CERAMIC 3D PRINTING: COMPARISON OF SLA AND DLP TECHNOLOGIES

VERONIKA TRUXOVA, JIRI SAFKA, MARTIN SEIDL, IAROSLAV KOVALENKO, LUKAS VOLESKY, MICHAL ACKERMANN

Technical University of Liberec, Liberec, Czech Republic

DOI: 10.17973/MMSJ.2020_06_2020006

veronika.truxova@tul.cz

Complex ceramic parts tend to be difficult or even impossible to produce by conventional methods. Therefore, the 3D printing technologies have started to spread widely in the area of ceramic parts production. The aim of this paper is to compare the efficiency of Stereolithography and Digital Light Processing technologies in 3D printing of ceramic parts. Firstly, indicative chemical analysis was performed on a chosen ceramic suspension. Secondly, sample parts of different shapes were designed and printed using both technologies. Next, printed samples were analyzed using thermogravimetric and optical analyses. Finally, printed parts were debound and sintered, and final ceramic parts were consequently re-analyzed. Both technologies show the best results in the printing of thin-walled and hollow models. The DLP was significantly faster, especially when the printing platform was close to full occupancy.

KEYWORDS

3D Printing, Stereolithography, Digital Light Processing, Ceramics, Sintering, Debinding

1 INTRODUCTION

Conventional manufacturing technologies are currently being replaced or supplemented by Additive Manufacturing (AM). The AM creates a number of new applications and allows processing a wide range of materials including but not limited to metals, thermoplastic or photopolymer materials. In addition, 3D printing is also applicable to ceramic materials, for which it offers the possibility of producing small and complex parts with high printing accuracy. On a global scale, 3D printing of ceramics is still in the research phase, mainly due to the difficult interconnection of manufacturing technology with the required mechanical properties and surface finish. For stereolithography (SL / SLA) and Digital Light Processing (DLP) technologies, suspensions of different chemical composition are used.

In this article, we are focused on suspensions with ceramics particles (SiO_2 and Al_2O_3). The first part of the article describes used printing technologies and possible applications of ceramic materials. Also, general proprieties of ceramic suspensions are briefly introduced. Next, the debinding and the sintering processes of green bodies are presented. In the practical part, used materials are widely described. Then, the methods of testing and evaluation of materials, as well as test models, are described. Finally, the obtained results and conclusions are presented.

2 MATERIALS AND METHODS

Ceramic materials can be generally divided into two main groups. The first group is bioceramics and the second group is technical ceramics. In the case of bioceramics, there is a wide range of applications. It can be used in medicine as dental implants, hip, and knee implants or for bone regeneration and reconstruction. The application options are shown in Figure 1. Technical ceramics can be used in engineering as pistons, bearings, nozzles, etc.

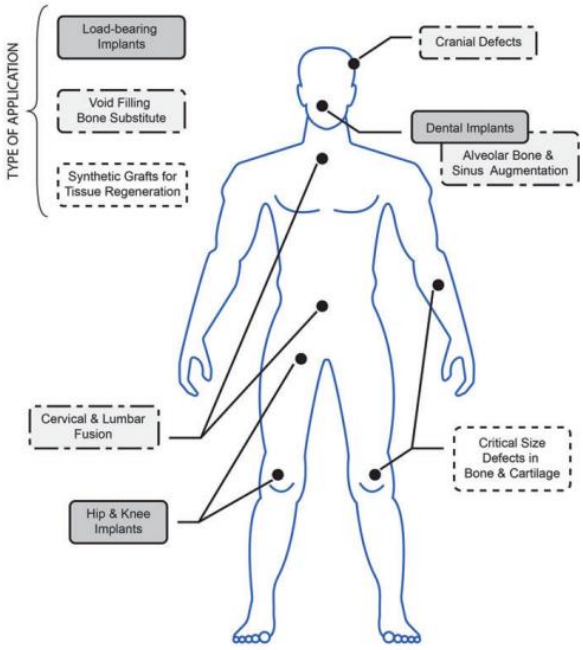

Figure 1. Applications of bioceramics. [Rodriguez 2017]

2.1 Stereolithography

The SLA is believed to be the most prominent and popular 3D printing technology that has been extensively used worldwide. It was first proposed and developed by Hull in 1986 and was later commercialized by 3D Systems Inc. The SL is a process in which a light source of a certain wavelength (usually in the ultraviolet range) is used to selectively cure a liquid surface in a resin vat containing mainly photopolymerizable monomer along with other additives in very small amounts, particularly photoinitiators. The light-activated polymerization process (i.e. a liquid monomer turns into a solid resin) generally proceeds point-to-line, line-to-layer, then layer-by-layer, along with the light scans on the liquid surface.

