

Binder development for the 3D printing of Ceramic

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Abstract:

The influence of monomer, plasticizer structure and concentration was evaluated on key properties required to achieve high performance binders for the 3D printing of ceramic using vat photopolymerization. A combination of monomers M1 and M5 featuring different structures and functionalities was mixed with controlled amount of plasticizer P1 and found to provide suitable balance of reactivity, green strength, viscosity, stability and residual ash content. These properties are allowing the additive manufacturing of complex structures on traditional stereolithography and Digital light processing printers.

Introduction:

Additive manufacturing (or 3D printing) of ceramic has been a subject of research for more than two decades and leads every day to new technologies and discoveries. These developments allow the creation of complex structures and design that would not be achievable using traditional methods. In most cases, the core principle behind each method remains similar, and consists of the solidification in a layer-by-layer fashion of a slurry made of UV-reactive binders mixed with ceramic powder to produce an object of the desired shape ^[1]. The green body is then placed in a furnace, and the binding resin is fired off the printed part, leaving a very brittle inorganic structure. This structure is then carefully sintered to obtain the final solid ceramic object.

Two main technologies using UV light to produce ceramic articles coexist and provide different challenges and benefits. The first approach uses a stereolithography (SLA) or digital light processing (DLP) technology to render an object from a combination of ceramic and UV-reactive ink ^[2]. The main benefit of this method comes from the high resolution it can achieve, producing parts with layer thickness down to 50 microns or lower. This fine resolution allows these parts to be easily used in many applications such as biomedical and energy ^[3]. One main challenge with this technology ^[3] comes from the viscosity limitations required during the printing process. As the resin needs to flow to be printable, it usually requires higher amounts of monomer, leading to lower density and/or higher shrinkage of the final part. An alternative approach to this technology is binder jetting. By depositing UV-curable resin into a bed of ceramic powder and exposing the infused powder to UV light, it becomes possible to print complex structures while maintaining high solids loadings and thus, higher density at lower shrinkage. The challenge with this technology lies in a reduction in resolution, that lands in the range of 200um or greater.

Even if the theory behind DLP and binder jetting technologies seems well understood, specific aspects still require improvement to ensure successful printing of technical ceramics at the highest density possible. Achieving those higher densities could in specific cases open up new industries, which can sometime be limited by the lower properties of the printed ceramics, compared to their powder-pressed equivalent^[4], ^[5]. One approach to overcome these technical challenges consists of improving the UV-curable resin by optimizing monomer, plasticizer composition and concentration ^[6]. Control of these inputs allows tuning of rheology, reactivity and thermal decomposition of the resin, improving final properties of the sintered ceramic part.

Experimental (methods, materials)

Monomers and plasticizers were first mixed with photo-initiators, photo-blockers and/or dispersants for sufficient time to allow appropriate dispersion of additives. Ceramic powder was added incrementally (10% maximum at a time) and mixed using high shear mixer for at least 4h between each increment. 3D printed green samples were produced using stereolithography process. Fabricated parts described in this work were printed using a 50um resolution to ensure good dimensional resolution of the 3D printed parts^[6]. Debinding and sintering were performed by heating the green parts in air from room temperature to sintering temperature, applying specific ramps and plateau to offer proper decomposition of the binder and solidification of the fillers.

Viscosity of the formulation was measured using a cone plate rheometer. Dispersion of the ceramic particles following mixing with the binders was evaluated by estimating the time required to achieve complete dispersion of the powder using the method described above and considering time superior to 4h per increment of powder to be significantly long (ranked 5) and time shorter than an hour to be significantly short (ranked 1). Stability of the formulation was estimated by evaluating the time needed for the powder to sediment after the mixing, taking in consideration the desired 3D printing application and thus the need for formulations to remain stable for approximately 8 to 12h. Stability lower than 2h were ranked 5 while stability superior to 8h were ranked 1. The re-dispersability of the formulations were evaluated by remixing formulations after sedimentation using tongue depressor. Impossibility to re-disperse the particles was ranked 5, significant efforts to re-achieve homogeneity of the formulation was ranked 4 and simple agitation of the container by hand was ranked 1.

