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STEREOLITHOGRAPHY CERAMIC 3D-PRINTING

Faculty of Engineering and Natural Sciences
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ABSTRACT

Teemu Vastamäki: Stereolithography 3D-Printing of Ceramics
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Additive manufacturing has been found to be suitable processing method for ceramic materials in recent years. For other material groups, like plastics and metals, the 3D-printing is widely studied and the industrial markets are growing. For ceramics, there is still a lot to study before its potential in ceramic manufacturing can be acquired. Stereolithography (SLA) is one method to 3D-print ceramics. Stereolithography uses photons to initiate polymerization reaction at monomer, oligomer or prepolymer solution. In stereolithography, the ceramic powder is dispersed in monomer medium and polymer network is printed around the particles. These monomer solutions can be the same as used in the plastic stereolithography 3D-printing. Usually the main components of the monomer solution are acrylates, methacrylates or epoxies. To polymerize the monomers, proper photoinitiators is added. Photoinitiator should be chosen according the photon wavelength that the SLA printer is using and the reaction type that it should initiate, radical initiators for acrylates and methacrylates and cationic initiators for epoxies. During this Master thesis work new slurry is tailored and commercial Lithoz GmbH manufactures slurries are studied.

Only small components can be made so far. One limiting factor is the layered structure that are prone to the delamination. Delamination leaves cracks and flaws at the surface, reducing the mechanical properties of the ceramic component and bigger components than few cubic centimeters could not be printed with sufficient mechanical properties. The overall processing time of the ceramic 3D-printing is long, even small component takes over a week to process. This is because of the heat treatments that are necessary for the process takes long time. The post thermal curing and polymer degradation at 3D-printed ceramic parts is studied in this Master thesis work. With the newly tailored slurry, consisting from the acrylate-monomer body and aluminium oxide particles, the heat treatment’s total time was reduced significantly compared to the commercial Lithoz GmbH’s slurries. Ceramic components are successfully made and printing properties are studied widely with all slurries.

This study also highlights the aspects in stereolithography ceramic 3D-printing that requires further studies.

Keywords: Ceramic 3D-printing, ceramic additive manufacturing, stereolithography, Lithoz GmbH

The originality of this thesis has been checked using the Turnitin OriginalityCheck service.
PREFACE

This Master Thesis work is done at the Faculty of Engineering and Natural Sciences, Tampere University. It was started at the Tampere University of technology that was combined with the Tampere University at the beginning of 2019.

Making this Thesis was actually pretty fun. I was lucky to get to do this Thesis based on my personal hobby, 3D-printing. Many thanks to my Master Thesis supervisors Erkka Frankberg, Jorma Vihinen and Erkki Levänen with the rest of ceramic group here at the Material Science department.

Tampere, 25.2.2019

Teemu Vastamäki
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LIST OF SYMBOLS AND ABBREVIATIONS

\( A \)  
Shape of the flaw and loading geometry constant \([m(MPaJ)]^{1/2}\)

\( \alpha_p \)  
molar absorptivity \([m^2/mol]\)

\( c \)  
Flaw size \([m]\)

\( c_c \)  
Critical flaw or crack size \([m]\).

\( C_d \)  
Curing depth \([m]\)

\( D_p \)  
Penetration depth \([m]\)

\( E \)  
Young’s module \([GPa]\)

\( E \)  
Light energy \([mW/cm^2]\)

\( E_c \)  
Critical light energy \([mW/cm^2]\)

\( F \)  
Failure probability

\( h \)  
Planck constant \([Js]\)

\( I \)  
Distance between upper loading rolls \([m]\)

\( K \)  
Loading factor depending on the loading type

\( K_{ic} \)  
Critical stress intensity \([MPa m^{1/2}]\)

\( L \)  
Distance between lower supporting rolls \([m]\)

\( M \)  
Monomer

\( P \)  
Load \([N]\)

\( PI \)  
Photoinitiator

\( \sigma \)  
Maximum stress causing the specimen to fail \([MPa]\)

\( \sigma_0 \)  
Characteristic strength \([MPa]\)

\( \sigma_f \)  
Fracture strength \([MPa]\)

\( \sigma_u \)  
Highest stress level at which point the specimen does not break

\( t \)  
Thickness of the specimen \([m]\)

\( T_g \)  
Glass transition temperature \([^\circ C]\)

\( T_m \)  
Melting point \([^\circ C]\)

\( v \)  
Photon’s wavelength \([m]\)

\( V \)  
Volume \([m^3]\)

\( w \)  
Width of specimen \([m]\)

\( \gamma \)  
Fracture surface energy \([J/m^2]\)

\( Y \)  
constant describing the geometry of a crack
1. INTRODUCTION

Additive manufacturing industry, also known as the 3D-printing industry, grew 80% from 2016 to 2017 and is expected to reach 20-billion dollar market value in 2022 [1]. All started from the Dr. Kodama’s work with stereolithography (SLA) method to produce plastics at the 1980s [2] [3], but the industry started to grow significantly just about 5-7 years ago [4] [5]. Plastics are easier to handle with 3D-printing and that’s why plastics are developed most since. Today, 3D-printing is more than just an industry scale manufacturing technique. Especially 3D-printing of plastics has already widely reached household consumers in the form of tabletop printers, most notably the fused deposit modeling (FDM) method. Metal 3D printing has followed after plastics and currently the metal material 3D-printing is spread widely to the manufacturing industry and 3D-printing machine manufacturers are also planning to bring the metal 3D-printing to table top scale. In addition, biomaterials 3D-printing is widely studied and has already gained some progress. The only major material that is not yet fully covered by the 3D-printing techniques are the ceramic materials. In particular the material group called engineering ceramics with high engineering properties, like strength and high temperature stability.

For me, the 3D-printing started as a hobby, printing some stuff to everyday use, like fishing gear. I used plastic FDM-printing, as mentioned earlier it is the easiest and cheapest way 3D-print stuff at home. The Material science department with the Mechanical Engineering and Industrial Systems department acquired a ceramic SLA 3D-printing machine from Lithoz GmbH, CeraFab 7500 [6] and have used their commercial materials to print Al₂O₃ and ZrO₂ components. They hired me to continue their research of the ceramic SLA 3D-printing and to find the critical points that has the greatest effects to the success to process.

In this master thesis work the main focus is get familiar with the current situation of the ceramic 3D-printing in the world and study the critical factors that are required to successfully produce printed ceramic components. This is done by developing and tailoring of own printable slurries of Al₂O₃ and ZrO₂. The 3D-printing of the ceramics by SLA is an indirect method to print ceramics, in fact the process prints a plastic network around the ceramic particles from the printing suspension. So, it is crucial to know the
chemical processes behind the photopolymerization and curing during the printing with the interactions of the ceramic particles.
2. THEORETICAL BACKGROUND

2.1. ADDITIVE MANUFACTURING

Additive manufacturing or 3D-printing, refers to series of individual methods to create three-dimensional objects by adding material layer by layer. The advantage of the 3D-printing is that almost any shapes or geometries can be formed to the object. This includes internal geometries such as hollow or honeycomb structures are possible to create with the same machine. Therefore, additive manufacturing techniques are an efficient way to quickly produce functional prototypes with high dimensional accuracy, which is why the 3D-printing is occasionally called “rapid prototyping”. The 3D-printer is a computer-controlled machine and uses STL-files (Standard Triangle Language -files) to create an object from the computer-aided design (CAD) models. To make the STL-file to the format that the 3D-printing machine understands, the STL-file needs to be sliced in to layers of wanted layer thickness. After the slicing, the g-code or some other controlling code is produced, which the 3D-printing machine follows.

Currently, the materials that can be used with 3D-printing includes numerous plastics, metals and ceramics. The most common 3D-printing methods are stereolithography (SLA), fused deposition modeling (FDM), selective laser sintering (SLS), direct laser sintering (DMLS), laminated object manufacturing (LOM), material- and binder jetting, and electron beam melting (EBM). Stereolithography uses a liquid monomer, oligomer or prepolymer resin that is photopolymerized with light. The SLS is used for thermoplastic and DMLS for metal powder to directly melt it and form a solid component with IR-lasers or LEDs. FDM uses a thermoplastic filament that is melted and then extruded to form an object as the melt solidifies. [7] [8]

The powder or resin is either placed to the tank where always after the melted or cured layer a new layer of resin or powder is spread on top of the previous layer by small quantities at the time. This makes the 3D-printing generally a slow process and the slowness makes 3D-printing a costly method to make products in high quantities compared to the established mass-production methods. Methods such as ceramic injection molding is used instead of the 3D-printing due to its low cost and quickness, however the freedom of design in CIM is inferior to 3D-printing techniques for example in the design of internal structures. One of the key aspects in the design freedom that the 3D-printing provides is that the model is stored to the computers CAD-software’s
memory, where the adjustments and modifications are able to be done by very short time if needed. [7] [8]

2.1.1. Stereolithography

The SLA is based on printing liquid resins that cures and solidify by a chemical reaction. The energy needed to start the chemical reaction is produced by a light source such as laser or LEDs that work mostly in the UVA- or UVB-wavelengths. The resin consists of organic molecules, monomers, oligomers or prepolymer, photoinitiators and other additives. When the resin cures, it provides a highly cross-linked polymer network. The monomers, oligomers and prepolymer make up the majority of the resin mass and they also determine the physical and chemical bulk properties of the resin and the formed plastic bulk. Usually the monomers, oligomers and prepolymer do not naturally react physically or chemically with the UV-light, so the photoinitiators is used to initiate the reaction by absorbing the photon, jumping to the higher energy state and becoming a chemically highly reactive with the monomers in the resin, which initiates the polymerization reaction. There is a great variety of photoinitiators that work with different photon energies. When the photon hits and get absorbed by the photoinitiator’s functional group which jumps to the higher energy level. This requires that the photon energy has to be at least as high as the difference between the photoinitiator electron’s ground state and the excited state. In addition, the initiation of the polymerization reaction requires a specific interaction between the photoinitiator molecule and the electric component of the incident radiation so that the dipole moment of the molecule changes during the interaction with the photon. [9, pp. 6-9]

The polymerization reaction is highly exothermic and spontaneous. After initiation, the reaction keeps going as long as there are other monomers left to react with or a separate termination reaction takes place. The polymers that are used in the SLA form a highly crosslinked 3D network of polymer chains that are infusible and insoluble to solvents. The polymerization initiates when the 3D-printer’s light source exposes the resin to photons and the photoinitiators absorbs the photons. After the initiation, the liquid resin starts to cure and solidify. There are two curing phases, first the gelation and second the vitrification. Gelation is an irreversible reaction of the resin where the viscosity increases fast and significantly, which is caused by the polymer chain and network growth. The gelation point is the phase when the resin does not flow freely anymore and turns into viscoelastic. Viscoelasticity occurs because there is already a small fraction of cross-linked polymer network mixed with the monomers and polymers still present in liquid form. As the gelation and curing proceeds, the resin starts to get a recognizable solid
form and the amount of the liquid resin decreases in the system. At this point, the mobility of the polymers and monomers decreases due to the increased viscosity, which leads to decrease in the polymerization rate. When the polymerization rate has sufficiently decreased, the vitrification starts to take place. Vitrification means that the proceeding of the reaction becomes diffusion controlled instead of kinetically controlled and the reactive pieces that are left needs much more time to diffuse through the structure and react. The vitrification determines the final degree of conversion and continuous long after the external energy output ends, which initiated the reaction. The polymerization rate and conversion degree is highly depended from parameters such as light intensity, temperature and the initiator concentration, so by increasing these factors usually lead to higher conversion rates, but in some cases, depending on the resin composition, they might also decrease it. [9, pp. 10-12] The polymer curing and kinetics is discussed in detail in the section 2.2

**Figure 2.1.** illustrates the two commonly used strategies in SLA 3D-printers to grow the model from the resin: either bottom down, so that the build platform lowers after every layer and the light comes from up, or by bottom up, so that the building platform rises after every layer and the light comes from beneath. With the method bottom up, **Figure 2.1.**, the machine lifts the model up after creating the layer and lowers it down again to the resin leaving a gap between the resin bath bottom and the model so that the gap height is the wanted layer thickness. The light source is located under the resin tank and the bottom of the tank is transparent. With the bottom down method, **Figure 2.1.**, the building platform lowers and sinks the printed model in the resin bath, so that the formed new layer gets wet from the resin and a sweeper spreads a new layer of the resin on top of the model evenly. The model’s top part is submerged to a depth selected to be the next layer thickness. The new layer is cured with the light so that only the shape of the new layer is cured, and the machine wets the new layer to start a new cycle. In this bottom down method, the model stays under the resin all the time. [9, pp. 12-13] [10]

These both methods require a waiting time, so that the possible air bubbles have time to escape, instead of being trapped inside the model. This is why low viscosity of the resin is important, which also allows the surface of the model to be wetted easier with the next layer. [9, pp. 12-13] [10]
In SLA the light is produced by a laser, by LEDs or by a projector. With the LEDs and the projector, the light source doesn’t move. Instead the light is reflected by a digital mirror device, consisting from many small moving mirrors, that form the whole image at once onto the resin. LEDs and projectors are used for example by the Lithoz GmbH CeraFab machine [6] and the ILIOS PHOTON 2 [12]. A laser instead sweeps over the resin surface writing the image of the model current layer to the surface of the resin. The laser beam can also be moved with mirrors, like in the Formlabs Form 2 SLA printer [13], but sometimes the laser itself moves horizontally on the resin surface, like mUVe 1 Laser 3D Printer [14]. The formed layer thickness is depended on that how much the light energy does the resin gain during the irradiation step. This is called the curing depth \( C_d \) [\( \mu m \)] and it is defined with the formula

\[
C_d = D_p \ln \left( \frac{E}{E_c} \right),
\]

where the \( D_p \) is the penetration depth [\( \mu m \)], \( E \) is the input light energy [mW/cm\(^2\)], \( E_c \) [mW/cm\(^2\)] is the critical light energy input that is required to initiate the reaction on the macroscopic scale and \( D_p \) is the resin’s characteristic constant indicating how well the light penetrates the resin taking account the light absorption and scattering. According to the formula (1) the cure depth can be controlled with the light exposure and increasing the exposure \( E \) increases the cure depth. Cure depth should be at least the layer thickness, and more preferably two or three layers thick or it is possible that the slurry does not polymerize and stick to the previous layer properly [15]. Of course, when the curing thickness is more than the layer thickness, there might be unwanted amount of curing at the overhangs of the part, which is called a z-overcure as presented at the Figure 2.2. Z-overcure error at the overhang areas, where the unwanted polymerization
has happened due the high curing thickness. This will increase the thickness error and has to be taken into account when the part tolerances are designed [9, pp. 12-15]

![Image](image.png)

**Figure 2.2.** Z-overcure error at the overhang areas, where the unwanted polymerization has happened due the high curing thickness [9, p. 87].