When the polymerization of the one layer is finished, the build platform or the resin tank moves upside or downside on the thickness of the layer. The moving direction depends on whether the building process is being operated in a top-down or bottom-up mode.

Sometimes, a wiper blade is required to level or mix the liquid surface after printing each layer. SL is capable of fabricating parts of high surface quality at fine resolutions down to the micrometer scale. A schematic diagram of the bottom-up SLA printer is shown in Figure 2.

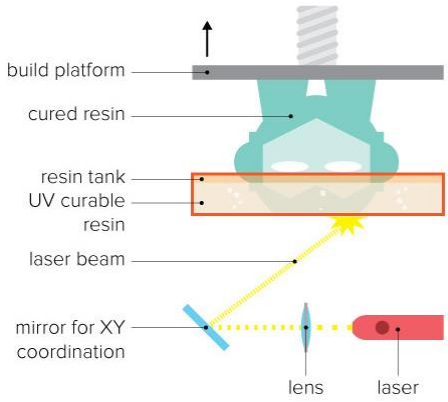

Figure 2. Schematic diagram of SLA technology. [Print 3DD]

2.2 *Digital Light Processing*

The digital light processing or digital light projection (DLP) technique is in fact a mask-based SL, in which an integral image is transferred to the photopolymerisable liquid surface by exposing the light source through a patterned mask once only. The original concept was first proposed by Nakamoto and Yamaguchi in 1996 [44] using physical masks. It was further developed and improved on by Bertsch et al. in 1997 [45] with the use of a liquid crystal display (LCD) as the dynamic mask generator. Since 2001, progress has been made by replacing LCDs with digital micromirror devices (DMDs) from Texas Instruments owing to their competitive fill factor and reflectivity (resulting in higher resolution and contrast in the light display).

The ultra-fast light switching and integral projection allow the DLP 3D printing process time to be dramatically reduced as it is much faster than the conventional SL point-line-layer scanning process. Moreover, very good feature resolution can be obtained, to several micrometres. These remarkable advantages of DLP technology have attracted considerable attention in the 3D printing industries, and it has been explored for fabricating parts with even higher accuracy and speed. [Chen 2019]

The schematic diagram of DLP technology is shown in Figure 3.

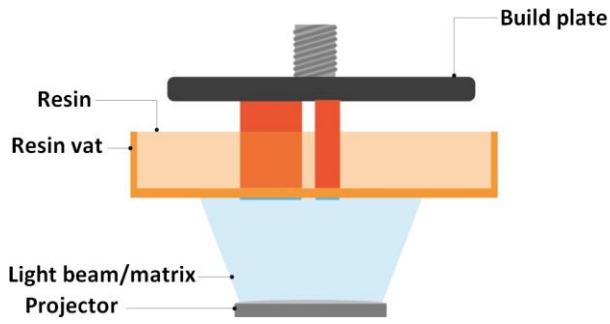

Figure 3. Schematic diagram of DLP technology. [DruckWege]

The key difference between the SLA and DLP technologies is in the type of used curing mechanism (shown in Figure 4). SLA technology uses ultraviolet (UV) laser and material is cured point by point. Compared to that, DLP technology uses a DLP projector and at the same time, a single layer is cured. Cured printed model is called “green body”.

2.3 *Suspensions*

Photopolymer ceramic material is used for SLA and DLP technologies. Suspension material is containing photosensitive polymer and fine ceramic particles. A general overview of ceramic materials is shown in Table 1.

Chemical Element	Chemical Formula
Aluminum Oxide	Al_2O_3
Zirconium Dioxide	ZrO_2
Silica	SiO_2
Tungsten Carbide	WC
Boron Nitride	BN
Aluminum Nitride	AlN
Silicon Carbide	SiC
Boron Carbide	B_4C
Titanium Diboride	TiB_2

Table 1. Ceramic materials. [Spring School 2019]

A candidate ceramic stereolithography suspension must satisfy several requirements. Since a high-quality ceramic is the goal, the freeform ceramic green body must have a high density, either for its refractory properties or so it can be readily sinterable to form a dense ceramic. [Griffith 1996]

The ceramic particles must be homogeneously and effectively dispersed in the photopolymerisable medium and remain stable without severe particle segregation for a reasonable period of time (e.g. hours to days). Unstable suspensions with rapid segregation could lead to material inhomogeneity in the fabricated parts. A good candidate for a ceramic suspension should also retain a satisfactory viscosity for proper flow during the printing process. At the beginning of ceramic SL development, suspension viscosity had to be comparable with that of commercial resin (less than 3000 mPa·s) [8], whereas current SL is also capable of working on suspensions of tens of Pa·s at a shear rate of 1000 s−1. However, this is often challenging because, on the one hand, a higher volume fraction of ceramic particles is favourable for less shrinkage and greater density (and thus mechanical strength) after sintering, while, on the other hand, a lower ceramic loading is usually required to minimise the viscosity and avoid possible segregation of the solid content. Therefore, compromises have to be made to prepare suitable ceramic suspensions for SL. [Chen 2019]

