UNIVERSITAT DE BARCELONA

Development and optimization of a Low Temperature Co-fired Ceramic suspension for Mask-Image-Projection-based Stereolithography

Joana Gonçalves Fernandes

CONLUSIONS AND HORIZONS

CHAPTER VI

The greatest achievement of this work is the possibility of printing complex geometry with a LTCC material, which has never been demonstrated before in the field of additive manufacturing. This is the beginning of new breakthroughs in multimaterial printing for electronic applications.

To accomplish this, the different steps of the whole process were successfully achieved, i.e, formulation of a LTCC photocurable suspension, its printability by MIP-SLA technology, and the post-thermal treatment of debinding and sintering.

The development and optimization of a LTCC suspension have been discussed in this work, based on the inherent requirements of the selected AM technology, i.e., viscosity lower than 5 Pa·s (at 2 s^{-1}) and high sensitivity to the visible light, maximizing the solid load for further thermal treatment. On this subject, the whole experiment was focused on the rheological and photocuring behavior of the LTCC suspension.

To accomplish these aims, an initial study of the dispersing medium based on photocurable resins was shown. The main requirements for the selection of the resin were its viscosity and the sensitivity to the light projected. Once the viscosity drastically increases by adding the ceramic particles, increasing also the light scattering which leads to the reduction of the cure depth, the viscosity must be as low as possible with the highest sensitivity to the visible light projector. Is was concluded that the spot-lv resin is the resin which presents the optimal balance between both characteristics.

The influence of the solid load was analyzed in terms of both photocuring and rheological behavior. The energy dose necessary to initiate the photopolymerization process (the critical energy dose) decreases for larger concentrations of ceramic powder, which corresponds to a larger surface occupied by inert particles. On the other hand, the sensitivity parameter decreases as a result of the addition of ceramic particles. This means that the maximum cure depth decreases for higher ceramic loads, due to the scattering of the light by the ceramic particles. Thus, the higher the solid load, the lower the sensitivity of the LTCC suspension.

Regarding the rheological behavior, it was demonstrated that the addition of ceramic powder drastically increases the viscosity, being more evident for volume fractions larger than 72 wt.%. The ceramic suspensions present a proper photocuring behavior for the MIP-SLA machine. However, the maximum viscosity for the MIP-SLA technology is 5 Pa·s (At 2 s^{-1}), therefore, although the photocuring behavior is appropriate for all studied suspensions, the viscosity must also be suitable for the printing process.

In this regard, after the dispersant concentration and dispersing time optimization, the maximum solid load was established at 67 wt.% LTCC with a 1.5 wt.% of dispersant, with respect to the solid load, with a viscosity of 4.5 Pa·s at 2 s^{-1}.

Furthermore, based on the previous results, the dispersing time was optimized for large-scale production in a horizontal ball mill. It was demonstrated that the viscosity of the suspension decreases during the dispersing process, which is mainly driven by the deagglomeration of the particles and the adsorption of the dispersant onto the particle surface. The optimal dispersing time, which corresponds to the minimum viscosity, was achieved in a range of 50 to 95 hours, with a viscosity of 2.8 Pa·s at 2 s^{-1}. For higher dispersing time, the viscosity increases due to the particle size reduction and lack of dispersant for the new particle surface area. Moreover, the photocuring behavior was studied along the dispersing time, where a direct correlation of particle size distribution and photocurable behavior was demonstrated. The particle size reduction leads to an increase in the light scattering, which attenuates the penetration of the light through the ceramic suspension, limiting the polymerization of the resin. In this regard, a decrease of the sensitivity of the suspensions was observed as the particle size decreases. However, as the volume of LTCC particles is constant along the experiment, the critical energy dose remains constant. This is explained by the substitution of the curable resin by inert ceramic particles, decreasing the energy dose necessary for the polymerization. This effect is related with the oxygen inhibition that occurs in acrylic systems, i.e., if a lower surface of resin is exposed to the air by increasing the ceramic powder load, a lower energy dose is needed to initiate the photopolymerization reaction.

It was demonstrated that the addition of an antifoam into the formulation improves air bubble elimination, slightly increasing the viscosity and maintaining photocuring behavior of the LTCC suspension. The stability of the suspensions was analyzed for five months and, although the suspensions presented an evident sedimentation, it was demonstrated that the optimized LTCC suspension could be reused after the five months. The recuperation of the optimized LTCC suspension was achieved applying a mechanical stirring, ensuring the same results in terms of rheology, particle size distribution, and photocuring behavior.

