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Enhancing photopolymer additive manufacturing via photoinhibition: An initial study

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Abstract
Vat photopolymerization (VPP) among other additive manufacturing processes has a great potential to rapidly print complex 3D components out of a matrix of photo-curable resin. Despite existing effort and current progress in VPP, there still lacks an effective approach to address the outstanding issues of over-curing, especially the lateral over-curing which critically limit the truly achievable resolution and smallest feature size. Photoinhibition has been demonstrated by leading research groups to be able to form a thicker deadzone that enables faster print and vertical micro-topography. However, the potential application of photoinhibition to improve VPP can go beyond vertical control for lateral over-curing control. The emerging concept of photoinhibition aided VPP (PinVPP) employs two concurrent optical masks for initiating and inhibiting the polymerization, respectively, at disparate wavelengths. This work is aimed to explore and establish PinVPP processes for tackling both vertical and lateral over-curing issues to enhance not only the print speed but also the three-dimensional accuracy, resolution, and precision. Specifically, two initial study cases of PinVPP are presented – one general VPP print for polymeric parts and one VPP of ceramic slurry. The preliminary results demonstrate the correlation of the two-wavelength exposure intensities with the inhibition zone thickness, the working curve, thus the critical energy and depth of penetration, and the effects on print speed and geometric properties in the PinVPP processes.

Additive manufacturing, photopolymer, photo inhibition, vat photopolymerization (VPP), over-curing, digital light processing

1. Introduction

Additive manufacturing (AM) has revolutionized the manufacturing industry by enabling the production of complex structures and functional parts using a wide range of materials, including metals, polymers, and ceramics. Among the various technologies used, vat-photopolymerization (VPP) gained widespread adoption, particularly in prototyping and moulding applications. Known to be one of the fastest, most accurate techniques to fabricate complex shapes, VPP involves converting a photo-responsive liquid resin into sequential solid layers, through selective curing by a light beam via photopolymerization. The photo-initiators present in the curing light act as catalysts, triggering the formation of chains of polymers (cross-links) among monomers and oligomers present in the photopolymer [1-3].

VPP has been broadly used for photopolymer printing and adapted for ceramic printing by adding ceramic powders to photopolymer resin. This has proven capable of overcoming challenges, generally associated with the traditional production of ceramics with complex 3D shapes. However, one outstanding challenge remains in controlling the over-curing, which is mainly caused by the photo-induced species diffusion, and can negatively affect the geometric properties of printed parts. Current research practices rely on formulating adequate resins, by using non-reactive light absorbers, or optimizing exposure parameters to address the over-curing but with limited performance [4-6].

Digital light processing (DLP) is a predominant VPP process, which uses a digital light projector, such as a digital micromirror device (DMD), to create a patterned light beam of a suitable wavelength, usually ultraviolet (UV). The DMD receives a grayscale image input, enabling selective activation of micromirrors to shape the light into an optical mask that matches the desired cross-sectional shape of the target object [7]. Each layer's input image consists of square pixels, which are projected into the resin vat to form small blocks called voxels. The lateral size of a voxel depends on the pixel size of the input image and the optical system's magnification factor, which can be determined through experimental calibration. The height of a voxel can be defined as either the layer thickness or the thickness of a part, creating column voxels in vertically discretized layers or parts. The light patters are directed through a liquid photopolymer resin, resulting in a solid 3D object by linking monomers/oligomers in the resin on a layer basis [8-10]. While advances of the DLP technology made possible the development of more sophisticated VPP processes [11], there is a critical lack of efficient, mature and effective methods to improve the resolution and accuracy [12, 13] of the build.

In this work, we present an initial, systematic study on a novel, two-wavelength DLP-based, photoinhibition-aided VPP process, referred as PinVPP, for polymer and ceramic printing. Specifically, we examine the effects the use of a two-wavelength DLP photopolymerization system has on the print speed and geometric accuracy of the build, through the use of parameters such as the inhibition zone thickness, the working curve and consequently the critical energy and depth of penetration [14]. The results obtained during this pilot study are promising and converge with the findings of the existing studies lead on PinVPP's ability to advance VPP printing of high-fidelity photopolymers and ceramics with decent print speed.

2. Methodology

2.1. Photo inhibited-VPP system

While conventional vat-photopolymerization relies on a single light source with a specific wavelength for photopolymerization,

our PinVPP process, in contrast, employs a two-wavelength approach. The PinVPP system we developed in our laboratory consists of two light sources – namely PRO4500PRO6500 from Wintech Digital Systems Technology, Carlsbard, CA –. These light sources emit two different beams of light, one for polymerization (blue light with a wavelength of 460 nm) and the other for photoinhibition (UV light with a wavelength of 365 nm). The generated mask is then transmitted to a precursor vat. The two light sources are positioned together with a movable build platform that includes a linear stage (LTS 150 from Thorlabs located in NJ). We have developed an in-house LabVIEW software to control the parameters of both photopolymerization and photoinhibition, including the intensity of irradiation and pattern parameters. This software also operates the build platform. Figure 1 illustrates the setup of the system. In this work, grey scale masks of various light intensities for UV and blue light are created using a MATLAB code, generating desired shapes to be projected into the vat.

