

Factors affecting measurement of cure depth and excess width for ceramic vat photopolymerization

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Abstract

Ceramic vat photopolymerization (VPP) is a process by which a ceramic particle-filled photosensitive resin is cured, layer by layer, via light projected with a certain intensity for a certain amount of time. The selection of exposure intensity and exposure time affects the amount of slurry that cures, both in the build direction (cure depth), and beyond the projected area within the projection plane (excess width). Cure depth and excess width, as measured from single layer samples printed over a range of exposure parameters, are key to process parameter optimization for VPP. The ratio of cure depth to layer thickness affects delamination, surface roughness, and microstructure of printed parts. Excess width determines dimensional accuracy and ability of printed parts to meet tolerances. However, there are currently no industry standards for printing single layers and obtaining measurements of cure depth and excess width.

This study investigates the effect of multiple factors, including sample shape, sample size, process parameters, and measurement system, on the values obtained for cure depth and excess width. Single layer samples were printed on a commercial ceramic VPP system using high purity alumina slurry. Samples were scanned in the green state with an Olympus OLS5100 laser scanning confocal microscope to determine cure depth and excess width. Results for excess width were compared to measurements obtained from a Keyence VHX-5000 digital microscope. The results indicate that methods for single layer printing and measurement significantly affect the resulting values for cure depth and excess width. This highlights an area where industry standardization and detailed reporting in literature are needed.

Keywords: ceramic, 3D printing, metrology, standardization

1. Introduction

Vat photopolymerization (VPP) is a form of additive manufacturing by which photosensitive resin is selectively cured, layer by layer, via a projected light or scanning laser. Ceramic VPP uses the same process with a slurry feedstock, which is composed of ceramic particles dispersed in photosensitive resin. After printing, the ceramic particle-filled polymer matrix composite (referred to as a “green” part) undergoes thermal processing to burn out the polymer binder and sinter the ceramic particles to maximum density.

The practice of print parameter selection remains a bespoke and expensive process for ceramic VPP, because the refractive properties of the ceramic particles introduce variation in the photopolymerization process due to light scattering. Building on experience from the polymer VPP field, ceramic VPP researchers have adopted the practice of printing single layers and measuring cure metrics such as cure depth and excess width to aid in process knowledge and process parameter development.

Single layer samples are printed by exposing slurry to light that is projected with a certain intensity (I) for a certain amount of time (t). These light engine parameters are often combined into one term, exposure energy (E_0), according to $E_0 = I \cdot t$

Equation 1.

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Equation 1

Cure depth (C_d) is measured as the thickness of the sample, while excess width (w_{ex}) is the distance between the contour of the printed sample and the designed sample contour. For simple geometries, this is often calculated as half of the difference between the measured sample width ($w_{measured}$) and the designed sample width ($w_{designed}$), as shown in $w_{ex} = (w_{measured} - w_{designed})/2$ Equation 2.

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When a relatively infinite vat of slurry is provided, both C_d and w_{ex} are linked to E_0 via physical models. These models ($C_d = S_d \cdot \ln(E_0/E_{c,d})$ Equation 3) are often called “working curves,” and they are derived from the Beer-Lambert law. The working curve equations include fitting parameters referring to sensitivity in the depth and width directions (S_d and S_w , respectively), as well as the depth and width critical energy dose ($E_{c,d}$ and $E_{c,w}$, respectively) required to initiate the photopolymerization reaction. The derivation was first developed by Jacobs for scanning laser polymer VPP [1], and later expanded for ceramic VPP by Gentry and Halloran [2].

$$C_d = S_d \cdot \ln(E_0/E_{c,d}) \quad \text{Equation 3a}$$

$$w_{ex} = S_w \cdot \ln(E_0/E_{c,w}) \quad \text{Equation 4b}$$

Cure metric results are used by researchers in several ways. Multiple groups have investigated the ratio between cure depth and layer thickness, and its effect on outcomes such as surface roughness, forming accuracy, and mechanical properties [3, 4]. Others have studied the link between excess width and forming accuracy and surface roughness [5, 6],