Additionally, when the light energy is increased, the light scatters to the sides increasingly, which is the case especially when the resin has a high solid particle filler content, like ceramic particles. The light scattering is increased if the fillers and resin have large difference in their refractive indexes and if the used wavelength of light is near the fillers particle size. For example, the scattering is greater with the lead zirconate titanate (PZT, refractive index 2.40) compared to silicon dioxide (SiO$_2$, refractive index 1.56) when mixed with 1,6-hexanediol diacrylate (HDDA, refractive index 1.458). [16], [17]

As mentioned before, the SLA materials are in form of resin that consist of polymerizable monomers, oligomers or prepolymer, photoinitiators, inhibitors, reactive or unreactive diluents and other additives. The bulk properties are determined by the monomers, oligomers and prepolymer that form the polymer network. Diluents are to decrease the viscosity of the resin and with additives some properties, such as glass transition temperature ($T_g$) and hardness can be modified. Photoinitiators are used to initiate the polymerization reaction and there are basically two different mechanism that are used with the SLA: radical and cationic curing.

With the radical curing mechanism, the photoinitiator forms a radical when it reacts with the proper light and the radical reacts with the covalent double bond between the carbon atoms, so that the radical passes on to the next carbon atom opening the double bond. The radical curing polymerization belongs to the chain-growth polymerization mechanism group. The chain growth mechanism works in that way that the unsaturated
monomer molecules attach to the polymer chain’s active end one at the time, so that the polymer growth happens only at the end of the chain. The reaction goes on as long as there are reactive components left or the termination reaction takes place. Acrylate, methacrylate and acrylic- and methacrylic acids polymerize with the radical curing mechanism and they also have a particularly fast curing reaction speed that does not proceed further after the light source is removed. For this reason, the resins that are based on the acrylate and methacrylate monomers are commonly used in SLA. Acrylate and methacrylate properties are variable and can be easily modified, because they are widely available with different molecular structures. The down side of the acrylates and methacrylates is that they exhibit a large shrinkage during the polymerization. For example, 1,6-hexanediol diacrylate (HDDA) shrinks about 18-22 vol-% \([18]\) generating internal stresses. The shrinkage is directly dependent on the carbon-carbon double bond conversion rate to carbon-carbon single bond. At the resin, monomers are linked together by the van der Waals forces and the distance is approximately 10^4 Å between molecules. Polymerization reaction changes the van der Waals forces to the covalent bonds between the monomers carbon atoms and then the distance is around 1 Å \([19]\). This is why oligomers and prepolymer are a lot used option for the SLA resins, since their double bond concentration is lower. On the other hand, with the larger acrylate or methacrylate monomer molecules the viscosity increases significantly. Higher viscosity makes the wetting of the build plate and the printable object surface more difficult, therefore, when formulating the resin, it is necessary to find an optimum between these two factors. The curing shrinkage might lead to inhomogeneous acrylate and methacrylate polymer network and possible poor adhesion between the polymer and the building platform surface \([20]\). More detailed this radical polymerization reaction of acrylates and methacrylates is covered at the section 2.2.1.

Other commonly used resin monomers are the epoxy-resins. Epoxies cure through the cationic curing mechanism, where the photolabile cationic initiator forms a Brönsted acid when it reacts with the incoming light. The curing kinetics of epoxies is significantly slower than that of the acrylates and the epoxies possess a property called dark curing. This means that the epoxy resin continues to cure long after the light exposure has ended, which happens by a monomer diffusion mechanism through the polymer network. Epoxies are generally tougher materials than acrylates and a major benefit is that they shrink significantly less during the polymerization, however they are also less reactive and have high viscosity and the reaction is harder to control. In SLA resins, the cycloaliphatic epoxies are often used due to their relatively fast curing kinetics, such as 3,4-epoxycyclohexyl-methyl-3,4-epoxycyclohexane carboxylate (ECC). ECC has a
curing shrinkage of only about 3.12 vol.%. Curing kinetics and behavior of the cationically cured ECC are demonstrated in the Figure 2.3. The epoxies “dark curing” phenomena means that it might take hours to reach the final conversion degree, since the conversion rate slows down. As the reaction propagates, the viscosity of the resin increases and the polymerization turns into diffusion controlled. [20] [21] More detailed this cationic polymerization reaction of epoxies is covered at the section 2.2.2.

Acrylate and epoxies do not copolymerize because of the different curing mechanisms, instead they form an inter-penetrating polymer network (IPN), in which the polymer networks are mixed together. This is proved by the fact that the polymer with IPN has only one glass transition temperature, somewhere between the value that the two components would have had separately. To use both acrylate and epoxy in the same resin grants many benefits, such as the acrylate polymerization shrinkage is reduced and the curing of the epoxy is more controllable since the gelation and the early solidification is done by the acrylate component. [20] [21] IPN’s will be discussed in more detail in the section 2.2.3.

Perhaps the most important component of the SLA resin is the photoinitiator. That is the component that initiates the polymerization reaction and the chosen photoinitiator has to be suitable for the used SLA printer. Basically, there is a photoinitiator for every wavelength of the light, but for the SLA, photoinitiators that works in the UV- or visible blue wavelengths are mostly used. For example the Formlab’s Form 2 SLA printer uses a 405 nm wave length laser [13] and Lithoz GmbH’s CeraFab uses 460 nm blue LEDs. A resin used for a certain SLA machine might not work if used directly with another machine. Figure 2.5. introduces the light absorbing wavelengths of some commonly
used photoinitiators, for example camphorquinone’s molar absorptivity $\alpha_p$ [m$^2$/mol] is greatest with the wavelength of approximately 460 nm.

There are two types of radical photoinitiators that can initiate the radical polymerization reaction: type I and type II. The difference is that the type I photoinitiators promote radical polymerization by photo-cleavage and type II by hydrogen abstraction. Therefore, the type I photoinitiators can work by itself, while the type II needs a co-initiator. Cationic photoinitiators initiates the cationic polymerization by creating an acidic molecule by interaction with light photon. Onium salts are very common choice at the SLA resins for this purpose. After the photo-chemical reaction of the cations, the formed cation and anion do not react back to the initial state due the low nucleophilicity of the formed anion, unlike the radical initiator that returns to the initial form quickly after photon activates it. This is the reason why the cationic initiated epoxy conversion exhibits the dark curing phenomena. The light absorbance of the cationic initiators are most often below 350 nm, but their absorbance can be modified by sensitizers like aromatic ketones or polycyclic aromatic hydrocarbons. [9, pp. 16-17] Photoinitiators are covered more detailed in the sections 2.2.1. and 2.2.2.

![Figure 2.5. Molar Absorptivities of some radical photoinitiators as a function of the wavelength [22].](image)

Resins can also consist of different amounts of inhibitors to increase the resin’s storage properties or to modify the curing properties. There are two common inhibitors mechanisms, radical scavengers and dyes. Radical scavengers work in a way that they react with the formed radicals of the resin and terminate quickly the ongoing polymerization reaction. Dyes work by reflecting the critical wavelength light away from the resin surface, but are otherwise inert component of the resin. In addition, the dyes also give a color to the resin and also for the polymerized plastic, therefore in many cases the use of dyes is limited due the aesthetic manners. Considering the ceramic 3D-
printing, the inhibitors and dyes should decompose, evaporate or degrade so that they do not make impurities to the final sintered ceramic. [23]

2.1.2. **3D-printing of the Ceramic Slurries with Stereolithography**

Stereolithography method has been used to 3D-print ceramics [17] [24] [23] [25]. SLA-printing of ceramics is very similar than the SLA-printing of plastics, basically because the ceramic 3D-printing slurry is monomer resin with high ceramic content. Ceramic particles in the resin are inert fillers that do not go through chemical reactions during the printing, unlike the resin around them. The cured resin binds the particles inside the polymer network and the polymer needs to be removed before sintering the ceramic particles. *Figure 2.6.* illustrates the particle binding induced by polymerization.

The total process of the SLA ceramic 3D-printing is illustrated in the *Figure 2.7.* It includes more than just the printing itself, it also requires various heat treatments to remove the binder and subsequent sintering of the remaining powder green body. Heat treatments are usually separated into two different categories, preconditioning and debinding. In precondition phase the printed parts are slowly heated to low temperatures, about 100 - 130 °C, so that the printed part thermally continue curing after the printing, or some volatile additives diffuse out of the network. Preconditioning phase is not always necessary needed if for example the resin does not thermally cure. Debinding is a necessary step prior to the sintering, in which the ceramic particles become in contact each other and can therefore can form a solid component by diffusion during the sintering process. Debinding should always done by sufficiently slow heating, because the polymers thermally degrade and form gases that may cause internal stresses. Effects of the debinding has been studied by Emil Johansson and coworkers [15] found that the some 3D-printed ceramic parts were severely damaged during the debinding phase, affecting their final mechanical properties when the thermal treatments are not made properly. In addition, the subsequent cleaning step can have great effects to the final quality of the green parts [26]. Lower viscosity slurries are easier to clean and the cleaning should be done with proper cleaning solvents and methods [15] [26], for example acetone dissolves very well many different organic substances, such as acrylate monomers. The acetone get swollen by the polymer network causing it to expand creating again internal stresses and possible delamination. Solvents like acetone can also dissolve uncured monomers or smaller polymers away from the printed structure possibly creating holes.
When mixing great amounts of ceramic particles into the monomer resin, obtaining a good dispersion of the particles is important. Oxide ceramics typically exhibit a slightly hydrophilic surface nature and that is why oxides can be difficult to disperse properly to the acrylate-type resins [27]. More information about the dispersion and the colloidal processing of ceramics in the section 2.4.

2.2. PHOTOPOLYMERIZATION

Photopolymerization is a polymerization reaction that is initiated by a photon. After initiation, the polymerization reaction proceeds by addition of new monomer units into the polymer chain and creation of polymeric macromolecules. There are two main mechanisms that the polymerization mechanism can follow: step and chain growth reactions. In the step growth reaction, the functional groups of the polymer react often by the substitution, elimination, addition or condensation reactions where the monomers attach to the other monomers, oligomers or polymers. In addition, the oligomers and polymers can attach to each other during the polymerization. Step growth reaction usually happens spontaneously in specific circumstances and the polymerization reaction speed is fairly slow. [28, pp. 3-6] [29, pp. 1-3]
In the chain growth mechanism, monomers are added to the chain one by one by the addition reaction through the radical induced reaction of opening carbon-carbon double bond and passing the radical to the next carbon atom or by cat- or anionic ring opening reaction. The speed of the chain growth reaction can be fast and a large polymer mass can be gained. Chain growth reaction is usually not spontaneous, instead it needs an initiator molecule and the right conditions. Initiator can be activated to start the polymerization reaction by heat, light, X-rays, γ-rays, microwaves, plasma, electron beam or sometimes pressure. Once the initiator is activated, it reacts with one monomer creating it the new reactive piece that react again with another monomer and so on. [28, pp. 3-6]

\[ PI + h\nu \rightarrow PI^\bullet + M \rightarrow PIM^\bullet + M \rightarrow PIMM^\bullet + M \rightarrow PIMMM^\bullet + M \rightarrow ... \]  

(2.1)

Usually the monomers are not directly sensitive to the visible- or UVA- and UVB-lights therefore a photoinitiator (Pi) is added. This photoinitiator adsorbs photons with a specific energy \( h\nu \) and gains an exited state. With the radical photoinitiator’s this creates a radical, with cationic Pi’s this creates an acid, cation or cationic radical and with the anionic photoinitiator’s this creates a base or an anion. There are basically two types of photoinitiators: type I creates the activated center by itself for example by self-cleavage and type II that requires an additional component or components to create the activated center, usually hydrogen. [28, pp. 3-6] [9, pp. 16-17]

Concerning the stereolithographic process, the gelation phenomena is essential to form solid structures from the low viscous resin. Gel point can be simply expressed as a point of curing degree where the monomers do not flow freely anymore inside the cured resin and the resin starts to form recognizable semi-solid 3D-structure that keeps it shape. The curing still continues by diffusion, however slower than before the gelation, due to the significantly increased viscosity. The curing that happens after the gelation creates internal stresses that weaken the mechanical properties of the polymer network, which is the case especially with acrylates and methacrylates due their high polymerization shrinkage. By increasing the curing degree at the gelation point reduces the internal stresses, but it keeps the polymer soft longer during the polymerization reaction and makes the forming of network more difficult and time consuming. Delaying the gelation point can be achieved by adding, for example, chain transfer agents, other monomers with different curing characteristics or non-reactive diluents. Modifying the gelation point of SLA-resin is a compromise between easier printing process and the final mechanical properties of the polymer. [30] [29, pp. 2-5]
2.2.1. Radical photopolymerization of acrylates and methacrylates

