Jetting Very High Viscosities With Piezo-Electric Drop-On-Demand Printheads For Increased Capability Of Photopolymer 3D Printing

Nick Jackson¹, Wolfgang Voit², Renzo Trip², Angus Condie¹, Xaar plc; ¹Cambridge, UK; ²Stockholm, Sweden

Abstract

The inkjet industry is constantly evolving to cater to the needs of emerging and changing markets, requiring new capabilities as well as a drive to increase productivity and reduce cost. Presented is how a new high viscosity and high productivity capability using the Xaar 1003 printhead can extend the application of inkjet for 3D printing of photopolymer materials - with improved mechanical properties and scalability, enabling inkjet to compete with the performance of other photopolymer 3D printing technologies.

Introduction

Inkjet has several advantages for 3D printing and additive manufacturing through its scalable nature; multiple materials with different properties (e.g. rigid, flexible, or soluble support) can easily be printed in the same layer at the same time by adding multiple printheads in series, while the build width can be scaled linearly by simply adding printheads in parallel with no loss in resolution. Printing only the exact volume required to create the printed part means that less fluid is wasted with no washing or depowdering required (other than support removal if present), and printing the entire layer at once means that inkjet has speed benefits over most other processes.

The main drawback to piezoelectric inkjet printing, however, is that that it is typically limited to viscosities below 25 mPa·s due, in part, to the resistance of flow through the ink fluid path and nozzle, resulting in an excessive drive voltage requirement, or ink starvation from the inability to replenish the nozzle. Xaar's TF Technology (Registered Trademark of Xaar plc. in US and other countries) ink recirculation overcomes this problem by keeping the channels and nozzles constantly primed at all times with a high flow rate well in excess of the ejection rate [1], while the open design of the Xaar 1003 printhead actuator keeps resistance to flow to a minimum, and the chevron actuator structure ensures there is enough inertia to eject at a reasonable voltage.

Extending this capability further, Xaar's unique High Laydown (HL) Technology [2] is a binary 4 dpd (droplets-per-drop) nearresonant single-cycle operation mode that makes much more efficient use of wall movements than the standard "3-Cycle" mode with no physical change to the printhead, resulting in two phases of drops firing from neighbouring nozzles rather than completely separate staggered cycles. This increase in efficiency means that the drive voltage requirements are reduced to between two thirds and a half for the same drop velocity at the same fluid viscosity, which in turn means that the viscosity can be increased further before the printhead voltage limit is reached.

The single-cycle operation of HL mode then results in an increase in print frequency by firing all active nozzles at once, significantly increasing the productivity from 0.5 μ l/s per nozzle with standard 3-Cycle mode to 2.4 μ l/s per nozzle in HL mode. This enables up to 80 μ m build height per layer at 423 mm/s from the

Xaar 1003 GS12 printhead, while also still allowing to switch to standard 3-Cycle greyscale mode, with a possible layer thickness as low as 2 μ m for 1 dpd at 423 mm/s, just by changing the operating mode with the same printhead.

With fluid recirculation keeping the nozzles primed, and actuator efficiency providing enough impulse to eject fluid through the nozzle, the ability to form droplets from the subsequent ligature is described by the Ohnesorge number, Oh, (Equation 1) [3], a dimensionless value that includes the fluid viscosity (η), surface tension (σ), density (ρ) and nozzle diameter (L), forming a ratio between the viscous forces, and both surface tension and kinetic forces such as inertia (Equation 2). The current understanding of inkjet printing [4] is that Newtonian fluids are limited to an Ohnesorge number less than 1 so that viscous forces do not dominate and impede droplet formation and ligature breakoff.

$$Oh = \sqrt{We} / Re = \eta / \sqrt{(\rho \times \sigma \times L)}$$
⁽¹⁾

$$Oh \approx viscous \ forces \ / \ \sqrt{(inertia \times surface \ tension)}$$
 (2)

This viscosity limit is of particular importance when considering the use of inkjet in 3D printing. A higher viscosity allows for resins with higher molecular weight polymer chains, and therefore mechanically tough and flexible parts, which therefore means that the use of inkjet in 3D printing is limited by the viscosity capability of the technology.