However, there is no standard practice for producing and measuring single layer samples. The process often requires working around the typical printer functions, so custom methods may be necessary. Nevertheless, there are a few parameters which intuitively affect the results of cure metric measurements. For example, different sizes and shapes of samples produce different light scattering patterns, affecting the depth and width of light penetration. Light intensity, a parameter which is not tunable in some VPP systems, also affects light scattering. Finally, different measurement methods are used in literature, with varying levels of accuracy. A NIST study on polymer VPP investigated three methods of cure depth measurement and reported that the measurement technique affected the resulting cure depth values for certain cases [7], but a similar study has not yet been published for ceramic VPP.

This study investigates how light intensity, sample size, sample shape, and measurement technique influence results for cure depth and excess width, with the goal of highlighting factors that should be the focus of standardization efforts and reporting in literature.

2. Methods

2.1. Design of Sample Geometry and Process Parameters

An array of sample geometries was designed to test the effect of sample size and shape on measurements of cure depth and excess width, as shown in **Figure 1**. The sample set consists of 2 mm, 4 mm, 6 mm, 8 mm, and 10 mm squares and circles. Three sets of process parameters were selected, as outlined in **Table 1**, to investigate the effect of increasing energy by increasing exposure time while holding intensity constant, versus increasing intensity and decreasing time while keeping energy constant.

Table 1. Process parameter values selected for this study

Parameter Set #	Exposure energy, E_0 [mJ/cm ²]	Exposure intensity [mW/cm ²]	Exposure time [s]
1	90 (low)	15 (low)	6
2	90 (low)	45 (high)	2
3	180 (high)	45 (high)	4

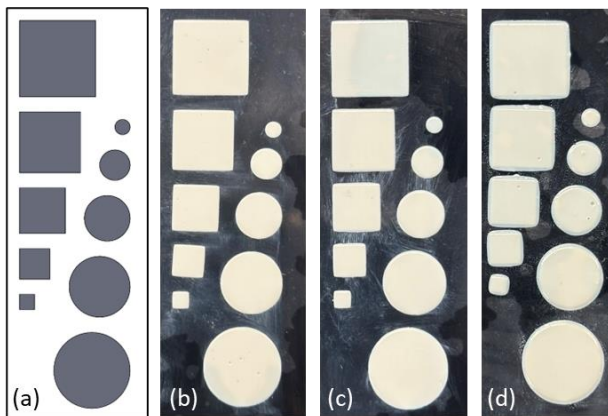


Figure 1. Schematic (a) and images of single layer geometric artifacts printed with parameter set 1 (b), set 2 (c), and set 3 (d). Sample sizes are 2 mm, 4 mm, 6 mm, 8 mm, and 10 mm.

2.2. Printing Single Layers

Samples were printed using digital light processing VPP, where light is projected to illuminate and cure each layer of a three-dimensional model. A commercially available high-purity alumina slurry (LithaLox HP500, Lithoz GmbH) was printed on a Lithoz CeraFab 7500 printer.

Service software available on the printer was leveraged to illuminate one layer of the shapes shown in **Figure 1(a)** with the desired exposure time and intensity. One set of shapes was printed for each parameter set. For each build, a miniature vat was filled 3 mm deep with slurry, to simulate an infinite supply of slurry. The miniature vats outlined the build area and were additively manufactured out of black polylactic acid (PLA) using material extrusion. A thin, transparent, flexible plastic sheet (provided by Lithoz GmbH) was used as a substrate on which each sample set was printed; the top side of the plastic sheet was treated by Lithoz to improve adhesion with printed samples. This sheet was placed on top of the vat plate surface, then the mini vat was placed on top of the sheet before filling with slurry.

2.3. Geometry Measurement Methods

Samples were scanned with a Keyence VHX-5000 digital microscope (DM) and an Olympus OLS5100 laser scanning confocal microscope (LSCM).

