AN INVESTIGATION OF THE EFFECTS OF QUANTUM DOT NANOPARTICLES ON PHOTOPOLYMER RESIN FOR USE IN POLYJET DIRECT 3D PRINTING

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ABSTRACT

The addition of quantum dot (QD) nanoparticles to additive manufacturing (AM) media provides the opportunity to create artifacts with complex geometry that also have unique optical characteristics. However, the addition of nanoparticles can significantly alter the rheology of a material and make it difficult to process in an AM context. In this study, quantum dots were added to a photopolymer resin in varying mass ratios to photopolymer, and their effects on the viscosity, surface tension, and jetting ability of the suspension were investigated. Results show that printability was not significantly affected by the presence of quantum dots in mass concentrations less than or equal to 0.5%. The nanosuspensions were deposited via inkjet to demonstrate the feasibility of creating optically-unique artifacts.

1. INTRODUCTION

Additive Manufacturing (AM) has allowed designers to create unique artifacts via selective placement of material that cannot be manufactured with traditional means. Objet's PolyJet direct-3D printing (3DP) process is unique among AM processes as it provides the ability to specify the placement of more than one material within a single build (Section 1.2). The PolyJet process is limited, however, to processing materials that can be deposited via inkjet and then solidified via UV irradiation. To circumvent this constraint, the authors look to develop new materials by incorporating nanoparticles into existing PolyJet photopolymer resin.

In this paper, the authors investigate the integration of Quantum Dots (QDs) into a PolyJet resin. QD nanoparticles are unique in their ability to absorb UV light and emit visible light (Section 1.1). By strategically placing quantum dots within AM parts, unique, three-dimensional, optical signatures may be created and embedded within additively manufactured parts. The resulting nanocomposites could find use in cryptography, optical temperature and pressure sensing, and programmable matter applications.

1.1 Quantum Dot Nanoparticles

A QD is a nanoparticle that ranges from 2 to 20 nanometers in diameter. Traditionally, QDs are made of chalcogenides (selenide or sulphate) of metals like cadmium or zinc (for example: CdSe and ZnS), but QDs composed of other materials also exist. The salient property of a quantum dot is that it absorbs ultraviolet (UV) light and emits the light in the visible spectrum [1]. This ability for a particle to receive one type of signal and produce a different type of signal is unique among nanoparticles and has been used in the areas of data storage and sensing devices (Section 2). The color of the quantum dot in visible and UV light is dictated by the size of the dot. For example, a 2 nm QD particle will appear light yellow in visible light and glow blue under UV light. Figure 1 shows orange quantum dots in visible light, while Figure 2 shows the same quantum dots glowing yellow-green in UV light. Since quantum dots have unique optical properties, integrating them into AM printing media will, theoretically, give the printing media (and the fabricated artifact) unique optical properties.

Figure 1: QD Powder in Visible Light (Orange Color)

Figure 2: QD Powder in UV Light (Yellow Color)

1.2 The Objet PolyJet Process

The Objet PolyJet process deposits photopolymer resin via inkjet printing onto a build substrate. As shown in Figure 3 below, the Objet process utilizes an array of inkjet nozzles that are arranged within the printing block. This bank of several hundred nozzles deposits two different build materials in addition to a support material. The inkjet nozzles have a diameter of approximately 60 microns and deliver a resolution of 600 dpi (for the Connex machine models). After a layer is formed, a leveling roller passes over the layer to smooth the surface. An ultra-violet (UV) light then passes over the layer to cure the polymer into a solid. Subsequent layers are added on top of the previously deposited layers and cured. In this fashion, an object is built up, layer-by-layer. The advantage of the PolyJet process is that the individual banks of inkjet nozzles can process different materials, which allows for the creation of multi-material objects. Characteristics of photopolymers developed for these systems include ABS-like properties, high temperature capability, transparency, rubber-like properties, biocompatibility, and others [2].

