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Characterization techniques for evaluation of micro scale vat photopolymerization-based additive manufacturing.

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Abstract
Vat photopolymerization-based Additive Manufacturing (VPAM) is a process in which a liquid polymer resin is exposed to UV light and cross-linked creating a tough structure. This technique allows to produce highly complex parts and has found its application in many fields e.g. hearing-aid components, dentistry and jewellery. The potential of VPAM makes it possible to be used in more advanced and demanding applications such as robotics, functional surfaces and soft tooling, just to name a few. These applications require manufacturing of features in micro scale with defined tolerances, thus, the current state-of-the-art calls for high precision and stability of the process as well as reliable characterisation techniques. This paper presents the efficiency of selected characterisation methods together with comparison between the influence of layer thickness and irradiance on the degree of curing as well as the dimensional and weight stability. By applying spectroscopic methods and geometrical measurements it was found that the two selected parameters have contradicting effect on the evaluated features. The results showed that the process is the most stable for two sets of process parameters: irradiance of 0.91 mW/cm^2 with layer thickness of 1 µm and 1 mW/cm^2 with layer thickness of 5 µm. The degree of curing was found to be higher for high light irradiance, with the thickness found to be an insignificant factor.

3D printing, Vat-photopolymerization, Characterization, FTIR

1. Introduction

Vat photopolymerization-based Additive Manufacturing (VPAM) is a process in which a liquid polymer resin is exposed to UV light and cross-linked creating a tough structure. The area exposed to irradiation is the cross-section of the produced part with a defined thickness. By moving the build plate in the vertical direction, subsequent layers are added thereby creating the entire structure. There are two variants of the built plate configurations: bottom-up, which allows higher control over the layer thickness because of resin entrapment between the built plate and the underlying glass and top-down, which allows a faster process due to bypassing of the additional built plate movement between each layer. In addition, there are two types of light excitation: scanning stereolitography, which uses a laser and mask-projection, which uses a high resolution projector.

On the molecular level, the polymer resin contains monomers and oligomers which define the physical properties and photoinitiators which react under a certain wavelength (usually in the UV spectra, between 380 and 450nm). The photopolymerization is achieved by a non-reversible chemical reaction, which is initiated by light excitation of a photoinitiator. Photoinitiator breaks its pair of electrons, creating free radicals which subsequently break the carbon-carbon double bond of the monomer and pair with the created free electron of this bond. The newly formed radical reacts with another monomer, creating branches, a process called propagation. The chain grows until the reactive branch joins another branch, leaving no free electrons, a step which is called termination.

In order to control the level of photopolymerisation, the process parameters, i.e. light irradiance and exposure time, must be adjusted to the type of material and minimum feature size which defines the necessary layer thickness and horizontal resolution of the light source. Current state-of-the-art in laser and projection techniques, allowed VPAM to produce highly complex parts and the technique has found its application in many fields e.g. hearing-aid components, dentistry and jewellery. The potential of the VPAM makes it possible to be used in more advanced and demanding applications such as robotics, functional surfaces and soft tooling, just to name a few [1]. These applications require manufacturing of features in micro scale with defined tolerances. In order to achieve such features the demands such as high-precision and stability of the process must be met as well as reliable characterisation techniques [2], which are able to correlate the dimensional stability of the parts together with the conversion of the resin. The most commonly used techniques involve geometrical measurements, by means of various instruments, e.g. callipers, profilometers and microscopes [4]. These techniques are useful for fast and simple evaluation, however they do not demonstrate the degree of curing of the photopolymer. This is particularly important for medical devices, where non-fully converted resin can release hazardous substances.

Commercial systems generally provide the material, which is finely tuned with its respective machine. These closed systems, allow an easy manufacturing process for the user since the profile parameters are pre-set by the manufacturers. However,

it also limits the user from using a third-party material and is confined to the default settings. For researchers it is a drawback, since it restrains from testing own materials or experiment with different combinations of process parameters to further study this technology. Understanding the material that is being used is imperative for a controlled manufacturing process and hence successfully manufactured components. The objective of this research is to select and apply additional characterisation techniques in order to provide a comprehensive correlation between the chemical reaction and dimensional stability of the parts produced with VPAM, with focus on biocompatible materials used in hearing-aid industry.