DM images were acquired with a Keyence VH-Z20T objective set to 150X zoom. Images were acquired using the stitching function with full coaxial illumination. Images were recorded using the Pixel Shift function, yielding 1.11 μ m resolution.

LSCM 3D scans were acquired using a 10X objective and the stitching function, with automatically determined z-range. This resulted in 1.25 μ m resolution in the X and Y dimensions, and 6.1 nm resolution in the Z (height) dimension. The LSCM simultaneously collects height and laser intensity images, as well as CMOS color images.

2.4. Cure Metric Quantification Methods

Two cure metrics were used to quantify and compare the geometry of single layer samples in this study: cure depth and excess width.

Cure depth (C_d) is defined as the thickness of the sample, and was measured from LSCM height data using native Olympus software. First, a second-degree polynomial form was removed from height data to account for any curvature in the flexible plastic substrate. The form was fit to user-defined regions of interest on the substrate, not overlapping with the sample (shown in **Figure 2a**). After form removal, horizontal and vertical line profiles were drawn across the center of each sample (**Figure 2a**), and an Olympus software tool was used to measure C_d , which was averaged for the two profiles. The technique used for cure depth measurement from a profile is shown in **Figure 2b**; it involved fitting a line to two user-selected points on the substrate region of the profile, then selecting a third point through which a parallel line passes, representing the top of the cured sample. The distance between these two parallel lines represents the value for C_d .

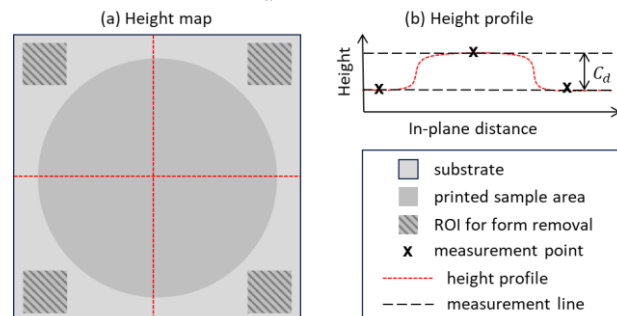


Figure 2. Diagram showing measurement method for cure depth, including regions of interest (ROI's) for form removal and profiles for cure depth measurements on a height map (a), and method for cure depth measurement from a profile (b).

Excess width (w_{ex}) is defined as the distance between the measured contour of the sample and the designed contour of the sample (Figure 3). w_{ex} was calculated using $w_{ex} = (w_{measured} - w_{designed})/2$ Equation 2 after measuring the width of squares and diameter of circles. These measurements were obtained from DM images using native Keyence software, and from LSCM images using native Olympus software. Both microscope systems include a parallel line tool to measure square width, and a three-point circle tool to measure circle diameter or radius (Keyence or Olympus, respectively), as shown in Figure 3. Each measurement of width, radius, or diameter was repeated five times per sample, and the average width or diameter was calculated for use in the excess width calculation according to $w_{ex} = (w_{measured} - w_{designed})/2$ Equation

2. After selecting a measurement point from the stitched image, the Keyence software zoomed into that tile of the stitched image to allow for accurate point selection along the edge of the sample. In the Olympus software, the loupe tool enabled zooming into any region of the stitched image for accurate selection of measurement points along the edge of the sample.

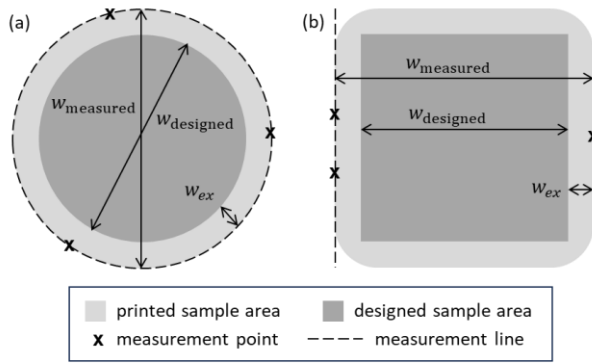


Figure 3. Diagram showing measurement methods for circular (a) and square (b) samples.

