Jetting of Reactive Materials for Additive Manufacturing of Nylon Parts

Saeed Fathi [a,], Phill Dickens [a], Richard Hague [a], Khosrow Khodabakhshi [b], Marianne Gilbert [b]; [a] Wolfson School of Mechanical and Manufacturing Engineering, [b] Department of Materials, Loughborough University; Loughborough, UK*

Abstract

The first stages in the research of a radically new digital fabrication process of nylon parts are presented in this paper. The fabrication process is based on additive layer manufacturing where two reacting mixtures are deposited via printing onto a moving surface. At elevated temperature, each layer is expected to start a reaction to polymerize nylon 6. The jetability of the mixtures consisting of caprolactam, catalyst and activator were investigated to find appropriate range of stable jetting parameters. Droplet formation characteristics were studied for the deposition stage. By overcoming the challenges in jetting and deposition of the reactive mixtures, this digital fabrication process could compete with the conventional casting and injection molding processes as it benefits from both rapid and tool-free aspects of additive manufacturing and high resolution and multi-material deposition of printing technology.

Introduction

The range of jetting materials, high throughput, computer aided design (CAD)-based process, multi-material jetting etc., have led ink-jet technology to be applied in a wide range of manufacturing applications namely electronics, medical, optics, and rapid prototyping/manufacturing (RP/M). In the first RP/M application of ink-jet technology, three-dimensional printing process was introduced by MIT in early 1990s [1].

Loughborough University has initiated research into a novel process based on layer by layer deposition of two reacting mixtures of caprolactam, catalyst and activator onto a moving hot surface through drop-on-demand (DoD) piezoelectric printheads. In appropriate conditions such as elevated temperature and moisture-free environment, the two mixtures are expected to start a polymerization reaction, where nylon 6 is made as a solid layer.

This paper reports the investigations undertaken for the jetability and droplet formation characterization of the reactive mixtures. Physical properties of the mixtures at jetting temperature will be presented. Jetability, jet array stability, interaction between jets and the nozzle plate and droplet formation characteristics namely droplets shape, size and kinetics were investigated in order to find the appropriate jetting conditions for a reliable deposition.

Materials, methodology and experimental setup

Nylon 6 in the melt state has too high a viscosity for jetting via the available ink-jet printheads. However, it is polymerized from mixtures of caprolactam having a viscosity as low as graphical printing ink at elevated temperatures. The appropriate composition of the reactive mixtures has been investigated by parallel research within the Department of Materials at Loughborough University. Optimized mixtures for faster reaction and better mechanical properties have been investigated in a conventional cast nylon process. The final mixture composition suggested for jetting consisted of 99% volumetric (vol.) caprolactam and 1% (vol.) of acetyl-caprolactam as activator and 1% (vol.) of magnesium bromide (MgBr) as catalyst. The mixtures dominated by caprolactam had a melt temperature of 68 °C. A reaction time of less than 1 minute between the two mixtures was achieved at a reaction temperature of about 150 °C via the conventional cast nylon technique. The composition with the faster reaction time showed mechanical properties similar to the available commercial cast nylon.

Caprolactam and the mixtures were characterized for physical properties. This could give an idea about the jetability and also help in studying the droplet formation characteristics of the mixtures. The dynamic viscosity of the molten caprolactam and the two mixtures were measured using a rheometer (MCR101 – Anton Paar Ltd). The surface tension was also measured using the pendent drop method (OCR 20 – DataPhysics GmbH). In addition, hot stage optical microscopy (DM LM – Leica Microsystems Ltd) was used to analyze the structure of the mixtures composition before jetting.

An experimental setup was integrated with jetting, heating, pneumatics, machine vision and depositing systems inside a glove box. A piezoelectric shear-mode DoD printhead (XJ126/80 – Xaar plc) was used with a maximum continuous operating temperature of 85 °C. Two jetting assemblies were provided in the setup for the two mixtures, each of which had a melt supply unit with thermal and pneumatic control. The mixtures were separately cast in bar cartridges as a feed for the process. The setup was designed to receive a bitmap image from the printhead software and deposit a pattern as a layer on a moving surface. Deposition integrated with a heating technique could provide the reaction condition in a controlled environment and with a motion control system, each layer could be fabricated in an additive manufacturing approach.