2. Materials and methods

2.1 Material and geometry

For this study the OTO-UHF BIO, a special acrylic-based resin for hearing-aids applications from 3Dresyns was used. The material is a mixture of alkenyl, ethenyl, allyl, vinyl and methacrylate. The main features of this material is durability, high hardness, sweat and water resistance and tensile strength above 40MPa [5].

The geometries used for this study were a series of dogbones following the ISO 527-2 2012, with two additional features. The first one was a small detachable cube. On the other side of the dogbone, a see-through hole, with a diameter of 0.4 mm, was added to the design to assess the resolution of the material. Figure 1 depicts the geometry of the specimen.

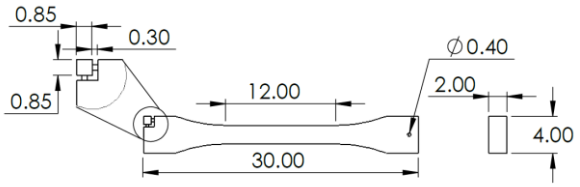


Figure 1. Geometry selected for the experiments.

2.2. Parts manufacturing

Two-level full factorial design of experiments (DOE) was conducted in order to investigate if the differences in process parameters will be reflected in the chosen characterization methods. The dogbones were manufactured at two different intensities and two layer thickness using the same exposure time of 1 s. Table 1 shows the factors and levels used in the DOE.

Table 1. Process parameters used in experiments.

Factor	Low level	High level
Layer thickness [µm]	1	5
Irradiance [mW/cm^2]	0.91	1
Exposure time [s]	1	1

To identify the samples, a code with two letters was applied, where the first letter refers to the layer thickness level, H for high level and L for low level, and the second letter refers to the irradiance level following the same logic as the previous letter. Table 2 summarizes this code.

Table 2. Identification code used for the printed samples.

ID name	Layer thickness [µm]	Irradiance [mW/cm^2]
HH	5	1
HL	5	0.91
LH	1	1
LL	1	0.91

An open VPAM high-resolution machine, developed at Technical University of Denmark, with a UV light mask projection system and vertical resolution of 0.625 µm was used for samples manufacturing. The machine uses a Visitech LUXBEAM® LRSWQ-HY projector with an integrated light engine DLP9000 DMD with a resolution of 2560x1600p and 7.54 µm pixel pitch. A bottom up built-plate setup was used for this purpose with a specially designed self-peeling vat configuration [6].

2.3. Characterization techniques

2.3.1 Determination of degree of curing

During the process of radical copolymerisation, the conversion of C=C bonds is not fully reached. The residual non-polymerized resin can lead to instability of physio-chemical characteristics of the parts and pollution of the surrounding medium due to unreacted volatiles. It is not possible to assess the degree of cure after the parts have been manufactured, therefore an IR methods can be applied in order to determine the content of C=C bonds [7]. Fourier Transform Infrared Spectroscopy (FTIR) was used to identify functional groups which have characteristic bands in terms of frequency (wave number or frequency) and intensity (absorption).

2.3.2 Geometrical measurements

A micro balance scale was used to measure the weight of samples and electronic slide micrometer was used to obtain the thickness of the dogbones in printing direction. This type of measurement a quick and simple method which can be done without any special preparation, however it is a manual process, relying on user to pick the area of measurement and apply the force needed to pinch the measured area.

3. Results

3.1. FTIR

The integrated peak values for each of the sets of process parameters were compared. The peaks which fell into the wavelength between 1680 and 1600 cm^{-1} were analysed, as the C=C bonds stretching occur in this range. Integration of the critical peaks is challenging as it is highly dependent on the chosen method of peaks analysis. The approach, which was chosen for this study, was to determine the internal reference for a prominent peak which is unchanged during polymerization process, in this case an aromatic C-C bonds in the proximity of 1608 cm^{-1}, which typically occurs in commercial methacrylate resins. The ratio between the area under the C=C bond peak to the area of the C-C bond peak was calculated [8]. Figure 2 shows the peaks obtained of FTIR measurements for a wavenumber between 1600 and 1660 cm^{-1}. As it can be seen, there is a difference between C=C bond conversion for different process parameters. In order to compare the degree of curing of the areas under the peaks were extracted and ratio of C=C to C-C was calculated. The procedure is done both for cured and uncured specimen and the ratio between the values is obtained as a degree of curing based on the formula [9]:

$$D(\%) = \left(1 - \frac{C}{U}\right) \times 100\%$$

Where *D* corresponds to *degree of curing* and *C* and *U* corresponds to molar ratio between C=C and C-C bonds for cured and uncured photopolymer, respectively. The uncured material was not analysed but based on the formula it is deducted that the lower the C=C to C-C ratio, the higher the degree of curing.

