Three-dimensional printing of blue-colored zirconia accessories using digital light processing-based stereolithography

Yanhui Li\textsuperscript{a,b}, Shengliang Wang\textsuperscript{a}, Minglang Wang\textsuperscript{a}, Xinyue Zhang\textsuperscript{a}, Binwen Lu\textsuperscript{a}, Yueliang Wang\textsuperscript{a}, Dongdong Dong\textsuperscript{b}, Fupo He\textsuperscript{a}, Wei Liu\textsuperscript{a} and Shanghua Wu\textsuperscript{b}

\textsuperscript{a}Institute of New Materials, Guangdong Academy of Sciences, Guangzhou, Guangdong, China; \textsuperscript{b}Guangdong University of Technology, Guangzhou, Guangdong, China

\section*{ABSTRACT}
Digital light processing (DLP) based stereolithography opens new possibilities for fabricating ceramic accessories with complex structures. The cure depth is a critical criterion for analyzing the production efficiency of ceramic accessories. As predicted using the absorption model, the absorbance from the photosensitizer and dye has a direct effect on the cure depth. In this study, blue-colored powder composed of 3 mol\% yttria-stabilized tetragonal zirconia polycrystals (3Y-TZP) and CoAl\textsubscript{2}O\textsubscript{4} powder was prepared through ball-milling. The cure depth of a single layer exposed to varying energy levels was measured, and the values of the depth sensitivity \(S_d\) and critical energy \(E_c\) were also calculated. The results showed that the absorbance of blue-colored 3Y-TZP powder increased with CoAl\textsubscript{2}O\textsubscript{4} content, which increased the critical energy \(E_c\) and depth sensitivity reciprocal \(1/S_d\). Compared with the pure 3Y-TZP, the cure depth decreased, which was attributable to the absorbance of CoAl\textsubscript{2}O\textsubscript{4}. In addition, blue-colored accessories were fabricated using the DLP method, and the microstructures of the accessories were characterized through scanning electron microscopy.

\section*{1. Introduction}
Colorful zirconia ceramics have wide applications in dental materials, ceramic knives and ceramic ornaments for their good biocompatibility, mechanical properties, bright color and metallic luster, and so on. Blue-colored zirconia ceramic is one of the most classical colorful ceramics. Colorful ceramic accessories with complex structures can be fabricated using conventional ceramic-processing methods, such as gel casting and injection molding [1–3]. Currently, these methods are still widely used. It is essential to use molds, but there are significant disadvantages in pertaining to their usage, such as high post-processing and shape limitations. Additive manufacturing (AM) is a toolless-forming method that is used to improve the fabrication of ceramic parts with more complex geometries, higher resolutions, and fewer post-processing than other ceramic forming [4–6]. Among the AM techniques used for ceramics, the stereolithography apparatus (SLA) is a direct approach of manufacturing ceramic parts without using molds or post-processing, and it is becoming popular owing to its high resolution and surface quality [6–9]. SLA uses a laser as the projector, which scans the photosensitive suspensions, resulting in its point-by-point polymerization. Then, the ceramic particles are locked in the resin networks to form a green ceramic body with a specific geometry, and the green body is later de-bound and sintered to the final ceramic part. Digital light processing (DLP) is a variant of SLA, in which an ultraviolet (UV) lamp is utilized to replace the laser, as a projector and digital micromirror device (DMD) are used [7,10]. When the photosensitive suspensions are exposed to the projector, the suspensions polymerize to form specific green parts layer by layer. Compared with the SLA method, the application of the DLP method yields a higher build speed due to its layer-by-layer formation and a higher output resolution due to its DMD. Therefore, the DLP method is a promising technique for fabricating ceramic parts with several potential applications, such as electronics, ceramic prototypes, and biomedical implants [11–13].

The cure depth is a particularly significant parameter used in evaluating the cure performance of photosensitive suspensions. The cure depth is determined using Beer–Lambert model (Equation (1)) during stereolithography (SL) processing [14].

\begin{equation}
C_d = S_d \ln \frac{E}{E_c}
\end{equation}

In Equation (1), \(C_d\) and \(S_d\) are the cure depth and depth sensitivity, respectively, and \(E\) and \(E_c\) are the incident energy and depth critical energy, respectively. John W. Halloran and others proposed an absorption model that is related to light attenuation, which is induced by the UV scattering from ceramic particles and absorption from the photosensitizer and dyes.