A range of BASF Ultracur3D (Registered Trademark of BASF 3D Printing Solutions GmbH in US and other countries) photopolymer resins were tested in collaboration with BASF 3D Printing Solutions to establish the capability limits of the Xaar 1003 printhead with respect to high viscosity, and hence the potential mechanical properties of printed parts. Ultracur3D photopolymers address a wide range of potential applications and performance characteristics in additive manufacturing with flexible, tough, rigid, and low viscosity materials available.

Results

Presented below are the results of tests performed with a number of different high viscosity fluids as summarised in Table 1 using the Xaar 1003 GS12 printhead (35 μ m nozzle diameter, *L*) in both standard 7 dpd greyscale 3-Cycle mode, and 4 dpd binary High Laydown printing mode, to establish the upper limit of viscosity with Xaar's TF Technology printheads.

Fluid	<i>T_{jetting}</i> [°C]	η [mPa·s]	ρ [g/cm³]	σ [mN/m]	Oh
ST 30 LVx	70	64.9	1.106	36.4	1.73
WS 07	30	60.0	1.121	28.5	1.79
PEG400	25	95.4	1.078	52.2	2.15
ST 30 LV	33	98.1	1.089	36.7	2.62

Table 1. Physical properties of key fluids tested

Standard Greyscale 3-Cycle mode

A Xaar 1003 GS12 printhead was loaded with a modified high viscosity Ultracur3D resin, ST 30 LVx, using a Xaar MIDAS 950C recirculating ink supply system [5] modified for high pressure and high temperature operation. When heated to 70 °C as measured at the printhead inlet, the fluid viscosity at constant 0.6 Pa stress was 65 mPa·s, which gives an Ohnesorge number of 1.73 – significantly above the conventional limit of 1.

Under these conditions, the drop formation appears to be good, with a consistent 6 m/s drop velocity for several lines of print as measured at 1 mm throw distance on a stroboscopic microscope system using a 20 μ s double-flash (not shown) at a drive voltage below the maximum possible for this printhead. With the exception of 1 dpd, the ligatures are short and few satellites are present for all drop sizes (Fig. 1). The longer ligature of 1 dpd still detaches before the typical 1 mm throw distance, and suggests that multi-drop printing has a significant effect on drop breakoff not captured by the variables in the Ohnesorge ratio (Equation 1).



Figure 1. 3-Cycle Drops in Flight for 1 dpd (left) to 7 dpd (right) at 6 kHz with BASF Ultracur3D ST 30 LVx test resin at 65 mPa·s jetting viscosity (70 °C, Oh = 1.73)

This performance can also be seen at low temperatures, where a support resin, BASF Ultracur3D WS 07, formulated to be jetted at 25 mPa·s at 50 °C, was lowered to 30 °C as shown in Figure 2. At 30 °C, the viscosity of 62 mPa·s and Ohnesorge number of 1.8 also jetted at 6 m/s for several lines of print, with good drop formation and a drive voltage below the printhead maximum.



Figure 2. 7 dpd 3-Cycle Drops in flight at 6 kHz with BASF Ultracur3D WS 07 at 62 mPa·s jetting viscosity (30 °C, Oh = 1.8)

Binary High Laydown mode

Initially, the performance of High Laydown was confirmed using the same modified Ultracur3D ST 30 LVx test resin previously shown in Figure 1 to have good jetting performance in 3-Cycle mode. In HL mode at 70 °C, the ligatures are similar in length to 3-Cycle mode, however now the next drop is ejected before the ligature detaches (Fig. 3). The drops still separate well before reaching the substrate, with little misting or satellites forming, and only a slight phase offset is visible between neighbouring nozzles.