3. Results and Discussion

In order to determine whether a certain factor (print parameters, sample geometry, or measurement system) has a significant effect on measurement of cure depth and excess width, the definition of *significant effect* must be established for each cure metric.

For evaluation of cure depth variation in this study, a *significant effect* is defined as one that creates variation equal to, or exceeding, one layer thickness (typically 25-50 μm). This metric was selected due to the prevalence of research which draws conclusions about print parameter optimization using a ratio of cure depth to layer thickness [3, 4]; failure to properly replicate cure depth results within one layer thickness will convolute results in this area of research.

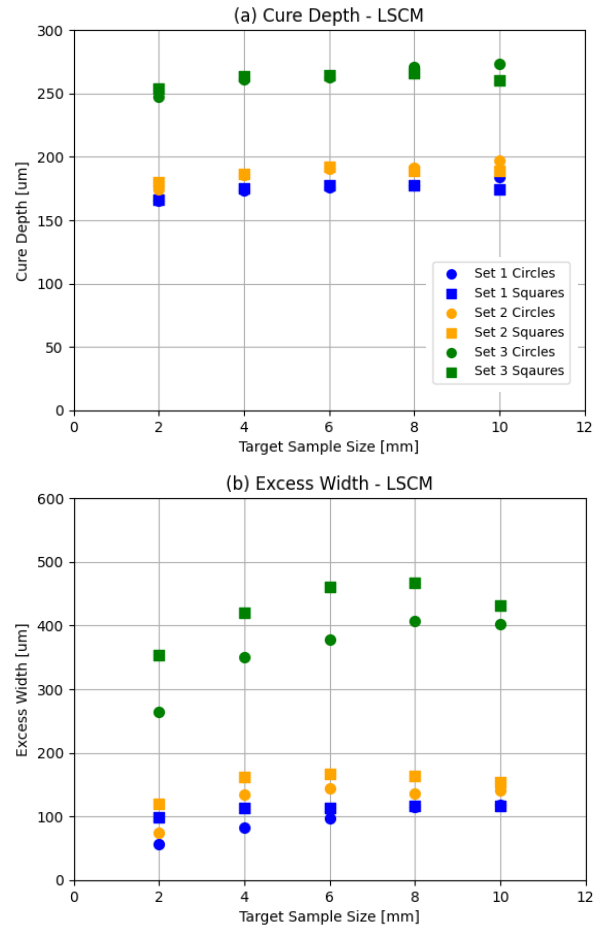
A *significant effect* on excess width is more difficult to define. Unlike cure depth, which can be compared to a process parameter (namely, layer thickness), excess width is best compared to dimensional accuracy and surface roughness, which are outcomes of a complex process. Additionally, the importance of dimensional accuracy and surface roughness are often application dependent. Therefore, evaluation of excess width in this study focuses on trends and comparison to

understand the effect of each factor, without declaration of significance.

3.1. The effect of process parameters

Process parameters have a strong effect on measured values for cure metrics. Values for both C_d (Figure 4a) and w_{ex} (Figure 4b, c) from samples printed with parameter set 3 are at least 100 μm greater than the values for comparable samples printed with parameter sets 1 and 2. This indicates that increasing exposure energy causes a significant increase in value of cure depth, an expected result due to the relationship between C_d and E_0 in $cd = S_d \cdot \ln(E_0/E_{c,d})$

Equation 3. The slight increase in values for C_d between samples from set 1 and set 2 indicates that increasing exposure intensity while maintaining the same exposure energy has a small effect; however, this increase of about 10-15 μm is less than a typical layer thickness (25-50 μm). The effect of exposure intensity on excess width is also present, but convoluted with the effects of size, shape, and measurement system.



