DOI: 10.1002/adem.201300020

Inkjet Printing of Quantum Dots in Photopolymer for Use in Additive Manufacturing of Nanocomposites**

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Much work has been done in the area of micro-patterning nanoparticles toward the fabrication of polymer electronics, micro-optical components, and complex nanocomposites.[1–5] Methods for micro-patterning include direct write, etching, lithography, microcontact printing, and inkjet.[5–9] Quantum dots (QD) are of particular interest in microscale patterning because of their size-dependent photoluminescence, narrow band of emission, and nonlinear optical properties.[6–8,10–12] The high-resolution patterning of QDs within bulk polymer, specifically, has potential in photonic and biomedical applications, as well as pressure and temperature sensing, cryptography, and programmable matter.[5,8,9,13–15]

Inkjet printing is a particularly effective method of patterning nanomaterials on the microscale. Nanomaterials incorporated into printing media cannot only be selectively patterned, but also placed among other materials to form complex composites.[16] Current approaches in deposition of nanoparticles primarily utilize solvents and relatively non-viscous polymers as the carrier fluid.[1,2,6,10,13] These materials are beneficial for the creation of thin films; however, they are not appropriate for fabricating macroscale objects.[15] This is a significant gap, as the ability to incorporate QDs into complex three-dimensional (3D) geometries would enable disruptive breakthroughs in current QD applications and enable QD applications in completely new frontiers.

Additive manufacturing (AM, also referred to as 3D Printing) is a class of fabrication processes that creates objects by building them layer-by-layer. In contrast to most subtractive manufacturing methods like etching or milling, AM allows the designer to have complete control over the topology of an artifact and is completed with very little user intervention and post-processing. A promising AM technology is the Objet PolyJet process.[17] In this process, photopolymer resins are selectively inkjet printed layer-by-layer and cured by a passing UV light. Through the deposition of multiple materials from different inkjet heads, this process is capable of fabricating functionally graded materials with up to a 32 μm resolution within each cross-section, and a 16 μm resolution (i.e., layer thickness) in the axis perpendicular to each cross-section (see Section 1.1).

While the PolyJet process enables the selective deposition of polymer drops at high resolution, the process is limited to ink-jettable and UV-curable materials. To develop new materials that are compatible with PolyJet process parameters, the authors look to incorporate nanoparticles into existing PolyJet photopolymer resin. With an ultimate goal of additively manufacturing complex, 3D, QD nanocomposites, the authors explored the rheological effects of adding QDs into existing AM photopolymer resin as a first step in toward modifying existing resin. In this study, QDs are added in varying mass ratios to photopolymer, and their effects on the viscosity, surface tension, and jetting ability of the suspension are investigated.

1. Results and Discussion

Visible fluorescence was used as a metric for determining sufficient concentrations of QD nanoparticles for testing as described in Section 1.1. Section 1.2 discusses rheological traits which were observed for varying mass percentages of QDs in photopolymer and compared with the control polymer (VeroClearFullCure 720, a commercially available resin that cures semi-transparent and is thus capable of providing visibility of the QDs when cured). Jetting calculations described in Section 1.3.1 were performed to assess the suitability of the QD-doped fluid for inkjetting. Jetting ability was demonstrated via deposition of the QD nanosuspensions via a single-nozzle inkjet test stand (Section 1.3.2). Finally, the QD-doped inkjet droplets were deposited onto a substrate and observed via fluorescent microscopy (Section 1.4).

1.1. Fluorescence

A QD is a nanoparticle that ranges from 2 to 15 nm in diameter. Traditionally, QDs are made of chalcogenides (selenide or sulfate) of metals like cadmium or zinc (for example: CdSe and ZnS), but QDs composed of other materials also exist. The salient property of a QD is that it absorbs ultraviolet (UV)

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[**] *The authors would like to acknowledge the Institute for Critical Technology and Applied Science (ICTAS) at Virginia Polytechnic and State University (Virginia Tech) for the funding of this project. Special thanks to Dr. Kathy Lu and Dr. Roe-Hoan Yoon for the use of their equipment and to their associates Edward Liang and Gwen Davis for the support in using this equipment.*