Figure 3. High Laydown drops in flight at 28 kHz with BASF Ultracur3D ST 30 LVx test fluid at 65 mPa·s jetting viscosity (70 °C, Oh = 1.73)

The viscosity was then increased further using a second modified version of Ultracur3D ST 30 LV with an intermediate viscosity of 76 mPa·s at 56 °C (Oh = 1.95), where a clean curtain of ejected drops was repeatedly jetted. The extremely high ejection throughput of High Laydown (approximately 1 ml/s per row of 500 nozzles) means that this curtain of drops is clearly visible with the naked eye without high powered illumination, as seen in Fig. 4.



Figure 4. Curtain of High Laydown drops jetting at 76 mPa·s (56 °C, Oh = 1.95)

A further increase in viscosity was then demonstrated using polyethylene glycol 400 (PEG400) with a viscosity of 95.4 mPa·s at 25 °C, and an Ohnesorge number of 2.15 (Fig. 5). At this viscosity, the drop formation was still acceptable with similar ligatures as seen with the modified Ultracur3D ST 30 LVx test resin in Figure 3, breaking off at broadly the same distance with few satellites formed. Even at 95.4 mPa·s, the drive voltage for 6 m/s drop velocity was still below the maximum drive voltage for the printhead.



Figure 5. High Laydown drops in flight with PEG400 model fluid at 30 kHz with 95 mPa \cdot s jetting viscosity (25 °C, Oh = 2.15)

Unmodified Ultracur3D ST 30 LV was then successfully jetted at 33 °C, where the fluid viscosity was 98 mPa·s (Oh = 2.62) (Fig. 6). Drop formation was still good and the drive voltage for 6 m/s was still below the printhead maximum.



Figure 6. High Laydown drops in flight at 27.6 kHz with BASF Ultracur3D ST 30 LV at 98 mPa·s jetting viscosity (33 °C, Oh = 2.62)

Discussion

Plotting the Weber and Reynolds values for the fluids tested (Fig. 7) shows that the results presented here lie outside of the conventional envelope of inkjet technologies [4]. The data in Figure 8 shows that the fluids are not shear-thinning in the nozzle, so this does not explain the ability to form droplets at these high viscosities.

Instead, this suggests that the current model, and the resulting Ohnesorge limit, does not apply to dynamic multi-drop systems with high recirculation rates such as with TF Technology. The high nozzle turnover rate could affect the dynamic surface tension of the meniscus by disrupting surfactant migration, while multi-drop jetting would influence the inertia, meaning that additional terms may be required in the dimensionless number to properly describe the observed results.



Figure 7. New successful high viscosity results for 3-Cycle (◊) and High Laydown (♦) compared to conventional Weber and Reynolds limits [4], and a typical UV curable ink formulated for conventional piezo drop-on-demand inkjet for comparison (●)



Figure 8. Flow curves of the fluids tested at respective jetting temperatures showing Newtonian behaviour.

A further benefit of high-flow recirculation is that the fluid can be continuously supplied at elevated temperatures, even when the printhead is idle, with less heat loss in the tubing due to a much lower dwell time. In the case of the Ultracur3D ST 30 LVx results above (Fig. 1 and Fig. 3), this photopolymer was heated to 70 °C to achieve the jetting viscosity of 65 mPa·s. As can be seen on the full temperature range in Figure 9, the room temperature viscosity of this fluid (dashed grey line) is above 600 mPa·s; far higher than conventional UV curing inkjet inks (solid black line). This has significant implications for fluid formulation by enabling much higher molecular weights than previously thought possible.



Figure 9. Viscosity at constant 0.6 Pa stress vs. temperature for a typical UV inkjet ink, PEG400 model fluid, and BASF Ultracur3D photopolymers

The different viscosity limits for 3-Cycle and High Laydown mean that there are two distinct operating ranges for the two modes from the same printhead. The higher viscosity capability for High Laydown of up to 100 mPa·s is offset by the much higher throughput, which results in an increase in build speed and the range of possible material properties is increased at the expense of some loss in feature size control due to the large binary drop volume. In contrast, the much smaller drop size and greyscale capability of standard 3-Cycle mode offers much finer feature size, but takes longer to produce parts as a result, with a lower maximum supported viscosity of 65 mPa·s.

