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Fabrication of ceramics using photosensitive slurries: A comparison between UV-casting replication and vat photopolymerization 3D printing

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Abstract

The development of photosensitive ceramic slurries for vat photopolymerization (stereolithography or digital light processing) has received much effort in recent years. However, many of these ceramic suspensions have high viscosity and they are suitable for use only on equipment, specialized in ceramic additive manufacturing. In this work, ceramic manufacturing using photocurable slurries was tested in a low-cost vat photopolymerization printer and in silicone moulds for UV-casting replication, with the latter approach still scarcely explored in the literature. Both processes were able to produce ceramic parts. The UV-casting replication was able to work with more viscous photocurable ceramic slurries and proved more suitable for the manufacturing of ceramic parts with larger cross-sections, providing pieces with improved flexural strength to those produced by additive manufacturing. This work presents the possibility of UV-casting photosensitive slurries to manufacture ceramics, an approach that could be easily adopted without high equipment costs.

Keywords: *additive manufacturing, photosensitive slurries, UV-casting, vat photopolymerization*

I. Introduction

Additive manufacturing (AM) of polymers is already well established [1] and polymer prototypes are easily obtained on a laboratory scale [2]. On the other hand, ceramics AM is the trend under the spotlight, aiming at the manufacturing of arbitrarily complex shapes that would be very challenging or even unfeasible by conventional manufacturing methods [1]. Such an approach allows manufacturing of small series, customized parts, or prototypes without the high cost of moulds [3–5]. However, there are still several challenges to ceramics AM such as the improvement of surface quality [6], dimensional accuracy, and mechanical properties [3].

Vat photopolymerization (VP) is an additive manufacturing process in which a liquid photopolymerizable material contained in a vat is selectively cured by light-activated polymerization [7]. This AM process stands out due to its printing resolution and surface quality in ceramics manufacturing. The development of photosensitive ceramic slurries for vat photopolymerization has received much effort in recent years and recently published review articles [8,9] summarized the state of the art on the subject. However, many of these ceramic suspensions have high viscosity and they are suitable for use only on equipment, specialized in ceramic additive manufacturing made by the major industrial suppliers as 3D Ceram, Lithoz, Admatec and Prodways [8,9] or developed devices with special apparatus for the recoating of the viscous materials [10–12].

Another ceramics processing technique capable of processing complex shapes is gel casting. In this tech-

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nique, ceramic powders are usually dispersed in an aqueous solution (Acrylamide-MBAM system) [13,14]. One of the main challenges of this method is to ensure sufficient strength of the green parts to remove them from the mould without damage [15]. On the other hand, green parts based on non-aqueous solutions have better mechanical strength [8,16], and the recent advances in photosensitive ceramic slurries could be a great fit.

Kotz *et al.* used photosensitive slurries of nanosilica to produce glass by both vat photopolymerization [17] and UV-casting using replication silicone moulds [2]. However, using UV-casting for producing crystalline ceramics is still unexplored. This method could provide a simple replication process for ceramic parts without high equipment costs.

In this paper, the manufacturability of ceramic bodies in a low-cost VP 3D printer and in a UV-casting replication method is evaluated and a comparison of the two processes is given considering the ability to work with different ceramic suspensions and to produce parts with large cross-sections and the flexural strength of the sintered parts. The choice to use a photoinitiator instead of a thermal initiator in the casting process is justified because a temperature-dependent polymerization would result in internal stresses due to temperature gradients, which would be more harmful to larger parts [18]. Furthermore, such a choice allowed the comparison between UV-casting and 3D printing process using the same ceramic slurry.

II. Experimental

Photosensitive ceramic suspensions were prepared, characterized and then used to fabricate ceramic parts by vat photopolymerization additive manufacturing and by UV-casting. Finally, these parts were sintered as described below.