Radical photopolymerization has a fast reaction speed with high controllability, that’s why it is highly popular among stereolithographic resins. In the radical photopolymerization, the reaction is triggered by the initiator that absorbs photon with a proper wavelength. Separate initiator is used, because most monomers by themselves undergo a photocleavage only with extremely low wavelengths of light. There are two types of the radical photoinitiators: type I promote a polymerization through photocleavage by itself when photon is adsorbed, like benzoin ethers, and type II which promote polymerization through a hydrogen abstraction, like camphorquinone, and requires a hydrogen donor as a co-initiator. Schematics of these photoinitiator of both types reactions is illustrated in the Figure 2.8. Radical polymerization induced by photoinitiator is easily controlled, because the photocleaved radicals are short lived and quickly react back to the initial form, also type II activated photoinitiators deactivates themselves quite quickly back to the initial form. Therefore, when the light irradiation is stopped, initiation reaction of the polymer ends basically immideately and new polymers does not form anymore. [28, pp. 103-118]

![Figure 2.8. Type I photoinitiator photocleavage (1) and type II photoinitiator hydrogen abstraction (2). Type I photoinitiator is hydroxyacetophenone and type II photoinitiator is camphorquinone with amine and silyl coinitiators as a hydrogen donors [31] [32].](image)

The rule of thumb can be hold that a type I photoinitiators absorbs light when wavelength is under 400 nm and type II photoinitiators absorbs when over 400 nm. Photosensitizers are molecules that can absorb light from a different wavelength than the used photoinitiator, usually from longer wavelengths. The role of the sensitizer is to absorb light and transfer the excess energy to the photoinitiator through the energy transfer
process. In that way the polymerization reaction can be induced also with different light’s wavelengths than the initial photoinitiator can absorb. [33, p. 356]

Acrylic and methacrylic monomers are used in the stereolithography due their flexibility of properties that are easily modified by additives and because of the high availability of different kinds of monomer backbone structures. By using these monomers, mechanical properties can be varied from soft to hard, flexible to rigid and T_g from -60 to 110 °C. In SLA applications, acrylics cure faster than methacrylates and in many cases are then preferred [34]. As the acrylics cures they exhibits a high shrinkage that is directly depended to the C=C-bonds conversion and resins C=C-concentration [19]. Shrinkage, for example, of the 1,6-hexanediol diacrylate (HDDA) can be even over 18 vol-%, when a monomer with a longer backbone, 15-mol ethoxylated trimethylolpropane triacrylate (TMPT(EO)15A), has much less polymerization shrinkage, about 6,5 vol-% [18]. After the gelation starts to take place, the shrinkage generated internal stresses starts to form inside the polymer structure significantly and keeps growing until the curing reaches its final conversion degree [30]. Crosslinking density increases when the functionally of the acrylate increases, but at the same time the viscosity also increases, while the monomers are more branched and larger in size.

Acrylics and methacrylics polymerize in free radical reaction, which is a part of the chain growth reaction. After the initiation of photoinitiator radical, the C=C-bond reacts with the radical, creating always a new radical at the end of the chain. Propagation happens also with the radical’s reaction with the monomer’s C=C-bond. At room temperature, the termination of the reaction mainly occurs through the combination of the chain end’s radical with the other radical from the other chain end or by the initiator radical. At higher temperatures, the termination by disproportionation starts to take place, exceeding the combination termination at some point. With the combination terminating reaction, the polymer can reach large chain lengths. In disproportionation, the chain ends with the C=C-bond that is prone to thermal degradation and might weaken the mechanical strength of the polymer. The acrylate and methacrylate reactions are presented at the Figure 2.9.
Acrylates and methacrylates are sensitive to oxygen inhibition. Air’s electron dense oxygen molecules react with radicals creating a hydroperoxyl radicals that are effective hydrogen scavenger and then terminates the polymerization, or at least retards the polymerization. The oxygen inhibition speed is determined mostly by the rate of oxygen diffusion to the resin. With fast polymerization reactions, the oxygen inhibition does not show such a major role, because after the oxygen presented already at the resin is consumed, the diffusion of new oxygen is negligible compared to the polymerization speed. Up on that, also when the viscosity increases during the polymerization, it hinders the oxygen diffusion further. [35, p. 269]

2.2.2. Cationic photopolymerization of epoxies

Cationic polymerization is a polymerization reaction initiated by a cation, which is a strong acid. Cationic photoinitiator is a molecule that breaks to a cation and its counter anion, by interaction with the light. The reaction is also called a photo-acid generator and it produces a Lewis- or Brønsted-acid [33, pp. 423-424]. Most used cationic photoinitiators are onium salts, like iodonium- and sulfonium salts, while also some other organometallic salts are used in minor cases. They consist of positively charged central atoms, such as iodium- or sulfonium-ions, which are attached by covalent bonds to variable number of benzene rings. Cationic photoinitiator’s organometallic anion can be for example BF$_4^-$, PF$_6^-$, SbF$_6^-$ and AsF$_6^-$. The role of the anion is to have a low nucleophilicity, so that it doesn’t react back with the cation to its initial form. Low
nucleophilicity is gained with a large size of the ion and low electron density. The low nucleophilicity, of the onium salt’s anion, means faster cationic polymerization rates, while the reactivity order is typically: SbF$_6^-$ > ASF$_6^-$ > PF$_6^-$ > SbF$_6^-$ . Typical onium salts are presented in the Figure 2.10. [28, pp. 289-294]

Onium salts absorb UV-light mostly below 300 nm wavelength. Light absorption causes the onium salt to undergo either homolytical- or heterolytical cleavage, and with additional steps the anionic portion of the molecule gains a proton and becomes a strong acid. Iodium- and sulfonium salts both have very similar decomposition properties and regarding the ceramic SLA, their performance are close each other. Onium salt’s cation is responsible of the UV-absorption and eventually gets neutralized after a multistep process that varies with each compound. During the process, also a phenyl radical might break off from the molecule. The anion then gains a proton from the additional hydrogen donor originating from the surrounding medium or from the cation during the decomposition. The photocleavage of the cationic photoinitiators are presented in the Figure 2.10. Due to the fact that onium salt’s anions have low nucleophilicity, they don’t react back to the initial form with a cation or a hydrogen proton very quickly. Instead, they stay separated and can further promote the curing process, dark curing. In addition the photoinitiator is not consumed by the polymerization reaction unlike with the radical initiator and -polymerization. [28, pp. 289-303] [33, pp. 423-429]

Recently, especially in dentistry, visible light cationic photoinitiators have been under research [36] [37]. It has been found that the initiating wavelength spectrum of the cationic photoinitiator can be modified by light photosensitizers, like camphorquinone. Photosensitizer absorbs the photon by its own characteristic absorption properties and the donates an electron to the cationic photoinitiator’s cation and becomes a cation by itself. If the photosensitizer is a type II radical photoinitiator, when it accepts a hydrogen from the co-initiator, it can grant an electron to the cation and the hydrogen to the anion of the cationic photoinitiator, creating an anion-hydrogen pair, a strong acid that initiates the polymerization [36] [33, pp. 442-446] [28, pp. 311-320]. These photosensitizing reactions are presented at the Figure 2.10.
Figure 2.10. Cationic photoinitiators and examples of cationic photoinitiator reactions, (1) and (2) are cationic photoinitiator's photocleavage reaction, (3) photosensitizer (ketone) donors an electron to the cationic photoinitiator, (4) reaction of the photosensitizer (ketone) radical and cationic photoinitiator (D=hydrogen donor molecule), (5) example of iodium salt, (6) example of sulfonium salt. [33, pp. 426, 446] [28, pp. 290, 311-320]
The epoxy-ring polymerization reaction’s initiation, propagation and termination with water is presented at the Figure 2.11. The photopolymerization of epoxy rings starts after the cationic photoinitiator is activated and strong acid is formed either from the photoinitiators anion or from the photosensitizer. The initiator ion transfer the positive charge to the epoxy ring’s oxygen and the reaction propagates by transferring the charge repeatedly to the new epoxy monomer. The charge always opens up a new ring’s covalent C-O – bond and results in a positively charged oxygen at the end. The reaction terminates when the positive charge of the monomer or initiator neutralizes with any anion provided in the resin. Water is really effective at terminating the epoxy’s cationic polymerization by donating OH⁻-ion or by absorbing the positive charge from the reaction. This is the reason why the cationic photoinitiator’s anion should have low nucleophilicity and a reason why it should donate the charge easily to the epoxy ring. In addition, all compounds that have a base like characteristics should be avoided in the resin’s composition, such as amines. The result from the epoxy polymerization is an ether polymer chain usually starting and ending to an OH-group. [36] [38, p. 158] [28, pp. 290, 311-320]

![Figure 2.11. Epoxy ring polymerization reaction, (1) initiation and propagation, (2) termination by water [36] [38].](image)

The cationic epoxy polymerization differs from the radical acrylate photopolymerization by its remarkably lower polymerization shrinkage, for example, only about 3 vol.% with ECC [21], but which also exhibits a lower curing speed compared to acrylates and a dark curing effect. The lower polymerization shrinkage is due the monomer’s covalent C-O –bond that brakes and creates a new covalent C-O -bond with another monomer.
during the reaction. The formed polymer network is well organized structure and the shrinkage stays low. The dark cure effect is due to the cationic photoinitiator’s characteristics, as mentioned earlier. Because of the relatively slow reaction speed of the epoxies, they are rather difficult monomers for the SLA 3D-printing compared to the acrylate and methacrylate resins.

**2.2.3. Inter Penetrating Polymer Network**

Inter penetrating polymer (IPN) network is a mixture of two or more different polymers that do not form significantly copolymeric networks by covalent bonds, but can not be separated and at least one component produces a crosslinked polymer network [39, pp. 3-5] [40, pp. 272-275]. There are different degrees of IPNs, which are distinguished by the polymer network structure. For example, a full IPN is a totally homogenic structure where all polymer components are crosslinked and so do not dissolve or flow, a semi-IPN has a linear polymer with a crosslinked polymer and a gradient IPN is where the overall composition and crosslinking density varies in the macroscopic scale [39, pp. 273-275]. The properties of IPN’s are something in between the properties of the single components, for example with a full IPN, the $T_g$ is between the single component $T_g$. As an example, the UV-cured IPN mixture of HDDA and ECC 50:50 molar ratio gives a $T_g$ of 153 °C, when it would be 140 and 190 °C in the single components [21].

IPNs are used in SLA 3D-printing resins [41] [42]. *In situ*-IPN network is generated when the SLA-resin includes both acrylate and epoxy monomers and also photoinitiators for both polymerization reactions, radical and cationic photoinitiators. The crosslinked networks of the acrylate and epoxy are formed simultaneously making homogenous network without any significant phase separation [39, pp. 275-276]. The gelation degree and speed are mainly dictated by the acrylic or methacrylic component of the resin due its much faster curing speed, while the epoxy conversion has to mainly take place after the vitrification phase by diffusion after the resin is solidified. Regarding of this SLA-printing of ceramic materials, IPN opens a possibility to create good after curing phase to the process which should increase the printed layer adhesion by creating chemical links also between the layers.

**2.3. THERMAL DEGRADATIONS OF POLYMERS**

Degradation of polymers include chemical reactions in the backbone of the polymer that leads to a material with different characteristic properties than the starting material. These reactions are initiated by the external physical or chemical stress that causes the
macromolecules to undergo the reversible or irreversible reactions that usually worsen the properties. Reaction might also affect the structure in useful ways such as compatibilization and stabilization of the polymer. Polymer degradation includes at least the following mechanisms: biodegradation, oxidation, pyrolysis, mechanical, photo- and catalytic-degradation. Every polymers have their own characteristics regarding their possible ways to degrade by the harmful environmental effects. These harmful effects can be caused by external chemical deteriogens: oxygen and its active forms, harmful anthropogenic emissions, humidity, pollutants, and physical stresses: heat, radiation, mechanical stress and ablation. [43, pp. 1-3]

Thermal degradation of the polymers occurs at the high temperatures by heat induced chemical changes without the involvement of any other reaction compound. In many cases, processing of the polymers requires high temperatures to for example reduce melt viscosity and it is important to recognize the thermal decomposition mechanisms to reduce or prevent their possibly harmful effects to the processing quality. In stereolithographic ceramic 3D-printing the knowledge about the thermal degradation is in high priority during the debinding phase of the process, so that the degrading process doesn’t cause unnecessary thermal stresses due the thermal expansion or the rising pressure when the polymers degrades and evaporates. [43, pp. 2-3]

Thermal degradation has three different reaction mechanisms to break the polymer chain, change the polymer composition or to reduce its molecular mass. These three mechanisms are: side-group elimination, random scission and depolymerization. Side-group elimination mechanism affects the polymer chain generally by two ways, first is the elimination of the small side group that forms a small molecule, like with PVC the eliminated Cl atom forms a HCl. Then the remaining polyene macromolecule further undergoes a reaction to form aromatic molecules. Side group elimination temperature is directly dependable on the polymer structure, for example, PVC can decompose slightly already at the room temperature. Random scission means breaking the polymer backbone and creating free radicals that further create C=C double bonds to the chains last carbon atoms at the broken section. The scission is random and can happen at any point of the polymer chain between carbon atoms with single bond, which decreases the molecular weight. The formed new smaller chains keep decomposing by random scission until the fragments are so small that they can evaporate into gas phase. For example, polyethylene decomposes by this process, creating molecules with unsaturated end-groups. Random scission usually requires over 400 °C to take place. Depolymerization is directly opposite reaction than the polymerization. During the
depolymerization, free radical is formed either to the middle of the polymer backbone by the random scission or to the unsaturated end-groups of the polymer chain. The radical induced depolymerization then propagates by splitting the polymer chain into monomers in a reverse step growth polymerization. Depolymerization is a common way of degradation to polymers such as polymethacrylates and polystyrene. Temperatures that it requires are depended from the composition of the polymer and can vary a lot. [43, pp. 31-32]