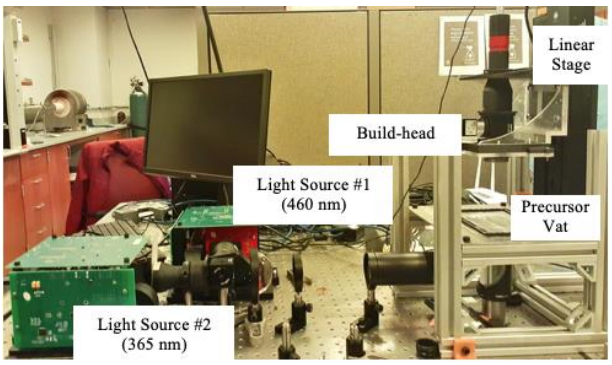

Figure 1. In-house physical setup for the PinVPP system.

The printing process relies primarily on photopolymerization reactions to create the polymer foundation for a green component. Meanwhile, photoinhibition is utilized to restrict the curing region, thereby accelerating the process and improving the properties of the final part.

2.2. Vat-photopolymerization for polymeric parts

The printable material system is developed based on a formulation described in a previous literature reference [3]. It consists of photo inhibitors, photo initiators, and monomers, which are detailed as follows. The resin used in our work contains a combination of 50% Triethylene glycol dimethacrylate (TEGDMA) and 50% bisphenol A glycidyl methacrylate (bisGMA) as monomers. For photo initiation, we utilize Camphorquinone (CQ) as a blue light photo-initiator, along with the addition of ethyl 4-(dimethylamino)benzoate (EDAB) as a co-initiator. To make the UV light-responsive photo inhibitor, 2,2'-Bis(2-chlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole (o-Cl-HABI) is dissolved in tetrahydrofuran (THF) as a 30 wt. % solution before being added to the monomer mixture. The non-monomer mixture is formulated with 0.2 wt. % CQ, 0.5 wt. % EDAB, and 3 wt. % o-Cl-HABI. This liquid resin is used to print polymers.

2.3. Vat-photopolymerization of ceramic slurry

The feedstock of ceramic slurry is obtained by mixing 50 wt. % of the prepared liquid resin (described in the previous section) with 50 wt. % of the ceramic suspension. This suspension is prepared by combining 50 wt. % Alumina powder, consisting of Aluminum Oxide (Al_2O_3) with 50 wt. % of alcohol containing 0.05 wt. % Stearic acid (SA). The latter is the dispersant which stabilizes the mixture by homogeneously dispersing the Aluminum Oxide in the liquid medium containing alcohol. This measure prevents the settling and aggregation of the ceramic particles, since the Stearic Acid creates a repulsive barrier between them, thus resulting in a uniformly distributed suspension which will not clump later. The ceramic suspension is stirred magnetically for 1 hour at a speed of 200 rpm, then heated up to 80 degrees Celsius to remove any alcohol from the powder.

3. Results and discussion

3.1. Two-wavelength exposure intensities effects on inhibition zone thickness

Figure 2 shows the working curve for printing polymers, while Figure 3 is for ceramics. In both study cases, the same exposure patterned is used with a fixed blue light intensity. The inhibition intensity I_{UV} and curing intensity I_{Blue} ratio (I_{UV}/I_{Blue}) is tested for varying values. The corresponding inhibition height is measured by using the spacer thickness minus cured thickness of sample. Indeed, the inhibition zone thickness increases proportionally with the I_{UV}/I_{Blue} ratio.

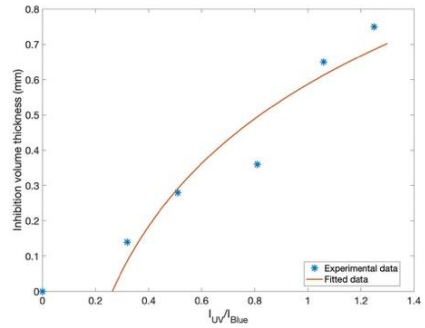

Figure 2. Variations of the inhibition zone thickness in relation to the inhibition/curing intensity ratio while printing polymers.

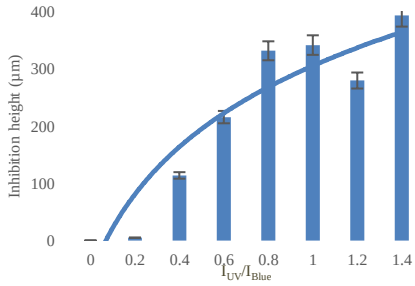

Figure 3. Variations of the inhibition zone thickness in relation to the inhibition/curing intensity ratio while printing ceramics.