2.1. Slurry preparation

Two photosensitive ceramic suspensions were prepared according to the route proposed by Camargo *et al.* [19]: i) mullite and ii) 3Y-TZP/mullite composite (4 mol% of mullite) slurries. Therefore, ground electrofused mullite powder with the mean particle size of 0.6 µm (MUB, Elfusa, Brazil) and/or partially stabilized zirconia powder with the mean particle size of 0.04 µm (TZ-3Y-E, Tosoh Corporation, Japan) were processed with the monomer (Poly(ethylene glycol) diacrylate, PEGDA $M_n = 250$, Sigma Aldrich, USA), dispersant (DISPERBYK-111, BYK-Chemie, Germany), and photoinitiator (Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide, Sigma Aldrich, USA) for 24 h in a ball-mill to create homogeneous slurries.

All the prepared suspensions had a ceramic loading of 40 vol.%, and the amount of used photoinitiator was 2 wt.% of the monomer. Also, the amount of the dispersant was defined as 3 wt.% of the ceramic powder, a proportion indicated as optimal for the used powders in related works [19,20]. The rheological behaviour of the prepared ceramic suspensions was characterized using a rotational viscometer (DV2T extra, Brookfield, Canada) between 23 and 25 °C. The relationship between curing thickness and exposure time to the light source was also characterized. For this purpose, the photopolymerizable slurries were poured into an opaque container (allowing light to be applied only in the desired direction) and positioned in a UV-light device (520 Light Polymerization, EXAKT). The ceramic suspensions were cured with different exposure times, as-created layers were rinsed with isopropyl alcohol (IPA) and their thickness was measured using a micrometre (Digimatic MDC-25PJ, Mitutoyo).

2.2. Ceramic forming and post-processing

The additive manufacturing of ceramic green parts was performed through a VP 3D Printer (LD-002H, Creality). In addition, the same device was used to manufacture standard resin parts that were used to create elastomeric moulds made of silicone. Next, the UV-casting replication was performed as follows: an amount of the photosensitive ceramic suspensions corresponding to a height of 0.3 mm was poured into the silicone mould, the spreading of the material was manually carried out, and it was cured using a UV-light device (520 Light Polymerization, EXAKT). The exposure time for each suspension was based on the performed photosensitive characterization and will be discussed in the next section. The process was repeated until the entire mould had been filled, cured and then the ceramic green parts replica was completed. When producing macroscopic objects, the entire mould cannot be filled at once because it would cause uncured material inside the part due to the limited light penetration, an intrinsic characteristic in photosensitive ceramic suspensions [21–23], which would cause problems (as cracking) in subsequent processing steps [24].

The green parts from both processes were rinsed with isopropyl alcohol, dried in the oven for 12 h at 100 °C and finally debound and sintered at 1600 °C for 2 h in a box furnace (Blue M, Lindberg). The adequate heating rates in the debinding were based on previous work [20], which studied the thermal decomposition of similar slurries by thermogravimetric analysis. Therefore, the heating rate was set as 0.5 °C/min up to 600 °C. Also, two one-hour hold points were added: at 400 °C (maximum decomposition rate) and at 600 °C to ensure that the organic portion was completely removed. Next, the heating rate was increased to 5 °C/min (up to the sintering temperature).

The density of the sintered parts was measured based on the Archimedes' principle in distilled water [25] using an analytical balance with a resolution of 0.01 mg (AUW220D, Shimadzu). Flexural three-point strength tests (span of 20 mm) were performed on bars ($\sim 25 \times 2 \times 1.5\,\text{mm}^3$) using a universal testing machine