2.4 *Printing process*

Both SLA and DLP are based on photopolymerization (Figure 5). Polymerization occurs under the influence of UV light. Oligomers and monomers in the suspension are linking in polymeric chains by the influence of photoinitiators and could be crosslinked after the UV exposure. During the process, additional covalent bonds are formed to a higher molecular polymer-based whole. The polymerization process is shown in Figure 4. The required model is supplemented with supports. Then the model is sliced in software into the layers depending on the selected layer thickness. Printing takes place in individual layers, where each layer is irradiated and cured under the influence of UV laser or projector. When the printed model contains both the cured photopolymer and ceramic particles green body is obtained. For getting the final ceramic part, the photopolymer should be removed from the green body before the sintering process.

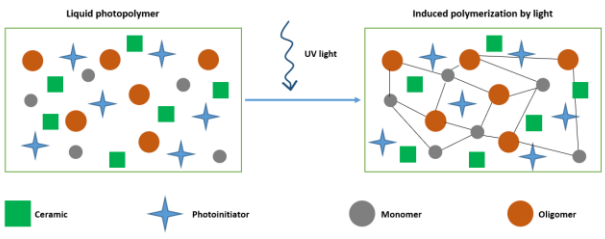

Figure 4. Graphical representation of polymerization. [Spring School 2019]

2.5 Debinding and sintering process, post-processing

To obtain the resulting ceramic parts post-processing is required. The whole process is divided into three parts – drying, debinding and sintering (Figure 5). In most cases, all three are held in a kiln in a one firing cycle. Sometimes chemical debinding can be required. During the heat treatment, the polymer is removed from the green body and desired mechanical properties are obtained.

After printing, the released particles are removed from the parts by isopropyl alcohol. Printed parts must be dry before the debinding process starts.

During the second phase of thermal treatment, the binding polymer should be removed. This phase is calling debinding. The degradation temperature of a photopolymer can be established by thermogravimetric analysis of green bodies.

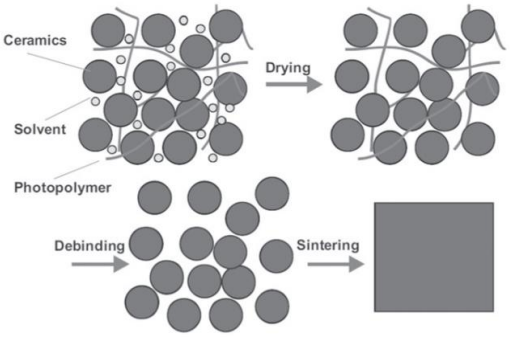

Figure 5. The firing processes. [Lantada 2016]

The specification of the heating cycle for removing the binder from green ceramic bodies, without introducing defects, is a difficult problem because of the coupling between the binder degradation kinetics and the mechanism of mass transfer within the green body, namely, gas permeation or diffusion. The controlling transport process of the decomposition products is determined by the volume fraction of binder in the space surrounding the particles. When the pore space is not completely filled and continuous porosity exists, the degradation products flow out of the body primarily via convection in a porous medium. When the binder nearly or completely fills the pore space, the degradation products reach the exterior of the green body mainly via diffusion in the remaining organic phase. [Lombardo 2016]

The debinding step is the most critical process. The used components have different evaporation or decomposition temperatures and behaviors. Thereby a reduction in weight and also in dimension occurs, which depends on the portion and composition of the organic components and especially on the temperature cycle. Furthermore, the physical characteristics of the ceramic powder, such as the particle size and the size distribution influence the debinding behavior. [Pfaffinger 2015]

The following step after the debinding is sintering. During this process, ceramic grains are sintered and compacted together. As a result, the density of the model increases but also the model shrinks volumetrically. The sintering process is shown in Figure 6. A different firing temperature profile is required for each material (consider also the size and shape of models).

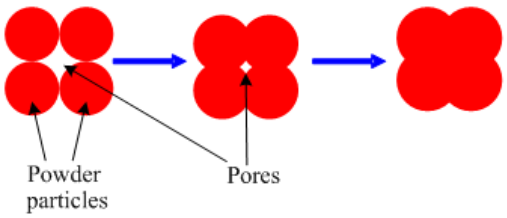

Figure 6. The sintering processes. [Kopeliovich 2014]

3 TESTED MATERIALS

Three industrially manufactured materials were chosen for testing. Ceramic Resin from Formlabs and Porcelite and Vitrolite material from Tethon3D. Each material is supplied with a material sheet. It is provided with recommended printing procedure, firing process and model design tips. Important information for each material is described below.