3.2. Critical energy and depth of penetration characterization

To understand the curing behaviour under the effect of inhibition, working curves of uninhibited and inhibited samples are measured during experimental prints under different inhibition and curing intensity ratios. As in typical VPP processes, critical energy E_c and penetration depth D_p are estimated. Jacobs introduced a crucial metric for investigating photopolymerization, as a standard design equation [15]. This equation has been widely employed in literature to extract values for critical energy, E_c and penetration depth, D_p from experimental data:

$$C_d = D_p \ln\left(\frac{E}{E_c}\right) \quad (1)$$

where $\boldsymbol{C_d}$ is the curing thickness, $\boldsymbol{D_p}$ is the penetration depth, $\boldsymbol{E}$ is the energy of the light source and $\boldsymbol{E_c}$ is the critical energy. By deriving these values, we can make predictions about the exposure energy and time required to achieve the desired

thickness. More importantly, we can examine the trends of $\boldsymbol{E_c}$ and $\boldsymbol{D_p}$ under different ratios of I_{UV}/I_{Blue}. Samples are printed for each given I_{UV}/I_{Blue} ratio with the curing time ranging from 20 s to 60 s. Note that an increase in the exposure time is accompanied with an increase in the exposure energy dosage. The plots in Figure 4 summarize the results.

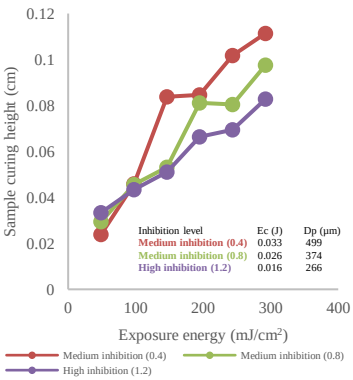

Figure 4. E_c - D_p working curve under different inhibition ratios. The higher the inhibition, the lower the curing height.

As the energy dosage increases, we can see an increase in the curing thickness for each. Albeit not linear, the increase is significant, and all ratios exhibit a similar trend, with the exception of I_{UV}/I_{Blue} = 0, due to potential inaccuracies in the measurements taken. This confirms the hypothesis that while the I_{UV}/I_{Blue} ratio directly determines the inhibition zone. We did more similar experiments using different blue light intensities and found that the curing light intensity I_{Blue} also affects its behaviour. This could be due to the changing concentrations of the interactive species which respond differently to varying I_{Blue} intensities. Indeed, inhibition allows to prevent the over-curing of the samples.

3.3. Inhibition role in confining 3D geometry

First, to demonstrate the effects inhibition has on the build geometry, testing is conducted for three groups of experiment, in order to print three types of polymeric pillar arrays, varying in configuration. Each group has a benchmark experiment using the traditional VPP process that does not employ any inhibition along with some comparison experiment using PinVPP. Group 1 allows to print two pillars, and has three processes (PinPAM_1.1, 1.2, and 1.3) that use the same overlapping inhibition pattern but different levels of surrounding inhibition intensity, in order to shed some light on the potential intensity sensitivity. Group 2 has one process (PinPAM_2.1) for printing four pillars spaced at 4mm between column. Finally, group 3 (PinPAM_3.1) has one process as well, to print four pillars spaced at 8mm between column. Figure 5 shows the results of the experiments.

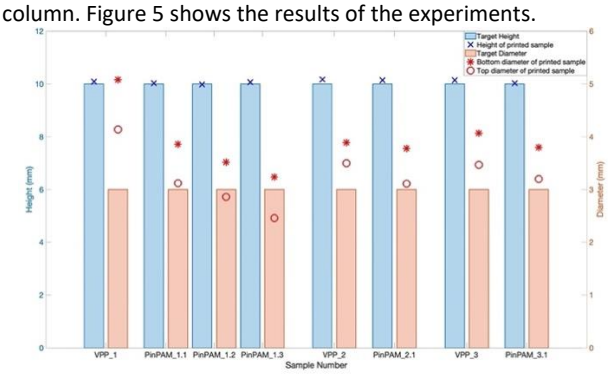

Figure 5. Case 1: PinVPP for polymers. Sample dimensions comparing VPP and PinVPP for printing three different arrays of polymeric pillars.

All the groups demonstrate PinVPP's ability to tackle the lateral and vertical over-curing issues. In all the processes used, both the top and bottom diameter values are closer to the target diameter than that in the corresponding traditional VPP process, indicating that the inhibition can significantly reduce lateral overcuring thus improve the lateral dimension. The observed deviations in diameter are mainly caused by the non-optimal inhibition intensity.

