Abstract

Incorporating liquid fillers in additive manufacturing processes can produce liquid-filled solid parts with unique properties. To develop this, the behavior of immiscible droplets in a polymer matrix subject to different kinds of flows is explored. Castor oil droplets, with a range of capillary numbers much higher than the critical capillary number, were injected in a matrix of Silicone oil and subjected to flows within a converging channel. The rate of change of capillary number as the droplet moves down the channel was measured to illuminate the effect of the die design. The affine state was not reached when the droplets were deployed in the center but was achieved when injected in an offset position. This data is valuable to understand the effect of the die on the deformation induced on immiscible droplets and is one of the preliminary steps to incorporate liquids in additive manufacturing.

Introduction

Polymer Based Additive Manufacturing (PBAM) is a manufacturing process where the polymer is deposited layer by layer to generate the required part. The deposited polymer is in the form of a thin filament which is melted and extruded in a die that is mounted on the print head. This manufacturing method is popularly used in polymer based additive manufacturing machines and its use is expected to grow soon.

Recent advances and innovations in this method include incorporation of solid fillers like glass fibers, carbon fibers and nanotubes in the polymer to manufacture composite parts. However, not much research has been done in integrating liquid fillers into the polymer matrix. The behavior and morphology of liquid additives in the polymer matrix has to be studied so that process parameters of a new manufacturing method can be established.

In order to investigate the behavior of liquid additives in a polymer based additive manufacturing method, a series of experiments was devised. A novel die that included a converging part with a subsequent straight section was used for this purpose. The objective was to determine the factors that control the injected liquid droplet morphology as the polymer matrix leaves the die. Clear polymer with streaks of colored liquid can be 3D printed with a control on the size and distribution of the droplet phase.

A range of operating conditions and initial droplet diameters were explored. The droplet shapes and dynamics of the process in a converging channel that imposes an extensional deformation on the droplet were studied to illuminate the conditions for the droplet to stretch and breakup into daughter droplets. When this phenomenon is modeled and explained, it has the potential to be incorporated into polymer based additive manufacturing dies where predictable droplet morphology can be obtained in a matrix polymer of the print.

Background

The breakup of droplets in a matrix is the basis for formation of emulsions. In industries, emulsions and polymer blends can be used to engineer desired properties by controlling the morphological behavior of droplets in a matrix. At a fundamental level, Rayleigh [1] proposed a theory based on the propagation of a disturbance as a sinusoidal wave on a liquid jet which causes the breakup of the jet when the disturbance wavelength exceeds a critical value based on cross sectional diameter of the jet. However, Taylor [2] first formulated the theory behind droplet breakup in physical flows like shear and extensional flows and modeled the normalized droplet size as a function of the viscosity ratio. This equation was a basis of research of many authors in the field, for over 50 years, all of whom aimed to make the equation applicable to other well defined flows. Tomatika [3] used Rayleigh’s theory and proved that Taylor’s equation can be theoretically derived.

Grace [4], in 1971, conducted a comprehensive set of experiments so that industrial standards could be established in formulation of emulsions, and it is a testimony to the work that the equations and graphs from his experiments are still being used. Bentley and Leal [5] conducted their own set of experiments using Taylor’s apparatus, with better control, and came up with a formal droplet breakup experimental procedure and characteristic curves, based on critical capillary number and viscosity ratio, in a series of flows ranging from simple shear to pure extensional. Stone [6] and Rallison [7], in their review papers, provided a comprehensive analysis of existing research performed in the area. However, there was a need to devise new experiments and models that
explained transient behavior of droplets after the flow is stopped.

Stone et al., [8] performed some of the first experiments, using Taylor’s apparatus, to address this and concluded that a critical aspect ratio of droplets must be attained before transient breakup occurs. They modeled this as a function of viscosity ratio and explained the phenomenon by assuming a normal stress drop at the neck of the bulb. However, their research does not address translating droplet behavior in zero shear regions of any given flow. Poiseuille flow is an example of such a flow where there is zero shear at the center of the channel but the fluid has an average velocity in the center.