Adding and mixing multiple materials within a single layer of a printed part can be difficult, if not impossible, with established 3D printing technologies such as Stereolithography Apparatus (SLA), Digital Light Processing (DLP), and Fused Deposition Modelling (FDM). Printing multiple different fluids such as a soluble support or a flexible rubber-like material with inkjet, in comparison, can be achieved by simply adding multiple printheads in series.

Figure 10 shows a structure printed with two Xaar 1003 GS12 printheads; one containing a flexible resin and the other containing a soluble support material. When the support is removed, this leaves the complex flexible lattice as shown.



Figure 10. A flexible matrix structure printed in situ with a flexible resin and a soluble support. Photograph supplied by BASF 3D Printing Solutions

Figure 11 shows the potential for combining rigid and flexible elastomeric materials in the same layer with inkjet. Here the two Xaar 1003 GS12 printheads in series allow for the boundary between the rigid rings and elastic bridge to be combined *in situ* before curing each layer, resulting in a strong bond that requires no post processing or assembly.



Figure 11. Test part consisting of rigid rings connected with a band of a second material demonstrating elastic (middle), and flexible (bottom) properties. Photographs supplied by BASF 3D Printing Solutions

Conclusion

The high fluid recirculation rate, combined with the high efficiency of the shared-wall chevron shear-mode actuator, means that Xaar printheads can be demonstrated as capable of jetting fluids with viscosities greater than 60 mPa·s in standard 3-Cycle mode, and in excess of 90 mPa·s using High Laydown mode, contrary to the commonly defined limit of approximately 25 mPa·s in established inkjet models.

Furthermore, if these viscosities are achieved by jetting at elevated temperatures as high as 70 °C, it becomes possible to jet fluids that have viscosities in excess of 600 mPa·s at 30 °C. This enables printing of specifically formulated inkjet resins to achieve improved mechanical toughness and/or flexibility at high resolution and high speed, as well as potentially enabling some existing SLA resins [6] [7] [8] to be printed with piezoelectric inkjet technology.

References

- M. Crankshaw, "Ink Recirculation Xaar TF Technology™: A Study of the Benefits", Int. Conf. on Digital Printing Technologies, pp. 207-244(5), 2016
- Xaar plc, "High Laydown Technology", [Online] Available: https://www.xaar.com/en/about/xaar-technologies/highlaydown-technology/, 2019
- [3] W. Ohnesorge, "Formation of drops by nozzles and the breakup of liquid jets", J. Applied Maths and Mech., vol. 16, pp. 355-358, 1936.
- [4] B. Derby, "Inkjet printing of functional and structural materials: Fluid property requirements, feature stability and resolution", Ann. Rev. Mater. Res., vol. 40, pp 395-414, 2010
- [5] Xaar plc, "Xaar MIDAS ink supply system", [Online] Available: https://www.xaar.com/en/products/systemscomponents/xaar-midas-ink-supply-system/, 2019
- [6] Forecast 3D, "SLA Materials", technical comparison chart, 2019
- [7] BASF, "Ultracur3D FL 60 Flexible Reactive Urethane
- Photopolymer", datasheet, 2019
 [8] BASF, "Ultracur3D RG 35 Rigid Reactive Urethane Photopolymer", datasheet, 2019

Acknowledgments

The authors wish to thank Fan Zhang and Andras Marton from BASF 3D Printing Solutions for supplying, and modifying, the Ultracur3D photopolymers.

Author Biography

Nick Jackson is a member of the Advanced Applications team at Xaar plc, Cambridge. He received his degree in Natural Sciences (Chemistry) from the University of Cambridge in 2007 and joined Xaar in 2008. In the past 11 years, he has built up extensive experience in printhead performance, developing several processes for product development and testing, as well as discovering the underlying technology for High Laydown.