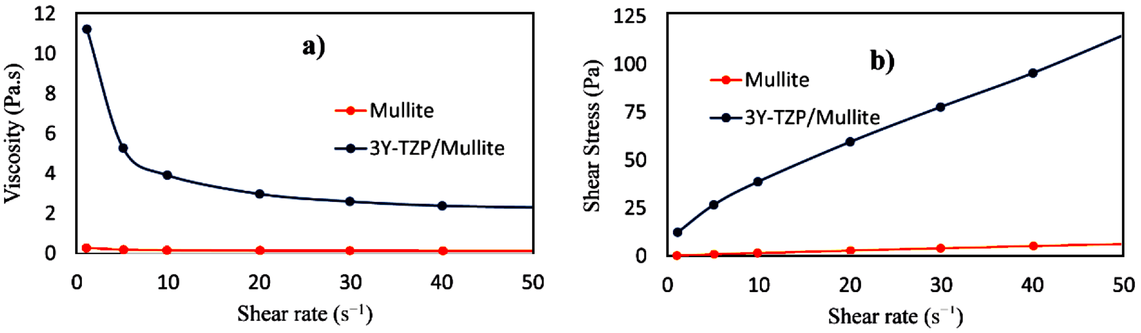

Figure 1. Rheological behaviour of mullite and 3Y-TZP/mullite composite slurries: a) viscosity curve and b) shear stress vs shear rate

(Bionix 370.02, MTS®) with a load cell of 15 kN and a crosshead speed of 0.2 mm/min. The phase composition of the sintered parts was identified by X-ray diffraction (XDR-7000, Shimadzu) and the prepared samples morphologies were analysed by a scanning electron microscope (SIGMA, WEISS).

III. Results and discussion

A comparison between the two manufacturing processes considering the ability to work with different ceramic suspensions, to produce diverse components and the flexural strength of the sintered parts are shown in this section.

3.1. Slurry characterization

Figure 1 presents viscosities of the two prepared photosensitive ceramic suspensions. While the mullite slurry showed very low viscosity (around 0.1 Pa·s at 30 s^{-1}) and negligible yield stress, the 3Y-TZP/mullite composite slurry has strong shear-thinning behaviour (decreased viscosity with increase in shear rate), higher viscosity (almost 3.0 Pa·s at 30 s^{-1}) and not significant yield stress. Such difference in the rheological behaviour is associated with the particle size of the raw materials since the 3Y-TZP presents much smaller particles (D_{50} = 0.04 µm) than the mullite powder (D_{50} = 0.60 µm). Finer particles usually result in higher viscosity suspensions [8,26]. Also, they have a greater tendency to agglomerate, which is responsible for the elastic response at rest [8,26,27]. Also, the agglomerates are deflocculated when the shear rate increases, causing the shear-thinning behaviour [8,26,28].

Figure 2 shows the relationship between curing thickness and exposure time to the light source of the polymerization unit for the prepared photosensitive ceramic suspensions. This was used to define the curing exposure time for each slurry to reach 0.3 mm curing depth. It was 3 min for the mullite slurry in the UV-casting replication and 10 min for the 3Y-TZP/mullite composite suspension. The chosen exposure times guarantee that all the material is cured, avoiding post-processing problems. The high exposure required for the zirconia-based slurry is explained by the refractive index of this material (~2.2) [8,29] being much higher than that of the used monomer (~1.46) [8]. According to the Beer-Lambert law, the cured depth thickness decreases with an increase in the difference between the refractive index of the medium and the particles [8,21].

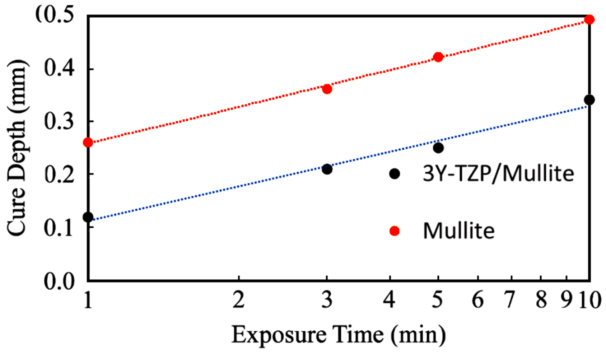

Figure 2. Cure depth vs. exposure time of the prepared photosensitive ceramic suspensions

3.2. Ceramic forming and characterization

The mullite suspension was successfully used for the additive manufacturing of the specimens and small parts. However, failures occurred for parts with larger cross-sections. For example, the manufacturing of a component inspired by a rotor of a centrifugal blood pump (maximum cross-section of 1500 mm^2) failed, as shown in Fig. 3a. The failure is associated with the periodic detachment between the part being manufactured and the bottom surface of the vat, which introduces unwanted stresses and deformation in the part being manufactured [30]. To reduce the detachment forces, the part was inclined (30°), significantly decreasing the maximum area of a section and thus reaching successful 3D printing of the rotor (Fig. 3b).