3.1 Ceramic Resin, Formlabs

Ceramic Resin (CR) is a composite resin from Formlabs company designed for Form 2 printers. CR is a polymer-based resin filled with silica ceramic parts. After firing CR is heat resistant over 1000°C, has a strong resistance to deformation over time and it is dinnerware safe when glazed. It is an experimental product is why it has a lower print success rate than standard Formlabs materials, and therefore benefits from a higher level of skill and attention than other Formlabs products. Ceramic Resin has special requirements for part design and print planning. Models should be designed with respecting specific rules that are required for the next heat treatment.

Ceramic Resin is best suited for printing small and thin parts. Wall thickness for fired parts should be between 2 and 10 mm. Thicker sections are more likely to crack during the burnout stage of firing and more likely to tear off supports during printing. Minimum wall thickness is 2 mm, ideal is 3 – 6 mm and maximum is 10 mm. Small walls and features may work under2 mm. Fillet internal edges to avoid stress concentrations and decrease cracking. Minimum fillet radius is 1 mm and ideal is 2 mm+. [Formlabs]

Shrinkage is caused by sintering, and gives Ceramic its strength by increasing the density of the part. General shrinkage occurs mostly uniformly across the part, and parts shrink by approximately 15% during sintering. Parts shrink more along the printed Z axis than the XY axis due to the lower concentration of ceramic particles between layers. If a model is printed at an angle, this causes a skewing effect when fired. Pre-scale the model in printed Z axis to correct this effect. The printed green part will be skewed, but the part shape will correct during firing. [Formlabs]

Ceramic particles can move during sintering, which means that the shape of the model is affected by gravity. Self-supporting structures maintain their shape, but unsupported overhangs tend to slump or collapse. Design structures that are self-supporting to minimize the volume of support structures and prevent slumping during firing. Unsupported structures, such as overhangs and bridges, are often unavoidable. There are two major ways to control the potential slumping effect. Print custom setter(s) (must be printed in the same orientation as part). Fire on supports. [Formlabs]

Due to its high filler content, Ceramic is fragile in the green (unfired) state, and requires more support than other Formlabs resins. Default support settings will typically work for small objects. Large objects may require large support touchpoints

and higher support density, especially for parts with thick cross-sections. Very small objects may be printable with smaller or fewer support touchpoints. After printing and removing supports, smooth the part surface with 120 grit sandpaper to smoothly remove support marks. Sanded support touchpoints disappear during the bisque fire. [Formlabs]

Vigorously shake the resin cartridge for one minute. If the cartridge has been sitting unused for several days, settled filler may obstruct the bite valve. Ensure the vent cap is closed, then gently push a toothpick through the pre-existing slit in the valve to clear the opening. Insufficient mixing of resin in the cartridge will result in inconsistent ceramic content within the resin, which will cause inconsistent shrinkage between the first and last prints from the cartridge. Ceramic Resin settles in the tank and must be fully mixed to print successfully. Before each print, remove the tank from the printer and use the wiper or scraper tool to fully mix resin in the tank. [Formlabs]

Wash the printed part for 5 minutes in isopropyl alcohol. Use a separate wash bucket to prevent loose ceramic particles from adhering to non-Ceramic parts. Ceramic Resin does not require post-curing, however parts must be fully dry before firing. Allow parts to fully dry before firing. [Formlabs]

Material Ceramic Resin, Formlabs is fired to a maximum temperature of 1271°C and the entire firing process takes approximately 28 hours. A graph of the firing process is shown in Figure 7.

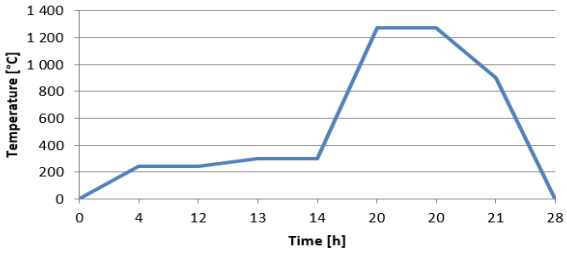

Figure 7. Firing profile for the Ceramic Resin, Formlabs. [Formlabs]

3.2 Vitrolite, Tethon3D

Vitrolite is a photopolymer based composite resin for SLA and DLP printers. After firing, Vitrolite is a glass-ceramic with high strength, low porosity/high density and thermal shock tolerance. Vitrolite does not conduct heat or electricity and is chemical resistant. Vitrolite is heavier than most 3D printing resins it may need a rough surface to adhere to the build platform. The Vitrolite resin same as Ceramic Resin from Formlabs has a special requirement for model design and printing planning.

