Understanding Inkjet Inks and Factors Influencing the Jetting Behaviour

Tri Tuladhar, Rob Harvey, John Tatum and Paul Drury; Xaar plc, Cambridge, UK

Abstract

An overview is presented of how and where key ink components influence the jetting behaviour during printing. Physical properties alone are an insufficient guide to ink performance. Small variations in ink viscoelasticity influence the upstream flow dynamics and jet break-up mechanism downstream. Recently developed novel techniques capable of quantifying fluid rheology of low viscosity complex inkjet inks at conditions similar to those during printing are discussed which have not been possible until recently. These techniques provide useful tools to differentiate between apparently identical inks but which show different jetting behaviour. This is often the case, where ink batch variations or a minor formulation alteration causes different jetting behaviour and influence print reliability.

Introduction

Recent innovative ideas and technological breakthroughs in (i) inkjet print-head (PH) designs capable of improved print speed, quality and resolution for a wider range of inks, and (ii) advances in inkjet ink chemistry and physics have extended inkjet technology to newly emerging markets and applications such as display fabrication, ceramic components, micro-arrays for biological screening, control-release drug delivery, anti-counterfeit and 3-D printing. New and existing applications demand (i) increased drop velocity, (ii) high print frequency, (iii) controlled drop size, and (iv) improved directionality. However, increased mist, or satellite drop formation and reliability issues (temporary or permanent line drop out, flooding, drop directionality and velocity fluctuation, etc) work against the achievement of these requirements. The effect can be mitigated to some extent by optimising the drive mechanism (waveform and drive amplitude) in drop on demand (DoD) devices and fluid modifications (composition and properties) within the window of PH operation. In extreme cases and, for novel applications, PH redesign and modification of drive electronics may be required.

Despite recent advances in ink chemistry and physics, one of the key challenges in ink formulation is to develop inks that are consistent. Ink formulations are maintained to keep key parameters within specifications, yet it is often noticed that there are marked differences in the jetting performance between batches or between colours of a CMYK set of apparently identical inks. As a consequence extensive and time consuming ink reformulation and validation (optimization and/or separate waveform development) needs to be carried out for each batch or between colours to achieve satisfactory jetting. This issue is further complicated when developing inks for niche applications which could contain special (i) pigments/particles with high loading concentration and density, (ii) polymers/binders of high molecular weight, (iii) carrier fluid with different physical and chemical properties. Any variations in the composition could change fluid physical properties (such as density, surface tension, viscoelasticity, speed of sound) beyond the existing PH operating windows.

A fundamental understanding of ink chemistry and the influence of individual components, as well as the ink as-a-whole, on dynamic flow behaviour in-channel, through the nozzle, in-flight and on-substrate during printing is vital to achieve targeted drop size, reduced satellite/mist formation, high print speed, frequency and print reliability. This understanding will help tailor inkjet fluids for new applications in existing and future PHs.

Influence of ink compositions and properties

Ejection of ink and subsequent drop formation are influenced by the physical properties of the fluid. For piezo-electric inkjet devices, high frequency voltage pulses (waveform) are applied to a piezo-electric element. This causes an ink-filled channel to deform, thereby creating a fluctuating pressure profile. Through fluid acoustics two or more consecutive waves are super-positioned which guide the pressure pulses towards the nozzle [1]. The required super-position is achieved via adjustments to the electrical signals driving the piezoelectric actuator i.e. waveform frequency, voltage amplitude and pulse duration [2]. As a result, a strong acceleration of fluid occurs inside the nozzle which overcomes the viscous dissipation and the energy associated with forming a new surface so that fluid is jetted at high speed. The propagation and reflection of acoustic pressure waves are function of fluid properties, PH design and constituent materials. The amplitude of the applied voltage pulse modifies the fluid acceleration in the channel and hence velocity of the jet ejected from the PH. The presence of any dissolved gas or bubbles slow the acoustic wave propagation and hence the jetting characteristics. Speed of sound, bulk modulus, density and pigments size and distribution influence acoustic waves and are important parameters for optimization of drive waveform.

Electric conductivity and pH of fluid have little influence on the jetting behaviour in the DoD. However, they are important parameters to consider in extending printhead life. Most printheads do not tolerate high conductivity fluid as it enhances attack on electrode and influences printhead performance. The low/high pH degrades the printhead material especially the bonds. Ideally, low conductivity and pH closer to 7 is preferable for DoD. Continuous inkjet ink requires some degree of electric conductivity in order to charge and deflect the droplet.