Next, the same slurry was used to successfully manufacture flexural specimens and the rotor using UV-casting replication. Figure 4 shows both rotors fabricated by UV-casting replication and vat photopolymerization AM with inclined configuration. The surface quality can be pointed out as the only drawback of the UV-casting part compared to the one produced by VP. In the UV-casting, a certain adhesion of the part being manufactured to the mould surface takes place at the

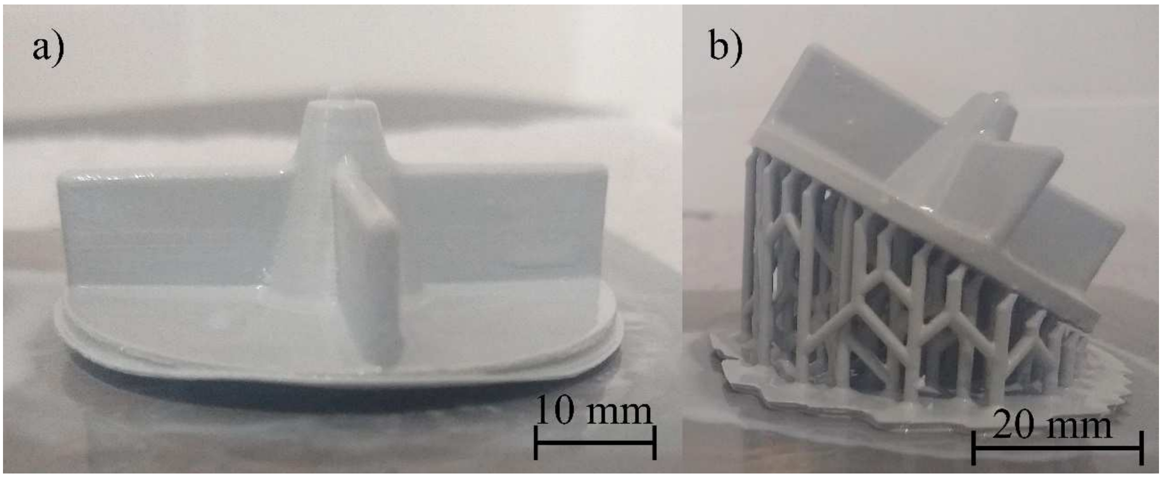

Figure 3. Mullite additive manufacturing in different printing configurations: a) failed 3D print with no inclination and b) successful 3D print with inclined orientation

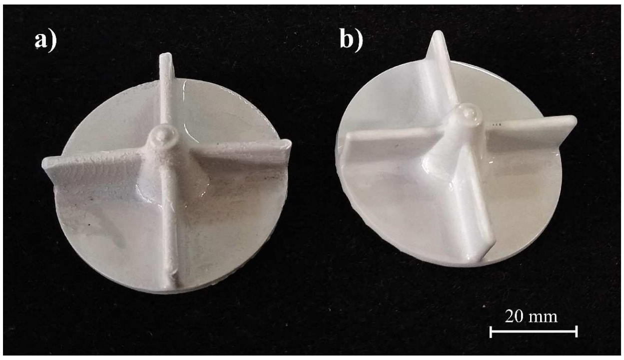

Figure 4. Rotor inspired by a centrifugal blood pump made of mullite slurry by different processes a) UV-casting replication, b) vat photopolymerization with inclined orientation

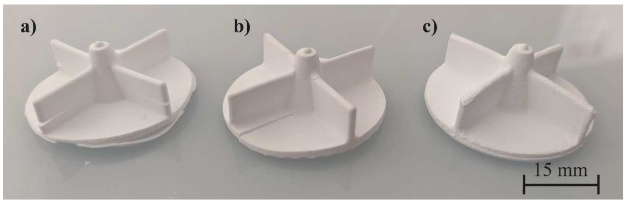

Figure 5. Sintered mullite rotor manufactured by different approaches a) vat photopolymerization with no inclination, b) vat photopolymerization with inclined orientation, c) UV-casting replication

same time that the material undergoes shrinkage due to the photopolymerization of the acrylic material, which hinders the surface quality. Future studies to circumvent this problem such as using additives to the ceramic photosensitive suspension and surface coating/greasing for the mould should be carried out.