Solid objects should be hollowed. The recommended wall thickness for Vitrolite material is in the range from 1 to 3 mm. After printing the uncured photopolymer should not be trapped inside hollowed models. If it is not possible to get by changing the shape of the model, wall halls should be added so the resin can escape. Trapped resin can cause cracks during sintering. Overhangs and bridges have to be supported by support structures with appropriate wall thickness. Thinner supports can warp. The designed model can be smaller than the supports.

Rounding outside and inside corners could help to reduce cracks during firing. Using ribs on the interior of a thin solid wall could help to reduce sagging during firing. A thin outer wall, with ribs supporting, will improve firing results

Vitrolite is heavier than most 3D printing resins. It may require increased contact size on supports. Increasing the density of the supports is also helpful. Clean your build platform with Isopropyl Alcohol. This ensures there is no other resin on the build platform that could interfere with Vitrolite adhering properly. Scratch the build plate if your parts are not sticking. Vitrolite is heavier than most 3D printing resins it may need a rough surface to adhere to the build platform. Increase the overall exposure time of the machine if prints are not sticking to the build platform. [Tethon3D]

Material Vitrolite, Tethon3D is fired to a maximum temperature of 1060°C using a slower heating ramp for thick parts over 5 mm. Subsequently, natural cooling occurs. The entire process takes up to 109 hours depending on the wall thickness of the objects. Density increases when the temperature is more than 1060°. But it is not recommended to heat above 1093°C. A graph of the firing process is shown in Figure 8.

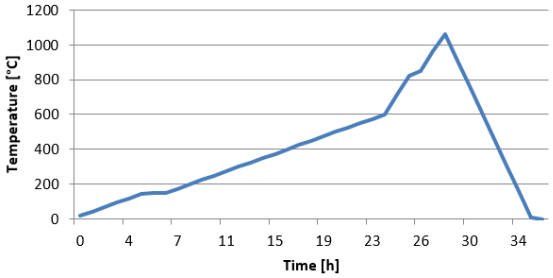

Figure 8. Firing profile for the Vitrolite, Tethon3D. Wall thickness is less than 5mm. [Tethon3D]

3.3 Porcelite, Tethon3D

Porcelite is a UV-curable porcelain resin suitable for 3D printers that utilize SLA, DLP or CLIP technologies with UV wavelengths between 350 - 405 nm. Porcelite is ideal for objects requiring high resolution details. It's capable of printing at 25 micrometer layer thickness. After firing, objects may be glazed with commercially available glazes. Glazed objects are food safe, microwave, oven, dishwasher and freezer safe. Applications for Porcelite include specialized manufacturing, fine art, engineering, architecture, design, and more. [Tethon3D]

Design recommendations are the same as for Vitrolite material (see in Chapter 3.2).

Porcelite is fired to a maximum temperature of 1240°C using a slower heating ramp for thick parts over 5 mm. Subsequently, natural cooling occurs. The entire process takes up to 112 hours depending on the wall thickness of the objects. A graph of the firing process is shown in Figure 9.

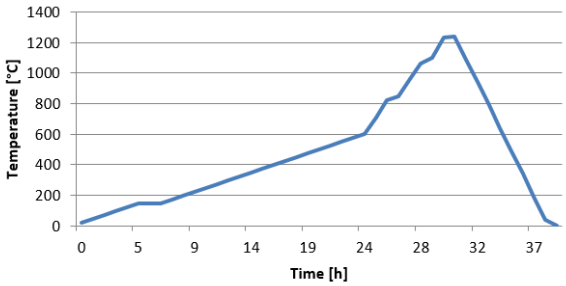

Figure 9. Firing profile for the Porcelite, Tethon3D. Wall thickness is less than 5mm. [Tethon3D]

4 RESULTS

Testing of Ceramic Resin was performed on the Form 2 SLA printer from Formlabs. Vitrolite and Porcelite materials from Tethon3D were tested on a DLP printer. Due to the unknown chemical composition of the ceramic suspensions, it was necessary to perform a chemical analysis for each material. The obtained chemical composition of materials is shown in tables: Ceramic Resin, Formlabs - Table 2, Vitrolite, Tethon3D – Table 3 and Porcelite, Tethon3D - Table 4.