\section*{CONTACT}
Yanhui Li (liyanhui@gdimm.com) Institute of New Materials, Guangdong Academy of Sciences, Guangzhou, Guangdong 510000, China; Shanghua Wu (swu@gdut.edu.cn) Guangdong University of Technology, Guangzhou, Guangdong 510006, China

This article has been republished with minor changes. These changes do not impact the academic content of the article.

© 2021 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group on behalf of The Korean Ceramic Society and The Ceramic Society of Japan. This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
model equation is expressed using Equation (2) [15, 16], as follows:

\[
\frac{1}{S} = S + A - \varphi A
\]  

(2)

where \( S \) is the scattering parameter due to the refractive index contrast between the resin and the ceramic particles, and \( A \) is the UV absorption term. Moreover, the model also includes a ceramic volume fraction \( \varphi \). As \( A \) originates from the photoinitiator and dyes, it is calculated using Equation (3):

\[
A = (1 - \varphi)(c_p\varepsilon_P + c_o\varepsilon_D)
\]

(3)

where \( c_p \) and \( c_o \) are the concentrations of the photoinitiator and dyes, respectively, and \( \varepsilon_P \) and \( \varepsilon_D \) are the molar extinction coefficients for the photoinitiator and dyes, respectively.

In another paper, Vladislava Tomeckova and John W. Halloran reported the details of a critical energy \( E_C \) model, where \( E_C \) is the minimum energy required to induce polymerization [17]. In a photosensitive suspension, the critical energy is mainly dependent on the absorption coefficients and concentrations of the photoinitiators and inert dyes, which could absorb photons. Furthermore, the critical energy model is influenced by the inhibitors that scavenge free radicals. Therefore, the critical energy model of the ceramic suspension is described as follows:

\[
E_C = (1 - \varphi)\frac{h\nu}{Q} \left(\gamma_Q Q + \gamma_O O + \gamma_D D\right) \frac{1}{\varepsilon_p c_p}
\]

(4)

where \( h \) and \( \Omega \) are the photon energy and quantum yield, respectively, \( \gamma_Q \) and \( \gamma_O \) are the potency of the inhibitor and oxygen inhibitor, respectively, and \( Q \) and \( O \) are the concentrations of the quinone-type and oxygen inhibitor, respectively. \( D \) is the number of radicals that are not generated because the photon is absorbed by an inert dye. The model predicts that the critical energy increases linearly with the additions of inert dye.

In previous studies, the cure depth model was based on the assumption that the ceramic is UV-transparent, but there is a dearth of literature on the cure performance of colorful photosensitive suspensions due to a higher absorbance of colorful ceramics. In addition, DLP method has a similar cure processing to stereolithography (SL). However, the cure depth and excess width models are not built until now due to the digital mirror device (DMD) scrolling the light distribution in DLP method. This study is focused on determining the effects of blue-colored 3 mol% yttria-stabilized tetragonal zirconia polycrystals (3Y-TZP) absorbance on cure behavior, mainly cure depth. The depth sensitivity and critical energy were also determined. Additionally, some ceramic accessories of blue-colored 3Y-TZP were produced using the DLP method.

2. Materials and methods

(1) Preparation and characterization of blue-colored powder

The blue-colored powder mixed 3Y-TZP powder \((D_{50} = 150 \text{ nm})\) with various mass ratios of \(\text{CoAl}_2\text{O}_4\) pigment \((D_{50} = 3 \mu m)\) was ball-milled and dried to obtain homogeneous blue-colored ceramic powder. X-ray diffraction (XRD, D8 Venture, Bruker, Germany) and scanning electron microscopy (SEM, SU8220, Hitachi, Japan) were carried out to characterize the blue-colored powder mentioned above. The absorbance of the prepared powder was also tested using a UV-Vis spectrophotometer (UV2450, Shimadzu, Japan).

(1) Preparation of the blue-colored suspensions

A ball-milling approach was then applied to prepare a uniform photosensitive resin, including ethoxylated pentaerythritol triacrylate (PPTA, Aladdin), 1,6-hexanediol diacrylate (HDDA, Aladdin), di-functional aliphatic urethane acrylate (U600, Aladdin), 1-octanol (octanol, Aladdin), and some other additives. In the next step, blue-colored photosensitive suspensions were prepared. This step involved the mixing of the above resin with the blue-colored 3Y-TZP powder using the ball-milling method for 2 h, and then the optimal photoinitiator, 1 wt% of photosensitive resin, was added to the suspensions. All the suspensions had the same solid content of 28 vol%, which is sensitive to cure properties.

