Advanced Ceramics Progress: Vol. 7, No. 2, (Spring 2021) 23-27

Materials and Energy Research Center
MERC

Contents lists available at ACERP

Advanced Ceramics Progress

Journal Homepage: www.acerp.ir

Technical Note Article

Preparation of High-Solid Filled Alumina Inks for Stereolithography 3D Printing Process

A. Khecho [a], S.A. Ghaffari [b] *, M. Behzadnasab [c], M. Rahmat [c]

[a] MS, School of Metallurgy and Materials Engineering, Iran University of Science and Technology, Tehran, Tehran, Iran
[b] Assistant Professor, School of Metallurgy and Materials Engineering, Iran University of Science and Technology, Tehran, Tehran, Iran
c Assistant Professor, Faculty of Polymer Processing, Iran Polymer and Petrochemical Institute, Tehran, Tehran, Iran

A R T I C L E I N F O

Article History:

Received 23 May 2021
Received in revised form 4 July 2021
Accepted 10 August 2021

Keywords:

Additive Manufacturing
3D Printing
DLP
Alumina
Rheology

A B S T R A C T

In ceramic additive manufacturing, it is important to fabricate parts with high solid contents to guarantee defect-free sintered parts. In stereolithography, low viscosity and especially shear-thinning behavior of the ink are the key factors in producing ceramic-resin parts. Therefore, there should be a correlation between solid loading and viscosity. In this study, Alumina-glass inks were printed using bottom-up and top-down approaches, and the rheological properties were investigated. The main objective of this study was to print a highly filled ceramic-resin part with a viscosity suitable for DLP printing. While use of suspensions with low viscosity was recommended for top-down digital light processing (DLP) printing, a new setup was designed to study the feasibility of the top-down approach for pastes for the top-down approach. According to the findings, ceramic-resin pastes with the solid content of maximum 75 wt% and viscosity of 47.64 Pa.s at the shear rate of 30 s^{-1} were easily printable via our hand-made top-down DLP printer. However, it was not possible to print inks with solid contents more than 60 wt% using the bottom-up DLP, mainly because the detachment force grew dramatically with an increase in viscosity.

https://doi.org/10.30501/ACP.2021.287468.1062

1. INTRODUCTION

Additive manufacturing is best known as an alternate shaping method for ceramics that ovecomes several problems in conventional shaping methods. In additively manufactured ceramic parts, the design of molds for complex-shaped structures is rejected and often, there is no need for mechanical process for sintered ceramic parts. Moreover, additive manufacturing provides fabrication of complex geometrical shapes with high dimensional accuracy [1,2]. In stereolithography, functioning based on the photopolymerization of the resin, the ceramic parts are formed by solidifying the ceramic-resin suspension. In each layer, the suspension is exposed to UV light according to a 3D pattern and photocurbale resin is polymerized for making a solidified layer. Finally, solidified layers consistute the final ceramic-resin part. In stereolithography, there is another method for printing called digital light processing (DLP) in which the laser light source is replaced by a UV projector, and each layer is cured all at once [3–5].

Depending on the light source position, stereolithography process is categorized into two approaches. The light source can be positioned either on the top (top-down approach) or at the bottom (bottom-up approach) of the suspension vat [6]. The bottom-up

* Corresponding Author Email: amirghaffari@iust.ac.ir (S. A. Ghaffari)
URL: https://www.acerp.ir/article_136415.html

Please cite this article as: Khecho, A., Ghaffari, S. A., Behzadnasab, M., Rahmat, M., "Preparation of High-Solid Filled Alumina Inks for Stereolithography 3D Printing Process", ***Advanced Ceramics Progress***, Vol. 7, No. 2, (2021), 23-27. https://doi.org/10.30501/ACP.2021.287468.1062