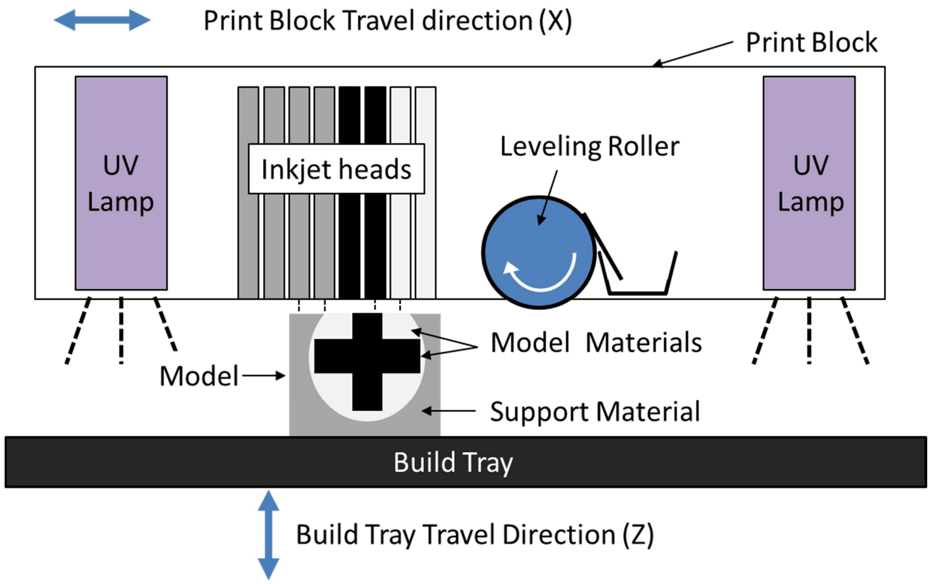

Figure 3: Objet PolyJet Print Head Assembly Block (adapted from Objet Training Manual)

1.3 How Inkjet Technology Works

PolyJet uses inkjet technology to deposit photopolymers as well as other AM media. Figure 4 below is an illustration of a drop-on-demand inkjet printhead. The printhead deposits drops of printing media by means of the following occurrences: first, printing media is supplied to the printhead chamber; second, a piezoelectric crystal receives a pulse of voltage and expands to create a positive pressure within the chamber; third, the positive pressure forces a small amount of the printing media out of the chamber through the nozzle, creating a droplet with some velocity.