Jetting trials were accomplished at the appropriate jetting temperature gained by studying the physical properties of the molten caprolactam and the mixtures. The start-up strategy for jetting was to have dripping of the melt to ensure that the printhead was filled. The nozzle plate was cleaned in order to remove any contamination. Then, an initial vacuum level was applied to control the flow of the melt inside the printhead. Three parameters of jetting voltage, frequency and vacuum level were varied to investigate the jet stability. The printhead's software was used to vary the jetting voltage signal amplitude and frequency within 5.0 V to 25.0 V and 1 kHz to 5 kHz respectively recommended by the printhead manufacturer. Thermal-dependency of the voltage

signals was taken into account when jetting at elevated temperature. The vacuum level over the melt was also varied within a range from 5 to 50 mbar.

Jet array (126 jets) stability was investigated by monitoring the nozzle plate via a microscope camera (AM211 – Dino Lite). Images of droplets in a single jet were captured by analysis of the images taken by a high speed camera (FastCam APX-RX – Photron Inc.) equipped with a long lens (12X Zoom – Navitar Inc.) and a transmitted backlight (ELSV 60 – Everest VIT Ltd.) with imaging rate and exposure time settings of 10,000 fps and 4 µs respectively. The images were then analyzed to obtain information of droplet's shape, size and kinetics at 1 mm distance from the nozzle (where droplets will impinge onto the surface recommended by the printhead manufacturer). The droplet edge definition error was ±1 pixel equivalent to less than ±7 µm.

Results and discussions

The dynamic viscosity of caprolactam, the dominant ingredient of the mixtures, was below 10 mPa.s at 80 °C. With the printhead's operating temperature limitation (85 °C), 80 °C was selected as the jetting temperature at which the surface tension of caprolactam, Acetyl-caprolactam and MgBr-caprolactam were 34.9 ± 0.3, 36.0 ± 0.1 and 34.9 ± 0.2 mN/m respectively, compared to the printhead's nozzle plate surface tension (40 mN/m). Caprolactam and acetyl-caprolactam had a dynamic viscosity of 9 mPa.s at 80 °C. However, MgBr-caprolactam had much higher viscosity of about 30 mPa.s. The origin of this higher viscosity was found by the optical microscopy in the mixture. Micro-crystals of MgBr-caprolactam were dispersed in the mixture with a size range from 20 to 100 µm. Due to the printhead's nozzle size (50 µm) and the two filtration units set in the jetting assembly, the micro-crystals were required to be molten before jetting. Their melting temperature was found to be around 150 °C. The dynamic viscosity of MgBr-caprolactam and its surface tension remained almost the same after the temperature dropped to 80 °C from 150 °C. This thermal cycle was considered as a start-up strategy for jetting the MgBr-caprolactam mixture.

Jetting of the molten caprolactam and acetyl-caprolactam was accomplished and the research is ongoing to jet MgBr-caprolactam in the near future. Due to the similarity of Acetyl-caprolactam mixture with caprolactam in physical properties at the selected jetting temperature, trials with the molten caprolactam were mainly carried out so far which is reported as follows.

One of the main objectives of this research was to investigate whether molten caprolactam could be jetted with the Xaar-type graphical industry printhead. A stable jet array of the molten caprolactam and acetyl-caprolactam was achieved. Figure 1 shows a trial with stable jet array of the molten caprolactam.

Jetting trials were sensitive to the jetting voltage and vacuum level. Jetting frequency did not play a significant role. At higher vacuum level, air ingestion and the consequent nozzle blocking occurred with instability in jet array especially when a high voltage was applied. At higher jetting voltage, the vacuum level needed to decrease and vice versa for jet array stability. Figure 2 gives a general guideline for setting the two parameters of voltage and vacuum level for a stable jet array of molten caprolactam and Acetyl-caprolactam in the setup.

Instabilities occurred in some trials within the parameter range of the stable jet array mainly due to contamination on the nozzle plate. The jet disturbance by contamination, could give a trajectory error in the disturbed jet causing droplet placement inaccuracy. In some cases, such trajectory error could lead to a jet failure in the jet array as Figure 3 shows. In such a case, a domino effect was observed leading to the whole jet array failure. This was when the failed jet bleeding from the actuating nozzle could influence the neighboring jets.