approach is beneficial due to the higher resolution of the ceramic parts; however, the detachment force applied to each layer is its main disadvantage, which causes deformation and increases the possibility of removing the sample from the build plate. In top-down, there is no need for any detachment force, since the light is exposed from the top. On the contrary, the layer thickness control is one of the challenging issues in the top-down approach which highly affects the resolution of the printed parts. Therefore, for top-down DLP printers, low-viscosity suspensions are recommended [7,8]. Generally, in DLP printing, self-levelling property is of singinificance in fabricating ceramic parts with minimized defects. As reported previously, ceramic suspensions suitable for stereolithography should have viscosities about <5 Pa.s with a shear rate of 30 s^{-1} and a non-Newtonian shear-thinning behavior [9]. In sintering, however, high solid-filled parts are required to develop a part with the lowest shrinkage and deformation, simultaneously characterized by acceptable mechanical properties [10]. Generally, the minimum solid loading is recommended to be 50 vol% to avoid further problems in sintering [11–14]. High solid loadings increase the viscosities and intensify the light scattering effect, both making the stereolithography process difficult. Therefore, the rheological properties and printability should be optimized for ceramic printing. Printing pastes with high viscosities can also be a solution to the aforementioned problems [14–16].

The present study uses a simple top-down DLP printing setup and high-viscosity paste for 3D print alumina parts. The effect of alumina solid load on rheology and printability of samples is also evaluated. Moreover, the thickness of the printing layer and curing time are changed to obtain the best green strength and interlayer bonding.

2. MATERIALS AND METHODS

2.1. Ink Preparation And DLP Printing

As initial ceramic powder, Alumina-glass mixture was produced by fast-milling of 70 g α-Alumina powder (d_{90}=5 µm and 99.99% purity) and 30 g soda-lime glass frit for 10 minutes and then, sieving by 270 meshes. The printable inks were prepared by mixing Alumina-glass powder with methacrylate-based photocurbale resin (Maan Polymer), as illustrated in Table 1. In order to prepare the inks, mechanical homogenizer (10,000 rpm speed) was used for the suspensions (H50 and H60) and for the pastes (U70 and U75). The resin and ceramic powder were firstly mixed mechanically and then, they were put in ultrasonic bath for two minutes to ensure the homogeneous preparation of the paste.

The suspensions were printed using Parsa 3D bottom-up DLP Printer with Vivitek 4000 Lumen projector. To print the pastes, a hand-made top-down DLP setup was designed with a UV projector light source (365 nm wavelength), and the printing pattern was changed to a cylinder as a simple pattern so that the feasibility of the top-down approach to paste printing could be examined. The curing time and the layer thickness were considered constant for both approaches, as shown in Table 1. The schematic of DLP printer approaches is shown in Figure 1.

TABLE 1. Alumina-resin printable inks' properties

Label	Powder wt%	Powder vol%	Curing Time (s)	Layer Thickness (µm)	Printing Approach
H50	50	23	2.3	30	Bottom-up
H60	60	31	2.3	30	Bottom-up
U70	70	42	45	200	Top-down
U75	75	48	45	200	Top-down

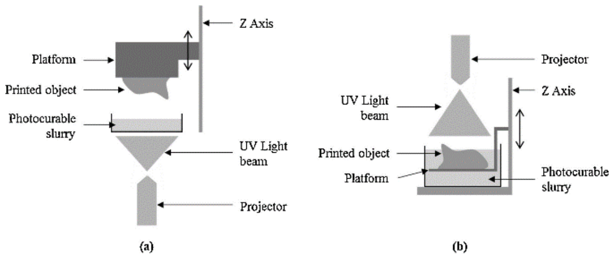

Figure 1. Schematic of DLP 3D printer approaches; a) bottom-up and b) top-down [7]

2.2. Characterization

The rheological properties of the inks were measured at room temperature using MCR301 and (Anton Parr, Austria) rheometer at shear rates of 0.1 to 1000 s^{-1}.

2.3. Sintering

Sintering was done in two steps. First, the ceramic-resin samples were heated to 400 °C at a rate of 5 °C/min and maintained for one hour for resin burn-out. Then, the samples were heated up to 1400 °C at a rate of 10 °C/min and sintered for 1.5 hours. The microstructure of the sintered samples was observed through scanning electron microscopy (Tescan, Czech Republic) images.