As per the characteristic curves of critical capillary number vs. viscosity ratio, droplet breakup can be achieved in either shear flow or extensional flow. Marks’ [9] performed experiments in shear flow and plotted non-dimensional time to droplet breakup vs. viscosity ratio. The breakup time scaled with the shear rate and simple shear flow needed an exorbitant amount of time to stretch the droplet and cause breakup for a given fluid system. Hence, simple shear flow was not an ideal candidate to be incorporated into the current experiment as it needed very long dies. Janssen and Meijer [10] performed experiments in plane hyperbolic flows and found that it takes much lesser time to achieve droplet elongation than in simple shear, although the deformation modes are different. Both Marks’ [9] and Janssen and Meijer [10] ran their experiments till droplet breakup occurred regardless of the length of the die needed. However, in polymer based additive manufacturing applications, the length of the die is fixed parameter. Some research to explore a different flow domain was done by Chin and Han [11] and Godbille and Picot [12] who used converging dies with straight walls to impose an extensional rate to the droplet. However, extensional rate in the die is not constant in the direction of flow at the center. Mulligan and Rothstein [13] designed microfluidic dies that have hyperbolic wall profiles which provide a constant extensional rate at the center of the channel. But the equation does not reveal the extensional rates at points other than the center.

In this research, the feasibility of using simple shear to breakup droplets in short dies was explored theoretically. Extensional flows were then explored in hyperbolic dies since converging dies with straight walls does not impose a constant extensional rate on droplets. The hyperbolic die was designed based on equations from Mulligan and Rothstein [13] which imposed a constant extensional rate on the droplet when deployed at the center of the channel. A straight section, subsequent to the converging zone, was designed by virtue of a length requirement based on critical aspect ratio from the experiments of Stone et al., [8]. Initial droplet dimensions, whose capillary numbers were much greater than the critical capillary number, and the flow conditions were varied to model the extensional deformation.

**Experimental development**

In this research, initial capillary numbers much higher than the critical capillary numbers are explored. Capillary number is given by the following expression.

$$Ca = \frac{a \gamma \eta_m}{\sigma}$$  \hspace{1cm} (1)

Where ‘a’ is the diameter of the droplet, ‘\( \gamma \)’ is the deformation rate, ‘\( \eta_m \)’ is the viscosity of the matrix and ‘\( \sigma \)’ is the interfacial tension between the droplet and the matrix. The critical capillary number for shear flow is around 0.4 for a viscosity ratio of one. Initially, a straight die was envisioned so that droplet breakup could occur in a simple shear flow. In simple shear, the average shear rate is given by

$$\gamma = \frac{V}{h}$$  \hspace{1cm} (2)

Where ‘V’ is the velocity and ‘h’ is the width of the die. The width of the die was assumed to be 4 mm and assuming a viscosity ratio of 0.6, Marks’ [9] non-dimensional time, which is shear rate times the actual time, has a value of 12 for the onset of the first bulb in the breakup process. So, for different velocities of the channel, the shear rates and the corresponding bulb onset times were calculated. The velocity of flow multiplied by the time for bulb onset gave the length of the die needed to produce that deformation and is shown in Table 1. This data is valid for droplets of any given capillary number higher than the critical capillary number.

<table>
<thead>
<tr>
<th>Velocity of flow (mm.s(^{-1}))</th>
<th>Shear rate in die (s(^{-1}))</th>
<th>Bulb onset time in die (s)</th>
<th>Minimum length of die required (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.5</td>
<td>24</td>
<td>48</td>
</tr>
<tr>
<td>4</td>
<td>1.0</td>
<td>12</td>
<td>48</td>
</tr>
<tr>
<td>6</td>
<td>1.5</td>
<td>8</td>
<td>48</td>
</tr>
<tr>
<td>8</td>
<td>2.0</td>
<td>6</td>
<td>48</td>
</tr>
</tbody>
</table>

Simple shear was not found to be an ideal candidate because it necessitates the usage of long dies which are impractical for a polymer based additive manufacturing method. Thus, converging dies were explored which
impose extensional deformation on the droplet whose magnitudes are much higher than in shear flow.

**Experimental design**

The experiment is centered on the design of the die which is presented in Figure 1. The die consists of three zones. The first is a section for the plunger movement, the second is a converging section that imposes an extensional deformation of droplets and the third is a long section where transient breakup of the droplet can be seen. The flow is from left to right as seen by the observer.

![Figure 1. 2D view of the experimental channel (Dimensions in mm)](image)

The die has a rectangular cross section with a depth of 20 mm. The width of the first straight section is 60 mm and the length is 70 mm. The converging portion has a length of 40 mm and has a curvature based on the equation

\[ y = \frac{600}{3x + L} \]  

The length ‘L’ of this converging portion is 40 mm and the width hyperbolically reduces from 60 mm to 20 mm. In this section, the extensional rate induced at the center for different flow rates is given by the equation

\[ e = \frac{2Q}{wLh} \]

Where ‘w’ is the downstream half width of the channel, ‘L’ is the length of convergence, ‘Q’ flow rate in the channel and ‘h’ is the depth of the channel. For different inlet velocities, different extensional rates can be thus obtained. The focus of this study is on the converging zone and the degree of deformation that can be achieved. In this zone, at any given plane into the channel, the velocity profile is a parabolic profile but with the added effect of convergence along the channel.