(1) Preparation and characterization of the single layer and accessories

The prepared suspensions were cured to a single layer of mesh under a UV light with a wavelength of 405 nm, and the single line of mesh was measured in terms of the cure depth using a thickness gauge (Mitutoyo Measuring Instrument (Suzhou) Co. Ltd., China).

The blue-colored 3Y-TZP accessories were fabricated using a photosensitive suspension with 3 wt% \(\text{CoAl}_2\text{O}_4\) using the DLP method. The accessories were exposed to the same wavelength of 405 nm at an energy of 25 mJ/cm². The prepared accessories were de-bonded following a two-step profile consisting of debinding including vacuum at 1°C/min to 600°C for holding 30 min and air pyrolysis 2°C/min to 900°C for holding 30 min, and then sintered at 5°C/min to 1500°C for 2 h in the air muffle furnace. In addition, the relative density and microstructure of the blue-colored accessories were analyzed using the Archimedes principle and SEM, respectively. Additionally, elements analysis of grains was used energy dispersive X-ray spectrometer (EDS) and the grain size was measured using Nano measure software.
3. Results and discussion

Figure 1(a) shows the XRD patterns of the ceramic powders. 3Y-TZP and CoAl$_2$O$_4$ peaks indexed in JCPDS 01-070–4427 and JCPDS 01-080-1678, respectively, are found in the pure ceramic powders. In both patterns of the mixture powders including 3 wt% CoAl$_2$O$_4$ before and after ball milling process, 3Y-TZP mainly appeared with some weak peaks belonging to CoAl$_2$O$_4$ observed, and no other peaks were detected. Besides, there are nearly no differences, which indicated that there was no reaction between the two components during the ball-milling process. The XRD result was consistent with the blue-colored 3Y-TZP powder. Figure 1(b-d) shows the SEM and EDS images of the blue-colored 3Y-TZP powder obtained during the ball-milling process. 3Y-TZP particles shown in Figure 1(b) had an average particle size of 150 nm and a uniform shape, and CoAl$_2$O$_4$ particles were irregularly shaped with an average size of 2 ~ 3 μm, as shown in Figure 1(d). Furthermore, EDS mappings of the main elements were measured to show homogeneous mixed particles. The element EDS maps are presented in Zr map, Al map and Co map. Zr occupied in the whole Figure 1(b), Al and Co were evenly distributed in the 3Y-TZP (Y$_2$O$_3$ stabilized ZrO$_2$) with some bigger zones enriched with Al and Co, which indicated that the homogeneous mixture could be obtained using ball-milling method.

The absorbance was measured using the UV-visible spectrophotometer to determine the effects of absorbance of blue-colored ceramic powder on cure behavior, and the results are displayed in Figure 2. Figure 2(a) shows the absorbance of the pure 3Y-TZP and CoAl$_2$O$_4$ under UV wavelengths varying from 350 to 800 nm. The absorbance of pure 3Y-TZP was almost maintained at a constant value of 0.083. However, the absorbance curve of the pure CoAl$_2$O$_4$ appeared as a broad absorption peak between 500 and 700 nm with an absorbance value of 0.20 at a wavelength of 405 nm, which was higher than that of the pure 3Y-TZP. It can also be observed that the absorbance of the blue-colored powder increased with the addition of CoAl$_2$O$_4$, as shown in Figure 2(b). When the CoAl$_2$O$_4$ content increased from 3 to 7 wt%, the absorbance values correspondingly increased from 0.134 to 0.166.