The sintered mullite rotors are shown in Fig. 5. Both additive manufactured parts presented visible cracks and delamination. Moreover, the rotor 3D printed with inclined orientation showed distortion which may be due to the difference in shrinkage between the building direction and the projection plane, which is intrinsic anisotropy of this layered process [5,19,20,26]. On the other hand, the UV-casted rotor showed no visible crack or delamination. The printed specimens showed a relative density of 85.5 ± 0.5 %TD and a flexural strength of 47 ± 4 MPa while the ones manufactured by UV-casting reached 81.4 ± 0.7 %TD and 63 ± 9 MPa of relative density and flexural strength, respectively. The considerable content of organic materials (60 vol.%) in the initial suspension may explain the relatively low density obtained. In addition, the lower flexural strength of the printed specimens is probably related to the stresses and deformation introduced by the periodic detachment. The influence of solid loading and additives on the properties of UV-casted parts may be the subject of future work.

Subsequently, all the attempts to 3D print ceramic parts with the 3Y-TZP/mullite composite suspension failed. In all tries, the first layer did not adhere to the build plate and stuck to the bottom of the vat, an issue named “sticking” in related work [31]. Such a problem may be associated with the increased detachment forces due to the rheological behaviour of the suspension. Conversely, the same slurry was successfully used to manufacture ceramic parts by UV-casting replication, as shown in Fig. 6.

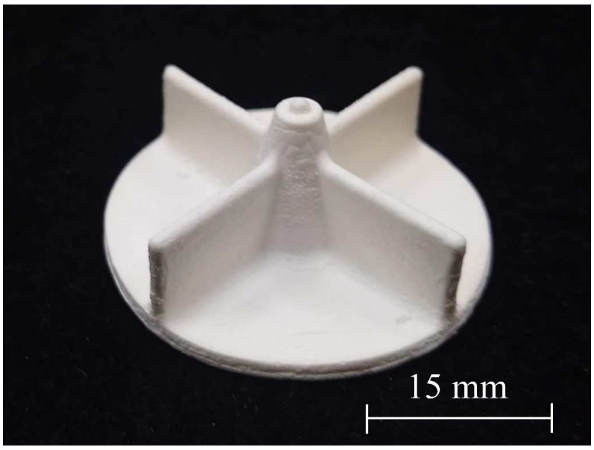

Figure 6. Sintered 3Y-TZP/mullite composite rotor manufactured by UV-casting replication