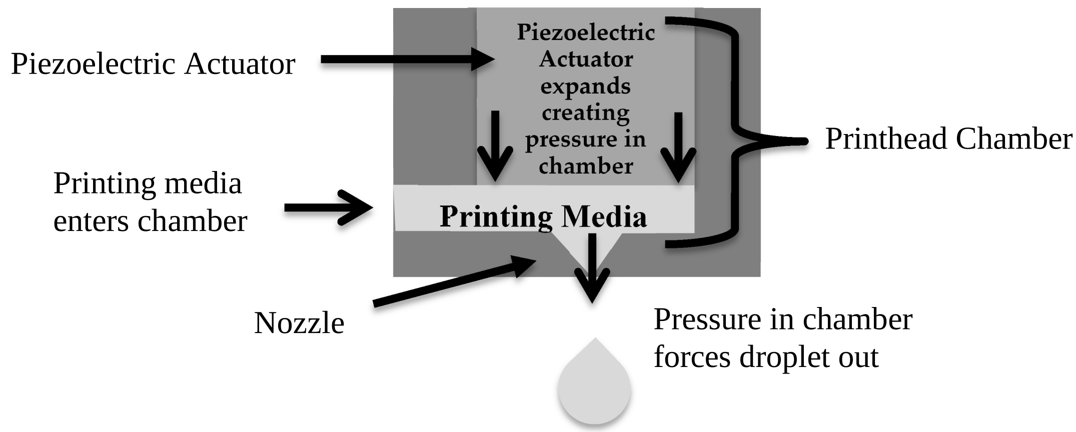

Figure 4: Diagram of a Drop-on Demand Inkjet Printhead

Because of the small size of the jetting chamber and the jetting nozzle, the rheology of the printing media is significant. Specifically, a highly viscous fluid or a fluid with a high surface tension would resist flow through the nozzle to a degree that cannot be overcome by the piezoelectric actuator. Similarly, if the surface tension of the fluid is too low, a splash of fluid will exit the nozzle instead of a cohesive droplet. Because of this sensitivity, adding particles into inkjet printing media (which can significantly affect the rheology of the media) to the degree that it is no longer jettable. Therefore, the goal of this study is to discover the effects of quantum dots on photopolymer rheology and the associated jettability.

1.4 Research Gap and Primary Research Question

The primary research question for this is work is the following:

Primary Research Question: What affects do Quantum Dots have on the viscosity, surface tension, and jetting ability of commercially available photopolymer?

Previous work in adding nanoparticles to inkjet media is discussed in Section 2. As discussed in Section 3, rheological traits were measured for varying mass percentages of quantum dots in photopolymer and compared with pure polymer. Jetting feasibility is also assessed via deposition of the QD nanosuspensions via inkjet and analysis of the resultant droplets. Areas for future work are presented in Section 4.

2. PREVIOUS WORK

2.1 Quantum Dots in Photopolymer

Characterization of quantum dot behavior within photopolymers has been well researched in the area of optical data storage and optical sensing. Li and authors have drop-casted eraseable, optical, thin-film data storage devices using a QD-doped photopolymer and were able to reduce flouresent power as well as change the refractive index of the QD-photopolymer mixture. The authors report that this is the first attempt at creating an "erasable multimode 3D bit optical data storage in a CdS QD-doped photorefractive polymer" [3]. Jorkaala and Stennenen have investigated the optical properties of ZnSe nanocrystals (a type of quantum dot) within polyvinyl alcohol photopolymer and have concluded that the nanocrystals increase optical output when temperature is decreased [4]. Xiangming and authors reported that by controlling the spacing between the QD's via holographic assembly, the defraction efficiency of the photopolymer/QD solidified mixture can reach 100 percent. This enables the creation of centimeter-sized, transmission Bragg gratings, a type of photosensor, which they created by casting QD's dispersed in photopolymer into films [5]. These are just a few of many efforts in the to study the interaction between quantum dots and photopolymer in the cured state for use in photosensing and optical data storage.

Using a variety of search terms and search term combinations (quantum dots, CdSe, nanocrystals, photopolymer, polymerization, etc.), only application-driven research was found, which focuses on the optical properties of the cured, QD-doped, thin film or functionalization of the QD's within the photopolymer. This can be attributed to the the fact that the work presented in this paper is the first attempt at characterizing the effects of QD's in bulk amounts of photopolymer.

2.2 Quantum Dots in Inkjet

Many Quantum Dot applications have benefited from the selective placement that inkjet technology is capable of providing. Wood and authors have created pattern pixels for flexible displays by printing QD's in a solution via inkjet. The QD's were suspended in a solution of hexan, octane, and a polyisobutylene matrix material and delivered by a thermal inkjet picofluidic dispensing system in 50-300 picoliter drop volumes. The result was a flexible, electroluminescent, thin film with the layers of glass, indium tin oxide, inkjet-printing Quantum Dots, and phosphor paste [6]. No mention of solids loading, rheological properties, or challenges in printing the QD-doped fluid were given.

Tekin and coauthors used inkjet nozzles to deposit QD's into films to create a nanocrystal-polymer composite. A contribution from this paper includes the addition of 1-2% volume ethylene-glycol to subdue the "coffee-stain effect," that is, how particles will migrate toward the outside of a droplet when introduced to a surface [7]. In a similar application, Haverinen and authors dissolved QD's in chlorobenzene to form their inkjet printing media. Their choice of a low-vapor pressure liquid as the main fluid of the printing media was also driven by the desire to reduce the "coffee-stain effect." The purpose of their research was to develop a simple process for creating light emitting diodes [8].