The blue-colored suspensions were exposed to varying energy doses to determine their respective cure properties. Figure 3 depicts the cure depth and excess width curves of the pure 3Y-TZP and blue-colored suspensions for varying CoAl$_2$O$_4$ contents. In Figure 3(a), the cure depth curves all increased linearly with the natural logarithm of the incident energy dose, consistent with Equation (1), while the cure depth decreased with increasing CoAl$_2$O$_4$ content under the same incident energy. The depth values of the pure 3Y-TZP ranged from 50.5 to 61.5 μm when energy was varied from 25 to 37 mJ/cm$^2$. Correspondingly, the cure depth of the 3 wt% blue-colored suspension increased from 45.4 to 60.4 μm, whereas that of the 7 wt% blue-colored suspension was from 39.5 to 55.5 μm when the energy increased from 25 to 41 mJ/cm$^2$. Compared with the pure 3Y-TZP, the depth of the 7 wt% blue-colored suspension for UV

![Figure 1](https://example.com/figure1.jpg)
attenuation decreased by over 31%, which might be due to the absorbance of the blue-colored CoAl_2O_4. As shown in Figure 3(b), the excess width has a nonlinear growth with natural logarithm of incident energy dose, and decreases with increasing CoAl_2O_4 contents at the same incident energy, which is similar to the cure depth curves, indicating that the ceramic absorbance has a positive effect on output resolution.

The depth sensitivity and critical energy versus suspension absorbance were plotted, as shown in Figure 4. Figure 3 shows the cure depth versus the natural logarithm of energy dose for the blue-colored 3Y-TZP suspensions at varying concentrations of CoAl_2O_4. It can be noticed that all the cure depth curves of the blue-colored suspensions linearly increased with the incident energy dose, which was consistent with Jacob’s Equation (i.e. Equation (1)). Therefore, the cure depth curves were applied to evaluate the attenuation factor 1/S_d from the slope and critical energy dose E_c from the energy intercept (fit to Equation (1)). When ceramic absorbance increased from 0.083 to 0.166, 1/S_d increased from 52.8 to 63.7 μm^{-1}, and E_c increased from 2.7 to 7.1 mJ/cm^2. In Figure 4, the 1/S_d curve of the blue-colored 3Y-TZP suspensions increased linearly with the ceramic absorbance, which agreed well with the absorbance model of photosensitive suspensions.
proposed by John W Hollaran (Equations (2) and (3)). Similarly, the critical energy increased with ceramic absorbance, not consistent with Equation (4), in which the ceramic is assumed to be transparent.

The suspension loading of 28 vol% consistent with above experiments, and the slice thickness of 20 μm, half of its cure depth, are applied to form the blue green bodies. The more CoAl₂O₄, the lower density. Therefore, blue-colored 3Y-TZP powder consisting 3 wt% CoAl₂O₄ is used as raw material. Figure 5(a,b) shows the green bodies of blue-colored ceramic which has a bright blue color and good cure properties prepared using the DLP-based stereolithography method. The green bodies had a uniform color, a higher resolution, and higher surface quality. The front surfaces of the bodies were smooth, but the profiles were slightly coarse. The green bodies were then subjected to a binder burnout and sintering process at 1500°C to obtain the final parts; the microstructure and grain size distribution are presented in Figure 5(c,d) and (g, h), respectively. The SEM images indicated that the blue-colored sample had a very dense microstructure with a small number of pores located at the grain boundaries. Some black grains were well distributed within the gray grains. From the EDS results, as presented in Figure 5(e,f), the black grains were confirmed to be CoAl₂O₄ particles, and the other grains were 3Y-TZP particles. The mean grain sizes of the particles were both between 0.25 and 0.3 μm. It is demonstrated that the CoAl₂O₄ colorant had slight effects on the microstructure, and the relative density of the sintered bodies was approximately 97%, which is suitable for ceramic accessories.

4. Conclusions

DLP-based stereolithography increases the opportunities for the application of colored accessories with complex structures. Cure depth is a critical parameter that should be considered in fabricating the green bodies of ceramic accessories. The results obtained from the cure depth model using the DLP method were similar to that of the Beer–Lambert model. As predicted using the model, the cure depth had a direct correlation to the light intensity.
attenuation, which is the sum of the attenuation coefficients from the ceramic and photosensitive components. The absorbance of the blue-colored 3Y-TZP powder increased from 0.134 to 0.166, with the addition of CoAl$_2$O$_4$ contents from 3 to 7 wt%. Correspondingly, 1/$S_d$ increased from 52.8 to 63.7 μm$^{-1}$, and $E_2$ increased from 2.7 to 7.1 mJ/mm$^2$. In addition, the cure depth decreased at the same incident energy and curing time, which was mainly due to the absorbance of the blue-colored CoAl$_2$O$_4$ powder. Furthermore, the blue-colored accessories prepared using the DLP method was sintered at 1500°C. The sintered particles had a uniform color with grain sizes of 0.25 and 0.3 μm for the 3Y-TZP and CoAl$_2$O$_4$ particles, respectively, and the relative density of the sintered bodies was approximately 97%.