2.3.1. Thermal degradation of Acrylate and Methacrylate

Acrylates and methacrylates thermally degrade by the free radical mechanism. There are basically three different reactions for thermal degradation: first is the scission of the head-to-head linkage, where the polymerization reaction has been terminated by the head-to-head mechanism. Second is the scission of the unsaturated chain-ends creating radicals or small volatile molecules. Third is the depolymerization initiated by the random chain-scission within the polymer chain. All the reactions are presented at the Figure 2.12. The rate of degradation and temperature needed to initiate degradation is mostly affected by the molecular weight. With higher molecular weight it is likely that there are less defects and chain ends, so the degradation is dominated by the random chain-scission. The polymerization technique does not have a strong effect on the degradation. Side group elimination of the PMMA is reported to happen, but it does not likely have a major effect to the degradation at the side of the other reactions. [43, pp. 97-103]

With PMMA, the scission of head-to-head linkage starts at the temperature around 180 °C. This probably does not greatly reduce the polymer mass in a short period, at least concerning the debinding phase of the ceramic 3D-printing, but it reduces the molecular mass of the chains. Scission of the unsaturated chain-ends takes place between temperature of 220-270 °C and in this way approximately 40-50 % of the polymer degrades. PMMA starts to greatly depolymerize over 300 °C and it is initiated by random chain-scission created radical. The radical propagates by splitting the polymer chain to smaller individual monomers, which become volatile. If there is any of the chains still left, over 400 °C the polymer starts to degrade by random chain scission between any carbon to carbon bond and the molecular mass degrades until the molecules are small enough to evaporate in to gas phase. The depolymerization is endothermic reaction, so it requires heat energy and for that reason does not happen significantly under 300 °C. The vaporization of uncured monomers and additives usually occur under 200 °C. [43, pp. 97-103]
If blending the PMMA to other polymers, such as epoxy, can create interactions inside the blend so that one of the polymers stabilize or destabilize. This might be a result from the different diffusion characteristics of the small and mobile molecules or radicals inside the polymer mixture. However, similar thermal degradation characteristics of single components can often be distinguished in the polymer blends. [43, p. 103]

![Figure 2.12. Degradation mechanisms of the acrylics and methacrylics. (1) Scission of the head-to-head linkage, (2) scission of the chain end (3) random chain scission. R₁ is hydrogen with acrylics and methyl with methacrylates, R₂ is the rest of molecule’s body. [43, p. 98]]

2.3.2. Thermal degradation of Epoxies

Cured epoxy resins generate polyethers: -C-O-C- links that dominate the thermal degradation process alongside the main body structure of the epoxy monomer. Having oxygen atoms in significant amounts in the polymer backbone, decreases the random chain scission temperature, for example, polyethylene oxide’s $T_{50}$ (temperature where 50% of its mass has degraded) is around 345 °C and polyethylene’s over 400 °C. Cured epoxy resin’s backbone starts to degrade from the ether groups around 350 °C, if there is no other functional group that degrades before, like benzene rings. Two widely used epoxy resins diglycidyl ether of bisphenol A (DGEBA) and 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (ECC) have different degradation characteristics, because in DGEBA and in other bisphenol derivates, the aromatic groups degrade forming phenols [44, pp. 64-66] and generally start to degrade at the lower temperatures than the aliphatic ECC. ECC degrades from the cured ether links by random chain scission usually before the random chain scission between the carbon-carbon single bonds occurs. Since with acrylates and methacrylates, the molecular mass has a significant effect to the degradation temperature, higher molecular mass polymer
network withstands higher temperatures. Highly cured ECC still has approximately 50% of its mass left at temperature 420 °C. Also, regarding the conversion degree, the curing agent has an effect to the thermal stability, and epoxies cured with the cationic-initiation have a high homogeneity in the polymer structure and they generally have good thermal stability. [44, pp. 61-70] [45] [46]

In the ceramic 3D-printing point of view the epoxy’s thermal degradation characteristics can be quite suitable. In the debinding phase, the temperature is risen relatively slowly and the epoxy’s temperature area of degradation happens in a wide temperature range, therefore the pressure from the evaporation of the degraded molecules does not increase the pressure too quickly to induce defects. Seok-Ho Hwang and co-workers found that the degradation of ECC takes place quite evenly between temperatures 360-450 °C with thermo gravimetry-studies (TG) with heating rate of 20 K/min. [46]

2.4. COLLOIDAL SYSTEM

In many ceramic manufacturing methods, the ceramic powder is mixed with a liquid medium to produce a slurry. This can the processing and handling of the powder easier, while dry powder can be hard to handle, and upon the packing, the particles do not necessary arrange in the densest form relative to each other. When particles are mixed with the liquid medium, the solution can be called a colloidal system. The colloidal system consists of at least two phases, continuous dispersion medium such as a liquid, and a dispersed particulate solid phase such as ceramic particles. The two phases can be solid, liquid or gas, in fact the only requirement is that the phases can be clearly separated. Typically, the dispersed solid particles dimension varies from 1 to 1000 nm in a colloidal system. When particle size is below 1 nm, the particle and medium physical properties are more close to the true solution and when they are over 1000 nm, particles separates from the medium by gravitation. [47, p. 141]

In the colloidal system between the ceramic particles and a liquid, there are always some interparticle forces creating either attraction on or repulsion interaction between the particles. In the dry powder, where there is nothing else than ceramic particles, the most dominating force is the short range van der Waals force that attracts the particles together. The thermal vibrational energy is negligible at the near room temperature, meaning that it can not overcome the attractive van der Waals forces. The attractive van der Waals force creates agglomerates that are not always desirable in ceramic processing. There are mainly two types of agglomerates: soft and hard agglomerates. Soft agglomerates are loosely bonded particles that create small flocs which flows as an
unit and requires only small external forces to brake. Hard agglomerates are interconnected fractal network with measurable yield stress [47, p. 98]. Hard agglomerates requires great amount of external forces to brake and sometimes they can not be broken to single particles again. In some cases the agglomerates are desirable feature at the powder, because it leaves porosity to the sintered ceramic object and porosity degrease for example heat conductivity [48, p. 506]. To counter the attractive van der Waals force, there are three ways to create repulsive forces at top of the ceramic particles surface mixed in the liquid medium: electrostatic, steric and electrosteric forces. Electrostatic force is based on the electrically charged ions creating a electric charge at the particle's surface. In the case of oxide ceramics, the acidic H⁺ and basic OH⁻ ions create a charge to the surface of the ceramic particle when adsorbed to particle's surface. Depending on the particle's surface chemistry and the subsequent equilibrium reaction, the particles generate an electric charge with the same sign, therefore they will have electric repulsive forces interacting between each other, as seen at the Figure 2.13. Ceramic materials has characteristic isoelectric point (IEP), when the pH of the liquid medium is at the IEP the electrostatadic forces are zero. Under the IEP the particles gains a positive charge and negative charge over it. The alumina’s zeta potential in water vs. pH is presented also at the Figure 2.13. For example, the IEP of the pure aluminum oxide in water is roughly at pH = 9, for zirconium oxide in water it is at pH = 4-5 and for silicon dioxide in water at pH ≈ 2. [47, pp. 142-164]
Figure 2.13. Left: surface charge of the SiO$_2$, right: zeta potential at the function of the pH for the Al$_2$O$_3$ and SiC. IEP is where the zeta potential is zero [49][50]

Steric repulsion force is based on the adsorption of non-charged polymers or surfactant molecules on the particle surface. Schematic picture is presented at the Figure 2.14. In this case, the polymer or surfactant main chain can attach to the ceramic particle surface by the van der Waals forces alone, but in most cases the polymer has a copolymer block or chain end that attaches more readily to the ceramic surface that the main body of the polymer chain. The surfactant molecule body has a ends with different chemical polarity or charge and works in a similar way than polymer, but surfactant is considered to be much smaller molecule than polymer. With the steric stabilization, the polymer or surfactant chains creates an obstacle between the ceramic particles to interact, so that the distance keeps long enough for the attractive van der Waals between the particles to stay negligible. In addition, the polymers and surfactant can change the surface properties of the ceramic particles from hydrophobic to more hydrophilic. The length of the chains should be taken to account, because too long chains can cause the chains to entangle and that can lead to the flocculation, where particles are stack together in bigger recognizable group of particles by the entangling. In general, enough polymer is needed
to form a uniform layer between particles, but entanglement and flocculation occurs with too great amount of the polymer. [47, pp. 164-171]

![Image](image.png)

**Figure 2.14.** Right: schematic from the electrostatic and left: steric repulsion at the particle’s surface [49].

Electrostatic and steric stabilization can be combined to electrosteric stabilization. Electrosteric stabilization is done using polymers that have an ionizable functional group, like carboxylic acid group, which creates a charge at the surface when it dissociates and the rest of the polymer chain adsorbs at surface of the ceramic creating steric repulsion. For this purpose, the polyacrylic acids and polymethacrylic acids and also their salts, like sodium polyacrylate acid, are commonly used. Carboxylic acids usually have a low dissociation coefficient in the acidic mediums, so controlling the pH of the medium is important to obtain the best stabilization between the particles. [47, pp. 172-176]

When the colloidal system is well stabilized it means that the particles can move more freely in relation with each other and for this reason the viscosity is a great way to measure the effect of stabilization and the interactive forces of the system. The viscosity gains it lowest value with the right amount of the dispersing agent. If too low amount, the repulsive forces can not defeat the attractive forces, and too high amount can lead to the entanglement of the dispersion agent’s polymer chains. In addition, too great electrostatic repulsion forces keeps the distance between particles great and hinders their movement relating each other. [50]

### 2.5. ENGINEERING CERAMICS

Ceramics are one of the four major material groups with metals, polymers and hybrid (composite) materials. Ceramics are characterized as an inorganic solid material, non-metallic, comprising of metal, metalloid or non-metal atoms primarily hold together by the ionic or covalent bonds [51, pp. 96-103]. Ceramics microstructure can appear as a crystalline or amorphous, giving them a large variety of different properties. The most specified properties for the whole ceramic group are the high hardness, low toughness,
high melting point, brittleness, chemical stability and thermal stability. Ceramics can be divided in many groups by considering of their properties in use, but this study focuses on the engineering ceramics. Engineering ceramics are a group of ceramics that are characterized by their extremely high properties considering of high melting point, good thermal and chemical stability, hardness and wear resistance, high elastic modulus with high compression strength and low density. Limiting factors of the engineering ceramics are brittleness, large deviation in strength, high costs, difficult machining, restrictions in shape and sizes due the current manufacturing methods and in many cases they are not standardized materials. [48, pp. 1-12]

In ceramics processing, everything starts from the ceramic powder. Because of the high melting point of the ceramics, like aluminum oxide’s (Al₂O₃) melting point ($T_m$) is over 2000 °C [51, p. 191], the melting is used only in special cases as a part of the manufacturing method. Instead the ceramic powder is sintered together by atomic diffusion movement with the help of high temperature and/or pressure. So, any properties and errors of the powder reflects also to the final sintered product, like in a domino effect. The driving force of the diffusion during the sintering is the external heat and the free energy contained in the surface of the ceramic particles. The free energy leads to densification and to the minimization of the surface area. Because the ceramic powder always contains some air or empty space, the part shrinks during the sintering when the density increases. [47, pp. 37-89] [48]

![Figure 2.15. Domino effect of the ceramic raw powder to the final product [51].](image)

Because of the brittleness of the ceramic materials, their strength is usually measured with the three or four point bending test rather than tensile tests. While using the ceramic in a particular application, it is necessary to take into consideration that the ceramics fail catastrophically before they show any plastic deformation as a warning sign. Therefore,
the fracture toughness is almost always used to define the strength of ceramic materials and one very important aspect is the flaw size and geometry at the surface or inside of the ceramic part. The flaw size can be used for theoretically estimating component bending or tensile strength by Griffith formula:

\[
\sigma_f = A \times \left( \frac{E \gamma}{c} \right)^{\frac{1}{2}},
\]

(2)

where \( \sigma_f \) is the fracture strength [MPa], \( E \) is Young’s module [MPa], \( \gamma \) fracture surface energy [J/m\(^2\)], \( c \) is the flaw length (\( c/2 \) if flaw inside the material) [m] and \( A \) is a constant depending from the shape of the flaw and loading geometry [m(MPaJ)]\(^{1/2}\) [51, p. 218].

Also, the strength under uniaxial stress is expressed as a fracture strength according to the formula:

\[
\delta_f = \frac{\gamma K_{ic}}{\sqrt{c_c}},
\]

(3)

where the \( Y \) is a dimensionless constant describing the geometry of a crack, \( K_{ic} \) is the critical stress intensity (fracture toughness) [MPam\(^{1/2}\)] and \( c_c \) is the critical flaw or crack size [m] [51, p. 218]. As it is seen from the formulas (2) and (3) the strength of the ceramic is not always isotropic and this might be caused for example by the manufacturing of the part, if the surface of the ceramic is grinded and it has left scratch at the surface. Shape and direction of the defect affects so that what a longer crack and sharper crack’s tip is, the more of the tension is concentrated to the tip. The effect of the crack is almost negligible if the crack is parallel and it has the most weakening effect if it is horizontal to the direction of the stress. This is opposite with the compressive stress, when the parallel cracks and flaws causes the weakness. Effect to the strength of the ceramic part is presented at the Figure 2.16.
Because the strength of ceramics is can vary even with the same manufacturing technique, it is matter of a probability on how does the flaws and cracks develops during the manufacturing and use. The failure probability of the ceramic material can be estimated with the Weibull statistics and in many cases strength is announced by e.g. $\sigma_{50}$ or $\sigma_{90}$ meaning that the 50% or 90% of the components made from the same material with same manufacturing methods can withstand the loading. [48, pp. 95-118]

To discover the true strength of the ceramic component, the shape and manufacturing method has to be examined carefully for example with finite element method (FEM) analysis to recognize the possible areas where the stress concentrates. With ceramics, the component size is also a major factor, because it is more likely that flaws and errors occurs in the big components rather than in small. The type and distribution of flaws throughout the specimens has to be able to be determined. One way is to examine the fractured surface of the broken part’s for example with microscopy. [51, pp. 581-593]

3-point or 4-point bending test is commonly used to define the strength of the ceramic materials. Bending tests are demonstrated at the Figure 2.17. In the bending test, the force is concentrated to the certain area of the specimen and it brakes on its weakest point, from flaw or crack, from that area. An adequate scratch or mark can be done at the surface of the specimen so that it will break at the scratched place and different kind of scratch geometry effects to the strength can be compared. The bending strength for the 3-point ($\sigma_{3b}$) and 4-point ($\sigma_{4b}$) bending test can be presented mathematically as:

$$\sigma_{3b} = \frac{3P + L}{2W + t^2}$$  \hspace{1cm} (4)
\[ \sigma_{4b} = \frac{3 \cdot P \cdot (L - I)}{2 \cdot w \cdot t^2} \]  

(5)

Here the \( P \) is the maximum load [MPa], \( L \) is the distance between lower supporting rolls [mm], \( I \) distance between upper loading rolls [mm], \( w \) width of specimen and \( t \) thickness of the specimen [mm]. [51, pp. 224-225]

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Figure 2.17. Demonstration of the 3-point and 4-point bending tests [51, p. 222].