The introduction of pigments to the carrier fluid produces considerable deviations from the Newtonian behaviour. This is due to particle association (by chemical bonds and/or physical interaction) during flow. The size and concentration of the pigment particles affect viscosity and the likelihood of nozzle blockage. Dispersants are added to stabilize the pigments. Additives such as resins are often present to bind other components of the ink and contribute to the properties of the ink once on the substrate (e.g. gloss, resistance to heat, chemicals and water). All of these additives influence the viscosity of the fluid and also elasticity due to their polymeric nature.

The fluid is subjected to high frequency pressure fluctuations in the channel during actuation and high shear at the nozzle wall. As the jet emerges from the nozzle, the viscosity and elastic stresses resist the necking motion of the liquid filament, whereas surface tension and inertia influence the resulting shape and form of the emerging drop. These opposing forces result in high extensional deformation of the jet and into a spherical drop. The optimum values of the surface tension and viscoelasticity becomes a compromise of what is required upstream (in the channel) and downstream (in-flight).

Surface tension

Surface tension is the driving force behind the jet pinch off and its role in inkjet ink is varied: (a) to enable proper jetting, (b) to form uniform droplets upon ejection and (c) to control spreading and contact angle of the drop on the substrate. It dictates the position of the ink meniscus within the nozzle along with drop quality in-flight. Inks with good wetting ability (low surface tension) are able to display a plug flow velocity profile through the channel and nozzle, where the velocity of the ink close to the wall of the channel is similar to that of the ink at the centre of the channel. Inks with poor wetting (high surface tension), display a more non-uniform velocity profile and the velocity of ink close to the wall are much lower than at the centre of the channel. Such non-uniformity in the velocity profile could lead to ink being left behind and influence drop and satellite formation. High surface tension requires an increase in drive voltage to jet and generate drops. In-flight, drops will be too small and may not spread enough on landing resulting in white space or under-banding and the image appearing too light. In contrast, too low surface tension may experience excessive nozzle plate wetting resulting in loss of jetting stability due to reduced ink ejection. In-flight drops may become too large, reducing resolution and on landing, droplets may spread too much causing excessive bleeding, wicking or over-banding.

The choice of surfactants and their concentration could have significant influence on the dynamic surface tension, jetting behaviour and reliability of apparently identical inks that have similar static surface tension. If the bulk surfactant concentration is near the critical micelle concentration level, it could cause wide fluctuation in the fluid's properties and could have detrimental effect during ink jetting by either preventing or delaying the pinch off of the ligature from the nozzle and cause jet reliability issues.

Marangoni flow caused by local changes in the surface tension between the high dynamic value of the jet at the nozzle and low static in the nozzle plate could cause the flow of the ink layer towards the actuated nozzle. Particles caught in this ink layer are likely to reach the jetting nozzle and may cause nozzle failure. For increasing the jetting stability of the PH, an ink layer near the nozzles should be prevented [1]. The absence of the ink layer would prevent transport of particles towards the nozzle.

At high speed, low viscosity liquid jets form satellite drops regardless of the presence of surfactant. Numerical simulation [3] show that the reduction in the size of satellite drops is achieved by the addition of weak surfactants of high surface diffusivity. In contrast, larger satellite drops are formed by the addition of strong surfactants of low surface diffusivity, i.e. surfactants with strength above the critical value at which the Marangoni stress reverses the capillary flow and draws liquid towards the satellite.

An ideal ink would possess a high dynamic surface tension to promote rapid meniscus recovery at high firing frequencies and a low static surface tension to achieve good substrate wetting. The static surface tension value of ink is usually dictated by the substrate wetting behaviour and typically set between 20-40 mN/m for DOD fluids by adding surfactants and dispersants to some extent.

Viscoelasticity

In the case of DoD, the acoustic waves which cause a droplet to be ejected are affected by ink viscosity. The acoustic waves will be dampened more with increased viscosity; therefore, the drive energy has to be increased in order to jet the fluid. In the channel, if the viscosity is too high, the ink may not flow through the PH and too low viscosity may cause the ink to leak out of PH. Once the jet detaches from the nozzle, high viscosity is preferable to reduce satellite formation in-flight and to avoid drop splattering or bouncing during landing. The ink viscosity is mainly dictated by the choice of carrier fluid and pigment loading. The operating temperature is varied to bring the fluid viscosity down to optimum operating window of 5-40 mPa.s for most DoD PH.

It is well known that addition of a small amount of polymer significantly influences the jetting behaviour due to subtle changes in their elasticity. High elasticity influences the jetting velocity, forms a thin ligature which breaks up at multiple points resulting in many satellites (or mist). In extreme cases, the jet does not detach from the nozzle and is either pulled back into the nozzle or floods the nozzle. Low or no elasticity results in satellite formation at high jetting speed. The presence of some optimum elasticity is required whereby the liquid filament connecting the main drop is instantly pulled into the main droplet after breaking from the nozzle giving a satellite free drop.