**Disclosure statement**

No potential conflict of interest was reported by the author(s).

**Funding**

This work was supported by the Major Science and Technology Project of Guangdong Province [2017B090911011]; Local Innovative and Research Team Project of Guangdong Pearl River Talents Program [2017BT01C169]; the Key R&D Program of Guangdong Province [2020B090923002]; Guangdong Academy of Sciences Projects [2021GDASYL-20210103065]; National Natural Science Foundation of China [52005114]; National Natural Science Foundation of China [51872052]; National Natural Science Foundation of China [52005113]; Postdoctoral Science Foundation [2020M682640]; the Natural Science Foundation of Guangdong Province [2021A1515012277]; Science & Technology Plan Project of Guangdong Province [2020B1212060049]

**References**

[1] Kuscer D, Stavber G, Trefalt G, et al. Brennecka, formulation of an aqueous titania suspension and its patterning with ink-jet printing technology. J Am Ceram Soc. 2012;95:487–493.
[2] Shang ZWQ, Lia J, Zhou G, et al. Gel-tape-casting of aluminum nitride ceramics. J Adv Ceram. 2017;6:67–72.
[3] Nuno Reis KA, Seerden M, Julian RG, et al. Ink-jet printing of wax-based alumina suspensions. J Am Ceram Soc. 2001;84:2514–2520.
[4] Chaoyin Zhou ZC, Eckel JH, Martin AJ, et al. Schaedler, additive manufacturing of polymer-derived ceramics. Science. 2016;351:58–62.
[5] John W. Halloran, ceramic stereolithography: additive manufacturing for ceramics by photopolymerization. Annu Rev Mater Res. 2016;46:19–40.
[6] Chen SKW, Miyamoto Y. Fabrication and measurement of micro three-dimensional photonic crystals of SiO$_2$ ceramic for terahertz wave applications. J Am Ceram Soc. 2007;90:2078–2081.
[7] Haidong W, Liu W, Rongxuan H, et al. Fabrication of dense zirconia-toughened alumina ceramics through a stereolithography-based additive manufacturing. Ceram Int. 2017;43:968–972.
[8] Liu W, Haidong W, Zhou M, et al. Fabrication of fine-grained alumina ceramics by a novel process integrating stereolithography and liquid precursor infiltration processing. Ceram Int. 2016;42:17736–17741.
[9] Griffith ML, Halloran JW. Freeform fabrication of ceramics via stereolithography. J Am Ceram Soc. 1996;79:2601–2608.
[10] Varghese MMG, Castro-Garcia M, Lópezz-López JJ, et al. Fabrication and characterisation of ceramics via low-cost DLP 3D printing. Boletín de la Sociedad Española de Cerámica y Vidrio. 2018;57:9–18.
[11] Yang XLY, Zheng X, Chen Z, et al. 3D-printed bimimetic super-hydrophobic structure for microdroplet manipulation and oil/water separation. Adv Mater. 2018;30:1704912.
[12] Shao XKH, Liu A, Sun M, et al. Bone regeneration in 3D printing bioactive ceramic scaffolds with improved tissue/material interface pore architecture in thin-wall bone defect. Biofabrication. 2017;9:025003.
[13] Song YC, Lee TW, Wu S, et al. Ceramic fabrication using mask-image-projection-based stereolithography integrated with tape-casting. J Manuf Processes. 2015;20:456–464.
[14] Vladislava Tomeckova JW, Halloran, cure depth for photopolymerization of ceramic suspensions. J Eur Ceram Soc. 2010;30:3023–3033.
[15] John W, Halloran SP, Gentry, absorption effects in photopolymerized ceramic suspensions. J Eur Ceram Soc. 2013;33:1989–1994.
[16] Susan P, Gentry JW. Halloran, depth and width of cured lines in photopolymerizable ceramic suspensions. J Eur Ceram Soc. 2013;33:1981–1988.
[17] John W. Halloran Vladislava Tomeckova, critical energy for photopolymerization of ceramic suspensions in acrylate monomers. J Eur Ceram Soc. 2010;30:3273–3282.