3. RESULTS AND DISCUSSION

3.1. Rheological Properties

Figure 2 shows the viscosity of the printable inks. Upon increasing the solid content from 50 wt% to 75 wt%, the viscosity of the inks would significantly increase, varying from 0.52 to 47.64 Pa.s at a shear rate of 30 s^{-1}. In addion, upon increasing the solid content to 70 wt%, the pastes exhibited different behaviors at low and high shear rates. In H50 and H60, the viscosity of suspensions gradually decreased with an increase in the shear rate, exhibiting a shear-thinning behavior. Viscosity would also decrease due to the presence of agglomerates, broken down by the shear stress, thus allowing the suspension to flow. Further, as observed, the shear-thinning behavior was attentuated and the viscosity became more stable as the shear rate increased, indicating the reconstruction of the suspension structures damaged at lower shear rates. However, H60 as the more viscose suspension has a viscosity of 1.45 Pa.s at a shear rate of 30 s^{-1}, characterized by suitable rheological behavior and acceptable viscosity for DLP printing [9,17,18].

For pastes, U70 and U75 exhibit shear-thickening behavior at low shear rates due to high solid loading and steric repulsion of the Alumina particles. In other words, the particls formed a 3D structure in which the paste resisted flowing. Of note, the rheological behavior changes to shear-thinning beahavior as the shear rate increases. This can be attributed to the destruction of the 3D structures. In fact, the newly formed 2D structures increase the flowability as the shear rate increases [19].

As observed in both pastes, the viscosity dropped down drastically at a shear rate of 100 s^{-1}. In other words, the paste is formed at this shear rate, thus helping a paddle spread the viscose paste by applying an appropriate force easily to form new layer. When removing the force, an increase in viscosity makes the layer stand still during the photocuring [8,15,20].

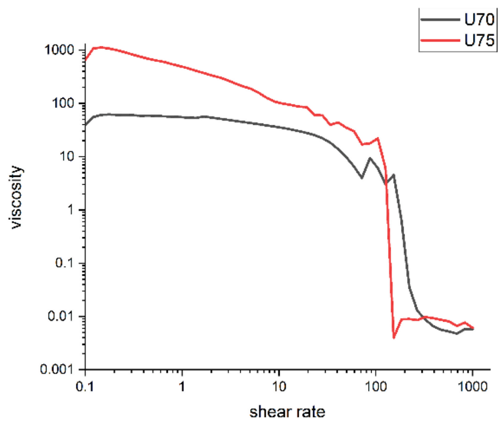

Figure 2. Viscosity variations of the inks; H50 and H60 exhibiting shear-thininng behavior, U70 and U75 showing shear-thickening and shear-thining behavior at low and high shear rates, respectively

3.2. DLP Printing

Figure 3a shows the H50 and H60 printed samples using the bottom-up DLP approach. In this approach, however, adhesion of the first layer was the main difficulty. As shown in Figure 3, H50 and H60 suspensions were printed with relatively high dimensional accuracy and layer thickness of 30 µm. It was not possible to print inks containing solid contents more than 60 wt% as the viscosity increased and exceeded the recommended viscosity range for DLP printing [21] (see Figure 2). Consequently, high viscosity and weakened self-flowing ability of the pastes made the bottom-up DLP process almost impossible due to the high detachment force required for each layer. The bottom-up DLP enjoys many advantages such as flexibility in layer thickness, high resolution, and surface quality, hence no detachment force is required. On the contrary, the top-down DLP is an interesting approach used in DLP printer [7,22]. In addition, in the top-down approach, the application of low viscosity suspension is recommended due to the difficulties in thickness control and spreading thin layers, hence making it a time-consuming process [8]. In the present study, printing of the pastes was made possible by applying the top-down DLP approach. In other words, the top-down setup designed in this study was totally appropriate for the printing pastes. Figure 3b shows the samples printed by the top-down approach. Accordingly, U70 and U75 Alumina-glass pastes were printed with an optimized layer thickness of 200 µm using this approach. By applying the top-down approach, the thickness of this layer increased up to 200 µm while maintaining acceptable dimensional accuracy. The thickness of this layer is significantly greater in value than that in studies that have previously targeted top-down approaches and printing pastes with high solid loadings [15,23,24].

In addition, the curing time reached 45 s since in the top-down approach, the photosensitive paste is directly in contact with oxygen which delays the photopolymerization [7]. In fact, besides the advantage of high solid print in the top-down approach, higher exposure time and lack of constant layer thickness are referred to as disadvantages, which reduce the printing accuracy and increase the printing duration, respectively. Moreover, it is mentioned that in the top-down approach, much more amount of ink is usually needed than that in the bottom-up approach [6,7]; however, the setup designed in this study requires a small amount of ink preparation. About five g of paste is printed on a cylinder with a diameter of about 1.4 mm and height of 5 mm, as shown in Figure 3. Hence, the material waste is minimized.