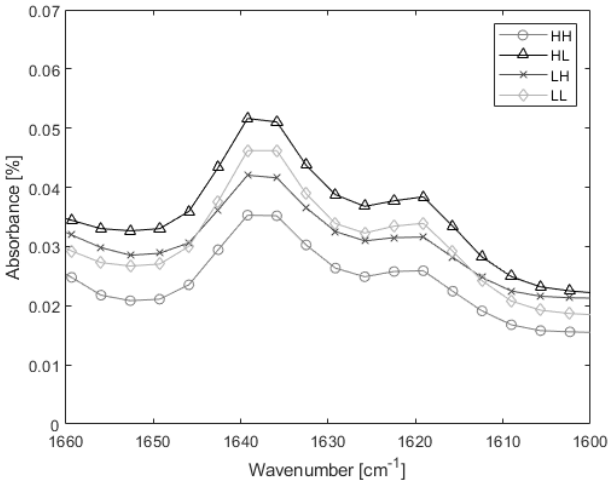


Figure 2. Obtained FTIR spectra for various process parameters.

As it can be seen in Figure 2, for each curve two peaks were identified in the region between 1600 and 1660 cm^{-1}. The peak occurring at in proximity of 1637 cm^{-1} is determined to represent the aliphatic group. The second peak, at 1619 cm^{-1}, is considered to represent an aromatic group. The areas under the peaks was extracted using the baseline and peak fitting tool. Table 3 depicts the resulting C=C to C-C ratios.

Table 3. Results of C=C to C-C ratio.

ID name	C=C/C-C
HH	2.040
HL	1.682
LH	1.802
LL	1.571

The obtained values are graphically presented in Figure 3.

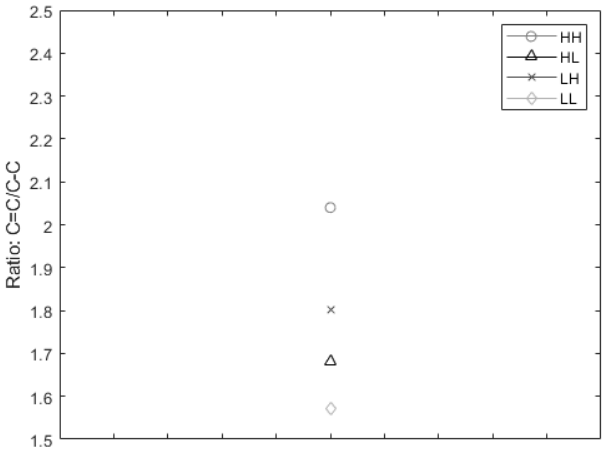


Figure 3. Comparison of resulting C=C to C-C ratios.

From the highest to the lowest ratio the process parameters sets occurs as following: HH, LH, HL and LL. This indicates, that the higher degree of curing occurs for polymer exposed to higher irradiance.

3.1. Thickness and weight measurements

Figures 4 and 5 depict the boxplot plots with standard deviation of thickness and weight measurements respectively.

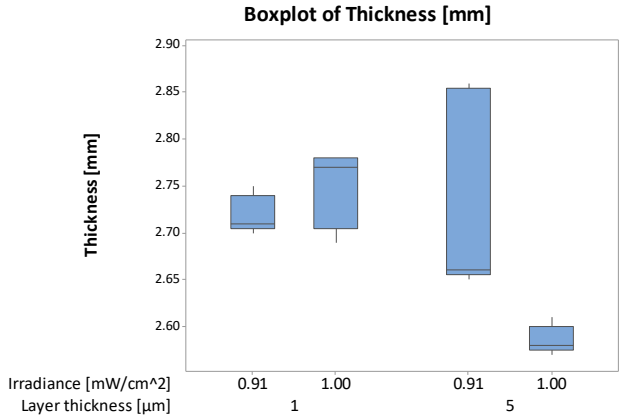


Figure 4. Boxplot of thickness in the printing direction.