Reactivity of the resins was evaluated by selectively exposing different sections of the resin to particular dosages of light. The resulting thickness was recorded and plotted to extract a critical energy to cure and depth of penetration, commonly referred to as E_c and D_p in the 3D printing industry^[7]. Archimedes' technique was performed to measure the density of the sintered parts using a scale equipped with a Satorius Imersion density kit. Thermogravimetric analysis (Q500, TA Instruments) was performed to study the behavior of the green samples during firing of the organic binder.

Results and discussion

1. Monomer selection

Monomers represent the key ingredient of the organic formulation, as they are necessary to achieve sufficient curing of the liquid system under UV light exposure. As literature ^{[9], [10]} and past experiments have already shown, structure of the monomers has a significant influence on all studied properties including viscosity profile, reactivity and thermal decomposition. Six monomers were designed for this study due to their expected greater debinding potential. Following table one shows the influence of those monomers on the viscosity, stability, re-dispersability, depth of penetration of the light upon curing, critical energy to achieve polymerization and residual ash content in air and in an inert atmosphere. Formulations are composed of 20.1% of the monomer of interest, 12.1% of plasticizer P1, 2.6% of dispersing agent D1, 65% of ceramic powder C1, 0.125% of Speedcure TPO and 0.04% of Benetex OB+.

| Monomer | M1 | M2 | M3 | M4 | M5 | M6 |
|--|-----------|-----------|-----------|------------------|-----------|-----------|
| Functionality | 2, MA | 2, MA | 2, MA | 1, A | 2, A | 2, A |
| Molecular weight (g/mol) | 336 | 736 | 254 | 220 | 226 | 308 |
| Family | polyether | polyether | Aliphatic | Cyclic Aliphatic | Aliphatic | polyether |
| Dp (mills) | 9.3 | 7.6 | 0.6 | 8.3 | 7.3 | 8.6 |
| Ec (mJ/cm ²) | 44.3 | 28.3 | 95.3 | 23.2 | 8.4 | 25.6 |
| Formulation Viscosity (Cp.s) | 1135 | 6386 | 878 | 2300 | 1216 | 1535 |
| Dispersion (ranked 1 to 5) | 2 | 5 | 2 | 1 | 1 | 3 |
| Stability (ranked 1 to 5) | 3 | 1 | 3 | 2 | 1 | 4 |
| Re-dispersability (ranked 1 to 5) | 5 | 2 | 4 | 1 | 1 | 4 |
| Residual ash content in air (%) | <0.1 | <0.1 | 0.3 | 0.7 | 0.5 | 0.2 |
| Residual ash content in N ₂ (%) | 0.2 | <0.1 | 1.2 | 1.5 | 2.0 | 1.0 |

Table 1: Monomer individual evaluation

As shown, each monomer provides different benefits on the measured physical properties. Those differences are greatly affected by the material design and show some interesting effects as we consider different molecular weights and monomer structures.

Acrylates (A: M4, M5 and M6) provide the lowest critical energy to induce polymerization (Ec) thanks to their faster kinetics compared to methacrylates (MA). This difference is common in radical polymerization and is due to the secondary radicals generated in the case of acrylates, which exhibit lower stability than the tertiary radicals generated from methacrylates. This lower stability is thought to increase the reactivity of the propagating end, inducing faster polymerization.

On the other hand, Poly Ether (PE) based (meth)acrylates tend to exhibit the lowest residual ash content in both air and inert atmosphere (N₂) thanks to the easy debinding process of the poly ether repeat units compared to aliphatic structures. In the case of PE-based (meth)acrylates, the binder easily decomposes itself into low molecular weight units while aliphatic structures tend to generate carbon residues of lower volatility and thus leading to a higher generation of ashes.

Acrylates also tend to exhibit higher residual ash content than methacrylates. This difference is supposed to be due to the higher degree of conversion achieved by acrylates when cured in similar conditions, leading to a higher degree of cross-linking with acrylates.

Despite being known for their poor thermal decomposition profile, cyclic aliphatic M4 shows better thermal decomposition in inert atmosphere than aliphatic M5, which is most likely due to the differences in functionality between the two molecules.