Ceramics can be machined before sintering (green machining) and after sintering (hard machining). Machining is used to form shapes for the ceramic component by removing material. When machining ceramics, the hardness of the material needs to be taken into account as many ceramics such as \( \text{Al}_2\text{O}_3 \) and \( \text{ZrO}_2 \) (zirconium oxide) are used as an abrasive by themselves. Therefore tools with high hardness and abrasion resistance is required for machining, such as diamond tools. Even the green machining might wear the tools severely. To increase the component strength for the machining, it is possible to pre-sinter it to the so called “white state”, where the sintering process has started, but the piece has not gained its full sintered density and hardness. If the component is machined in green or white state, it has to be noticed that the ceramic shrinks still when it is sintered to the full density, so the green state machining only gives the shape, not the final dimensions of the component. After sintering, it is often necessary to machine the component to gain the adequate dimensional tolerances and proper surface quality. Polishing the component highly increase it strength by removing surface cracks and flaws [51, pp. 269-270]. Machining the sintered ceramic component is slow difficult and expensive process that requires skills and knowledge from the machinist [51]. 3D-printing of ceramics is developed and studied for this reason: shaping and producing different geometries to ceramics is particularly difficult. With 3D-printing, all shapes and geometries are equally easy to manufacture while it doesn’t change the basic properties of the ceramic.
2.5.1. Aluminum oxide

Aluminum oxide ( alumina), a chemical compound with the formula Al\(_2\)O\(_3\), is the most used engineering ceramic, owning over 35% of the engineering ceramics market share [52]. Refractories are the most used application form of the Al\(_2\)O\(_3\), others include abrasives, whiteware and spark plugs and engineering ceramics. The alumina’s most important properties that make it a good engineering ceramic are: it is an electrical insulator with relatively high thermal conductivity, excellent dielectric properties and low dielectric constant, good hardness, stiffness, wear resistance, strength and thermal stability, strong resistance to the acids and alkali attacks at elevated temperatures and also good corrosion resistance properties. Cons of the alumina is that it has a poor thermal shock resistance, only about 100 °C [51, p. 278], and stress corrosion resistance at the highly humid or under water environment when silica is used as an additive with alumina [53, pp. 524-533]. Water molecules grows the cracks at the glassy grain boundaries where silica locates.

Only rarely the alumina consist of pure 100 % Al\(_2\)O\(_3\), additives like SiO\(_2\) and CaO is used as sintering aids and for example ZrO\(_2\) and long SiC particles are used to strengthen the alumina to improve its fracture toughness [48, pp. 418-423]. Zirconia strengthening works in a way that the zirconia particles remain separate from the alumina and after sintering they are in a metastable state. During the crack growth in the alumina, the zirconia particles gain energy from the crack propagation and the phase transformation takes place creating compressive stress which can inhibit the crack growth. Another way to improve the fracture toughness is to add long SiC particles (SiC whiskers) so that they makes solid bridges, kind of like fibers, over the propagating crack making its movement more difficult. The ZrO\(_2\) and SiC toughening mechanisms are presented at the Figure 2.18. In addition, because the grain boundaries are usually the weak link between the grains at the alumina, decreasing the grain’s size makes the crack harder to propagate due it needs to make more surface and so needs more energy. To decrease the grain size, smaller particle sizes in the powder is required, while it makes the handling of the powder more challenging [51].
Zirconium oxide (zirconia) is another frequently used engineering ceramic that exhibits favorable properties. These good properties are: hardness, wear resistance, low friction coefficient, chemical inertness, ionic conductivity, electrical insulating properties, low thermal conductivity and high melting temperature. The fracture toughness is one of the best in the group of engineering ceramics and can yield over 1000 MPa bending strength with the yttrium stabilized zirconia. This means that the zirconia can withstand larger cracks and flaws than for example alumina without fracturing. It is important to notice that when using the pure zirconia, its density is not thermally stable over temperature of 1000 °C, in which it experiences a phase transformation and the density changes. Zirconia exhibits three polymorphic phase changes at the atmospheric pressure [51, pp. 105-107]. Under 1000 °C, zirconia occurs mainly in the monoclinic crystal structure and its density is around 5,83 g/cm³. Around 800 - 1170 °C the zirconia’s crystal structure transforms to the tetragonal form and density increases to 6,1 g/cm³. About at 2370 °C, zirconia gains a cubic crystal structure with density of 6,06 g/cm³ and around 2680 °C it melts.

To prevent the phase transformation the zirconia is mixed with other oxides such as MgO, CaO, CeO₂ and Y₂O₃, that fully or partially stabilize the crystal structure of zirconia. In fully stabilized zirconia (TZP = tetragonal zirconia polycrystal), the crystal structure is locked to tetragonal form and the crystal structure remains same at least from 0 to
1200 °C [51, p. 106]. In the partially stabilized zirconia (PSZ = partially stabilize zirconia), the crystal structure is mainly cubic with dispersion of tetragonal precipitates. In PSZ, the density does not change that dramatically than with the pure zirconia, when the PSZ experiences a phase transformation. Thermal expansions can be seen from the Figure 2.19. The TZP is can be done by mixing of $\text{Y}_2\text{O}_3$, usually about 3 mol-%, or $\text{CeO}_2$ to the pure zirconia. The PSZ can also be achieved with many other additives, for example with the $\text{MgO}_2\text{O}$ or $\text{CaO}$. In engineering applications, the yttrium oxide stabilized zirconia (Y-TZP) is commonly used, while mixing the zirconia with $\text{Y}_2\text{O}_3$ lowers ceramic's fracture toughness, the bending strength increases and can be over 1000 MPa.

![Figure 2.19. Thermal expansion of different zirconia compositions as a function of temperature, from the left: first pure zirconia, then TZP and PSZ. [51, pp. 105-107]](image)

Zirconia particles can be used as a toughening agent in other ceramic materials, like in alumina. Zirconia toughened ceramic (TTC = transformation-toughened ceramic) works in a way that the zirconia particles are in the metastable phase, tetragonal form, inside the ceramic matrix. When the crack occurs and hits the zirconia particle, it absorbs energy from the crack and undergoes a transformation from tetragonal to monoclinic phase with about 3 – 5 % volume expansion. This will induce pressure towards the crack, limiting its progression. [51]

Zirconia has relatively high thermal expansion coefficient, compared to the other ceramic materials, which might be limiting factor in applying zirconia. However, the thermal expansion coefficient is near the one of cast iron and steel, so it can be effectively used together with those metals in applications which include large temperature changes. This property, including zirconia's good thermal insulating properties, is used for example in the turbine blades as a thermal insulating coatings. [51]
2.5.3. **Silicon oxide**

Silicon dioxide (silica, SiO\(_2\)) does not find many applications in the field of high performance engineering ceramics. It is still widely used material and cheap. Pure silicon is the second most abundant element in the earth’s crust and 90 % of the earth’s mass is made from minerals that include silicon. Therefore, silicon dioxide is a widely available material. Compared to the alumina and zirconia, the silica has a lower melting temperature, fused silica \( T_m = 1650 \) °C [51, p. 191]. World wide, most of the silicon oxide goes to the construction industry’s use and majority of the rest is used to make silica-based glasses. When melted and cooled rapidly or with certain mixture of oxides, the silicon oxide gains an amorphous form and transparency with low refractive index. Silicon dioxide is also highly resistant to the acids, except hydrofluoric acid, so chemical containers are commonly made from it. Silicon dioxide is formed naturally at the surface of the other silicon based non-oxide ceramics, like silicon nitride, to prevent and protect the material from further oxidation. [54] [55]

2.5.4. **Silicon nitride**

Non-oxide engineering ceramics are more difficult to manufacture due their readiness to oxidize at the elevated temperatures. Nevertheless, many of them are highly suitable for the engineering ceramic applications because of their excellent properties. Silicon nitride, Si\(_3\)N\(_4\), has many good properties, of which the most impactful properties are high temperature strength, superior thermal shock resistance, low density, good fracture toughness, excellent wear resistance, good resistance to mechanical fatigue, creep and oxidation. Down side of silicon nitride is that it is difficult to manufacture and the properties are highly dependable from the manufacturing method. Silicon nitride maintains its mechanical properties even at high temperatures, over 1200 °C and it can withstand quick thermal shock of over 800 °C. These two properties makes it wanted material for example in the combustion engines. [51]

The creep properties of silicon nitride vary greatly with the amount of the sintering aids, however, the less sintering aids are used, the harder the densification process becomes and more creep resistance the silicon nitride gains. Sintering aids, such as SiO\(_2\) and MgO melts at the sintering temperatures of Si\(_3\)N\(_4\), forming high viscosity liquids. When sintered, the silicon nitride particles grow into long grains randomly orientated and interlocked to each other. When cooled down, the sintering aids form solid glass structures between the grains, however they soften again at the elevated temperatures. The silicon nitride powder needs to be sintered in an inert atmosphere, for example in
vacuum or in nitrogen gas, so that the oxidation of the silicon does not occur. For the sintered and dense silicon nitride material, a thin oxidized layer at the top of the material is essential, because it chemically protect the bulk material from oxidizing further at the elevated temperatures. [47, pp. 365-440]
3. EXPERIMENTAL PROCEDURE

3.1. MATERIALS AND METHODS

3.1.1. Printing Materials

In this study three different printing precursor slurries have been used for printing and their printing and heat treatment behavior was examined. These materials are LithaLox HP 500, LithaCon 3Y 610 purple from LITHOZ GmbH [56] and a newly developed Al₂O₃-printing slurry OMA Al₂O₃. In addition, the viscosity and curing depth were measured for the first prototype of a new ZrO₂-printing slurry’s (OMA ZrO₂).

LithaLox HP 500 consists of Al₂O₃-powder and multifunctional methacrylate-based photosensitive medium [57] [58]. Al₂O₃-powder solid loading is 49 vol-%. LithaCon 3Y 610 purple consists of 3 mol-% yttrium stabilized (Y-TZP) ZrO₂-powder with a solid loading of 39 vol-%, and a photosensitive medium made of methacrylic ester and 2-Hydroxyethyl methacrylate [59]. Basics of the OMA Al₂O₃ and OMA ZrO₂ recipes are discussed in the section 4.1.

The OMA Al₂O₃ slurry developed and tailored during this study is based on monomers that were kindly donated to us by SARTOMER. The additives were bought from the Sigma-Aldrich or kindly donated to us by BASF. The Al₂O₃-powder is from ALBEMARLE® and ZrO₂-powder was also kindly donated by Saint-Gobain ZirPro.

For the LithaLox HP 500 and LithaCon 3Y 610 purple, heat treatment programs are already provided by Lithoz and they are presented at the Figure 3.1.
3.1.2. Equipments, Softwares and Machines

The 3D-printer used is Cerafab 7500 from Lithoz GmbH [6] along with all the additional equipment that Lithoz GmbH offers for it. Furnaces were TERMAKS SERIES TS8000 for precondition, CARBOLITE RHF 1500 for preconditioning and debinding and ENTECH ECF 40 / 17 for sintering. For rheology measurements, we used Anton Paar
Physica MCR301 with a cylinder geometry. Dilatometer ADAMEL LHOMARGY DI-24. Infrared spectroscopy was BRUKER TENSOR 27 with diamond ATR-unit. Thermogravimetry was NETZSCH TG 209 F3 Tarsus. Differential scanning calorimeter was (DSC) NETZSCH DSC 214 Polyma. Electron microscopes are PHILIPS XL30 and Field emission scanning electron microscope (FESEM) Zeiss ULTRA plus and JEOL JSM-IT500.

Ball milling was done with the Materials Science Laboratory’s custom ball mill with zirconia balls. Curing depth measurements were carried out with a custom LED-bench and the LEDs used in the bench were LED ENGIN LZ1-00B202 Blue LED emitter 457nm [60] with the measured light intensity of 39,5 mW/cm².
4. RESULTS AND DISCUSSION

4.1. PRINTING

For developing the new $\text{Al}_2\text{O}_3$-printing slurry, precursor acrylate and methacrylate monomers curing speed was tested with the IR-spectrometry. After 10 s of irradiation with the test bench, it was clearly noticeable that the acrylate monomers cure faster than the methacrylate monomers. The difference in curing speed of acrylates vs. methacrylates was also stated by Samuel Clark Ligon-Auer and coworkers [20] and also by E. Schwarzer and coworkers [26]. Therefore, acrylates are selected for the main component for the new slurry’s photosensitive medium, slurry is called OMA. Lithoz has chosen methacrylates for their slurries photosensitive medium’s main component. This is also confirmed with the IR-spectrometry from the LithaLox HP 500 and LithaCon 3Y 610 purple. OMA-slurry was mixed in a manner that the dispersion agent, additives and photoinitiators were first mixed well to the monomers, and after that, the ceramic powder, $\text{Al}_2\text{O}_3$ or $\text{ZrO}_2$, is dispersed in to yield a solid content of 50 vol-% in the slurry. All slurry components were first mixed with impeller stirring to have the components visibly dispersed and then the slurry was ball milled at least for 24h with the speed of approximately 2 rps. All the stirring and ball milling was done either at the dark room or room deprived from the wavelengths of visible blue light.