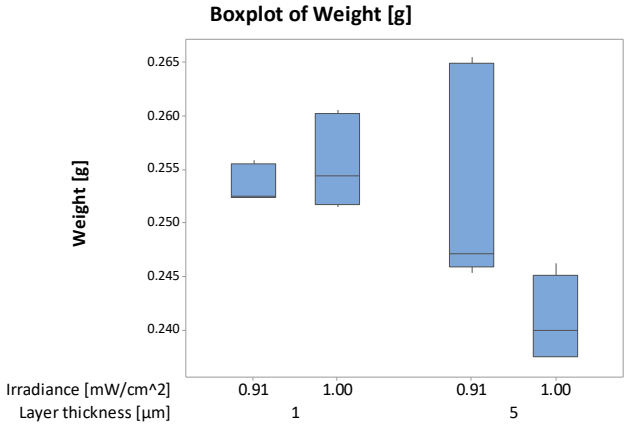


Figure 5. Boxplot of weight.

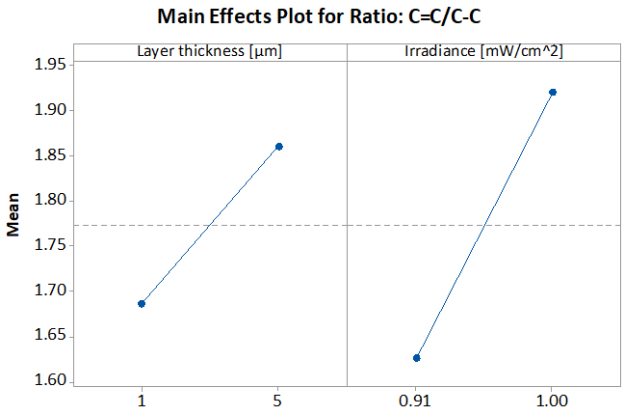
As it can be seen the deviations differ significantly between different sets of process parameters. Table 4 shows the deviations for thickness and weight. It is evident that the process is the most stable for two sets of process parameters: irradiance of 0.91 mW/cm^2 with layer thickness of 1 µm (LL) and 1 mW/cm^2 with layer thickness of 5 µm (HH).

Table 4. Standard deviations of thickness and weight.

ID name	St Dev Thickness [mm]	St Dev Weight [g]
HH	0.0136	0.0035
HL	0.0976	0.0091
LH	0.0366	0.0039
LL	0.0179	0.0015

4. Discussion

In order to evaluate the influence of the process parameters, main effects plots based on Tables 3 and 4 were made. Figure 6 depicts results of FTIR C=C to C-C ratio. In this case, the irradiance had higher influence on the performance, with higher degree of curing for higher amount of the light amplitude. Based on the plots the layer thickness influence can be concluded as less significant. Figure 7 and 8 show the main effects plots for thickness and weight. The influence of the process parameters is similar in case of thickness. From Figure 8, it can be seen that the layer thickness has also higher influence on the weight stability.



. **Figure 6.** Main effects plot for FTIR data.

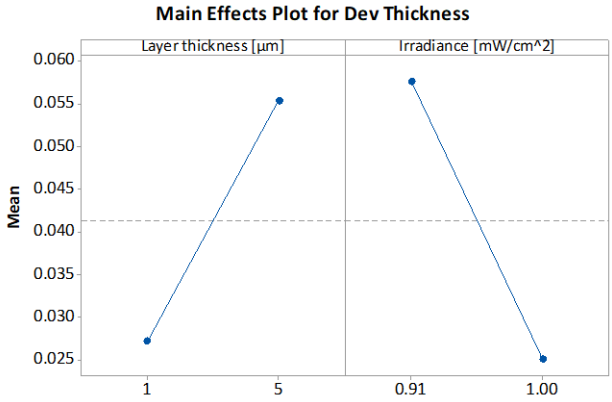


Figure 7. Main effects plot for standard deviation of thickness.