Secondly, using the ceramic slurry, samples are printed for four I_{UV}/I_{Blue} ratios, with the curing time ranging from 20 s to 60 s. The curing blue light intensity remains constant. Plotting the curing thickness and diameter variations, respectively, as a function of exposure time for varying I_{UV}/I_{Blue} ratios, allows us to see that a high inhibition allows to get a thickness around 600µm for exposure times of 60s, 80s and 100s. The dimensional accuracy is therefore preserved, since the cured diameter is close to a value of 8000µm (see Figures 6 and 7).

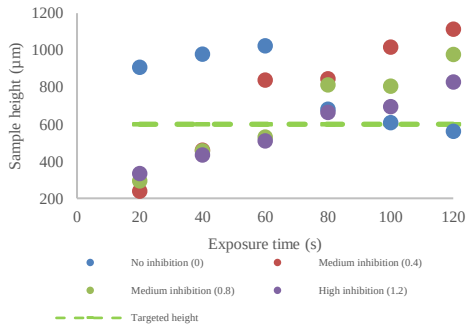

Figure 6. Case 2: PinVPP for ceramics. Thickness variation plots as function of exposure time using different inhibition ratios. The use of a high inhibition ratio allows to reach the desired height of 600µm.

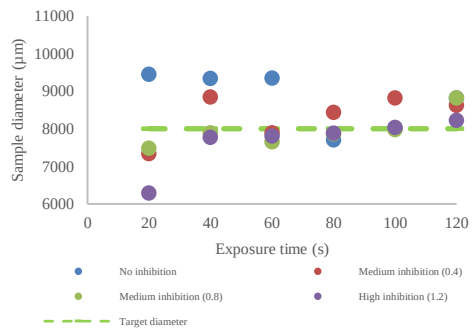

Figure 7. Case 2: PinVPP for ceramic. Diameter variations in relation to the exposure time using different inhibition ratios. The use of a high inhibition ratio allows to reach the target diameter of 8000µm.

3.4. Inhibition effects on printing speed

In order to understand potential bottlenecks for the process optimization, we evaluate the vertical printing speed, for different inhibition ratios in the 2nd case of ceramic PinVPP. From Figure 8, it appears that a high inhibition level of I_{UV}/I_{Blue} = 1.2 allows to cure the sample the fastest for an exposure time of 20s. Despite still being slower than a pure blue light, the use of a high inhibition level guarantees the prevention of an overcuring of the build. Moreover, for a longer exposure time – higher than 80s – a medium inhibition ratio of I_{UV}/I_{Blue} = 0.4 cures the samples the fastest, followed by a medium inhibition of I_{UV}/I_{Blue} = 0.8, a high inhibition of I_{UV}/I_{Blue} = 1.2, and lastly by a pure blue light I_{UV}/I_{Blue} = 0. Therefore, while a high inhibition ratio isn't the fastest, it still results in a more controlled and monitored process, with builds averaging a curing height closer to the target height of 600µm.

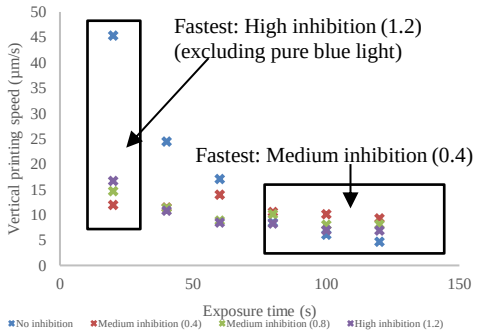

Figure 8. Vertical print speed variations with respect to exposure time for all inhibition ratios I_{UV}/I_{Blue} tested in PinVPP of ceramic parts.

4. Conclusion

This research focuses on exploring a novel photoinhibition aided VPP process, for polymers and ceramics. The aim is to investigate the effects of using a two-wavelength DLP system on print speed and geometric accuracy, while addressing the challenge of over-curing. By utilizing parameters such as inhibition zone thickness, working curve, critical energy, and depth of penetration, the study aims to improve the resolution and accuracy of the build. The developed mask projection system allows for precise control over both photopolymerization and photoinhibition parameters, including exposure time, intensity, and pattern. Optimal greyscale mask projections are utilized to refine the print and enhance the build without compromising its structural integrity.

Overall, this research provides valuable insights into the potential of the PinVPP approach, for achieving high-fidelity printing of photopolymers and ceramics. The integration of photoinhibition offers the opportunity to enhance three-dimensional accuracy, improve print speed, and achieve enhanced resolution in additive manufacturing processes. Further investigation and optimization of the PinVPP method holds promise for advancing the field of additive manufacturing, and expanding the PinVPP applications in various industries. This research study serves as a proof-of-concept for future development of the PinVPP method at a larger scale and for different materials.

5. Acknowledgments

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