According to the findings, in case the powder amount increases to more than 75 wt%, the powder and resin do not mix well and the excess powder will remain unmixed and agglomerated, which indicates a saturation point in 75 wt% solid content for the methacrylate-based resin used in this work. This amount of solid content is equal to 48 vol%, which can be considered an acceptable solid load for sintering to obtain fully dense parts [4,25].

Therefore, the top-down approach to DLP printing can be employed as a method for developing high-filled ceramic-resin composites.

3.3. Sintering

The printed samples containing 70 and 75 wt% Alumina-resin, with the highest solid loadings, were sintered at 1400 °C. Figure 4 shows the microstructure of the 70 wt% sample. As expected, due to the existence of glass powder in the composition and high solid content, the sample with 75 wt% was fully densified at 1400 °C, resulting in 97% relative density, 2% open porosity, and 1.3% shrinkage.

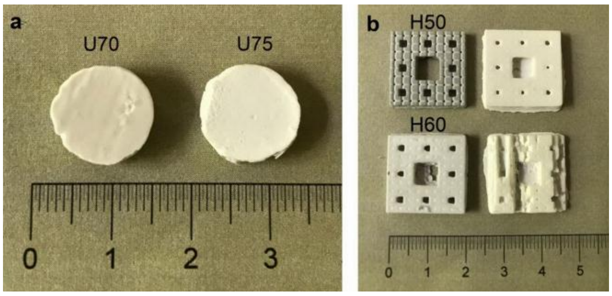

Figure 3. Printed samples via a) top-down and b) bottom-up approaches

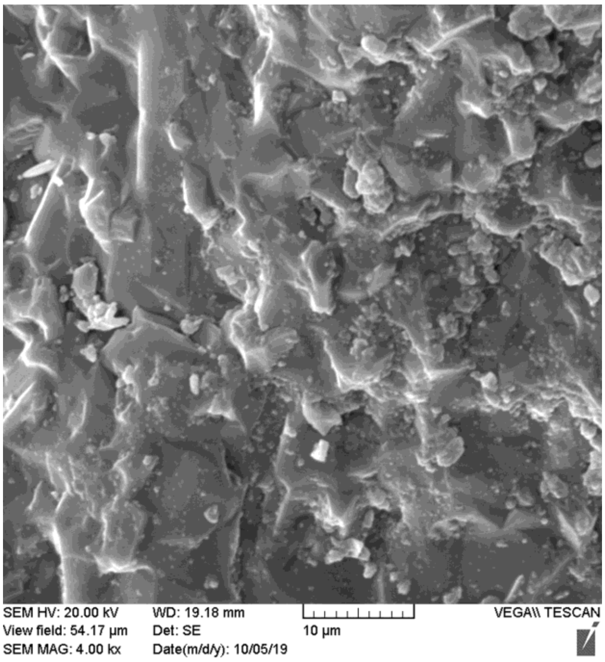

Figure 4. Cross-sectional SEM image of 70 wt% sample printed via top-down approach and sintered at 1400 °C

4. CONCLUSION

In this study, investigation of solid content and its effect on rheology indicated that the bottom-up DLP printer was suitable for the printing of the Alumina-glass suspensions containing maximum 60 wt% solid. As the solid content increased and the suspensions were converted to pastes, the bottom-up DLP printing was not doable since the detachment force highly increased. However, by employing our hand-made top-down DLP setup, the high-solid loading pastes were printable. Despite the recommendations about low viscosity in top-down approach, we were able to print highly-filled Alumina-glass samples with acceptable dimensional accuracy and high layer thickness and without any material waste.

ACKNOWLEDGEMENTS

The authors thank colleagues from Iran Polymer and Petrochemical Institute for their collaboration and their great assistance in this research.