Chemical Element	Content before the firing process [%]	Content after the firing process [%]
O	64,8	64,9
Si	28,1	27,2
Al	3,4	4,2
Na	2,5	2,7
K	1,0	0,9
Mg	0,3	-

Table 2. *Chemical composition of material Ceramic Resin, Formlabs.*

Chemical Element	Content before the firing process [%]	Content after the firing process [%]
O	57,2	65,2
Si	17,5	23,4
C	16,2	-
Al	6,6	8,0
Ca	1,1	1,4
Na	0,9	1,5
Mg	0,2	0,4
K	0,1	0,1

Table 3. *Chemical composition of material Vitrolite, Tethon3D.*

Chemical Element	Content before the firing process [%]	Content after the firing process [%]
O	52,3	58,6
C	23,8	10,1
Al	13,2	17,7
Si	8,8	11,7
Ca	1,3	1,6
Mg	0,2	0,4
K	0,1	-

Table 4. *Chemical composition of material Porcelite, Tethon3D.*

Thermogravimetric Analysis (TGA) was performed to determine the beginning and end of degradation (Graph 4) for each material. The percentage of ceramics and polymer in ceramic suspensions for each material was also found (Table 5).

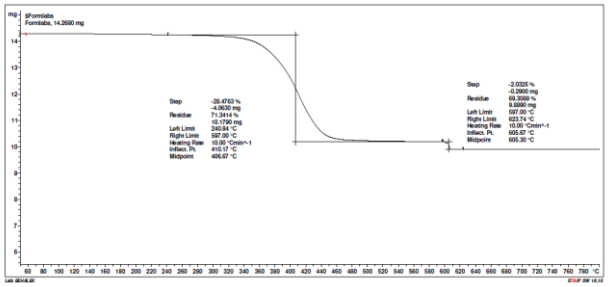

Figure 10. Results of TGA for material Ceramic Resin, Formlabs.

	Ceramic Resin (Formlabs)	Vitrolite, Tethon3D	Porcelite, Tethon3D
IDT [°C]	224,64	221,80	210,86
T50% [°C]	427,40	420,31	426,41
FDT [°C]	594,57	592,14	599,03
Residue - ceramics [%]	69,31	60,87	63,07
Residue - polymer [%]	30,69	39,13	36,93

Table 5. *Results of TGA for material Ceramic Resin, Vitrolite and Porcelite.*

The materials did not have the desired final properties during the testing. Even if the manufacturer´s instructions for each material were followed. For this reason, the models (Figure 11) were changed during the testing as well as printing parameters and firing profiles (debinding and sintering process). Unfortunately, none of the changes led to the complete elimination of the main problem – cracking of samples, especially in layers of printing (Figure 12 and Figure 13).

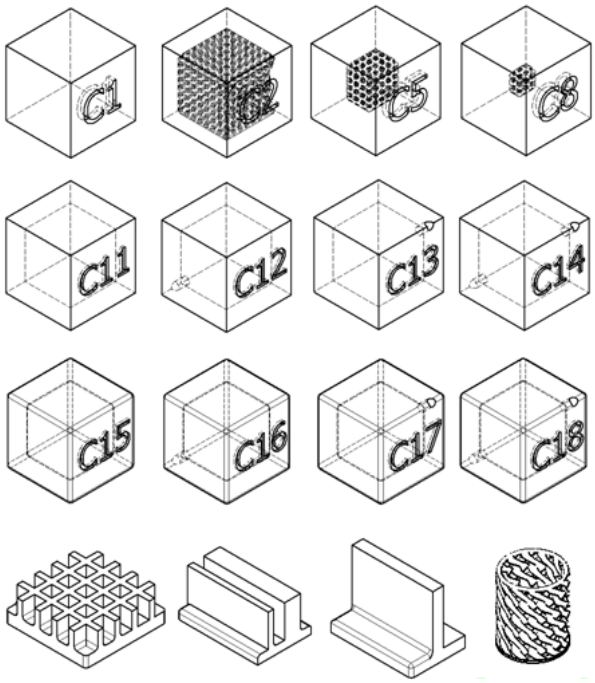

Figure 11. Printed models during the materials testing.

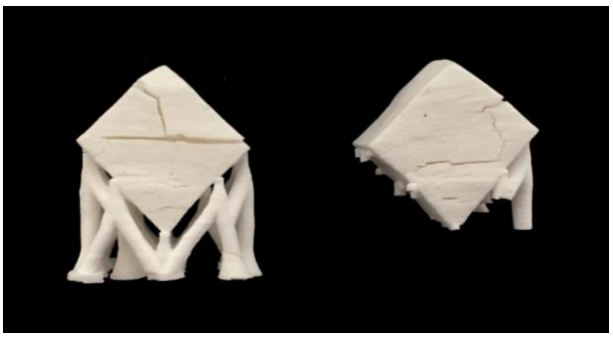

Figure 12. Models C11 and C14 (material Porcelite, Tethon3D) after the firing process.