2.3 Inkjet with High Particle Loading

Brian Derby has provided an extensive review of work related to inkjet of highly particle-loaded printing media [9]. A major contribution in this review is the region of jettability for varying values of the Weber number versus the Reynolds number. The ratio of the square root of the Weber number (*We*) to the Reynold's number (*Re*), called the Ohnesorge number (*Oh*), is what dictates printability. These equations are shown below, where ρ is density, *V* is drop velocity, *D* is the nozzle diameter, γ is surface tension, and μ is viscosity.

$$We = \frac{\rho V^2 D}{\gamma} \quad (1) \qquad Re = \frac{\rho V D}{\mu} \quad (2) \qquad Oh = \frac{\sqrt{We}}{Re} \quad (3) \qquad Oh = \frac{\mu}{\sqrt{\gamma \rho \frac{d}{2}}} \quad (4)$$

Equation 4 suggests that the most important variables in predicting jettability are viscosity, surface tension, density, and nozzle diameter. Derby cites that jettability generally occurs when the inverse of the Ohnesorge number (1/*Oh*) is less than 10 and greater than 1. To predict viscosity of a fluid containing particle loading under 0.01 volume fraction, the Einstein equation shown below may be employed [10]:

$$n_r = 1 + 2.5f \quad (5)$$

where n_r is the relative viscosity and f is the volume fraction of hard sphere particles. These equations in combination have been used to predict jettability of wax that is highly loaded with sub-micron sized alumina particles for the creation of ceramic artifacts via direct 3D printing [9].

3. EXPERIMENTAL PROCEDURE, RESULTS, AND ANALYSIS

The primary goal of the experiments described in this work is to determine the effects of the integration of QD nanoparticles on a photopolymer resin. Specifically, the rheological properties of the pure polymer (control sample: 0% QDs) is compared with that of six experimental suspension samples that contain various mass percentages of QD's (0.005%, 0.01%, 0.02%, 0.1%, 0.2%, and 0.5%). The type of polymer (Objet VeroClear) and the size of the quantum dot (approximately 4-5 nanometers in diameter) were held constant across all experimental samples.

The QDs were prepared by hot-injection synthesis according to an established procedure [11]. The QD's were separated via centrifugation from the liquid in which they are initially dispersed, washed with water, and then freeze-dried to remove the remaining moisture. The QD powder was then dispersed in Objet VeroClear photopolymer – a commercially available resin that cures semi-transparent, and thus is capable of providing maximum visibility of the QD's when cured. Dispersion was achieved by alternating stirring and sonication [12]. Specifically, six samples of various concentrations were prepared by stirring for 30 minutes. Sonication followed for 10-30 minutes to break up any visible aggregates. Since the particles have not been functionalized to remain dispersed within the photopolymer, the samples were continuously stirred to avoid settling and aggregation of the particles (preliminary results show that settling occurs within 2-3 days without continuous stirring).

3.1 Fluorescence

Since the primary function of the QD is to add visible characteristics to the additively manufactured artifacts, it was decided that the desired concentration should fluoresce with an intensity that can be detected with the naked eye. To determine the appropriate mass concentration of each of the samples, varying ratios of quantum dots to photopolymer were prepared and photo-cured into thin films. These thin films were investigated under UV light in a dark room for visible glowing from the QDs. It was determined that a mixture of at least 0.1% quantum dots is required to produce visible fluorescence under an 8 watt UV lamp, as seen in Figure 5.

0.5 % QD's 0.2% QD's 0.1% QD's 0.05% QD's

Figure 5: Varying concentrations of QD's in Vero Clear photopolymer cured under UV light (365 nm) into thin films (~300 microns thick) to determine visibility

3.2 Rheology

As previously stated (Section 2.3), the two major fluid characteristics that govern jettability are viscosity and surface tension [9].