There are many factors that have an effect to the curing thickness of the slurry and they have been studied widely by many different research teams [15] [17] [23] [25] [61] [62]. For determining the curing depth, the formula (1) is used. From the formula (1), the $D_p$ and $E_c$ are characteristic factors for each slurry. Choosing fast curing monomers and increasing the photoinitiator concentration decrease the $E_c$. Increasing the ceramic loading and adding inhibitors to the slurry increase the $E_c$ and decrease the $D_p$ at the same time. Inert dyes slightly increase the $E_c$ but do not affect to the $D_p$, because it only absorbs or reflects the light away from the slurry. Inert dyes do not react in any way with the monomers or photoinitiators at any point of the process. For the SLA-slurry or -resin, it is crucial to have a low $E_c$ so that the slurry starts to solidify fast enough at macroscale during the light irradiation. The $E_c$ and $D_p$ and the final properties of the printed green body is affected by the characteristics of the photopolymerization process. Higher curing degree can be achieved with the proper slurry composition, high gelation point and proper amounts of the photoinitiator and other additives with highly polymerizable
monomer composition [63]. Curing rate can be affected with the choice of monomers, additives and photoinitiator concentration [64]. While the increase of photoinitiator concentration increase the curing rate, it also might decrease the final curing degree of the slurry. The advantages or disadvantages of the selection depends from case to case, for example the lower curing degree gives lower mechanical properties to the green body, but it also decreases the polymerization shrinkage and lowers the thermal degradation temperature. Adding plasticizers to the slurry has been found to increase the gelation point and decrease the delamination between the layers [65]. All of these factors are taken to concern when the OMA slurry’s photosensitive medium is developed.

4.1.1. Curing Depth

Before the slurry can be printed, the curing depth as a function of the light energy has to be determined for each slurry. The slurry was irradiated with multiple different exposure times, washed with ethanol and the thickness measured with a micrometer. Cure depth $C_d$ as a function of irradiation energy $E$ is presented in the Figure 4.1.

![Figure 4.1. Cure depths as a function of irradiation energy of LithaLox HP 500, LithaCon 3Y 610 purple, OMA Al2O3 and OMA ZrO2 slurries at room temperature.](image)

From the Figure 4.1, the plotted trend line of each formula gives the $E_c$ when the $C_d$ is 0 μm. $D_p$ is the slope of trend line. $E_c$ and $D_p$ of each slurries is collected to the Table 4.1.
When the slurry is printed, the $C_d$ should be at least 3-4 times the intended layer thickness to ensure good layer adhesion and prevent delamination [15]. In addition, it was noticed that long light exposures, when $C_d$ is >10 times the layer thickness, cause delamination between the layers, like at the Figure 4.2. Moreover, the light scattering with high exposure times increases, creating dimensional inaccuracy in XY-direction, as seen in the Figure 4.2. It is found that to decrease the light scattering effect, the particle size should not be near the same size as the wavelength of the light. Another issue to cause increased light scattering is the refractive index differences between the monomer medium and particles surface [17]. This is especially problem when the ZrO$_2$ is used in the slurries. For example, HDDA has refractive index is 1,40 [17] and ZrO$_2$ has 2,13 [66]. The increased light scattering causes over curing in the horizontal direction of the printing platform and in that way causes inaccuracy in the green body dimensions.

**Table 4.1. $E_c$ and $D_p$ of the slurries. Data from the Figure 4.1.**

<table>
<thead>
<tr>
<th>Slurry</th>
<th>$E_c$ [mJ/cm$^2$]</th>
<th>$D_p$ [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMA Al$_2$O$_3$</td>
<td>59,5</td>
<td>142,5</td>
</tr>
<tr>
<td>OMA ZrO$_2$</td>
<td>57,4</td>
<td>67,2</td>
</tr>
<tr>
<td>LithaLoxHP500</td>
<td>16,4</td>
<td>116,7</td>
</tr>
<tr>
<td>LithaCon3Y610 Purple</td>
<td>19,8</td>
<td>94,8</td>
</tr>
</tbody>
</table>

Figure 4.2. Left picture of severely delaminated LithaCon 3Y 610 purple printed part and, right horizontally over-cured 2x2x25mm sticks that are united by light scattering polymerization. All exposures were done in a blue light protected room.
The OMA $\text{Al}_2\text{O}_3$ $\text{C}_d$ was also measured at the temperature of 40 °C. Higher temperature had no significant effect on the $\text{C}_d$ as it was exactly the same as measured at room temperature.

4.1.2. Viscosity

Viscosity as a function of shear rate was measured for the LithaLoxHP500, LithaCon 3Y 610 purple, OMA $\text{Al}_2\text{O}_3$ and OMA $\text{ZrO}_2$ and the results are presented in the Figure 4.3. With low shear rates all the slurries have a shear thinning behavior and as the shear rate increases, the slurries become shear thickening. While the pure monomer solutions were measured to have linear Newtonian fluid viscosity characteristics, the slurries appear to exhibit non-Newtonian behavior. Shear thinning behavior at low shear rates is most likely occurs because the ceramic particles are weakly flocculated and break down under relatively small shear stress. With high shear rates, the particles collides more frequently with each other creating new flocculates and therefore the shear thickening. LithaCon 3Y 610 purple and OMA $\text{ZrO}_2$ slurries exhibit the shear thickening behavior with lower shear rates compared to LithaLox HP500 and OMA $\text{Al}_2\text{O}_3$ slurries, and in addition, the shear thickening effect is also stronger. Zirconia particle’s iso electric point (IEP), pH = 4-5 in water medium, is lower than that of the alumina’s, pH = 9 in water medium [47, pp. 142-164]. The IEP might explain at least partially the differences in the viscosities with the OMA $\text{Al}_2\text{O}_3$ and OMA $\text{ZrO}_2$, while the same monomer solution medium and dispersing agent was used with both powders. In addition, zirconia particles in the OMA $\text{ZrO}_2$ have a smaller average particle size than the alumina particles in OMA $\text{Al}_2\text{O}_3$. Increasing the particle size has been found to decrease the viscosity [47, pp. 266-269] [61].
Temperature has a major influence on the viscosity of monomer solutions [67] as can also be seen with the ceramic 3D-printing slurries. The temperature effect on the viscosity can be seen from the Figure 4.4. In all of the four measured slurries, the viscosity profile remains similar with different temperatures, however the absolute viscosity changes as a function of temperature. For example, the OMA ZrO₂ starts to shear thicken when the shear rate increases, but increasing the temperature increases the highest shear rate where the slurry is still shear thinning.
Figure 4.4. Viscosities as a function of shear rate of LithaLox HP500, LithaCon 3Y 610 purple, OMA Al$_2$O$_3$ and OMA ZrO$_2$ at the temperatures of 22, 30, 40 and 50 °C.

4.1.3. Printing Parameters

The slicing software of the CeraFab 7500 printer allows user to use the printer with multiple different settings depending on the situation and material. Perhaps the most important setting is the light exposure time and intensity. The CeraFab 7500 maximum intensity setting (100%) yields intensity of 51.2 mW/cm$^2$ and the exposure time can be changed with 0.01 s accuracy. The layer thickness can be alternated between 25 - 100 μm with 1 μm accuracy. Before the actual part is printed, the glass building platform needs to be covered with the cured slurry so that the part will stick to it properly, referred to as backlight exposure. Velocities of the vat movement up and down is better
to keep slow so that the print does not get fractured when it is lifted from the vat bottom. The separation of the vat and building platform and general movement of a similar kind of bottom-up SLA process is studied by Xiangquan Wu et al. [68]. When the part is lowered to the vat again for the new layer, the printer waits a certain time so that the part surface wets properly and that any air bubble can escape. The slicing program also allows to input size correction factors for each axels X, Y and Z, to compensate the shrinkage that occurs during the heat treatments. Parameters that have the highest impact to the printing process are presented in the Table 4.2.

Table 4.2. Printing parameters of the three materials for the CeraFab 7500 slicing program.

<table>
<thead>
<tr>
<th>Material</th>
<th>LithaLox HP 500</th>
<th>LithaCon 3Y 610 purple</th>
<th>OMA Al2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer thickness</td>
<td>25 μm</td>
<td>25 μm</td>
<td>50 μm</td>
</tr>
<tr>
<td>backlight exposure</td>
<td>1,6 s</td>
<td>2,0 s</td>
<td>5,0 s</td>
</tr>
<tr>
<td>backlight exposure waiting time</td>
<td>180 s</td>
<td>300 s</td>
<td>120 s</td>
</tr>
<tr>
<td>Exposure time</td>
<td>3 s</td>
<td>2,5 s</td>
<td>4,2 s</td>
</tr>
<tr>
<td>Intensity</td>
<td>80 %</td>
<td>80 %</td>
<td>80 %</td>
</tr>
<tr>
<td>Exposure</td>
<td>122,9 mJ/cm²</td>
<td>102,4 mJ/cm²</td>
<td>200,1 mJ/cm²</td>
</tr>
<tr>
<td>Waiting time general</td>
<td>4 s</td>
<td>6 s</td>
<td>4 s</td>
</tr>
<tr>
<td>Compensation X/Y</td>
<td>1,245</td>
<td>1,354</td>
<td>-</td>
</tr>
<tr>
<td>Compensation Y/Z</td>
<td>1,275</td>
<td>1,356</td>
<td>-</td>
</tr>
</tbody>
</table>

LithaLox HP 500 and LithaCon 3Y 610 purple achieve a good back layer adhesion with the building platform, which is why only short back light exposure is needed. For OMA Al₂O₃ slurry, the adhesion needs to be helped with curing a 0,5 - 1 mm layer of the slurry on top of the building platform glass by hand before printing. Waiting time needs to be the longest for the LithCon 3Y 610 purple, because it has the highest viscosity and therefore the air bubbles need more time to escape. The light energy input for LithaLox HP 500 was chosen based on the Lithoz recommendations, which is 122,9 mJ/cm², and according to the Table 4.1 and the formula (1), it corresponds $C_d$ of 235 μm. LithaCon 3Y 610 purple’s recommended exposure is 102,4 mJ/cm², which equals $C_d$ of 156 μm. For OMA Al₂O₃ slurry, the light exposure of 200,1 mJ/cm² was determined from the Table 4.1, in order for that the exposure to correspond roughly three to four times of the wanted layer thickness of 50 μm, which corresponds to $C_d$ of 173 μm.
For OMA ZrO$_2$, many different printing parameters were trialed. The printing of OMA ZrO$_2$ was found to be generally more difficult regardless of the chosen printing parameters. The $D_p$ is low compared to other slurries, which is most probably caused by the high refractive index difference between the monomer medium and the zirconia particles. After the printing process, the whole vat was polymerized, which left the rest of the slurry unusable for further printing.

The recommended compensation factors from Lithoz for dimensions for LithaLox HP 500 and LithaCon 3Y 610 purple were used, as presented in the figure Figure 3.1. The Z-axis compensation is higher than the XY-compensation for both Lithoz slurries. This is probably because the parts can experience creep along Z-axis during the sintering if sintered in the same printing orientation.

### 4.1.4. Cleaning

After the printing, the green body is still covered with uncured slurry. The uncured slurry also covers the small details, like holes, and needs to be removed, or it can have affect to the small detail dimensions. E. Schwarzer and co-workers[26] and Emil Johansson and co-workers [15] have studied the cleaning of the printed parts. They found that low viscosity slurries are easier to clean and that details are easier to preserve during the cleaning. In addition, the cleaning liquid needs to be selected carefully. Acetone dissolves well many organic solutions, but in this case, it also causes severely delamination by getting swallowed between the layers of the green body. Ethanol has moderate cleaning properties and it also causes moderate delamination. Organic esters like dibasic esters [69] have moderate to great cleaning properties and generally cause no delamination. The effects of acetone and ethanol were noticed also in this study. In this study, all printed parts were cleaned by first soaking it in the LithaSol20, cleaning liquid from Lithoz, or dibasic ester and kept at the low power ultrasonic bath for 10 minutes. Then the parts were washed with LithaSol20 or dibasic ester with help of the compressed air to get all small details visible. The ultrasonic bath wash was repeated multiple times if necessary. Finally, the parts were flushed with mixture of 70/30 ethanol/water or with pure water and dried with compressed air.

Many of the as-printed parts were broken in this cleaning phase, simply because the cleaning was done manually and is prone to human error. The printed parts might be stuck too tightly to the build-platform and the removal brakes the part. In addition, the backlight exposure layer needs to be cut off by a razor blade or some other sharp tool.
The cleaning of a single batch can all together take about 0.5 - 2 hours, depending from complicity of the printed parts.

Parts printed with OMA Al₂O₃ slurry withstood acetone, ethanol and water better than the LithaLox HP 500 and LithaCon 3Y 610 purple printed parts. LithaLox HP 500 and LithaCon 3Y 610 purple were significantly delaminated when they were soaked in acetone or ethanol for over 12 h. However, when OMA Al₂O₃ printed parts were kept under acetone or ethanol or water over 12 h, they did not delaminate as can be seen from the Figure 4.5 with the reference untreated part. However, as can be seen from Figure 4.5, the acetone, ethanol and water did have an effect to the surface quality of the printed part. Reference surface is smooth with only few defects, while all cleaning liquids roughened the surface, most likely because they dissolve material out of the surface. At the surface, there might be left some not completely cured slurry that has acquired less light exposure, for example, because of the light scattering to the sides and therefore partly dissolves away. There are also some bubbles on the surface that might have appeared when the liquid is swollen by the polymer network swelling the structure.
4.1.5. Conclusion of Printing

Quality of the printing process affects greatly to the final sintered component properties. Mistakes and errors made in the printing and cleaning phase cannot be repaired later. One source of surface errors are the supports that are required to print overhangs to the component. Characteristically to SLA, the CeraFab 7500 can print only one material at a time. Therefore, the support structures are printed with the same material as the component itself and need to be removed to reach the final shape of the printed part. The removal is most easily done during the cleaning phase or after the preconditioning phase. However, the removal of supports can leave an uneven or a rough surface on the printed piece. The optimization of support structures is a high priority design challenge in the future, so that they do not significantly affect to the quality of the final product, but still provide necessary support during the printing.