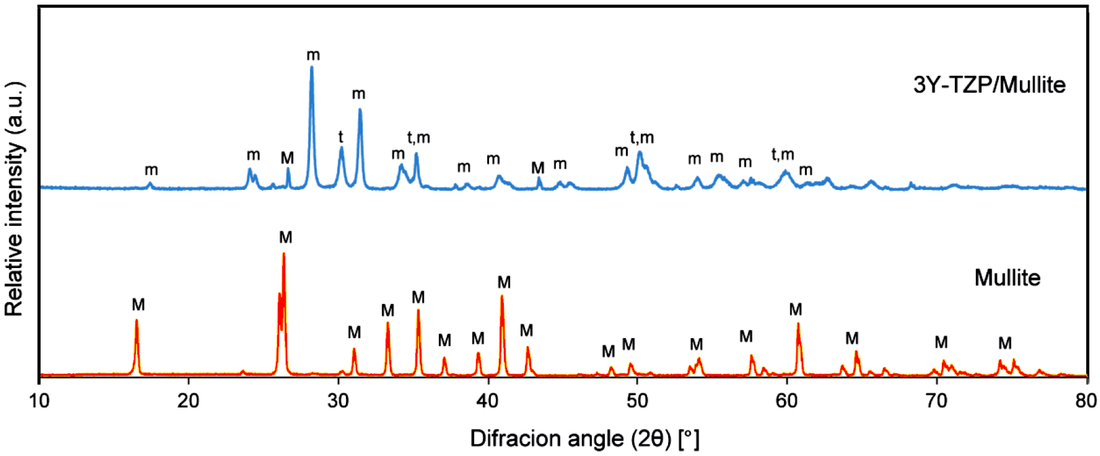

Figure 7. X-ray diffraction patterns for the sintered parts manufactured by UV-casting (peaks of mullite are marked with "M", monoclinic zirconia with "m" and tetragonal zirconia with "t")

Moreover, Fig. 7 shows X-ray diffraction patterns of the sintered parts manufactured by the UV-casting replication indicating that no significant crystallinity change occurred in the mullite part. In this case, the raw material used (electrofused powder) was already composed only of the stable mullite phase. On the other hand, for the 3Y-TZP/mullite composite, the addition of mullite affected the zirconia stabilization, and a large amount of monoclinic phase was generated. A significant portion of the doping agent (yttria) diffused into the mullite structure, allowing the tetragonal-monoclinic phase transformation, similar to what has been described in related work [32].

Lastly, Fig. 8 presents the SEM images of the manufactured parts. The higher porosity of the mullite sample (Fig. 8a) is related to the high organic content, characteristic of the photosensitive ceramic suspensions, which generates a limited powder packing density in the green parts combined with the low reactivity of the electrofused powder used as raw-material. In contrast, for the 3Y-TZP/mullite composite sintered at the same temperature, the porosity was significantly reduced, and a higher density (89.0 ± 0.9 %TD) was obtained due to the use of the fine 3Y-TZP powder with high sintering reactivity. Also, the addition of electrofused mullite powder contributed to the formation of a microstructure composed mostly of uniform zirconia grains with limited size.

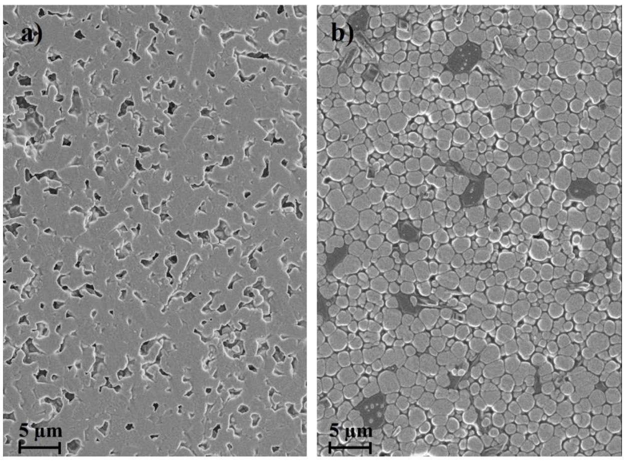

Figure 8. SEM images of the sintered parts manufactured by UV-casting. a) mullite, b) 3Y-TZP/mullite composite

Based on the presented results, UV-casting replication proved to be a promising technique in ceramic manufacturing, allowing fabrication based on photosensitive ceramic suspensions that could not be used in additive manufacturing by vat photopolymerization using low-cost 3D printers. Different formulations can be easily tested using a minimum amount of material, as there is no need to fill the vat or loss of material during cleaning, as occurs in the compared additive manufacturing process. The use of low-cost commercial resins as a substitute for high purity monomer and photoinitiator used in this work can be an alternative to lower the raw material costs and make the technique even more viable. For that, rheological behaviour, stability and thermal decomposition of such suspensions may be the subject of future work. Also, the curing behaviour of the photosensitive slurries and alternative light sources may be considered to optimize the process.