Variations in the jetting of identical fluids

Small variations of polymeric additives (concentration and/or molecular weight) in these low viscosity inkjet inks (< 50 mPa.s) have detrimental effect on the inkjet printing behaviour to the extent that it may not jet at all even though the bulk properties are same. We often encounter inks where the first few formulations are unreliable and do not jet properly. With several subtle modifications to the formulations, it is able jet reliably with minimal satellite though all formulations have apparently identical composition and physical properties.

Figure 1 shows the effect of increased polymer concentration on the jettability of five model monodispersed Polystyrene PS110 (110,000 g/mol mol. wt.) solutions of different concentrations (0-1.0 wt %) but matched viscosity of 17 mPa.s. The matched bulk viscosity were achieved by varying the proportion of high viscosity dioctylphthalate, DOP, (50 mPa.s) and low viscosity Diethylphthalate, DEP, (10 mPa.s) as a carrier fluid. The jettings were carried out at 25°C using a Xaar 1001 PH using the standard waveform. The drive amplitude was adjusted to achieve a drop velocity of 5 m/s at 1 mm distance the nozzle. The number of satellite reduced with increasing polymer concentration and negligible or satellite free drops were obtained for 0.2% PS110. However, further increases in PS concentration resulted in no jetting even when the drive amplitude was significantly increased.

Others have also reported similar observations from their controlled experimental [4-5] and simulation [6] studies. Influence of polymer concentration and structure can be associated with the differences in elasticity. These results demonstrate that there is an optimum elasticity which reliably gives satellite free drops. Low elasticity results in satellite drop formation and very high elastic fluids do not jet at all.

Unlike viscosity, it is difficult to quantify the degree of elasticity of inkjet fluids (as a result of dispersant, binders and other additives) using standard tools and hence it is difficult to control during formulation. There is clearly benefit in appropriate measurement or testing methods that can be used to evaluate inkjet fluids before they are loaded into the print heads – either as a batch to batch quality assessment tool or as an aid in the development of fluid formulations. The measuring techniques should be capable of detecting subtle changes in ink properties at conditions similar to that experienced during jetting i.e. high frequency (10-100 kHz) in the channel, high shear rates (10^5-10^6 s^{-1}) in the nozzle, extensive extension in-flight and high impact on landing.

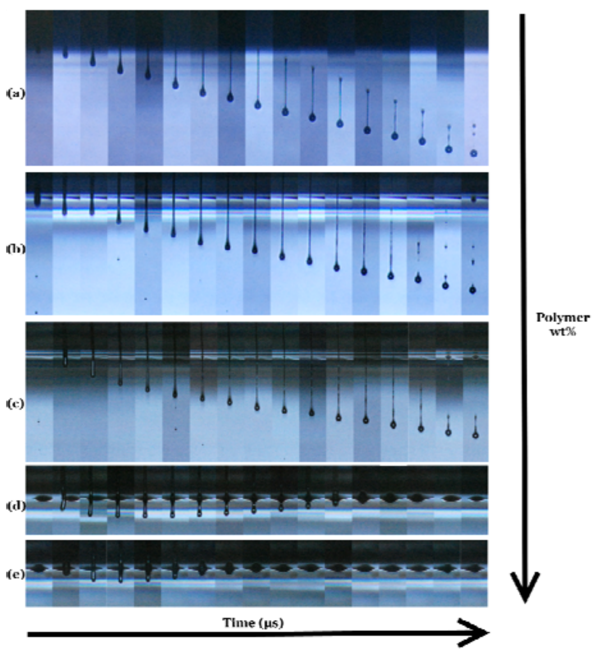

***Figure 1**. Jetting photographs of five 17 mPa.s PS110 solutions of varying concentration: (a) 0%, (b) 0.1%, (c) 0.2%, (d) 0.5% and (e) 1.0%. Images obtained from Xaar 1001 PH using Spark Flash Rig. Photo courtesy: Amit Mulji and Damien Vadillo, Cambridge University.*

Measuring techniques at print conditions

Two techniques are proposed in this paper: the Cambridge TriMaster and the Piezo Axial Vibrator (PAV) to link between fluid rheology, drop-on-demand jet formation and printability.