The mechanical properties of the parts printed with Lithoz slurries and the newly developed OMA Al$_2$O$_3$ and OMA ZrO$_2$ are different. Prints made with Lithoz slurries are rigid and hard, while parts done printed with OMA Al$_2$O$_3$ and OMA ZrO$_2$ are soft and

*Figure 4.5. OMA Al$_2$O$_3$ printed parts washed with different solvents for 12h, a) reference, b) acetone, c) ethanol, d) water. Acquired with optical microscope. The scale is 500 μm long in each figure.*
flexible. The difference comes from the polymer network, and for the OMA slurries, flexible acrylate monomers were selected. As a result, the flexible OMA parts cleaning is significantly easier and only few parts were broken during the cleaning phase, in comparison to the parts printed with the Lithoz slurries. The lower viscosity of OMA $\text{Al}_2\text{O}_3$ also helps in with the cleaning process. On the other hand, the rigid and hard nature of Lithoz slurries makes it possible to print smaller details compared to OMA slurries. For example, the printed sections of OMA $\text{ZrO}_2$ were so soft that the printing was only possible only with a relatively large wall thickness.

Microscope images from the OMA $\text{Al}_2\text{O}_3$ and LithaLox HP 500 after printing are presented at the Figure 4.6. In addition, the layered structure of the printed parts can be seen in the Figure 4.6.

![Microscope images](image1.png)

**Figure 4.6.** Layered structure of the SLA 3D-printed ceramic parts a) and b) from OMA $\text{Al}_2\text{O}_3$, c) from LithaLox HP 500 and d) LithaCon 3Y 610 purple. Bigger particles have been worn out of the surface during the grinding of the sample. Acquired with SEM.

Delamination was observed to happen more likely along the layer lines than across them, as can be seen from the Figure 4.7.
4.2. PRECONDITIONING

Preconditioning phase in this study is defined as thermal post processing of the printed green parts at low temperatures. As seen from the Figure 3.1, the precondition phases of the printed parts take a large portion of the total process time with Lithoz slurries. The temperature is slowly risen from room temperature to 120 °C and dwelled at certain temperatures for several hours. Reason why the precondition phase is required and how the heat in this phase affects to the green body is studied in this chapter. LithaLox HP 500, LithaCon 3Y 610 purple and OMA Al₂O₃ is studied in this chapter.

4.2.1. Differential scanning calorimeter

First all three slurries are measured with DSC to see if they undergo any chemical or physical reactions under 200 °C. The results are presented at the Figure 4.8. DSC measurements of the slurries, heating rate 10 K/min in nitrogen atmosphere.
LithaLox HP 500 and LithaCon 3Y 610 purple undergo an exothermic reaction starting from 94 °C for LithaLox HP 500 and 84 °C for LithaCon 3Y 610 purple and ending around 176 °C and 179 °C with the peak power values at around 140 °C and 135 °C. This exothermic reaction indicates that the LithaLox HP 500 and LithaCon 3Y 610 purple cure thermally during the heating by a radical polymerization reaction. Radical polymerization reaction of polyacrylates is found to be an exothermic reaction [35, p. 20]. Some photoinitiators can be activated by the heat and an incomplete curing can continue at elevated temperatures. The curing degree only rarely increases to the final degree during the printing and heat induced curing is used to improve the curing degree of the formed plastic in 3D printing when there is an initiator that activates by heat [70]. The OMA Al₂O₃ slurry shows no thermal curing phenomena, there was no exothermic reaction under 200 °C. Therefore, it cannot be thermally cured to e.g. increase the curing degree of the monomers.

Next the printed parts were measured with the DSC. The parts were printed with the parameters showed in the Table 4.2. Results of the DSC measurements are presented in the Figure 4.9. LithaLox HP 500 showed a clear thermal post curing behavior, while LithaCon 3Y 610 purple cured only very slightly. As could be expected based on the results of the slurry DSC, OMA Al₂O₃ printed part did not show any thermal curing

**Figure 4.8.** DSC measurements of the slurries, heating rate 10 K/min in nitrogen atmosphere.
behavior. LithaLox HP 500 has a large exothermic maximum between 120 °C and 180 °C, which means that there are still quite a lot of uncured monomers after the printing light exposure.

![DSC measurements of the OMA Al₂O₃, LithaCon3Y 610 purple and LithaLox HP500 printed parts during the precondition processing phase. Heating rate was 10 K/min in a nitrogen atmosphere.](image)

**Figure 4.9.** DSC measurements of the OMA Al₂O₃, LithaCon3Y 610 purple and LithaLox HP500 printed parts during the precondition processing phase. Heating rate was 10 K/min in a nitrogen atmosphere.

### 4.2.2. Dilatometer

The thermal dilation of the printed parts was measured with a dilatometer. The dilatometer results are presented in the **Figure 4.10**. For all the three materials, the dilatometer measurement showed a clear shrinkage at the preconditioning temperatures. All the materials generally expand or shrink at different temperatures, which is expected since their composition is different. LithaLox HP 500 and LithaCon 3Y 610 purple started to shrink at around 60 °C and steadily shrank until 150 °C where the material was dwelled for one hour. At the same time, the polymer binder network thermally expands and the final shrinkage can be seen only after cooling back to the room temperature. The linear shrinkage is totally about -1.7 % for the LithaLox HP 500 and about -2.2 % for the LithaCon 3Y 610 purple in the horizontal printing direction (XY-direction). Because of the CeraFab 7500 printer characteristics, the printed part is homogenous in X- and Y-direction. For the OMA Al₂O₃ part, the shrinkage starts around 90 °C and it shrinks
steadily as the temperature rises. Total shrinkage of OMA Al\textsubscript{2}O\textsubscript{3} is about -1.5% when cooled to the room temperature.

![Graph showing strain vs temperature for LithaLox HP 500, LithaCon 3Y 610 purple, and OMA Al\textsubscript{2}O\textsubscript{3} printed parts. Heating rate was 0.5 K/min and induced an 1 hour dwell at the peak temperature.]

**Figure 4.10.** Dilatometer measurements of the LithaLox HP 500, LithaCon 3Y 610 purple and OMA Al\textsubscript{2}O\textsubscript{3} printed parts. Heating rate was 0.5 K/min and induced an 1 hour dwell at the peak temperature.

When the dilation of the parts was measured a second time to the same temperature, it was noticed that they did not shrink anymore. Exception was the OMA Al\textsubscript{2}O\textsubscript{3} part, which still shrunk to a small extent. The second heating cycle is demonstrated in the **Figure 4.11.**
Figure 4.11. First and second heating cycle of the printed parts with the same heating program, a) LithaCon 3Y 610 purple and b) OMA Al₂O₃. Heating rate was 0.5 K/min and included a 1 hour dwell at the peak temperature.

4.2.3. Thermogravimetry

Thermogravimetric analysis (TGA) results at the precondition temperature below 200 °C is shown in the Figure 4.12. Thermogravimetry studies revealed that the OMA Al₂O₃ and LithaCon 3Y 610 purple will experience mass loss during the precondition stage. LithaCon 3Y 610 purple starts to lose mass slightly around over 75 °C and the mass loss rate increases slowly up to 115 °C, after which it starts to lose mass more significantly. OMA Al₂O₃ slurry’s mass loss begins significantly below 100 °C and the mass loss rate stays high throughout the whole precondition phase. LithaLox HP 500 starts to lose mass at higher temperatures than the previous two. LithaLox HP 500 starts to lose mass after the temperature is risen over 120 °C and the mass loss rate greatly increases after that.
Figure 4.12. Thermogravimetric measurements on the LithaCon 3Y 610 purple, LithaLox HP 500 and OMA Al₂O₃ printed parts at the precondition temperatures. Measurement was done with heating rate of 5 K/min in nitrogen atmosphere.

Although the LithaLox HP 500 does not lose mass under temperature of 120 °C, it was noticed that at this temperature it exudes brownish liquid on its surface. This exuded liquid mass was determined to be 8 - 9 wt.-% from the total mass of the printed LithaLox HP 500 parts. Most probably it consists of unreactive diluents, additives and uncured monomers of the slurry that diffuse out of the polymer network when heated, but do not significantly evaporate yet below 120 °C.

4.2.4. Conclusion of Precondition

The preconditioning phase is demonstrated to be very important phase for the whole ceramic 3D-printing process. As can be seen from the Figure 4.8, Figure 4.9. and Figure 4.10. LithaLox HP 500 and LithaCon 3Y 610 purple undergo a thermal polymerization during the precondition phase and experience polymerization shrinkage due to the radical polymerization reaction. To ensure that the green body shrinks evenly, the heating needs to be done slowly. Polymethacrylates have a low heat conductivity, for example, PMMA has 0,1922 W/mK at room temperature [71]. Uneven shrinkage,
caused for example by uneven heating rate or varying geometry, leads to twisting of the printed piece as seen in Figure 4.13.

Figure 4.13. An unevenly shrunk 3D-printed ceramic part after sintering from LithaLox HP 500, because of poor positioning inside the oven. The side suppose to be straight, but the side has shrunk more during the preconditioning than the other side and twisted the whole component. This is because the twisted side got heated up way faster.

For the OMA Al$_2$O$_3$ printed parts, the precondition phase can be seen as unnecessary. As we see from the Figure 4.8. and the Figure 4.9. the OMA Al$_2$O$_3$ slurry and printed parts do not experience any thermal polymerization. There is no polyacrylate’s polymerization shrinkage. It does still shrink, as can be seen from the Figure 4.10., however it is because of the diffusion and evaporation of the uncured monomers and additives that can be seen as a mass loss as was confirmed with the TG-studies in the Figure 4.12. In addition, the Figure 4.11. indicates that the shrinking occurs still when heated for a second time and to the mass loss continues. The LithaLox HP 500 and the LithaCon 3Y 610 purple were also shown to experience an outward diffusion and evaporation of uncured monomers and additives from the printed part.

The total processing time for the OMA Al$_2$O$_3$ slurry with SLA printing can be determined to be significantly shorter compared to the LithaLox HP 500 and LithaCon 3Y 610 purple. This is because the over 70h long preconditioning phase can be fully skipped with the OMA Al$_2$O$_3$ printed parts. For the LithaLox HP 500 and LithaCon 3Y 610 purple, the alternative ways of doing the precondition can be investigated in the future and see if it is possible to reduce the long preconditioning time. One way might be to use light to post cure and to finish the polymerization. Light based post curing has been used with the fully polymer based SLA printed parts to post cure the polymer and to improve the mechanical properties. An example of this is the formlabs' Form Cure [72].

After the preconditioning, the LithaLox HP 500's and LithaCon 3Y 610 purple’s polyacrylate and polymethacrylate network have the highest mechanical properties when the polymer mass of the cured polymer is high and no significant degradation has not happened yet [73]. The support structures should be removed by grinding at this point
when the part is strong enough that it does not fracture while grinding and soft enough that it is easy to grind.

### 4.3. DEBINDING

In the heat treatments of the SLA printed ceramic parts, and ceramics processing in general, the debinding is referred as the heating phase where the polymer binder network is removed. During debinding, the polymer degrades, diffuses and evaporates away, and at the end only ceramic particles are left and they are bonded together by attractive van der Waals forces. The characteristics of the debinding process depend strongly on the polymer network’s composition and the used additives, for example in a manner E. Johansson and co-workers have found out [15]. Because the degradation makes gases inside the part, the internal pressure might increase if they don’t have enough time to diffuse out of the structure. Ceramic particles make this diffusion more difficult, the holes between the particles typically are about only tens of nanometers wide and may cause capillary stresses. Eventually capillary stresses can brake the part or cause uneven shrinkage and dimension instability [47, p. 14]. The debinding phase is next studied with DSC, dilatometry and TG measurements with LithaLox HP 500, LithaCon 3Y 610 purple and OMA Al₂O₃ printed parts to find and study the critical steps that characterize the debinding phase of the ceramic SLA printing process.

#### 4.3.1. Differential Scanning Calorimetry

The endothermic degradation reactions happening during the debinding phase can be studied with the DSC measurements. The DSC measurement results are shown in the Figure 4.14. LithaLox HP 500 does not have any sharp endothermic maxima, instead the whole curve shows fairly constant endothermic reactions that steadily happen throughout the debinding phase. After about 330 °C, the degradation reaction most likely changes, or alternatively, one part of the polymer network degradation is finished and other reaction starts. This hypothesis is probable because there is small drop of the enthalpy before the acrylate starts to degrade, reaching the maximum at 370 °C. When the temperature rises over 400 °C, the polymer network around the ceramic particles is completely degraded, where only some residual carbon might be left, which also evaporates from the green body before reaching 500 °C. LithaCon 3Y 610 purple has a major endothermic spike around the polymethacrylate degradation temperature of 270 °C. Between 300 - 400 °C the printed part enthalpy shows minor endothermic reactions to take place and after 400 °C the majority of the polymer network is degraded
and only some residual carbon remains. OMA Al₂O₃ printed parts have more clear endothermic spikes than the previous two slurries. Under 300 °C there are two minor endothermic reaction spikes, around 190 °C and 270 °C. These spikes likely indicate the additives diffusing and evaporating out of the polymer network. Major maxima at 370 °C and 430 °C originate from the single bonds scission of C-O and C-C in the polyacrylate network. After 450 °C the polymer network is degraded totally and only residual carbon remain.