**Materials**

The fluid system chosen for this research was Silicone oil (Consolidated Chemical & Solvents) that had a viscosity of 1000 cSt. The droplet phase was commercially available Castor oil with a viscosity of 600 cSt. The interfacial tension between the two fluids was assumed to be 0.004 N/m [10]

**Methods**

The channel was filled with Silicone oil and the plunger was placed in a position just touching the oil. The Castor oil droplets were injected using a syringe into the channel. The approximate size of each droplet was controlled by the markings on the syringe which were related to the diameter of the droplet by volumetric equivalence. The motor that controlled the plunger movement received input voltage regulated using an Arduino Uno board. The PWM input was related to the speed of the plunger and the required PWM value was input to the Arduino. The plunger movement was regulated so that the droplet was positioned just before the converging zone began. Since the droplet size was not very accurately controllable, a range of initial capillary numbers much higher than the critical capillary number was generated as required. Data collection commenced at this point and Table 2 shows the experimental conditions.

![Table 2. Experimental conditions and initial capillary numbers for pure extension](image)

<table>
<thead>
<tr>
<th>Trial no.</th>
<th>Arduino PWM setting</th>
<th>Plunger speed (mm/s)</th>
<th>Initial droplet size (mm)</th>
<th>Initial Capillary number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>34.08</td>
<td>3.10</td>
<td>7.67</td>
</tr>
<tr>
<td>2</td>
<td>120</td>
<td>42.02</td>
<td>2.77</td>
<td>8.47</td>
</tr>
<tr>
<td>3</td>
<td>140</td>
<td>49.96</td>
<td>3.10</td>
<td>11.28</td>
</tr>
<tr>
<td>4</td>
<td>160</td>
<td>57.90</td>
<td>2.61</td>
<td>10.85</td>
</tr>
<tr>
<td>5</td>
<td>180</td>
<td>65.84</td>
<td>2.52</td>
<td>11.94</td>
</tr>
<tr>
<td>6</td>
<td>200</td>
<td>73.78</td>
<td>2.65</td>
<td>14.11</td>
</tr>
</tbody>
</table>

In order to see the effect of changing the location of droplet injection, some droplets were injected 5 mm deeper into the channel from the center so that combined shear and extension effects could be observed. Table 3 shows the experimental conditions.

![Table 3. Experimental conditions and initial capillary numbers for combined shear and extension](image)

<table>
<thead>
<tr>
<th>Trial no.</th>
<th>Arduino PWM setting</th>
<th>Plunger speed (mm/s)</th>
<th>Initial droplet size (mm)</th>
<th>Initial Capillary number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>10.26</td>
<td>2.30</td>
<td>1.68</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>18.20</td>
<td>2.66</td>
<td>3.48</td>
</tr>
<tr>
<td>3</td>
<td>65</td>
<td>20.18</td>
<td>2.83</td>
<td>4.33</td>
</tr>
</tbody>
</table>

As the Castor oil droplet moved down the channel, it was recorded using a high speed camera (Chameleon3 by Point Grey Technologies). Frames of interest at the
required positions along the channel were extracted from the high speed video. Adobe Photoshop was used to analyze the frames for the pixel locations of the droplet at various points along the channel. Data for droplet length, width and the velocity of front and rear end were extracted and plotted.

**Results and discussion**

A series of images as the droplet moves down the channel is shown in Figure 2 for one of the test cases (Initial Ca = 7.67). In this first set of experiments, the droplet is at the center of the channel (into the plane). The seven frames were extracted from the high speed video when the droplet was at different points of interest along the channel.

Figure 2. Deformation of a droplet deployed at the center of a converging channel (Initial Ca = 7.67)
Plotting the capillary number, as it changes with changing width of the droplet, at five equally spaced divisions of the converging channel, trends can be observed across all the test cases with different initial capillary numbers. This is depicted in Figure 3.

A linear least squares fit was done on the data. Within the experimental error, it was observed that droplets with a higher initial capillary number experience a steeper drop than droplets with lower initial capillary numbers. This was corroborated by observations from the plot of droplet length vs position along the channel at the same locations. This is depicted in Figure 4.