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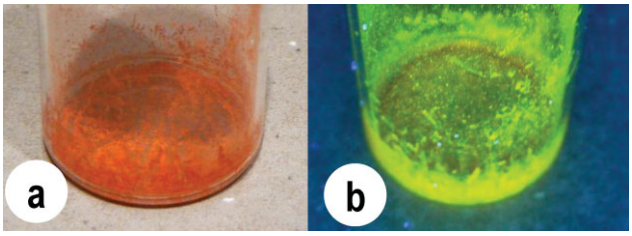

Fig. 1. Cadmium selenim (CdSe) quantum dots with an approximate diameter of 6.6 nm under (a) visible light and (b) UV light.

light and emits the light in the visible spectrum. This ability for a particle to receive one type of signal and produce a different type of signal is unique among nanoparticles.[18] The color of the QD 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 1a shows orange QDs (≈6.6 nm in diameter) in visible light, while Figure 1b shows the same QDs glowing yellow-green in UV light. Since QD have unique optical properties, integrating them into AM printing media will give the printing media (and the fabricated artifact) unique optical properties.

Since the primary function of QDs is to add visible characteristics to the additively manufactured artifacts, the authors prepared nanosuspensions with different QD loadings and cured them into thin films to determine the minimum concentration necessary to detect fluorescence signature with the naked eye. The following concentrations of QDs in photopolymer were used: 0.5, 0.2, 0.1, and 0.05 wt%. These thin films were investigated under UV light in a dark room for visible glowing from the QDs. It was determined that 0.2 wt% QDs was sufficient concentration to produce visible fluorescence under an 8 watt UV lamp, as seen in Figure 2.

1.2. Rheology

The Objet PolyJet process utilizes an array of inkjet nozzles that have a diameter of approximately 60 μm and deliver a resolution of 32 μm (for the Objet Connex machine models). As the layer is formed, a leveling roller passes over the layer to smooth the surface. A UV light, which is integrated into the print block, cures the polymer into a solid. Subsequent layers are printed on top of the previously deposited layers and cured. In this fashion, an object is built 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. Various photopolymer materials have been developed for these systems including plastics, rubbers, temperature resistant, transparent, and biocompatible polymers.[17]

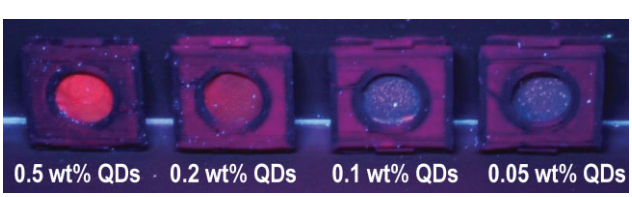

Fig. 2. Various concentrations of quantum dots in Objet VeroClear photopolymer cured under UV light (365 nm) into thin films (≈300 μm thick) to determine visibility.

Inkjet printing is the key enabling technology used by the Objet PolyJet process. Efforts in adding particles to inkjet media can affect the rheology, and therefore the jettability, of the media. Derby and co-authors have provided an extensive review of work related to inkjet of highly particle-loaded printing media.[19] From this work, it was determined that jettability can be predicted by the Ohnesorge number (*Oh*), which is the ratio of viscous forces to surface tension and inertial forces.

$$Oh = \frac{\mu}{\sqrt{\gamma \rho \frac{D}{2}}} \tag{1}$$

Equation 1 identifies that the principal variables in predicting jettability are an ink's viscosity (μ), surface tension (γ), density (ρ), and the inkjet nozzle diameter (D). Jettability generally occurs when the inverse of the Ohnesorge number ($1/Oh$) is less than 10 and greater than 1.[19] To predict viscosity of a fluid containing particle loading under 0.01 volume fraction, the Einstein Equation shown below may be employed[19]:

$$n_r = 1 + 2.5f \tag{2}$$

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 highly loaded with sub-micron sized alumina particles for the creation of ceramic artifacts via 3D printing.[4]

Prior work in jetting of viscous fluids cites that viscosity and surface tension are the governing material properties that determine jettability of a fluid.[1,3,4,6,20,21] Therefore, viscosity and surface tension of our photopolymer (control) and the QD-doped photopolymer (experimental) samples were examined in detail as described in Sections and 1.2.2.