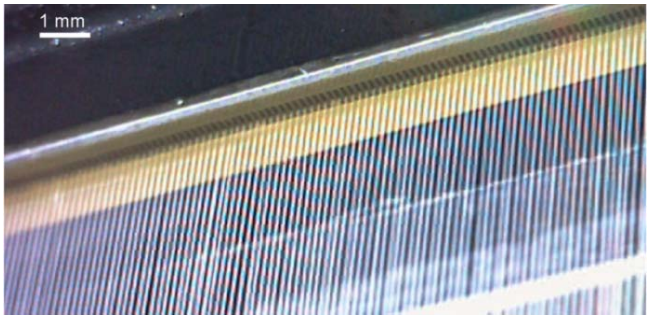

***Figure 1**. Jet array of the molten caprolactam (Jetting conditions: 17.5 V and 5 kHz, 25 mbar)*

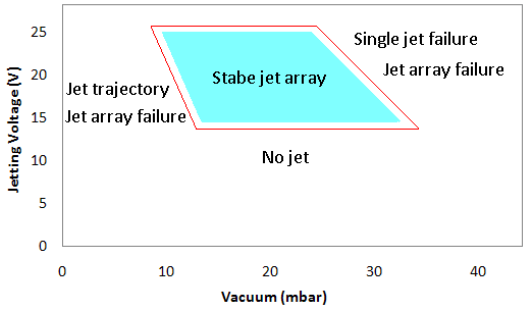

***Figure 2**. Process window for stable jet array when jetting the molten caprolactam*

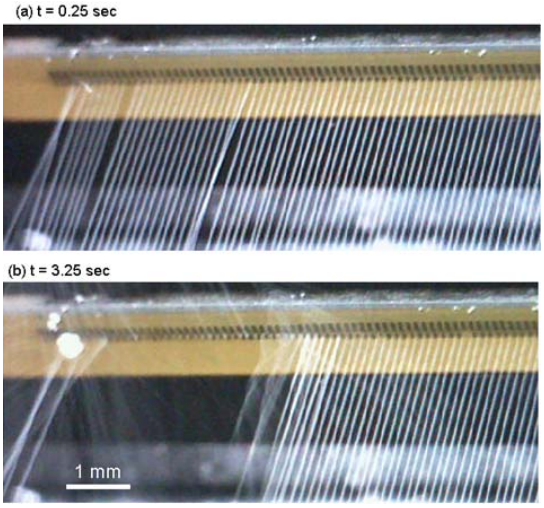

***Figure 3**. Jet instabilities during jetting of the molten caprolactam, (a) trajectory error at 0.25 sec from start of jetting, (b) domino effect in jet array failure (Jetting conditions: 15.0 V, 5 kHz, 30 mbar)*

The characteristics of a jet of molten caprolactam were investigated to understand phenomena associated with the formation of droplets. Oscillation of the melt meniscus on the nozzle and formation and separation of a single droplet were studied by high speed imaging. The study was expected to determine the appropriate values for the jetting parameters (voltage and frequency) within the range of stable jet array (Figure 2) to be found for the deposition stage. Therefore, a single jet of the molten caprolactam was produced with varying jetting voltage and frequency (15.0 ~ 25.0 V with 2.5 V increments and 1 ~ 5 kHz with 1 kHz increments respectively) at a fixed vacuum level (25 mbar).

The nozzle plate was cleaned and dried before jetting started to study the melt/nozzle plate interaction. However, after jetting started, wetting developed around the actuating nozzles. After about 1 second, the wetting area covered the adjacent nozzles. This was a repeatable behavior for all the range of jetting voltages and frequencies.

All droplets were accompanied with formation of a tail within the range of jetting parameters. However, the tail formation characteristics varied with the jetting parameters. Frequency had no significant effect on tail formation. However, the voltage signal defined the amount of melt being expelled from the nozzle. With increasing voltage, longer tails were formed. Figure 4 shows short and long tails formed with low and high jetting voltage.

Within 100 µs after separation from the nozzle, the tail either disintegrated into satellite droplets flying behind the main droplet (higher jetting voltages) or rejoined the main droplet (lower jetting voltages). Droplets generated with 15.0 V had a short tail with no disintegration to form any satellite droplets. The rejoining of the tail to the main droplet for this voltage occurred at about 250 µm from the nozzle. The tail formed with 17.5 V jetting voltage also rejoined the main droplet without disintegration. However, the rejoining distance increased to about 550 µm for droplets generated with this voltage. In contrast, with the jetting voltages higher than 17.5 V, the tail disintegrated into several satellite droplets. The disintegration distance increased to 1550 µm for the droplets formed with 25.0 V. The tail evolution from formation to rejoining/disintegration occurred within 200 µs of the nozzle actuation for all voltages. This suggested that the appropriate jetting voltages to avoid formation of satellite droplets for better layer deposition were equal or less than 17.5 V.

