelastic characteristics of inkjet fluids. Polymer and Pigment loading effects have been identified as two different sources of LVE and the viscoelasticity developed with their loading. For the polymer, a Maxwell like behaviour with an increase of G' as a power law with index of 2 has been observed, whereas for the pigment, an almost linear evolution has been measured. The "Cambridge Trimaster" filament stretcher has been used to demonstrate the effect of the polymer loading on the transient filament thinning profile, the extensional viscosity and the breakup time. Different behaviours have been observed for different fluids and a link exists between fluid rheology and processing behaviour.

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Author Biography

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