**Figure 4.14.** DSC measurements data from the LithaLox HP 500, LithaCon 3Y 610 purple and OMA Al₂O₃ printed parts during the debinding phase. Heating rate was 10 K/min at a nitrogen atmosphere.
4.3.2. Dilatometry

Dilatometer measurements during the debinding phase were done after the precondition phase with the LithaLox HP 500, LithaCon 3Y 610 purple. Precondition phase with the dilatometer is covered at the section 4.2.2. For the OMA Al₂O₃ the precondition was determined to be unnecessary at the section 4.2. The results are shown at the Figure 4.15.

LithaLox HP 500 starts to shrink around 160 °C and quite steadily continues shrinking until 300 °C. At the 300 °C the shrinking slows down and at 420 °C the green body starts to expand most likely due the thermal expansion of the alumina particles. The shrinkage starts by diffusion and evaporation of the additives, uncured monomers and by smaller molecular size pieces of the polymer network. LithaLox HP 500’s polymethacrylate components of the network degrades between 220 - 320 °C and polyacrylic components degrade around 400 °C. When the polymer degradation advances, the ceramic particles become in contact with each other and that most probably causes the shrinkage to slow down after 300 °C. LithaCon 3Y 610 purple has a very similar start in the debinding phase compared to LithaLox HP 500. It starts shrinking around 160 °C and strongly shrinks until 260 °C, however the shrinkage rate decreases after 220 °C. Also, with LithaCon 3Y 610 purple, the shrinkage starts by diffusion and evaporation of the additives, uncured monomers and smaller molecules of the polymer network. The degradation of the polymer networks main component, polymethacrylate, is clearly seen by the large shrinkage between 200 - 270 °C. After 270 °C, the shrinkage slows down significantly most likely due to the establishment of contacts between the ceramic particles. Around 400 °C, the majority of the polymer network is degraded and evaporated away and only ceramic particles remain. OMA Al₂O₃ starts to shrink already at 80 °C by the diffusion and evaporation of additives and when reaching 200 °C the shrinking starts to slow down. Between 280 - 390 °C no shrinkage happens, most likely due to the ceramic particles becoming in contact with each other. The polyacrylate’s degradation is still clearly seen by small shrinkage spike around 400 °C and burnout of the residual carbon.

Unlike was expected, the LithaCon 3Y 610 purple shrinks less in total than the two others as seen in figure Figure 4.15., although it has the lowest ceramic particle concentration and therefore relatively high polymer concentration. The most likely reason is that the LithaCon 3Y 610 purple already shrinks the most during the preconditioning phase, as was noticed in the Figure 4.10. In addition, the ZrO₂ has a slightly higher thermal expansion coefficient than Al₂O₃ [74] and it makes the printed green part to thermally
expand more. The differences between the LithaLox HP 500 and OMA Al$_2$O$_3$ total shrinkage can occur because OMA Al$_2$O$_3$ did not go through a preconditioning phase.

![Figure 4.15. Dilatometer measurements of the debinding phase of the LithaLox HP 500, LithaCon 3Y 610 purple and OMA Al$_2$O$_3$. Heating rate was 0,5 K/min at air an atmosphere. The shrinkage is in the XY-direction.](image)

### 4.3.3. Thermogravimetry

To study the debinding phase, the TG measurements give valuable information regarding the degradation of the polymer binder. TG measurement results of the debinding phase are presented in the Figure 4.16. LithaLox HP 500 and OMA Al$_2$O$_3$ printed parts have a clear maximum in the mass loss rate around the polyacrylate’s degradation temperature of 400 °C. LithaLox HP 500’s unreactive diluents, additives and uncured monomers diffuse and evaporate out of the polymer binder network most probably under 200 °C. Between 200 - 300 °C the polymethacrylates starts to degrade. The polymethacrylate’s degradation accelerates a mass loss rate maximum around 370 °C, after that the rest of the mass loss takes place because of the polyacrylate’s degradation. With OMA Al$_2$O$_3$, the mass loss starts by diffusion and evaporation of the additives, unreactive diluents and uncured monomers under 250 °C. The OMA Al$_2$O$_3$ does not thermally post-cure, however the polymer mass distribution might be wide and the lower mass polymer chains and pieces of network diffuses and evaporates out of the structure early in the bedinding phase. The choice of the acrylates as the main component leads to slow degradation between 250 - 310 °C and fast degradation at the
polyacrylate’s degradation temperature around 400 °C. LithaCon 3Y 610 loses half of its mass around the polymethacrylate’s degradation temperature between 220 - 330 °C. The degradation continues with high and steady mass loss rate by degradation of the leftover polymethacrylate and methacrylic ester. When the temperature reaches over 400 °C there is mostly residual carbon left and finally it also evaporates away.

**Figure 4.16.** Thermogravimetry measurements from printed parts of LithaLox HP 500, OMA Al₂O₃ and LithaCon 3Y 601 purple. Heating rate of 5 K/min at nitrogen atmosphere.

OMA Al₂O₃ printed parts were also measured in synthetic air atmosphere. The measurement and comparison with nitrogen atmosphere can be seen in the **Figure 4.17.**
The oxygen of the synthetic air starts to affect the degradation after 250 °C by increasing significantly the degradation rate between 300 - 380 °C compared to the degradation in the nitrogen atmosphere. The degradation in air leaves more residual carbon, which is finally burned away between. This is seen as a mass loss between 430 - 500 °C, and in that temperature the mass loss rate is lower at the nitrogen atmosphere. The oxygen decreases the polyacrylates degradation temperature to under 400 °C, most likely because of the carbon atoms react with oxygen and create heat inside the printed part.

![Figure 4.17. TG measurement of OMA Al₂O₃ printed in synthetic air (80/20 N₂/O₂) and in nitrogen atmosphere, heating rate was 5 K/min.](image)

**Figure 4.17.** TG measurement of OMA Al₂O₃ printed in synthetic air (80/20 N₂/O₂) and in nitrogen atmosphere, heating rate was 5 K/min.

### 4.3.4. Conclusion of Debinding

Debinding phase was found to be a major source of flaws and lowers part quality if it is not done properly. Too fast heating delaminated the printed part and created bubbles on the part’s surface. Delamination and bubbles of the debinded part can be seen in the **Figure 4.18.** which were created by too fast heating. Slow heating rate with dwelling of several hours at the critical temperatures are necessary. The critical temperatures can be identified from TG-, dilatometer- and DSC-studies. The critical temperature was defined as a maximum of the degradation speed. The LithaLox HP 500’s and LithaCon 3Y 610 purple’s heat treatment programs according to the **Figure 3.1.** follows well the measurement results. The dwelling temperatures follow the mass loss spikes acquired measured with TG.
Figure 4.18. OMA Al₂O₃ printed part, which is debinded and sintered. During the debinding the degradation gases have created bubbles (example is shown with red arrow) at the surface and delamination inside the component. In the left image, part is illuminated by light so that the delamination can be detected (example is shown with red arrow) more clearly.

For OMA Al₂O₃ printed parts, the TG- and DSC-measurements give major degradation spikes between 350 - 430 °C in nitrogen atmosphere. As a consequence, if the heating is done too fast in this temperature range, the results are poor similarly to the Figure 4.18. TG-measurement in synthetic air lowered the critical temperature to 270 - 390 °C. While the dilatometer measurement gave the most deformation under 300 °C, the soft and flexible nature of the withstands the evaporations of unreacted monomers and inert additives even when the heating rate is higher than with Lithoz slurries under 250 °C. The debinding heat treatment program for OMA Al₂O₃ is presented at the Table 4.3.

Table 4.3. Debinding program of OMA Al₂O₃.

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Total [h] 81,06
After the OMA Al₂O₃ was dwelled at 350 °C for 4 hours, the majority of the polymer network is degraded to small enough molecules to evaporate away without further degradation. In that phase, the ceramic particles have porosity between them and the evaporated molecules and gases can escape more easily without the need of diffusing through the structure. The debinding can be done significantly faster for OMA Al₂O₃ compared to the LithaLox HP 500 and LithaCon 3Y 610 purple. One reason most probably is that the average particle size for OMA Al₂O₃ is higher than LithaLox HP 500 and LithaCon 3Y 610 purple creating larger channels and porosity between the particles.

After debinding, the ceramic particles are arranged densely relative to each other, which is seen in the Figure 4.19. In addition, the Figure 4.19 shows that a stable dispersion was obtained for the ceramic particles in the OMA Al₂O₃ slurry. Possible delamination can also be clearly seen to take place along the layer lines with debinded parts in the Figure 4.19.

![Figure 4.19. OMA Al₂O₃ debinded surface against the layers a) without delamination b) with delamination cracks. Direction of the layer lines are presented with the red arrows.](image)

### 4.4. SINTERING

In this study characterization of the sintering process is not performed. Sintering and densification of used slurries ceramic powders are done with the slurry or powder manufacturer instructions. For Lithoz slurries sintering is done according to the Figure 3.1. For OMA Al₂O₃ the powder manufacturer’s instructions are to hold the temperature at 1600 °C for 2 hours to obtain high density. The total heat treatment programs are presented in the Figure 4.20. while the detailed OMA Al₂O₃ debinding program was shown in the Table 4.3. Debinding program of OMA Al₂O₃ Table 4.3.
Figure 4.20. The full heat treatment programs including possible precondition (optional), debinding and sintering. Temperature data as a function of time, for OMA Al₂O₃, LithaLox HP 500 and LithaCon 3Y 610 purple materials. Furnace changes are seen in data sections were temperature drops to 20 °C. Furnace change is required, because no furnace that can handle low and high temperatures at the same time were available during this study.

The total heat treatment time of OMA Al₂O₃ is about 110 hours. This is less than half of the total time compared to LithaLox HP 500 because of the absence of the preconditioning phase.

According to the Lithoz, over 99 % for LithaLox HP 500 and over 98 % for LithaCon 3Y 610 purple relative density can be achieved after sintering [56]. Thermally etched surfaces of sintered LithaLox HP 500 and LithaCon 3Y 610 purple can be seen in the Figure 4.21
Figure 4.21. Surface and grains of the sintered a) LithaLox HP 500 thermally etched at 1400 °C and b) LithaCon 3Y 610 purple thermally etched at 1300 °C.
5. CONCLUSION

In this Master Thesis work, additive manufacturing of ceramic materials by stereolithography method was studied. New printable Al₂O₃-slurry was developed and ZrO₂-slurry was tested. New OMA Al₂O₃-slurry was compared to the already existing slurries manufactured by Lithoz. This study was started by literature review of 3D-printing of ceramics by stereolithography method. We found that the 3D-printing of ceramic materials is a young field of research compared to the other 3D printable material groups such as plastics and metals. In 3D-printing of ceramics, understanding the characteristics of the light curable monomers is essential for the successful 3D-printing of high quality engineering ceramics.

During this study, it was noticed that one of the major problems with the existing commercial slurries, LithaLox HP 500 and LithaCon 3Y 610 purple, is that they delaminate relatively easily along the printing layer lines. These cracks and flaws, caused by the delamination, makes the mechanical properties highly variable depending from the geometry of the printed part. Delamination is the main reason why bigger parts than couple cubic centimeters were not successfully printed with good mechanical properties and accurate dimensions. The delamination was noticed to occur also along the layer lines with OMA Al₂O₃, slurry fabricated in this study. This delamination phenomena should of high concern in the future studies regarding ceramics 3D-printing.

The mechanical response of the green parts after printing with Lithoz slurries and OMA Al₂O₃ was found to be very different. Lithoz slurries produce tough and rigid green parts, while OMA Al₂O₃ produces soft and flexible green parts. Neither of these properties were found to be optimal. Tough and rigid Lithoz slurries were difficult to clean after printing and they did not withstand large cross-sectional area prints well during the printing without delamination or fracture. On the other hand, considerably small details were possible to print out. On the contrary, the small detail printing was found to be hard with OMA Al₂O₃, and the printed parts were easy to clean. In addition, the flexibility of the green parts provided better durability when large cross-sectional area parts were printed. In further slurry tailoring, the properties of the optimal green part should be something between the Lithoz and OMA Al₂O₃ slurries, moderately flexible and tough. For OMA ZrO₂ the same monomer medium with same amount of photoinitiators as with the OMA Al₂O₃ was found to be difficult to print. Therefore, it is clear that the ZrO₂ powder requires a different monomer medium to be successfully printed.
The heat treatments regarding the polymer degradation during the SLA 3D-printing of ceramics has been found to be a critical manufacturing phase to gain high quality engineering ceramics. In this study heat treatments have been of high concern for studies. It has been found that while the precondition and debinding takes the majority of the total processing time, precise controlling the precondition and debinding phases is important. The 3D-printed green part experiences significant dilation and deformation during these phases. The deformation occurs because of the thermal curing shrinkage and mass loss related to degraded polymer network and evaporated gases. During the debinding phase, the gases produced during the degradation of the polymer network, additives and uncured monomers need time to diffuse and escape out of the structure. Otherwise the printed green part can delaminate or create surface bubbles due to increased internal gas pressure. OMA Al$_2$O$_3$ was able to be tailored so that the precondition phase is unnecessary and the total processing time was able to get much shorter compared to the commercial reference slurries. To further reduce the total processing time, the precondition and debinding phases should be studied in detail. One way to reduce the total time could be changing the monomer composition and properties.

So far, the printable engineering ceramics are limits mostly to the dense Al$_2$O$_3$ and ZrO$_2$. Further studies are required to increase the ceramic material selection to for example porous ceramics and non-oxide ceramics.

The scale between printed part and sintered finished part is presented at the **Figure 5.1**. More examples of the parts printed during this study are presented in the **Figure 5.2**.

*Figure 5.1.* The scale between the part after printing (right) and sintering (left). Printed with LithaLox HP 500.
Figure 5.2. Printed and sintered parts from a) LithaLox HP 500, impellers, conefilters and mesh structures, b) OMA Al₂O₃, mesh structures and pipework with mesh structure inside, c) LithaLox HP 500, nozzles for plastic FDM 3D-printer E3D V6 hotend.
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