The optimized LTCC suspension has a viscosity of 3.6 Pa Pa·s at 2 s^{-1}, meaning a viscosity 90 times higher than the spot-lv resin without ceramic particles. On the other hand, the sensitivity decreases 95 % with the addition of the ceramic particles: the sensitivity is 850 µm for the resin and 41 µm for the optimized LTCC suspension. Concerning the critical

energy dose, the values obtained were 48 mJ·cm^{-2} for the resin and 15 mJ·cm^{-2} for the LTCC suspension, meaning a reduction of 69 % of the energy needed to initiate the polymerization process when the ceramic particles is added.

The printability features of the optimized LTCC photocurable suspension were studied regarding the influence of the layer thickness, the printing area, and the resolution in the XY-plane and Z-direction.

The printing process was performed at different layer thicknesses while maintaining the applied energy dose, demonstrating that the printed pieces do not present delamination between layers. Moreover, excellent accuracy was obtained in the z-direction for the layer thickness of 25, 50, and 75 µm.

However, an overgrowth of 10 % was detected in the z-direction. This effect is explained due to the surface tension effects which lead to a shrinking of the liquid LTCC suspension to minimize the surface area. Some strategies could be applied to minimize this effect, such as increasing the wait time, the reorientation of the piece minimizing the area of the last printed layers, and, if possible, reducing the layer thickness.

The studies summarized in this chapter provide conclusive evidence that the shrinkage of the printed pieces presents significant differences in the X and Y-axes. It was demonstrated that the shrinkage in the X-axis is 1.8 ± 0.8% and the shrinkage observed for the Y-axis is 2.9 ± 0.7 %.

Moreover, the excess width in the XY-plane is not uniform along the printing area and presents different values on both axes. It was demonstrated that the X-axis presents less excess width than in the Y-axis. In the X-axis the variation of the excess width is 90 µm along the printing area, however the excess width in the Y-axis is 166 µm. Likewise, the values of the excess width are higher in the Y-axis than in the X axis, with values ranging between 50-215 µm and 60-150 µm, respectively.

The energy distribution of the pixels, with a higher energy density along the Y-axis, could directly affect the shrinkage of the pieces and increase the value of the excess width. The effect of inhomogeneities along the platform could be explained by the parallelism of the

light projection, which lead to different path lengths of the light, varying the energy dose. Another important factor is the focus level, i.e., not all the points are equally focused.

Regarding the fidelity of the patterns over the printing area, the experiments demonstrate that the worst results are placed where the difference between the dimensional variation in the X-plane and the Y-plane is greater, considering both excess width and shrinkage.

As expected, it was proven that the excess width does not affect the accuracy in the z-axis. However, in all axes the effect of rounding of the perimeters were observed for the cavities printed in all the planes (XY, XZ, YZ). Nevertheless, in the ZX plane and ZY plane, the patterns are reduced by the excess width, but not the height of the cavities. Regarding the Z-direction, the geometry is affected by the print-through effect, mainly for the quadrangular cavities. Thus, the minimum detail possible to print in the XZ and YZ planes is 500 µm side/diameter, taking into consideration that the printed cavities are reduced by the excess width and height by the print-through effect. The minimum feature size in XY-plane is 500 µm for the circular cavities and 1000 µm for the quadrangular ones. As mentioned, the rounding of the corners is present in all quadrangular cavities printed in the XY-plane, limiting its resolution. For patterns above 500 µm, the excess width has the same effects, with a value of 90 µm for the optimized LTCC suspension. On the other hand, for the patterns below 500 µm, the excess width is higher with a value of 150 µm. As the pattern size decreases, the effect of the edges becomes more significant, increasing the excess width.

In this sense, to ensure a correct pattern transfer of a quadrangular shape the details must be higher than 500 µm in the XY-plane, considering that the corners are rounded if the same energy dose is applied in 2D image, with a total size reduction of 180 µm. On the other hand, the circular shape could be designed with 500 µm, knowing that the final shape will be reduced to 200 µm.

Regarding the debinding process, the presence of oxygen in the debinding atmosphere negatively affects the process due to the polymerization of the residual monomer. As a result, the debinding process could not be successfully obtained in air atmosphere, even for samples with 500 µm of wall thickness and lowering the temperature rate at 0.1 $^{o}C \cdot min^{-1}$.

The debinding process was analyzed and performed in two different atmospheres: oxidative and non-oxidative. The exothermic peaks related to the polymerization of the uncured monomer were observed for both atmospheres, however the energy peak intensity is higher for the experiments performed in the oxidative one. This result is explained by the oxidation of the radical monomer in the presence of oxygen, which is also associated with an energy release. As a result, the exothermic peak in the oxidative atmosphere presents a higher specific enthalpy and higher intensities, because polymerization of and oxidation of some radical monomers occurs simultaneously, and both phenomena involve exothermic reactions.