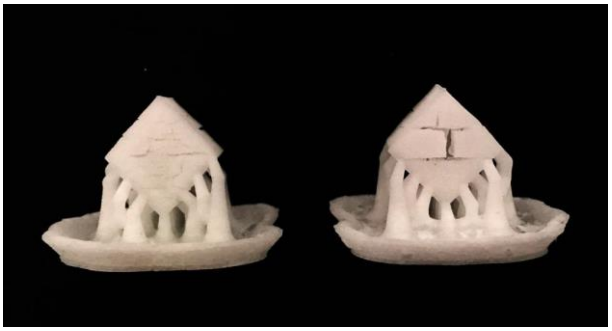

Figure 13. Models A11 and A14 (material Ceramic Resin, Formlabs) after the firing process.

A detailed image of the surface for Ceramic Resin before and after the firing process is shown in Figure 14.

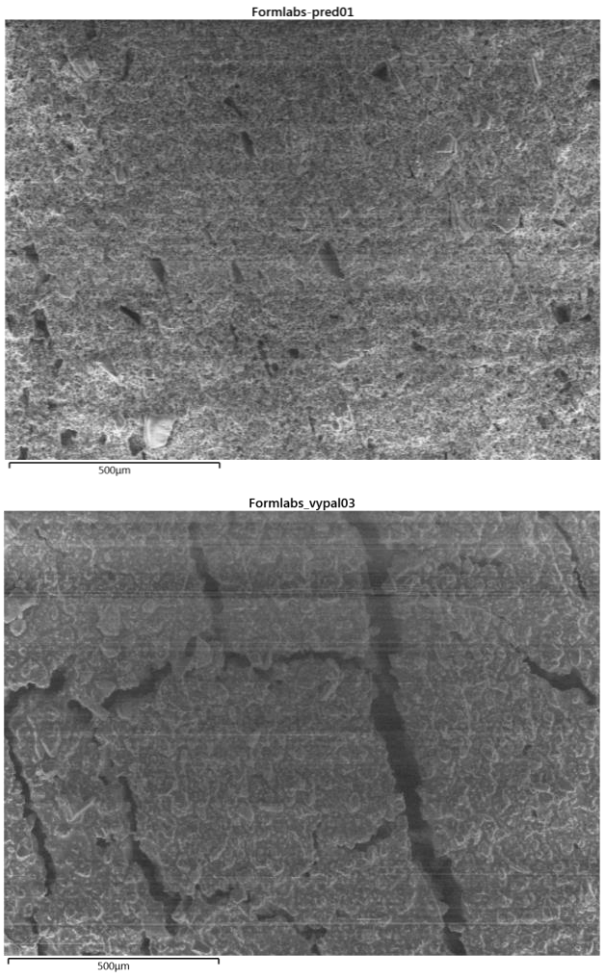

Figure 14. Image of Ceramic Resin, Formlabs before (above) and after the firing process (below).

The best influence on the reduction of cracks was the change of samples to thin-walled models (Figure 15 and Figure 16).

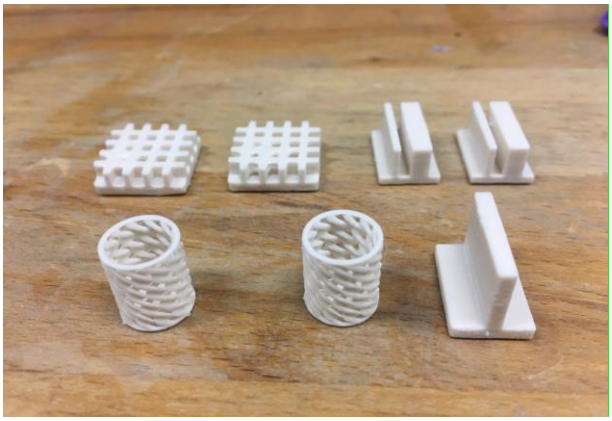

Figure 15. Thin-walled green models after the DLP printing (material Porcelite, Tethon3D).

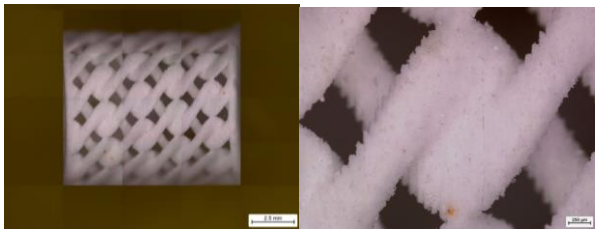

Figure 16: Thin-walled spiral model after the sintering (material Porcelite, Tethon3D).