Viscosity

Viscosity of each prepared sample was measured using an AR-2000 model rheometer configured with a 40mm diameter, 2° angle rheometric cone. Three samples were measured from each test concentration at a shear rate of 10 seconds^{-1} and the printing temperature of the Objet Connex, which is 72 °C. Using Equation 5, it is predicted that for a sample with 0.5% QD's, the relative viscosity is 1.0025, meaning a very little change in viscosity is expected. This analysis was corroborated by experimental results: the average measured viscosity of pure polymer and the suspension with the highest QD loading (0.5%) was 0.20 ± 0.0012 Pa-s and 0.20 ± 0.0015 Pa-s, respectively. Figure 6 shows one standard deviation from the average viscosity collected for pure polymer highlighted in grey. As shown, the average viscosity for all sample concentrations lies within one standard deviation from the average viscosity found for pure polymer. Therefore, it was concluded that adding QD's in mass concentrations less than or equal to 0.5% does not significantly affect the viscosity of the polymer.

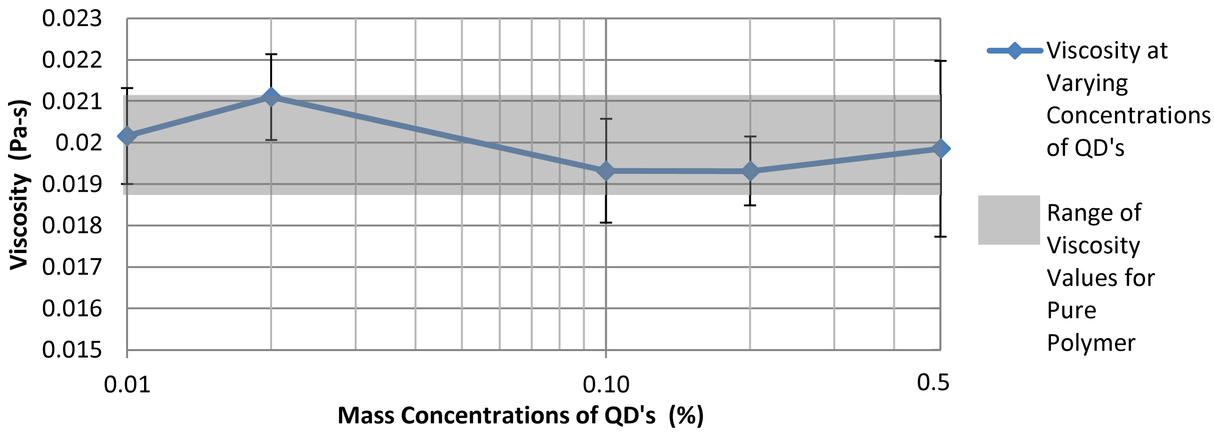

Figure 6: Viscosity of QD's + Photopolymer

Surface Tension

Surface tension was measured using the Wilhelmy Plate Method with a 20mm-length aluminum plate. The samples were heated to approximately 72 °C (Objet printing temperature) before taking the surface tension measurement. Figure 7 shows a slight increase in surface tension with increasing concentration of QDs. This can be attributed to the increased presence of QD's, whose agglomerative forces may intensify surface tension effects. Although a trend is evident, the overall increase in surface tension does not significantly affect the jettability of the samples, as discussed in Section 3.2.