REFERENCES

1. Wu, Z., Liu, W., Wu, H., Huang, R., He, R., Jiang, Q., Chen, Y., Ji, X., Tian, Z., Wu, S., “Research into the mechanical properties, sintering mechanism and microstructure evolution of Al_2O_3-ZrO_2 composites fabricated by a stereolithography-based 3D printing method”, ***Materials Chemistry and Physics***, Vol. 207, (2018), 1–10. https://doi.org/10.1016/j.matchemphys.2017.12.021
2. He, R., Liu, W., Wu, Z., An, D., Huang, M., Wu, H., Jiang, Q., Ji, X., Wu, S. Xie, Z., “Fabrication of complex-shaped zirconia ceramic parts via a DLP-stereolithography-based 3D printing method”, ***Ceramics International***, Vol. 44, No. 3, (2018), 3412–3416. https://doi.org/10.1016/j.ceramint.2017.11.135
3. Wu, H., Liu, W., He, R., Wu, Z., Jiang, Q., Song, X., Chen, Y., Cheng, L., Wu, S., “Fabrication of dense zirconia-toughened alumina ceramics through a stereolithography-based additive manufacturing”, ***Ceramics International***, Vol. 43, No. 1, (2017), 968–972. https://doi.org/10.1016/j.ceramint.2016.10.027
4. Schmidt, J., Elsayed, H., Bernardo, E., Colombo, P., “Digital light processing of wollastonite-diopside glass-ceramic complex structures”, ***Journal of the European Ceramic Society***, Vol. 38, No. 13, (2018), 4580–4584. https://doi.org/10.1016/j.jeurceramsoc.2018.06.004
5. Johansson, E., Lidström, O., Johansson, J., Lyckfeldt, O., Adolfsson, E., “Influence of resin composition on the defect formation in alumina manufactured by stereolithography”, ***Materials***, Vol. 10, No. 2, (2017), 138. https://doi.org/10.10.3390/ma10020138
6. Zakeri, S., Vippola, M., Levänen, E., “A comprehensive review of the photopolymerization of ceramic resins used in stereolithography”, ***Additive Manufacturing***, Vol. 35, (2020), 101177. https://doi.org/10.1016/j.addma.2020.101177
7. Santoliquido, O., Colombo, P., Ortona, A., “Additive Manufacturing of ceramic components by Digital Light Processing: A comparison between the “bottom-up” and the “top-down” approaches”, ***Journal of the European Ceramic Society***, Vol. 39, No. 6, (2019), 2140–2148. https://doi.org/10.1016/j.jeurceramsoc.2019.01.044
8. Bártolo, P. J., Ed., ***Stereolithography: Materials, Processes and Applications***, Springer Science & Business Media, New York, (2011). https://doi.org/10.1007/978-0-387-92904-0