Overall, monomer M5 appears to provide interesting balance of properties, exhibiting low viscosity, suitable reactivity but poor decomposition in inert atmosphere. Combination of monomers was thus evaluated as a potential solution to achieve formulations exhibiting all targeted properties. Following table two shows the same properties measured with formulations composed of 10% of the monomer of interest, 10% of M5, 12.1% of plasticizer P1, 2.6% of dispersing agent D1, 65% of ceramic powder C1, 0.125% of Speedcure TPO and 0.04% of Benetex OB+.

| Monomer | M1 + M5 | M2 + M5 | M3 + M5 | M4 + M5 | M5 + M6 |
|--|-----------|-----------|-----------|------------|----------|
| Functionality | 2, MA + A | 2, MA + A | 2, MA + A | 1.5, A + A | 2, A + A |
| Dp (mills) | 13.7 | 7.4 | 2.3 | 8.9 | 12.5 |
| Ec (mJ/cm ²) | 64.9 | 28.4 | 75.2 | 17.4 | 25.2 |
| Formulation viscosity (Cp.s) | 1232 | 9492 | 1758 | 4481 | 2820 |
| Dispersion (ranked 1 to 5) | 1 | 2 | 1 | 1 | 2 |
| Stability (ranked 1 to 5) | 1 | 1 | 2 | 1 | 3 |
| Re-dispersability (ranked 1 to 5) | 1 | 1 | 1 | 1 | 2 |
| Residual ash content in air (%) | <0.1 | <0.1 | 0.6 | 0.6 | 0.2 |
| Residual ash content in N ₂ (%) | 1.4 | 0.5 | 2.3 | 1.7 | 1.6 |

Table 2: Combined monomers evaluation

Significant improvement in the stability, dispersion and re-dispersability can be observed from this second set of experiments combined with very promising viscosity, reactivity and residual ash content. Combination of M1 and M5 shows viscosity lower than 1500 Cps, making it printable on most SLA-DLP printers while providing stability sufficiently high to make the resin printable.

2. Plasticizer selection

Plasticizers are diluents used to improve firing of the binder and reduce internal stress generated during UV-curing ^[11]. Thanks to their non-reactivity, the plasticizers strongly help reducing curing shrinkage and thus delamination generated between adjacent layers during the 3D printing process. They also play a key role during the firing process through two complementary mechanisms. First and as explained above, their non-reactivity helps reducing the cross-link density, hence assisting decomposition of the polymerized network. The second key benefit comes from their low boiling point. Once the temperature reaches the boiling point of the plasticizer, the chemical starts to flow out of the cured system, reducing the stress within the parts and assisting the polymerized binder in its own decomposition, providing lower residual ash content in the final ceramic parts and reduced amounts of cracks in the structure.

As they represent a significant portion of the organic formulation, the plasticizers affect the rheology, stability and reactivity of the resin. Incorporation of these ingredients further reduces cross-linking density and can either increase or reduce the viscosity of the formulation. In order to accurately evaluate their influence in the formulations, two structures of plasticizers have been evaluated and compared to a reference monomer. Table 3 displays the influence of plasticizers P1 and P2 on the viscosity of the sole organic formulation, viscosity mixed with 50% of ceramic C1, 10% of M1, 10% of M5 and 2.6% of dispersing agent D1 and re-dispersability of the filled formulation compared to a reference PE-based di-functional acrylate.

| Plasticizer | Ref | | | P1 | | | P2 | | |
|---|------|------|------|------|-------|-------|-----|-----|------|
| | 742 | | | MW1 | | | 92 | | |
| Molecular weight (g/mol) | | | | | | | | | |
| %wt | 20 | 35 | 50 | 20 | 35 | 50 | 20 | 35 | 50 |
| Binder Viscosity (Cp.s) | 12.5 | 21.8 | 30.8 | 7.85 | 16.2 | 25.8 | 896 | 967 | 1003 |
| Viscosity w/ 50% Ceramic (Cp.s) | 75 | 78.5 | 110 | 74.8 | 158.4 | 164.3 | / | / | / |
| Dp (mills) | 9.4 | 10.6 | 7.1 | 6.4 | 6.4 | 6.7 | / | / | / |
| Ec (mJ/cm ²) | 16.8 | 19.3 | 10.4 | 11.5 | 12.7 | 14.6 | / | / | / |
| Re-dispersability (ranked from 1 to 5) | 4 | 4 | 4 | 1 | 1 | 1 | 5 | 5 | 5 |