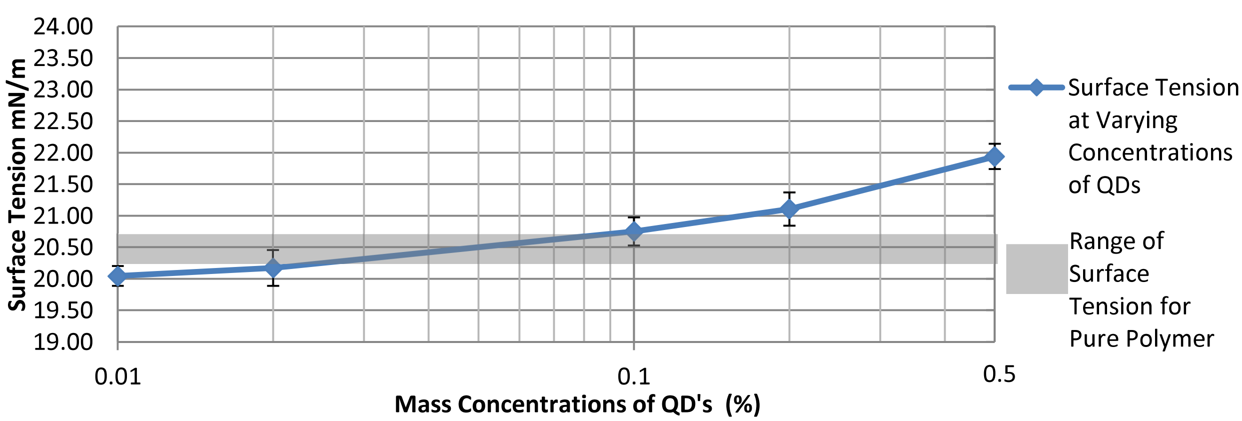

Figure 7: Surface Tension of Objet VeroClear and Varying Concentrations of QD's

3.2 Jetting

Jetting Calculations

As previously mentioned, the ability to create droplets via inkjet is predicted by the Ohnesorge number [9]. For nozzle diameter of 60 microns and a fluid density for VeroClear of 1.08 g/ml, the inverse of the Ohnesorge number (1/*Oh*, Equation 4) was found to be 1.75 for pure polymer and range from 1.65 to 1.91 for the maximum and minimum values of surface tension and viscosity of the QD-doped samples. Table 1 below contains these values and the corresponding 1/*Oh* calculation:

Table 1: Maximum and Minimum Values for Viscosity and Surface Tension and Corresponding Calculated 1/*Oh* Values

Viscosity (Pa-s)	Surface Tension (N/m)	Oh	1/Oh
0.021 (max)	0.020 (min)	0.61	1.65
0.021 (max)	0.022 (max)	0.58	1.73
0.019 (min)	0.022 (max)	0.52	1.91
0.019 (min)	0.020 (min)	0.55	1.82

Since 1/*Oh* is within the printable range (less than 10 and greater than 1) for all concentrations, it can be concluded that the addition of quantum dots at such low concentrations did not shift the rheology of the photopolymer out of the printable region.

Jetting Performance

Droplet formation via inkjet was observed using an inkjet test stand produced by MicroFab Technologies. The setup consists of a single, 60 micron inkjet nozzle, a fluid reservoir, pressure and temperature-regulating electronics, and a strobe and coupled camera, which enable the imaging of the jetted fluid. The fluid reservoir on the jetting apparatus contains external heaters that were used to heat the nozzle and reservoir to the photopolymer printing temperature, (72 °C). The fluid passes through a 7 micron filter before entering the nozzle chamber. Jetting images were taken with varying voltage and dwell settings as shown in Figures 8 and 9 below. These two parameters are typically varied to determine the optimum waveform in terms of droplet volume and velocity [13].