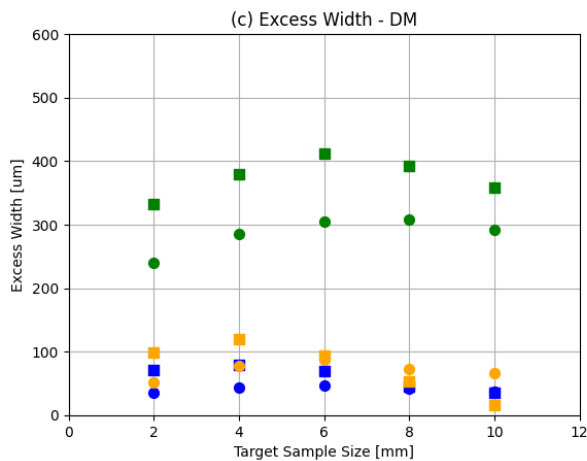


Figure 4. Data showing trends in cure depth (a) and excess width (b), as measured by LSCM, and excess width as measured by DM (c).

3.2. The effect of sample geometry

In order to understand the effect of sample geometry, C_d and w_{ex} were plotted in **Figure 4** with the target sample size along the x-axis and the marker shape differentiating between circular and square samples (**Figure 4**). Circular samples exhibit cure depth that increases with sample size, while square samples reach a maximum value of cure depth for samples with 6-8 mm dimensions, after which cure depth decreases with increasing sample size (**Figure 4a**). As a result, greater cure depths are measured from squares with small dimensions and circles with large dimensions. The effect of sample shape on cure depth values is largest at the extremes of sample size (2 and 10 mm).

For samples in parameter sets 1 and 2, printed with the same exposure energy (the only factor captured by $cd = S_d \cdot \ln(E_0/E_{c,d})$ Equation 3), sample geometry and exposure intensity introduce cure depth variation with a range of 31.5 µm, greater than one 25 µm layer thickness (**Figure 4a**). For parameter set 3, with no effect from exposure intensity, the range of cure depth variation introduced by sample geometry is 26.2 µm (**Figure 4a**). This means that the variation in working curves presented in literature would be significantly decreased if additional factors such as print parameters and sample geometry are clearly described or standardized.

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3.3. The effect of measurement system on excess width

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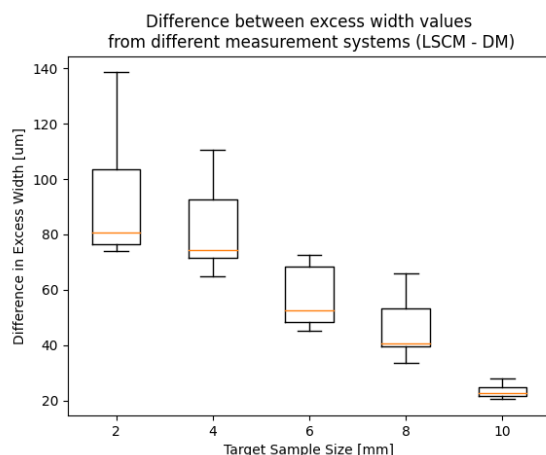


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4. Conclusions

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Exposure energy had a significant effect on cure depth, as described in the working curve equation ($cd = S_d \cdot \ln(E_0/E_{c,d})$ Equation 3a).

Exposure intensity, sample shape, and sample size did not independently have a significant effect on cure depth values. However, the combined effect of these factors, which are not included in $cd = S_d \cdot \ln(E_0/E_{c,d})$

Equation 3a, is significant to cure depth.

Excess width varies more than cure depth with respect to sample size and sample shape. Additionally, the choice of microscope affected the appearance of excess width trends as well as the magnitude of excess width values.

The results of this study indicate that neglecting to publish sufficient details about print parameters, sample geometry, and measurement technique limits the reproducibility and impact of results related to cure depth and excess width. This highlights an area where development of standard practices would be beneficial.

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