Cambridge Trimaster

The Cambridge Trimaster device, developed at Cambridge University, employs filament stretching and thinning techniques to simulate jet break-up under in-flight conditions. Filament stretching techniques are employed to investigate the visco-capillary thinning of slender filaments that have a distinctive dependence on time and material properties [7-9]. The key feature of the Trimaster is its ability to handle low viscosity fluids such as inkjet inks. The filament stretching technique provides a simple way of extracting the surface tension and the extensional viscosity of Newtonian fluids, or alternatively the single relaxation time of viscoelastic fluids, by analysing the diameter variation of the fluid thread [8]. In the Trimaster setup, a small volume of fluid is placed between two plates which are then rapidly displaced (~ 0.5-1.0 m/s) to a set separation. The filament stretching and subsequent thinning profiles are captured using a high speed camera, synchronised to the initial motion of the pistons, and photographs of the whole filament profile as a function of time are recorded. Image analysis software developed for Trimaster was used to calculate the mid-filament diameter. The detail of Trimaster is described in Vadillo et al. [9].

Figure 2a shows an example of a normalised filament diameter of the thinning process after the cessation of piston movement for five Polystyrene (PS) solutions of varying mol. wt. (20,000 to 488,000 g/mol) in DEP which have apparently identical viscosity (~24 mPa.s) and surface tension (36 mN/m). The PS concentration was lowered with increased mol. wt. to achieve the same viscosity. The inset shows the high speed photographs of the filament thinning sequences for one fluid. The filament diameter of low mol. wt. PS20 (20,000 g/mol) and PS70 (70,000 g/mol) decreased linearly with time suggesting Newtonian fluid. The higher mol. wt. solutions PS110 (110,000 g/mol), PS210 (210,000 g/mol) and PS488 (488,000 g/mol) exhibited different behaviour where the filament diameter decreased exponentially with time. This exponential decay profile probably originates from an initial Newtonian response of the solvent followed by viscoelasticity dominance of high mol. wt. PS at the later stage. This suggests that these high mol. wt. polymer solutions have a higher degree viscoelasticity though they have a low polymer concentration and are of similar viscosity. An “ideal” fluid for satellite free jetting would be one that just deviates from linear decay to exponential decay represented by “ideal region” in Figure 2a. Filament stretching has been used as a quality control tool [8-9] to correlate and match the filament stretching behaviour with the inkjet printing behaviour of inkjet fluids. Close inspection of the filament shape of the thin ligature just before break can be linked to in-flight jet ejection and break-up mechanism (detailed discussion in [9]).

Piezo-Axial Vibrator (PAV)

The PAV is a squeeze-flow rheometer developed by Prof. Pechhold at the University of Ulm. The high frequency rheology of fluids is measured using the PAV at conditions that mimic those experienced in PH channel. It has a frequency range from 1 Hz to 12 kHz, close to the pulse width in a PH channel (~10-50 kHz.). The PAV can distinguish between the two components of complex viscosity, η*; the elastic (G’) and viscous (G’’) modulus. At high frequencies, the inkjet fluid exhibits a low level of non-Newtonian behaviour, which strongly influences the fluid jet-ability. The