1.2.1. Viscosity

Using Equation 2, it is predicted that adding 0.5 wt% QDs to the control polymer will increase the viscosity by 0.23%. Experimental results showed and average of 0.15% increase in viscosity, with the average measured viscosity of the control polymer and the suspension with the highest QD loading (0.5 wt%) being 0.01982 ± 0.0012 and 0.01985 ± 0.0015 Pa s, respectively. Figure 3 is a plot of the viscosity results when measured at the Objet printing temperature of 72 °C. The plot shows the standard deviation from the average viscosity collected for the control polymer highlighted in gray. As shown, the average viscosities for all sample experimental concentrations lie within one standard deviation from the average viscosity found for the control polymer. To determine the impact of the change in viscosity of the polymer due to the addition of QDs, jettability calculations were performed and are described in Section 1.3.1.

1.2.2. Surface Tension

The samples were heated to approximately 72 °C (Objet printing temperature) before taking the surface tension measurements. The surface tension results are shown in

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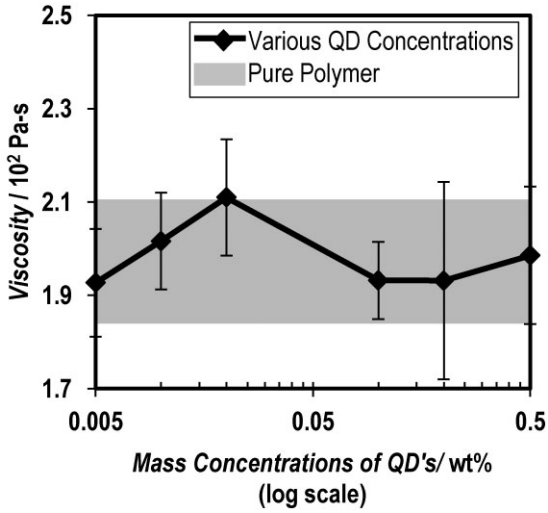

Fig. 3. Viscosity of nanosuspensions with different QD loadings taken at 72 °C.

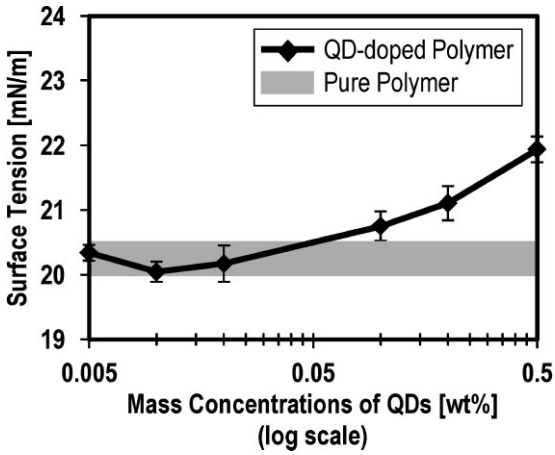

Fig. 4. Surface tension of Objet VeroClear and varying concentrations of QDs.

Figure 4. An increase in surface tension can be seen with increasing concentration of QDs. This can be attributed to the increased presence of QDs, whose attractive 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 1.3.1.

1.3. Jetting

1.3.1. Jetting Calculations

PolyJet uses drop-on-demand inkjet technology to deposit photopolymer resin. As shown in Figure 5, drop-on-demand inkjet printheads deposit drops of printing media by means of the following occurrences: first, the 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.

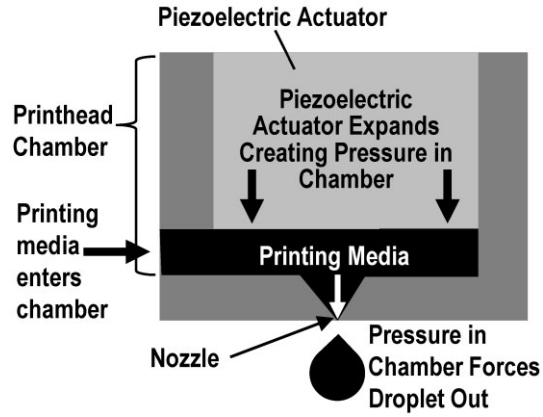

Fig. 5. Diagram of a drop-on demand inkjet printhead.

To determine jettability of the prepared QD nanoink, the authors calculated its $1/Oh$ number (Equation 1). For nozzle diameter of 60 μm, a fluid density for the control polymer of 1.08 g/ml, and the surface tension and viscosity measurements presented in Figure 3 and 4, $1/Oh$ was found to be 1.75 for the control polymer and range from 1.74 to 1.81 for the maximum and minimum values of surface tension and viscosity of the sample with the highest concentration of QDs (0.5 wt%). Table 1 contains these values and the corresponding $1/Oh$ calculation. Since $1/Oh$ is within the printable range (<10 and >1) for all concentrations, the authors concluded that the addition of QDs at such low concentrations (but which fluoresce to the naked eye) did not shift the rheology of the photopolymer out of the printable region.