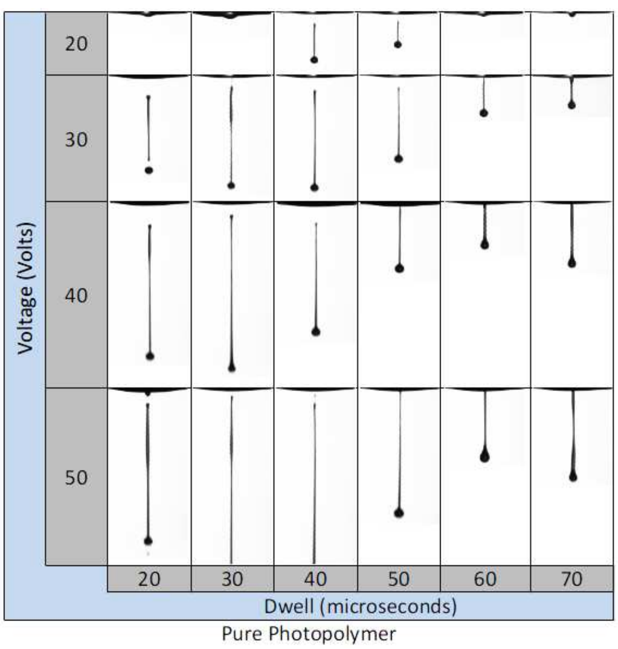

Figure 8: Images of pure photopolymer - drops formed for varying values of voltage and dwell

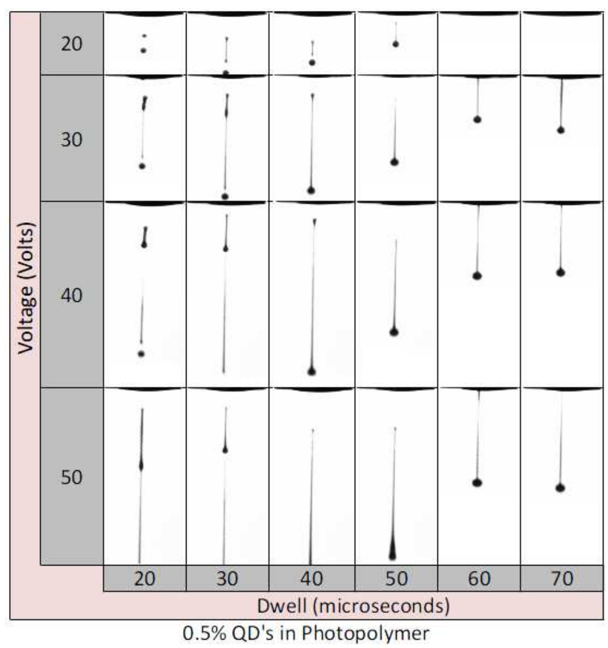

Figure 9: Images of photopolymer with 0.5% mass QD's - drops formed for varying values of voltage and dwell

All images in Figures 8 and 9 were taken at a jetting frequency of 600 hertz and at 200 microseconds after the beginning of the pulse. The drops were imaged with the tip of the inkjet nozzle visible in view (at the top of the image). The structure of the drop consists of the drop and the tail. As dwell increases the tail becomes shorter and eventually recedes into the drop mass. Some tails however, separate from the drop mass to form satellite drops, as prominently shown for a dwell of 20 microseconds in Figure 9. Also, increasing the voltage given to the piezoelectric actuators in the printhead increases the velocity of the droplet, which increases the droplets distance from the nozzle in the images. Furthermore, the interaction of velocity and dwell produces a wave-like pattern of droplet position as seen for values of 40 and 50 volts.

Upon comparing Figures 8 and 9, some differences between the pure polymer droplets and the QD-doped droplets are noted. First, the drop volumes for the QD-doped polymer are visibly smaller than for pure polymer. Also, for two settings of voltage and dwell (20 volts, 20 and 30 microsecond dwell times), the QD-doped polymer succeeds in droplet ejection while the pure polymer does not. Although the difference may seem significant, these results are within the observed typical variation of the jetting device when jetting this particular polymer. An example of a significant difference in the pure polymer and the QD-doped polymer would be an inability to eject droplets at several data points. Therefore, it can be concluded that the jetting characteristics of the photopolymer is not significantly affected by the presence of quantum dots in up to 0.5% mass concentrations.