9. Zhang, S., Sha, N., Zhao, Z., "Surface modification of α-Al_2O_3 with dicarboxylic acids for the preparation of UV-curable ceramic suspensions", ***Journal of the European Ceramic Society***, Vol. 37, No. 4, (2017), 1607–1616. https://doi.org/10.1016/j.jeurceramsoc.2016.12.013
10. Li, H., Liu, Y., Liu, Y., Zeng, Q., Wang, J., Hu, K., Lu, Z., Liang, J., "Evolution of the microstructure and mechanical properties of stereolithography formed alumina cores sintered in vacuum", ***Journal of the European Ceramic Society***, Vol. 40, No. 14, (2020), 4825-4836. https://doi.org/10.1016/j.jeurceramsoc.2019.11.047
11. Gentry, S. P., Halloran, J. W., "Light scattering in absorbing ceramic suspensions: Effect on the width and depth of photopolymerized features", ***Journal of the European Ceramic Society***, Vol. 35, No. 6, (2015), 1895–1904. https://doi.org/10.1016/j.jeurceramsoc.2014.12.006
12. Hu, K., Wei, Y., Lu, Z., Wan, L., Li, P., "Design of a Shaping System for Stereolithography with High Solid Loading Ceramic Suspensions", ***3D Printing and Additive Manufacturing***, Vol. 5, No. 4, (2018), 311–318. https://doi.org/10.1089/3dp.2017.0065
13. Chartier, T., Dupas, C., Lasgorceix, M., Brie, J., Delhote, N., Chaput, C., "Additive manufacturing to produce complex 3D ceramic parts", ***Journal of Ceramic Science and Technology***, Vol. 6, No. 2, (2015), 95–104. https://doi.org/10.4416/JCST2014-00040
14. Dehurtevent, M., Robberecht, L., Hornez, J. C., Thuault, A., Deveaux, E., Béhin, P., "Stereolithography: A new method for processing dental ceramics by additive computer-aided manufacturing", ***Dental Material***, Vol. 33, No. 5, (2017), 477–485. https://doi.org/10.1016/J.DENTAL.2017.01.018
15. Liu, W., Li, M., Nie, J., Wang, C., Li, W., Xing, Z., "Synergy of solid loading and printability of ceramic paste for optimized properties of alumina via stereolithography-based 3D printing", ***Journal of Materials Research and Technology***, Vol. 9, No. 5, (2020), 11476–11483. https://doi.org/10.1016/j.jmrt.2020.08.038
16. Wu, H., Cheng, Y., Liu, W., He, R., Zhou, M., Wu, S., Song, X., Chen, Y., "Effect of the particle size and the debinding process on the density of alumina ceramics fabricated by 3D printing based on stereolithography", ***Ceramics International***, Vol. 42, No. 15, (2016), 17290–17294. https://doi.org/10.1016/j.ceramint.2016.08.024
17. Griffith, M. L., Halloran, J. W. H., "Freeform fabrication of ceramics via stereolithography", ***Journal of the American Ceramic Society***, Vol. 79, No. 10, (1996), 2601–2608. https://doi.org/10.1111/j.1151-2916.1996.tb09022.x
18. Nie, J., Li, M., Liu, W., Li, W., Xing, Z., "The role of plasticizer in optimizing the rheological behavior of ceramic pastes intended for stereolithography-based additive manufacturing", ***Journal of the European Ceramic Society***, Vol. 41, No. 1, (2021), 646–654. https://doi.org/10.1016/j.jeurceramsoc.2020.08.013
19. Zhang, K., Xie, C., Wang, G., He, R., Ding, G., Wang, M., Dai, D., Fang, D., "High solid loading, low viscosity photosensitive Al_2O_3 slurry for stereolithography based additive manufacturing", ***Ceramics International***, Vol. 45, No. 1, (2019), 203–208. https://doi.org/10.1016/j.ceramint.2018.09.152
20. de Camargo, I. L., Morais, M. M., Fortulan, C. A., Branciforti, M. C., "A review on the rheological behavior and formulations of ceramic suspensions for vat photopolymerization", ***Ceramics International***, Vol. 47, No. 9, (2021), 11906–11921. https://doi.org/10.1016/j.ceramint.2021.01.031
21. Chen, Z., Li, J., Liu, C., Liu, Y., Zhu, J., Lao, C., "Preparation of high solid loading and low viscosity ceramic slurries for photopolymerization-based 3D printing", ***Ceramics International***, Vol. 45, No. 9, (2019), 11549–11557. https://doi.org/10.1016/j.ceramint.2019.03.024
22. Taormina, G., Sciancalepore, C., Messori, M., Bondioli, F., "3D printing processes for photocurable polymeric materials: technologies, materials, and future trends", ***Journal of Applied Biomaterials & Functional Materials***, Vol. 16, No. 3, (2018), 151–160. https://doi.org/10.1177/2280800018764770
23. Hu, C., Chen, Y., Liu, H., Huang, X., Huo, Y., Jia, Z., Wang, H., Hu, L., Sun, H., Wang, C., "Effect of SiC powder on the properties of SiC Slurry for Stereolithography", ***Ceramics International***, Vol. 47, No. 9, (2021), 12442–12449. https://doi.org/10.1016/j.ceramint.2021.01.101
24. Liu, C., Qian, B., Liu, X., Tong, L., Qiu, J., "Additive manufacturing of silica glass using laser stereolithography with a top-down approach and fast debinding", ***RSC Advances***, Vol. 8, No. 29, (2018), 16344–16348. https://doi.org/10.1039/C8RA02428F
25. Li, K., Zhao, Z., "The effect of the surfactants on the formulation of UV-curable SLA alumina suspension", ***Ceramics International***, Vol. 43, No. 6, (2017), 4761–4767. https://doi.org/10.1016/j.ceramint.2016.11.143