1.3.2. Jetting Performance

Upon predicting that the QD-doped polymer was within the jettable range of the $1/Oh$ number, an inkjet test stand was used to observe droplet formation. The test stand utilized is produced by MicroFab Technologies and is the typical equipment used for jetting characterization.[5,6,20,21] The setup consists of a single 60 μm inkjet nozzle, a fluid reservoir, and pressure and temperature-regulating electronics. A strobe and coupled camera are also mounted on the stand and enable the imaging of the jetted fluid. The fluid reservoir on the jetting apparatus contains external heaters that heat the nozzle and reservoir to the photopolymer printing temperature (72 °C). The fluid passes through a 7 μm filter before entering the nozzle chamber. Jetting images were taken at a dwell value of 60 μs and pulse voltage of 30 V. Dwell and voltage are the two principal parameters typically varied to determine the

Table 1. Maximum and minimum values for viscosity and surface tension and corresponding calculated 1/Oh values.

Viscosity [Pa s]	Surface tension [N m^{-1}]	$1/Oh$
0.0208 (max)	0.0218 (min)	1.74
0.0201 (min)	0.0221 (max)	1.81

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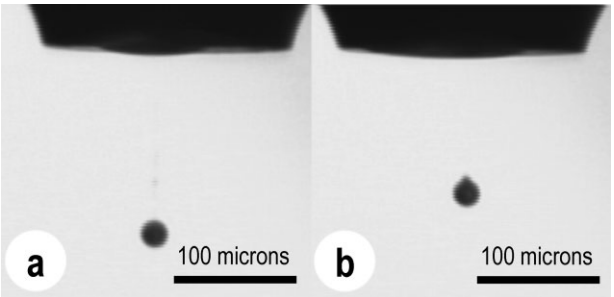

Fig. 6. Image of an inkjet droplet of photopolymer with (a) 0.5 wt% mass QDs and (b) pure photopolymer (no quantum dots).

optimum waveform in terms of droplet cohesion, volume, and velocity.[22]

Figure 6a and b are images of two jetted polymer droplets with 0.5 wt% QDs and the control polymer, respectively. The images were taken at a jetting frequency of 600 hertz and at 275 μs after the beginning of the inkjet pulse. The drops were imaged with the tip of the inkjet nozzle in view (at the top of the image). In observing jetting performance, critical droplet characteristics include cohesion, velocity, and volume and are heavily influenced by fluid properties.[23] A cohesive droplet is without any trailing fluid such as a ''tail'' or satellite droplets, and achieving a cohesive droplet is a major goal in inkjet droplet formation. Jetting velocity can be assessed by measuring the distance of the droplet from the nozzle after a controlled amount of time. Droplet volume can be calculated by measuring the circumference of the droplet profile and assuming a spherical droplet. Although differences in velocity and cohesion between the droplets in Figure 6a and b are noticeable, these differences were found to be within the observed variation of the inkjet test stand. From these observations, it was concluded that the presence QDs in up to 0.5 wt% does not significantly affect the cohesion, velocity, or volume of jetted droplets.

1.4. Fluorescence Microscopy

Inkjet drops containing 0.5 wt% QDs were deposited 375 μm apart via the aforementioned inkjet device onto a substrate, cured under UV light (365 nm wavelength) for 20 s, and examined via microscopy. Figure 7a and b show the inkjet-deposited drops under visible light and ultraviolet light, respectively. Figure 7b gives insight to the dispersion of the QDs within the jetted photopolymer AM media. The ''glowing'' spots within the round drop profiles are the actual QDs glowing due to excitation. Each drop can be seen to contain regions of higher concentrations of the QDs, which implies non-uniform dispersion of the QDs within the polymer. The circular profile of the drops is typical of drops deposited via inkjet. Overall, the microscopy reveals that, although the QDs are not evenly dispersed within the fluid, the circular deposition profile is very typical of inkjet fluids and evidences that the presence of QD nanoparticles should not significantly impact the inkjet deposition properties of the photopolymer. Future work will include a study of the topology of the deposited drop as well as efforts to disperse the QDs evenly within each drop.