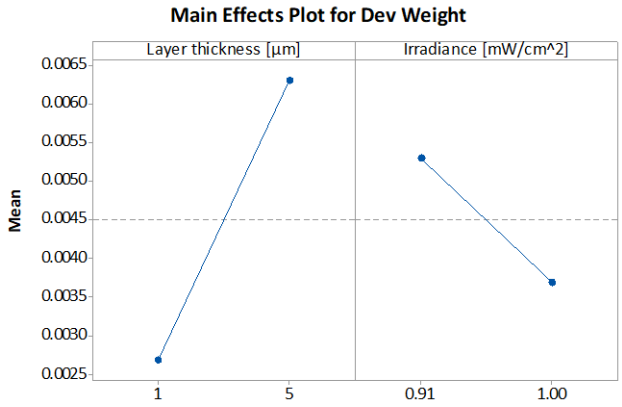


Figure 8. Main effects plot for standard deviation of weight.

Based on the main effects plots it is evident that layer thickness and irradiance have very different influence on the evaluated features. The discrepancy shows that the real process window should be narrowed in order to achieve sufficient degree of curing and geometrical and weight stability.

Moreover, dimensional and weight measurements do not correlate with the degree of curing, therefore it is necessary to apply other methods as FTIR to determine it, and have a thorough characterization procedure. Although measurements with caliper and scale can serve as tools for quick and easy determination of the stability of the process, they are not sufficient for a full evaluation of the VPAM process.

5. Conclusion

With this work different approaches for evaluation of degree of curing for a commercial resin were presented. It was found that FTIR can be applied for the material with unknown formulation in order to determine the differences in influence on the degree curing for various process parameters. It must be noted, that the obtained values should not be taken as an absolute result but as a tool for relative comparison.

It was also found that the influence of the process parameters is different when evaluating the degree of curing and process stability by means of thickness in the printing direction and weight. This indicates that a special care must be taken when determining the process window in order to achieve sufficient degree of curing and geometrical and weight stability.

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References

[1] Stansbury J W and Idacavagec M J 2016 3D printing with polymers: Challenges among expanding options and opportunities *Dental Materials* vol. 32 p 54-64

[2] Santos I C, Almeida H and Bartolo P J 2014 Overview on additive manufacturing techniques for scaffold-based cartilage tissue engineering *High Value Manufacturing: Advanced Research in Virtual and Rapid Prototyping* vol. 8 p 175-186

[3] Futh, J Y H, Lu L, Tan C C, Shen Z X and Chew S 2006 Curing characteristics of acrylic photopolymer used in stereolithography process *Rapid Prototyping Journal* vol 40, p 71-76

[4] Bennet J 2017 Measuring UV curing parameters of commercial photopolymers used in additive manufacturing *Additive Manufacturing* vol 18 p 203-212

[5] 3Dresyns 2018 Otoplastic 3Dresyn OTO-UHF basic color & bio-based <https://www.3dresyns.com/collections/otoplastic-3dresyns-oto-uhf-clear-and-basic-colors/products/otoplastic-3dresyn-oto-uhf-basic-color-bio-based-1>

[6] Ribo M M, Danielak A H, Nielsen J S, Islam A, Pedersen D B 2019 Optimization of a self-peeling vat for precision vat photopolymerisation setups euspens's 19th International Conference & Exhibition, Bilbao, p 1-4

[7] Kurmaz S V, Poshchupkin V P and Kocheva I S 2002 IR spectroscopy for studying the conversion of double bonds in the radical copolymerisation of oligodimethacrylates with styrene *International Polymer Science and Technology* vol. 25 p. 43-48

[8] Moraes L G P, Rocha R S F, Menegazzo L M, Araujo E B, Yukimitu K and Moraes J C S 2008 Infrared Spectroscopy: A tool for determination of the degree of conversion in dental composites, Journal of Applied Oral Science vol. 16 p. 145-149.

[9] Rueggeberg F A, Hashinger D T and Fairhurst 1989 Calibration of FTIR analysis of conterporary dental resin composites *Dental Materials* vol. 6 p. 241-249