IV. Conclusions

Vat photopolymerization was used to manufacture ceramic parts using low-viscosity photosensitive suspensions. Nevertheless, this process presented problems for parts with large cross-sections. This issue could be partially solved by rotating the building direction. This approach allowed large parts to be 3D printed without visible defects. However, cracks, delamination and distortion were observed in the sintered parts. On the other hand, UV-casting lamination allowed the ceramic manufacturing of large parts even with high-viscosity suspensions with yield stress resulting in parts with improved flexural strength compared to those produced by additive manufacturing. Thus, UV-casting replication proved capable of producing ceramic components using the recently well-studied photosensitive ceramic suspensions.

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References

1. Z. Chen, Z. Li, J. Li, C. Liu, C. Lao, Y. Fu, C. Liu, Y. Li, P. Wang, Y. He, "3D printing of ceramics: A review", *J. Eur. Ceram. Soc.*, **39** (2019) 661–687.
2. F. Kotz, K. Plewa, W. Bauer, N. Schneider, N. Keller, T. Nargang, D. Helmer, K. Sachsenheimer, M. Schäfer, M. Worgull, C. Greiner, C. Richter, B.E. Rapp, "Liquid glass: A facile soft replication method for structuring glass", *Adv. Mater.*, **28** (2016) 4646–4650.
3. R. Galante, C.G. Figueiredo-Pina, A.P. Serro, "Additive manufacturing of ceramics for dental applications: A review", *Dent. Mater.*, **35** (2019) 825–846.
4. M. Schwentenwein, J. Homa, "Additive manufacturing of dense alumina ceramics", *Int. J. Appl. Ceram. Technol.*, **12** (2015) 1–7.
5. K. Zhang, R. He, G. Ding, C. Feng, W. Song, D. Fang, "Digital light processing of 3Y-TZP strengthened ZrO_2 ceramics", *Mater. Sci. Eng. A*, **774** (2020) 138768.
6. C. Revelo, H. Colorado, "3D printing of kaolinite clay with small additions of lime, fly ash and talc ceramic powders", *Process. Appl. Ceram.*, **13** (2019) 287–299.
7. ISO/ASTM 52900:2015, Additive manufacturing - General principles - Terminology, 2015.
8. I.L. de Camargo, M.M. Morais, C.A. Fortulan, M.C. Branciforti, "A review on the rheological behavior and formulations of ceramic suspensions for vat photopolymerization", *Ceram. Int.*, **47** (2021) 11906–11921.
9. S. Zakeri, M. Vippola, E. Levänen, "A comprehensive review of the photopolymerization of ceramic resins used in stereolithography", *Additiv Manuf.*, **35** (2020) 101177.
10. I.L. de Camargo, R. Erbereli, J.F.P. Lovo, C.A. Fortulan, "DLP 3D Printer with innovative recoating system", pp. 609–616 in *Proc. 6th Brazilian Technol. Symp.*, Springer, Cham, 2021.
11. J.C. Wang, H. Dommati, "Fabrication of zirconia ceramic parts by using solvent-based slurry stereolithography and sintering", *Int. J. Adv. Manuf. Technol.*, **98** (2018) 1537–1546.
12. O. Santoliquido, F. Camerota, A. Rosa, A. Ortona, "A novel device to simply 3D print bulk green ceramic components by stereolithography employing viscous slurries", *Open Ceram.*, **5** (2021) 100089.
13. J. Yang, J. Yu, Y. Huang, "Recent developments in gelcasting of ceramics", *J. Eur. Ceram. Soc.*, **31** (2011) 2569–2591.
14. F. Wang, J. Yin, K. Zuo, Y. Xia, D. Yao, Y. Zeng, "Effect of organic additives on mechanical properties of SiC ceramics prepared by a modified gelcasting method", *Process. Appl. Ceram.*, **10** (2016) 227–233.
15. G.V. Franks, C. Tallon, A.R. Studart, M.L. Sesso, S. Leo, "Colloidal processing: enabling complex shaped ceramics with unique multiscale structures", *J. Am. Ceram. Soc.*, **100** (2017) 458–490.