Table 3: Plasticizers family evaluation

As expected, plasticizers have a strong influence on the rheology and stability of the formulations. In the case of plasticizer P2, the slight incompatibility of the plasticizer with the binders led to the formation of solid spherical aggregates of ceramic. This unique type of structuration is supposed to be due to a phase separation between the monomers and the plasticizer, which was not observed before the addition of the ceramic powder. Due to stronger compatibility of the plasticizer P2 with the ceramic rather than with the monomer, phase separation occurred, leading to the formation of those large spherical aggregates. On the other hand, too low compatibility between the organic binder and the ceramic such as illustrated with the reference sample led to a very poor stability of the composite resin, leading to the quick and persistent sedimentation of the ceramic in a very short amount of time.

With P1, offering an intermediate alternative to Ref and P2, a stable and low viscosity formulation was achieved while providing acceptable reduction of the viscosity.

The influence of the molecular weight of the plasticizer P1 (MW1) on the rheology and thermal decomposition was then evaluated by comparing various plasticizers of similar structures but higher or lower molecular weight. Plasticizer of molecular weight twice as high as P1 are disclosed as having a molecular weight of 2*MW1. Plasticizers having half the molecular weight of P1 are disclosed as MW1/2. Results are displayed in table 4 and compare the influence of those molecular weight variations on the sole viscosity of the binder (M1 + M5), viscosity of the binder mixed with 68% of ceramic C1 and 2.6% of dispersant D1, stability and re-dispersability of the filled formulation and residual ash content of the binder upon thermal decomposition.

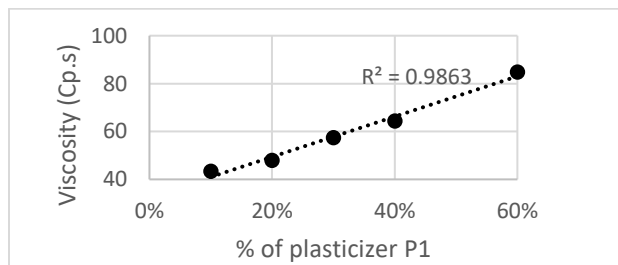
| Molecular weight (g/mol) | MW1/2 | MW1/2 | MW1 | 2*MW1 | 5*MW1 | 10*MW1 |
|---|-------|-------|------|-------|-------|--------|
| Percent of Plasticizer in sole binder (%) | 37.5 | 50 | 37.5 | 37.5 | 37.5 | 37.5 |
| Binder viscosity (Cp.s) | 11.7 | 16 | 16.6 | SOLID | SOLID | SOLID |
| Viscosity w/ 70% Ceramic (Cp.s) | 6245 | 1345 | 1769 | SOLID | SOLID | SOLID |
| Stability (ranking from 1 to 5) | 5 | 3 | 1 | SOLID | SOLID | SOLID |
| Re-dispersability (ranking from 1 to 5) | 4 | 2 | 1 | SOLID | SOLID | SOLID |
| Residual ash content (ppm) | 92 | 71 | 83 | SOLID | SOLID | SOLID |

Table 4: Molecular weight of plasticizer influence

Results in table 4 clearly show the existence of a threshold above which formulations tend to solidify, threshold being correlated to the melting temperature of the considered plasticizer. Above MW1, considered plasticizers are solid at room temperature and mixing with monomers appear not sufficient to achieve liquid formulations at 37.5% of plasticizer loading.