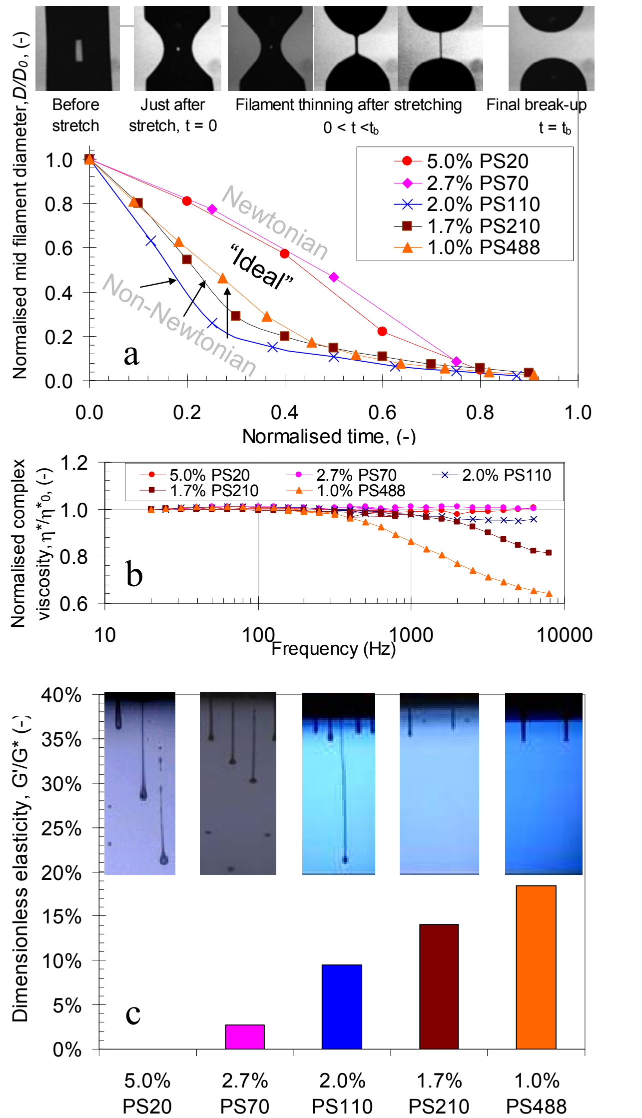

Figure2. *Effect of PS concentration and molecular weight (20–488,000 g/mol) on viscoelastic properties and jetting behaviour of 17 mPa.s fluid at 25°C. (a) Trimaster filament thinning profile (inset: high speed photographs of the thinning process); (b) PAV high frequency complex viscosity profile; and (c) Elasticity of the fluid at 5 kHz (inset: DoD jetting images obtained with Xaar 126 PH; courtesy: Steve Hoath, Cambridge University).*

high frequency rheometer can be used to study the jet-ability of inks.

Figure 2b shows the frequency sweep of normalised complex viscosity using the PAV. All fluids looked almost identical at lower frequencies (<200 Hz). However, high mol. wt. PS solutions deviate at higher frequencies showing thinning behaviour. This clearly indicates that these fluids are not identical at printing conditions and thus suggest different printing behaviour. From the ratio of elastic to complex modulus (G*), obtained from the PAV measurements, the elasticity at high frequency can be deduced. Figure 2c shows the dimensionless elasticity (ratio of G' to G*) obtained at higher frequency and ink jetting images is shown in the inset. For the Newtonian (no elasticity) fluid such as PS20, satellite drops were evident during jetting. The PS210 and PS488 jets did not detach from the nozzle despite increasing the drive voltage and showed high elasticity (> 10%). Fewer or negligible satellites were obtained between PS70 and PS110, where it had some degree of elasticity but less than that of PS210 and PS488 suggesting an optimum elasticity of 4-10% for these PH conditions.

Conclusions

The subtle changes in the ink properties at the printing are important as far as the jetting of the fluids are concerned. Novel rheological techniques to quantify fluid properties close to printing conditions can provide quantitative correlations between jetting and rheological properties. These techniques have proved useful as a prescreening tool to rank inks by detecting subtle changes in ink properties between batches and colours. They can also be exploited during formulations by being able to quantify, control and match higher frequency viscoelasticity and extensional properties of the ink. Further techniques capable of detecting viscoelasticity at PH resonance frequency, dynamic surface tension in microsecond time domain, meniscus and pressure profile during jetting, and mists at the print condition have to be explored to obtain more detailed insight into fluid properties and jetting.

Acknowledgements

We would like to thank all members of the "Next Generation Inkjet" consortium, particularly Prof. Malcolm Mackley, Dr. Damien Vadillo and Amit Mulji of Chemical Engineering Department and Dr. Steve Hoath of Inkjet Research Centre, Cambridge University for their significant contributions and discussions in this field.

References

[1] B Beulen et al., Exp Fluids, 42:217–224 (2007).
[2] N Reis et al., Applied Physics, 094903-1-6 (2005)
[3] V Dravid et al., Chem. Eng. Sci, 61, 3577-3585 (2006).
[4] AV Bazilevskii et al., Fluid Dynamics, 40(3), 376-392 (2005).
[5] S Hoath et al., J. Image Sci. Tech, 53(4), 041208(2009).
[6] J-D Yu et al., J. Computational Physics, 220, 568-585 (2007).
[7] GH McKinley, in Rheology Review, D.M. Bindings and K. Walters (Eds.), The British Society of Rheology, 1-49 (2005).
[8] TR Tuladhar, MR Mackley, J. Non-Newtonian Fluid Mech., 148, 97-108 (2008).
[9] DC Vadillo, TR Tuladhar, AC Mulji, MR Mackley, S Jung, and SD Hoath, "The development of the "Cambridge Trimaster" filament stretch and break-up device for the evaluation of ink jet fluids", J. Rheol, submitted (2009).

Author Biography

Tri Tuladhar received his PhD in Chemical Engineering from the University of Cambridge (2001). He has over 10 years experience in R&D in academia and industry. Recently, he has focused on rheology of inkjet printing ink and developed measurement techniques to link fluid rheology to jetting behaviour. Currently, he heads Xaar's development in the rheological characterisation of inks in the inkjet environment.