16. X.B. Li, H. Zhong, J.X. Zhang, Y.S. Duan, D.L. Jiang, "Powder characteristics on the rheological performance of resin-based zirconia suspension for stereolithography", *J. Inorg. Mater.*, **35** (2020) 231–235.
17. F. Kotz, K. Arnold, W. Bauer, D. Schild, N. Keller, K. Sachsenheimer, T.M. Nargang, C. Richter, D. Helmer, B.E. Rapp, "Three-dimensional printing of transparent fused silica glass", *Nature*, **544** (2017) 337–339.
18. L.G. Ma, Y. Huang, J.L. Yang, H.R. Le, Y. Sun, "Effect of plasticizer on the cracking of ceramic green bodies in gelcasting", *J. Mater. Sci.*, **40** (2005) 4947–4949.
19. I.L. de Camargo, R. Erbeteli, H. Taylor, C.A. Fortulan, "3Y-TZP DLP additive manufacturing: solvent-free slurry development and characterization", *Mater. Res.*, **24** (2021) e20200457.
20. I.L. de Camargo, R. Erbereli, C.A. Fortulan, "Additive manufacturing of electrofused mullite slurry by digital light processing", *J. Eur. Ceram. Soc.*, **41** (2021) 7182–7188.
21. M.L. Griffith, J.W. Halloran, "Freeform fabrication of ceramics via stereolithography", *J. Am. Ceram. Soc.*, **79** (1996) 2601.
22. C. Hinczewski, S. Corbel, T. Chartier, "Stereolithography for the fabrication of ceramic 3D parts", *Rapid Prototyp. J.*, **4** (1998) 104–111.
23. C. Hinczewski, S. Corbel, T. Chartier, "Ceramic suspensions suitable for stereolithography", *J. Eur. Ceram. Soc.*, **18** (1998) 583–590.
24. C.J. Bae, J.W. Halloran, "Influence of residual monomer on cracking in ceramics fabricated by stereolithography", *Int. J. Appl. Ceram. Technol.*, **8** (2011) 1289–1295.
25. J. Zygmuntowicz, M. Piątek, A. Miazga, K. Konopka, W. Kaszuwara, "Dilatrometric sintering study and characterization of alumina-nickel composites", *Process. Appl. Ceram.*, **12** (2018) 111–117.
26. J. Sun, J. Binner, J. Bai, "Effect of surface treatment on the dispersion of nano zirconia particles in non-aqueous suspensions for stereolithography", *J. Eur. Ceram. Soc.*, **39** (2019) 1660–1667.
27. L.F.G. Setz, A.C. Silva, S.C. Santos, S.R.H. Mello-Castanho, M.R. Morelli, "A viscoelastic approach from α-Al_2O_3 suspensions with high solids content", *J. Eur. Ceram. Soc.*, **33** (2013) 3211–3219.
28. M.C. Newstein, H. Wang, N.P. Balsara, A.A. Lefebvre, Y. Shnidman, H. Watanabe, K. Osaki, T. Shikata, H. Niwa, Y. Morishima, "Microstructural changes in a colloidal liquid in the shear thinning and shear thickening regimes", *J. Chem. Phys.*, **111** (1999) 4827–4838.
29. D.A. Komissarenko, P.S. Sokolov, A.D. Evstigneeva, I.A. Shmeleva, A.E. Dosovitsky, "Rheological and curing behavior of acrylate-based suspensions for the DLP 3D printing of complex zirconia parts", *Materials*, **11** [12] (2018) 2350.
30. O. Santoliquido, P. Colombo, A. Ortona, "Additive manufacturing of ceramic components by digital light processing: A comparison between the "bottom-up" and the "top-down" approaches", *J. Eur. Ceram. Soc.*, **39** (2019) 2140–2148.
31. M. Roach, D. Keicher, E. Maines, B. Wall, C. Wall, J. Lavin, S. Whetten, L. Evans, "Mechanical challenges of 3D printing ceramics using digital light processing", in *Proc. 29th Annu. Int. Solid Free. Fabr. Symp.* - An Additive Manufacturing Conf., 2018.
32. H. Aydın, "Effect of La_2O_3 addition on the thermal, mi-

crostructure and mechanical properties of mullite-zirconia composites”, *Iran. J. Mater. Sci. Eng.*, 16 (2019) 10–19.