4. FUTURE WORK

With jettability for QD suspensions verified, examination of the effects of quantum dots on the curing properties of the photopolymer will be conducted next. Photo-curing is a critical aspect of the PolyJet process, as it affects part quality and process energy and throughput. Since the photopolymer and quantum dots react in different ways with UV light, photopolymer curing is expected to be affected by quantum dots. This behavior cannot be predicted by observing the effects of other types of nanoparticles on curing, as the quantum dots not only refract UV light but also absorb it (and fluoresce at visible wavelength). Such behavior could increase the critical exposure necessary for curing, which could significantly alter the curing process.

Figure 10 below contains preliminary results that show the effect of QD's on curing depth. Each sample was given a dose of 52 mJ/cm^2 (30 second exposure under an 8-watt UV lamp) at a wavelength of 365 nanometers. As shown, cure depth decreases as QD concentration increases, with the 0.5% QD samples having a cure depth of less than half of pure polymer cure depth. Once curing properties are understood, the PolyJet Process can be employed to create geometrically complex, three dimensional objects with embedded quantum dots.

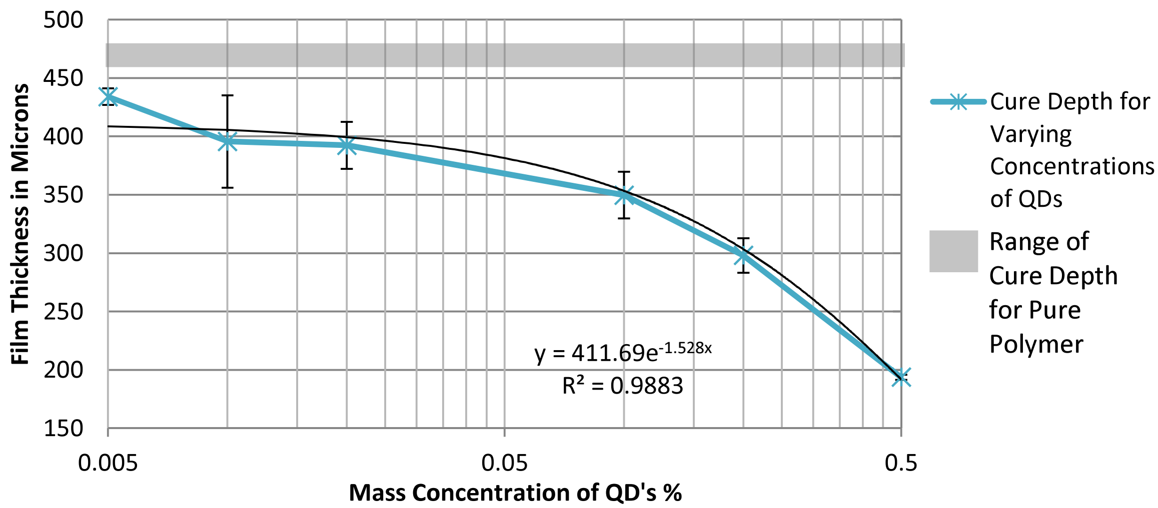

Figure 10: Curing Depth for varying mass ratios of QD's in Photopolymer

5. CLOSURE

This work is a preliminary step toward the creation of geometrically complex artifacts with unique optical properties via Polyet Direct 3D Printing. Quantum dots (QDs) were added to Objet Vero Clear Resin in varying concentrations, and their effects on viscosity, surface tension, and jetting ability were examined. The addition of quantum dots in small percentages (up to 0.5% by mass) produces QD fluorescence that is visible with the naked eye and does not significantly affect the ability to process via inkjet. Jettability predictions have been established by measuring the viscosity and surface tension of QD-doped photopolymer and calculating jettability using established means (the Ohnesorge number) [9]. Jettability was verified by using a single-nozzle inkjet test stand to produce droplets with the QD-doped photopolymer. Results were comparable to droplets formed with pure, un-doped polymer at the same voltage and dwell settings.

6. REFERENCES

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