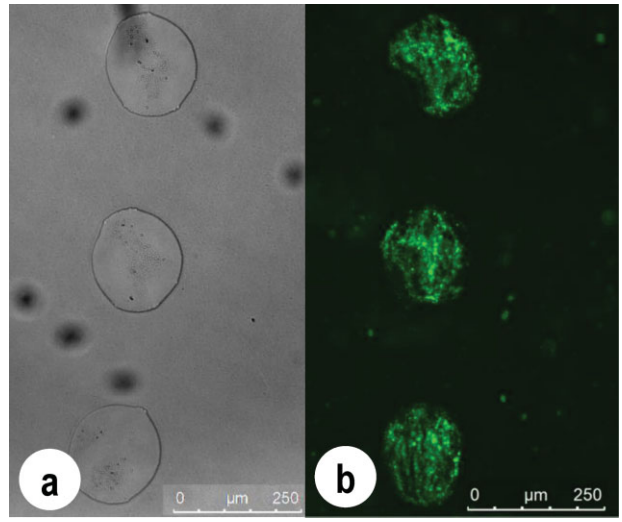

Fig. 7. Drops of quantum dot-doped photopolymer deposited onto a substrate shown (a) under visible light and (b) fluorescing under UV light.

2. Conclusions

QD were added to Objet VeroClear resin in varying concentrations, and their effects on viscosity, surface tension, and jetting ability were examined. The addition of QD in small percentages (up to 0.5 wt% 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).[19] Jettability was verified by using a single-nozzle inkjet test stand to produce droplets with the QD-doped photopolymer and results were comparable to droplets formed with the control polymer at the same voltage and dwell settings.

Jetting is one of two major process steps within the Objet PolyJet process. The second major step in PolyJet is photocuring – the transition of the liquid photopolymer to a solid. QDs absorb UV light in the same region at which the photopolymer cures. Thus it is likely that the rate and depth of photocuring will be influenced by the presence of QD nanoparticles. Future work will include the study of the effect of the QD nanoparticles on the curing characteristics of the AM photopolymer.

This work's focus on the jettability of QD nanoinks is a first step toward the creation of geometrically complex artifacts with unique optical properties via PolyJet Direct 3D Printing. The ability to fabricate such nanocomposites could have a significant impact on existing QD applications (e.g., LEDs, sensing, data storage, etc.), while also opening new opportunities that would benefit AM itself (i.e., using embedded

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QDs as markers for anti-counterfeiting or visual indicators of increased temperature).

3. Experimental

3.1. Materials

Cadmium oxide (CdO) (99.95%), selenium powder (200 mesh, 99.999%), Tri-*n*-octylphosphine (TOP) (90%), Tri-*n*-octylphosphine oxide (TOPO; 98%), and 1-tetradecylphosphonic acid (TDPA; 98%) were purchased from Alfa Aesar and used as received. Objet® Vero Clear resin was purchased from Objet and used as received.

3.2. Synthesis of CdSe QDs and Nanosuspension Preparation

The QDs were prepared by hot-injection synthesis according to an established procedure [24]. The QDs were separated via centrifugation from the solvent in which they are initially dispersed, washed with ethanol and then with water, and then freeze-dried to remove the remaining moisture. The QD powder was then dispersed in Objet VeroClear photopolymerresin. Dispersion was achieved by alternating stirring and sonication [13]. Specifically, six samples of various concentrations were prepared by stirring for 30 min. Sonication followed for 10–30 min 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).

3.3. Methods

Viscosity of each prepared sample was measured using an AR-2000 model rheometer configured with a 40 mm diameter, 2° angle rheometric cone. Three samples were measured from each test concentration at a shear rate of $10\,s^{-1}$ and the printing temperature of the Objet Connex, which is 72 °C. Surface tension was measured using the Wilhelmy Plate Method with a 20 mm-length aluminum plate. This method utilizes a plate with a specific size and surface finish. The plate is slowly pulled through the surface of the fluid, and the force exerted on the plate by the fluid surface is measured. Fluorescence images were acquired by using the Leica Microsystems DMI6000B inverted microscope equipped with Leica EL6000 external light source for fluorescence excitation. A TxR (Texas Red) filter cube was used in detecting the emission of the CdSe QDs for visualization of printed drops.

Received: January 18, 2013
Final Version: March 13, 2013
Published online: May 22, 2013

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