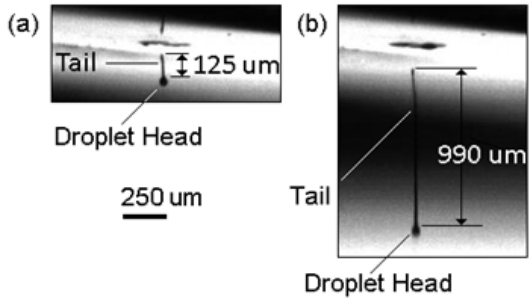

***Figure 4**. Tail length measurements after separation when jetting caprolactam at 3 kHz frequency (a) 15.0 V, (b) 25.0 V*

Figure 5 shows the evolution of a droplet and tail generated with high jetting voltage (25.0 V). The figure also demonstrates the meniscus oscillation in the adjacent nozzles due to the Xaar-shared-wall technology in the printhead's design. After 67 µs (Figure 5(c)), it is seen that two further adjacent nozzles on both sides of the ejecting nozzle were also actuated partially to make a total of four nozzles being affected by an individual nozzle actuation.

Figure 5(c) also shows a moment just before the tail was separated from the nozzle at 67 µs. It is clearly seen that the tail end became very thin before separation due to necking. With the thinning shape of the tail in Figure 5(c), it seems that the meniscus could be inside the nozzle from which the upper side of necking was not visible. The deflection could be a result of instability of the tail end upon separation and possibly touching the nozzle edge as reported by Hutching *et al* [2]. The deflected end of the tail can be seen in Figure 5(d) after the tail was separated. The tail end deflection was a repeatable behavior in the trial within the range of jetting voltages and frequencies in both nozzle (plate) conditions (wet/dry). The satellite droplets made by the tail end were found to be deflected by 10 pixels from the droplet head.

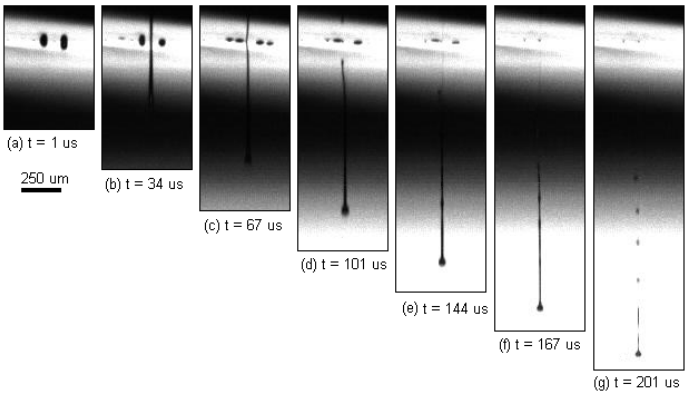

***Figure 5**. Evolution of a tail (formation and disintegration) in jetting with voltage of 25.0 V at 3 kHz frequency at a vacuum level of 25 mbar*

The droplet diameter was almost constant at around 50 µm which was also the nozzle size. This shows that the droplet size was not affected by the jetting parameters and was a factor of the nozzle size. As the droplets produced at 22.5 and 25.0 V had satellites, the main droplet was a proportion of the whole material jetted and so results for kinetics energy, Weber number and Reynolds number will be less accurate.

The variation of the kinetics of droplets with jetting voltage and frequency was quantified. It was found that frequency had little effect on droplet kinetics. However, increasing jetting voltage increased droplet velocity linearly as Figure 6 shows, due to the increase in the pressure wave magnitude propagated from the melt channel to the meniscus surface.

Quantifying the droplet diameter and velocity could be useful for studying droplets spreading behavior by calculating the droplet impact energy, Weber and Reynolds numbers. The latter two were increased linearly with jetting voltage within a range of 5 ~ 70 and 10 ~ 40 respectively. Both the Weber and Reynolds numbers were relatively low which would indicate little tendency of the droplets to make a splashing effect on the surface during impingement [3]. From the results it can be predicted that for all the range of jetting

voltage and frequencies there will be droplet spreading with no secondary droplets from splashing.

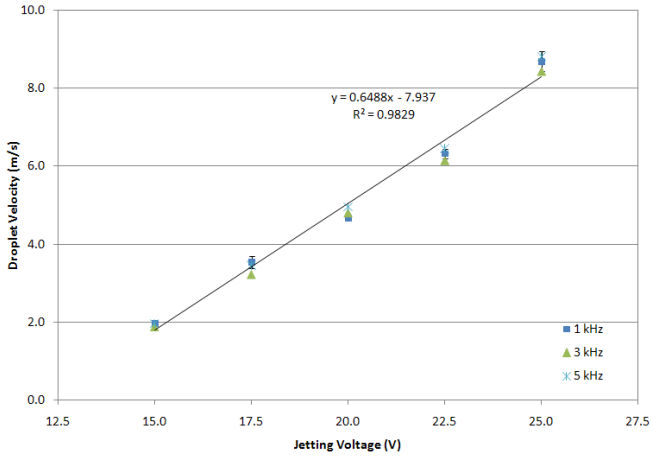

Figure 6 *Droplet velocity vs. jetting voltage at different frequencies for the molten caprolactam*