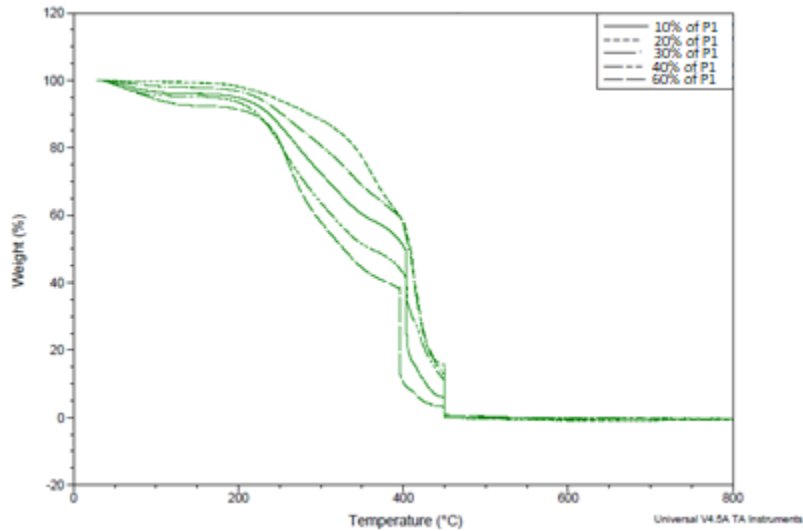
On the other side of the spectrum, lowering molecular weight of the plasticizer at equivalent percent of plasticizer proved to have a negative influence on the filled properties of the resin by reducing the stability and re-dispersability of the composite resin while also impacting negatively the viscosity of the filled resin despite lower binder viscosity. Those observations are expected to be due to higher compatibility of lower molecular weight plasticizers with the monomers, leading to lower stability of the ceramic particles. In addition, shorter chains led to lower plasticizing effect during the firing of the resin, leading to higher residual ash content.

It can still be noticed a positive influence of lower molecular weight plasticizers when compared at equivalent viscosity, leading to lower residual ash content and acceptable stability of the resin. However, further tests displayed below show the negative influence of too high content of plasticizers on the green strength of the resin. Viscosity of five formulations containing incremental percent of plasticizer P1 mixed with monomer M7 and photo-initiator PI1 was evaluated, showing the following linear increase of the viscosity at increasing percent of plasticizer.



Graph 1: Influence of percent of plasticizer P1 on the viscosity

Thermal decomposition of the considered organic formulations was also evaluated in air, showing a clear trend of the decomposition of the plasticizer preceding the decomposition of the binders. This earlier decomposition provides lower tendency to initiate cracks during the actual burning of printed ceramic parts as the plasticizer is not chemically bounded to the surrounding network, and thus decomposes smoother while initiating micro to nano paths for the binder to decompose afterward.



Graph 2: Influence of percent of plasticizer P1 on the thermal decomposition

Printability of the previous formulations following to the addition of 65% of ceramic powder C1 and 0.36% of dispersant D1 was finally evaluated, showing similar to slightly higher depth of penetration of the light when considering higher amount of plasticizers.

| % of P1 | 10 | 20 | 30 | 40 | 60 |
|--------------------------|------|------|------|------|------|
| Dp (mills) | 2.1 | 2.2 | 2.0 | 2.3 | 2.5 |
| Ec (mJ/cm ²) | 0.02 | 0.11 | 0.18 | 0.32 | 0.51 |

Table 5: Influence of percent of plasticizer P1 on reactivity

In addition, in the case of low amounts of plasticizers, printed calibrations parts tend to bend/curl due to the significant shrinkage induced by the binder while printed formulations at higher loadings of plasticizers show lower shrinkage/bending/curling (see picture of Working Curve 1 compare to picture 2 below). However, reactivity (measured as the critical energy to induce polymerization) and green strength significantly drops when increasing the loading of plasticizer over 40% as can be seen from the following pictures. No actual values can be measured at this point but the printed part clearly shows that it cannot hold itself properly, leading to an unprintable formulation in those specific cases.

| % of P1 | 10 | 20 | 30 | 40 | 60 |
|--------------------------|----|----|----|----|----|
| Working curve appearance | | | | | |