The polymerization of the monomer is not uniform along the cured depth, and as a consequence, the degradation of the resin occurs differently along the green body. In this regard, thermal degradation proceeds uniformly when a non-oxidative atmosphere and slow temperature rates are applied during the debinding process. The exothermic peak, associated with the polymerization of the residual monomer, decreases in intensity due to the reduction in temperature rate and using a non-oxidative atmosphere. Moreover, the energy released is also minimized under this condition, preventing the formation of cracks during the debinding process.

The delamination for the debinded pieces also occurs when the process is performed under a non-oxidative atmosphere. However, this defect occurs for debinding rates higher than 0.5 $^{o}C \cdot min^{-1}$. For rates higher than 0.5 ºC/min, both exothermic peak intensity and the amount of energy release during the polymerization of the residual monomer increases, causing the cracking of the pieces. The cracks are the consequence of the stress relaxation, in this sense for lower temperature rates this relaxation is performed in a controlled manner and does not cause crack formation. On the other hand, if the temperature rate is too high, this relaxation occurs through a crack formation. Moreover, it is known that the polymerization shrinkage during the printing process causes built-in stresses which can also lead to the deformation and delamination during the debinding process. Thus, the crack formation from the stresses produced during the printing process could also be minimized, reducing the temperature rate. In conclusion, the maximum debinding rate is 0.5 $^{o}C \cdot min^{-1}$ in a non-oxidative atmosphere, for a certain geometry and printing conditions, i.e., for

cylinders of 10 mm diameter, a height of 5 mm and a wall thickness of 2 mm, printed with 25 µm of layer thickness with 10 seconds of exposure time, which means a cure depth of 150 µm. By increasing the layer thickness to 50 and 75 µm, using the same energy dose, some slight delamination was observed after the debinding process. In this regard, the relation between cure depth and layer thickness is optimal when the cure depth is six times higher than the layer thickness, preventing the cracking of the pieces during the thermal debinding.

During the debinding process under a non-oxidative atmosphere, the carbon residues from the thermal degradation are eliminated in a previous step of the sintering process, in an oxidative atmosphere. At the sintering step, a dwell at 500 ^{o}C is performed for its elimination, followed by the densification of the pieces at 870 ^{o}C. It was demonstrated that if the pieces do not present defects after the debinding process, the sintering could be performed at a higher rate ensuring a correct densification, without cracking. The final density after the whole optimized thermal treatment is 3.213 g·cm^{-3}, meaning 95 % with respect to the theoretical density.

Regarding the nanoindentation, it was demonstrated that the sintered piece shows an isotropic behavior in terms of mechanical properties, independent of the layer-by-layer strategy. The observed differences of the Young's modulus values are associated with the LTCC phases, resulting in E value around 140 GPa for the contribution of the hardest phases and around 80 GPa for the contribution of the softest phases. Moreover, the distribution of the Young's modulus values is uniformly distributed over the piece in concordance with the uniform distribution of the different phases of the LTCC.

The successfully fabrication of complex pieces validates the whole process: from the LTCC suspension to the final thermal treatment.

Moreover, the initial proof-of-concept of AM hybridization was demonstrated by a multimaterial printed piece, demonstrating that the number of silver layers printed by the inkjet system is critical for the debinding and sintering processes.

To conclude, the development and the optimization of a photocurable LTCC suspensions was successfully achieved for the MIP-SLA technology, resulting in a final ceramic pieces with a high level of geometrical complexity and resolution.

Horizons

The knowledge developed throughout this thesis could be explored with other ceramic materials, expanding the range of applications. Furthermore, once the technological limits are well established, new developments could be focused on the new possibility of design freedom, redesigning existing products, or even the development of new products.

Nowadays the hybridization of AMT is a clear tendency that will greatly develop the field of multimaterial printing and which will surely pave the way to new breakthroughs in printing electronics. The hybridization of AMT presented in this work allows for the fabrication of electric circuitry embedded within 3D ceramic structures, and that holds the promise of exploring and designing new materials with new levels of functionality and customization.

From this point of view, the optimization of the hybrid process and multimaterial printing is one of the most promising challenges for further work. One possibility to accomplish this challenge is to use an inkjet system with a higher nozzle diameter to deposit a higher amount of conductive materials. Another approach, which has been studied, is the hybridization of the MIP-SLA with a Direct Ink Writing system, allowing to work with conductive inks at higher solid loads. Not only nanoparticles could be worked with, but other particle sizes could be used for ink development as well. In this regard, the materials formulation and optimization is also needed for the success of hybridization of AMT.