Figure 7 shows how the presence of contamination could lead to a trajectory error which would then cause droplet placement inaccuracy when layer patterning on the surface. In Figure 7(a), the position of the contamination to the left of the actuating nozzle is seen. Also, the meniscus oscillation in the adjacent nozzles is also seen. Figure 7(b) which is a just after a droplet was ejected shows there was no residual melt left around the nozzle. However, over time the nozzle area was wetted locally as seen in Figure 7(c) and (d) but the wetting was not symmetric to the actuating nozzle. The asymmetric wetting caused the tail of the ejecting droplet to deflect toward the centre of the wetting area (left of the actuating nozzle). This situation led the trajectory change of the jet after ejection of 3,607 droplets. The contamination could attract the contact line of the oscillating melt meniscus of the partial actuation (to the left of ejecting nozzle) by surface tension forces. Over time, the nozzle wetting developed towards the contamination.

Conclusions

The concept of a new additive manufacturing process for nylon based on jetting reactive mixtures was introduced. The jetability of the mixtures was studied by investigating their physical properties, namely dynamic viscosity and surface tension. Appropriate jetting start-up conditions were considered in an integrated experimental setup. Jetting trials with the molten caprolactam as the dominant component of the mixtures and Acetyl-caprolactam were accomplished.

Amongst the range of the jetting parameters varied, it was found that jetting frequency had little effect on the stability and droplet formation characteristics. However, jetting voltage and vacuum level were the two main parameters. The stability of the jet array was achieved in a range which was narrowed down by the droplet formation characterization to find optimized jetting condition for the deposition stage. The droplets were found to have similar shape and kinetics within a trial.

A tail was formed with the droplets. With higher jetting voltage, the tail disintegrated into satellite droplets whereas with lower voltages, the tail rejoined to the main droplet. This was used as a criteria to narrow down the range of jetting voltage with a stable jet array to 15.0 to 17.5 V for the deposition stage to avoid the satellite droplets.

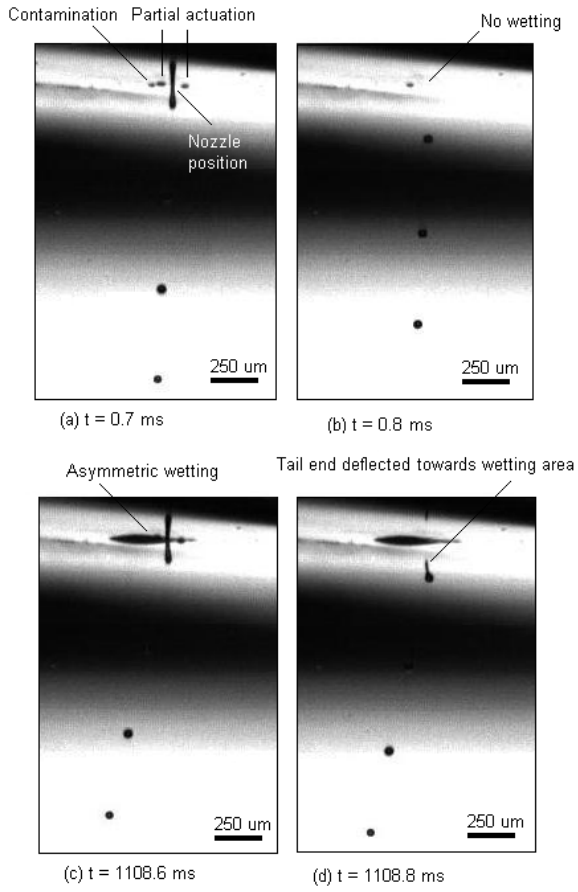

Figure 7*. Significant droplet placement inaccuracy due to an unbalanced wetting of the nozzle plate (Jetting conditions: 15.0 V and 4 kHz)*

References

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Author Biography

Saeed Fathi, BSc MSc MPhil, joined Loughborough University as a PhD student in 2007 with a background in Manufacturing Engineering. He researched on continuous ink-jetting of high viscosity bio-degradable resins for medical applications with a focus on droplets train/moving substrate interactions during layer fabrication. As the theme of his research now, Saeed has been researching a radically new process in rapid manufacturing of nylon parts via jetting of two reacting mixtures in an additive-layer approach.