The actual volume shrinkage of the models was higher than given shrinkage by the manufactures of the materials. This causes internal stresses during the firing process and cracking of the samples. Especially in models with larger wall thickness. For Porcelite the manufacturer (Tethon3D) reports a volume shrinkage from 13% to 17%. The actual volume shrinkage is more than twice higher as shown in Table 6.

	Volume shrinkage [%]
C1	36,66
C3	31,81
C4	32,94
C5	37,02

Table 6. Volume shrinkage of models after the firing process, material Porcelite, Tethon3D.

During the testing, SLA and DLP printing technologies were compared. DLP printer has a 30-50% shorter printing time compare to SLA. The printing time of the DLP printer depends on the total layer numbers that depend on the height of the models and the layer thickness. Also, the exposure time of each layer and the waiting time between layers influences the printing time. Thanks to each layer of all models are printed at one time, total printing time does not depend on platform occupancy.

Compared to that, for an SLA printer, printing time depends on a number of models. Due to the necessity to cure each model point by point, printing time is longer when multiple models are printed. The printing time also depends on the layer thickness and size of the models.

It has been found that the DLP printer can print small models (Figure 17) in higher quality compared to the SLA printer.

Figure 17. Fine detail models after the DLP printing process (Porcelite, Tethon3D).

5 CONCLUSION

Despite that instructions were provided for each material by suppliers and followed during the testing. The models did not achieve the desired and appropriate final properties. The instructions are not entirely appropriate for the real process and several adjustments are needed to be changed to achieve the required results.

Several changes were done during the testing. However, it is necessary to know the composition of each ceramics suspension to accurately optimize individual technological parameters. The unknown exact composition of suspensions, including grain size, has proved to be a significant limiting factor during the testing.

For further research in the field of printing polymer ceramic materials, it is recommended to use non-commercial materials, where the content and proportion of individual chemical elements including grain size will be fully known.

It is also recommended to divide the process of debinding and sintering and then evaluate which of the processes has the effect of model cracking. Then adequately change the firing profile considering previous results and chemical composition of materials.

ACKNOWLEDGMENTS

This publication was written at the Technical University of Liberec as part of the project (SGS-2019-5012) "Research and application of 3D printed functional parts in the Formula Student project at TUL." with the support of the Specific University Research Grant, as provided by the Ministry of Education, Youth and Sports of the Czech Republic in the year 2020

REFERENCES

[Aniwaa 2019] The 13 best resin 3D printers (SLA/DLP/LCD) in 2019, September 2019. Available from www.aniwaa.com.

[Chen 2019] Chen, Z. and Li, Z. Journal of the European Ceramic Society, April 2019, Volume 39, Issue 4, 661-687

[DruckWege] Direct Light Processing (DLP), Available from www.druckwege.de.

[Formlabs 2018] Formlabs, 2018, May 2018. Available from www.formlabs.com.

[Griffith 1996] Griffith, M. L. and Halloran, J.W. Journal of the American Ceramic Society, October 1996, Volume 79, Issue 10,2609-2618

[Hull 1986] Hull, C. W. Apparatus for production of three-dimensional objects by stereolithography, 1986, US Patent 4,575,330. doi: 10.1145/634067.634234.

[Kopeliovich 2014] Kopeliovich, D. Substances & Technologies, 2014. Available from www.substech.com.

[Lantada 2016] Lantada, A. D. and Schwentenwein, M. Smart Materials and Structures, April 2016, Volume 25

[Lombardo 2016] Lombardo, S. J. Journal of the American Ceramic Society, October 2016, Volume 100, Issue 2,529-538

[Petit 2019] Petit, F. Spring School: 3D Printing and ceramic processes, Maubeuge, April 2019

[Pfaffinger 2015] Pfaffinger, M. and Mitteramskogler, G. Materials Science Forum, July 2015, Volume 825-826, 75-81, ISSN 1662-9752

[Print 3DD] Print 3DD, Available from www.print3dd.com.

[Rodriguez 2017] Rodriguez, C.A. and Padilla, H.L. 3D Printing and Biofabrication. Springer International Publishing AG, part of Springer Nature 2018. ISBN 978-3-319-40498-1

[Spring School 2019] Spring School Maubeuge - UPHF, 3D

[Tethon3D] Tethon3D. Available from www.tethon3d.com.
Printing and ceramic processes, April 2019.

CONTACTS:

Ing. Veronika Truxova
Technical University of Liberec, Department of Manufacturing Systems and Automation
Studentska 2

461 17 Liberec 1

Email: veronika.truxova@tul.cz

Tel: 00420 485 35 3801