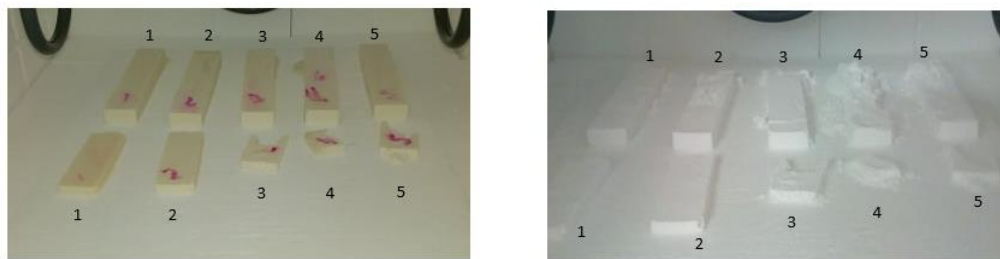
Table 6: Influence of plasticizer P1 content on green strength

In order to evaluate the influence of the plasticizer on the density, various size bars of the ceramic-filled formulations were cured and density was then measured prior burning (meaning prior firing and sintering) and after. As can be seen from the table below, density pre-burning doesn't follow specific trend, most likely due to the experimental error coming from preparing the formulations. However, a trend can clearly be identified in the density post-burning where a significant increase of the density can be observed, proving the positive influence of the plasticizer on improving the densification of the ceramic during the burning process.

| Wt% of plasticizer | 10% | 20% | 30% | 40% | 60% |
|--|------|------|------|------|------|
| Density pre-burning (g/cm ³) | 1.93 | 1.87 | 1.79 | 1.81 | 1.81 |
| Density post-burning (%) | 83% | 89% | 93% | 93% | 99% |

Table 7: Influence of plasticizer P1 content on cured density

However, as can be seen from the following pictures, a too high amount of plasticizer (40% in sole binder or above) is usually not desired as it is expected to lead to a too fast gas generation following the decomposition of the plasticizer. As can be seen with the samples 4 and 5, this fast gas generation causes the shattering of the samples and is not desired in the process of sintering 3D printed parts of high resolution.



Picture 1: Influence of plasticizer P1 concentration on the firing

An existing solution to control this phenomenon is to reduce heating ramp or apply specific plateau around the decomposition temperature of the plasticizer, which is expected to give it appropriate time to decompose and thus escape from the cured part without creating damages, cracks or holes.

Overall, the use of higher amount of plasticizer (over 20%) is preferred to prevent over-reactivity induced by the cross-linkers and monomers and leading to dimensional curling, bending or shrinkage of the printed parts. Significant amount of plasticizer (20% or higher) is recommended to generate dual decomposition of the organic system during the burning, leading to the removal of the plasticizer first, followed by the cross-linkers and monomers and thus reducing the tendency to initiate cracks as can be observed in formulations only comprising monomers and/or cross-linkers. This dual decomposition also offers better sintering process of the ceramic due to the lower amount of cracks or micro-void domains generated in the part during the firing.

The percentage of plasticizer is thus recommended to be in the range of 20 to 40% in sole binder, providing lower internal stress and better thermal decomposition while keeping sufficient amount of monomer to achieve acceptable green strength.

Conclusion

This evaluation of the various components of the formulations shows their interdependence on all key properties required to achieve successful printing of ceramic filled resins using SLA-DLP process. As an example, it was found that monomers play a key role on all main properties (reactivity, viscosity, stability and residual ash contents) of the filled formulations but that they should be chosen carefully as specific compatibility challenges arise from mixing specific organic compounds either with other organic products or with specific inorganic particles.

It was thus found that selecting a suitable monomer or combination of monomers should be the first key step to ensure suitable base for the organic formulation as the reacting agent drives most properties. Formulations then need to be optimized by carefully selecting compatible plasticizer, leading to slight reduction of the reactivity, higher stability and better thermal decomposition of the binders.

In this fashion, combination of M1 and M5 appears to provide suitable viscosity, while maintaining controlled reactivity and low residual ash content. Combining those monomers with 20 to 40% plasticizer P1 has allowed improved thermal decomposition of the formulations while maintaining sufficient green strength and reactivity during the 3D printing process, allowing the additive manufacturing of complex parts on traditional SLA and DLP printers.

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