Droplet lengths are normalized with initial droplet diameter. It can be seen from the plot that droplets with higher capillary numbers elongate at a faster rate than lower capillary number droplets. Marks [9] reported that two different sized droplets exposed to the same shear rate (and thus, different capillary numbers) reach the deformed state at the same time. This means that higher capillary numbers must deform at a faster rate and this is clearly evident from the plot and is valid for extensional flow as well.

From the experiments, it was observed that the droplets do not reach the affine state in the converging zone. The reduction in capillary number is not adequate to cause breakup as well. Hence, different points in the channel were investigated to see the effect of the varying extensional rate on the droplet.

In the second set of experiments, some droplets were deployed 5 mm away from the center of the channel (into the plane). Three different capillary numbers (1.68, 3.48 and 4.33) were investigated at this position. In all the three cases, the droplets experienced a different degree of deformation than what was observed in the first set of experiments. A series of images from one of the test conditions (Initial Ca = 3.48) is shown in Figure 5.
Evidently, the droplet experienced a different deformation rate. The capillary number vs position and normalized length vs position were plotted for all the three test cases and are shown in the Figure 6 and 7.

A trend that is similar to the droplets deployed at the center can be seen in this case as well. Droplets with higher capillary numbers experienced a faster rate of capillary number drop as well as became affine quicker than the other test cases.

From Figure 7, it can be seen that there is a large rate of increase in length of the droplet for each of the capillary numbers. In some cases, the droplet was longer than the field of view as well. Figure 8 shows the difference in the velocities between the front and rear end of the droplet as it moves down the channel.

The vast difference between the front and rear end velocities on the droplet further confirms the rapid stretch and attainment of the affine state. As the center of the droplet hits 40 mm, which is the end of the converging section, this difference is reduced since the droplet experiences a state of reduced shear. Calculations for the precise deformation rate in the converging zone are more complicated since the deformation is a combination of shear and extension. The velocity does not grow at a linear rate as well and the vorticity tensor induces a spin to the droplet which means that it does not deform along a straight line as well.

**Conclusion**

Additive manufacturing industry is growing at a rapid pace and innovations in polymer based additive manufacturing are the need of the hour to sustain the growth. Conventional additive manufacturing setups usually use a single material or add solid fillers to achieve...
the required properties. Liquid fillers in polymer based additive manufacturing have not been explored as an innovation and this research seeks to address it.

In this study, droplets immiscible in a polymer matrix were subjected to high capillary numbers in a converging die in order to reveal the effect of the die on the deformation experienced by it. Initial calculations revealed that simple shear was not adequate to induce deformation and needed long dies of inconvenient lengths to achieve it. Extensional deformation that can be induced in converging channels overcomes this by inducing a much rapid stretch to the droplets. Six different droplets of different initial capillary numbers were chosen and subject to the calculated extensional rates. It was seen that droplets of higher initial capillary numbers deformed at a faster rate than lower ones. However, the affine state was never reached in the converging zone for droplets deployed at the center.

Some investigations into droplets deployed deeper into the channel revealed a different degree of droplet stretch. This was attributed to the combined shear and extensional deformation which have higher magnitudes than simple extension. In this case as well, it was observed that droplets of higher initial capillary numbers deformed at a faster rate than lower ones and reached the affine state.

This research has the potential to change polymer based additive manufacturing scenario as liquids can be incorporated into the process. This method can be used to additively manufacture clear polymers that have channels of colored liquid embedded in them. Robust control on the droplet stretch as well as daughter droplet distribution can be achieved. Future research focus will be on exploring the transient behavior of stretched droplets as well as working on incorporating the technique in actual polymer based additive manufacturing machines.

**Future work**

The next step in this research would be to model the droplet deformation at different starting points in the channel (into the plane). The influence of combined shear and extension on the droplet is not fully understood and it would be desirable to incorporate it into polymer based additive manufacturing. For this, the rate of deformation tensor and its changes as the droplet moves along the converging channel needs to be accurately developed and related to the observed deformation.

Another avenue into the research is to explore the effect of the straight section, subsequent to the converging section. At the center of this section is a region where stretched droplets do not experience any shear rate despite being in a flow field. It would be important to find the size of the region around the center of the channel where the shear rate is low enough to cause transient breakup of the stretched droplet, resulting in daughter droplets. This can be used to achieve the required droplet distribution using the transient breakup methodology.

**Acknowledgement**

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**References**
