
Light-box set-up for the development of resins for vat polymerization additive manufacturing

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Abstract

Vat polymerization additive manufacturing (VPAM) technologies, such as stereolithography and digital light processing, possesses several key advantages over conventional manufacturing techniques. This is of particular interest in the medical field, especially for the production of personalized medical devices. Photo-polymer resins used in VPAM are complex mixtures of several components, each with a specific role in the printing process, including monomers, oligomers, photo-initiators, and inhibitors. Optimization of the liquid photo-polymer resin composition is crucial for achieving a stable process, as well as the final properties of the printed parts. However, the iterative optimization process often used for resin formulation is rather cumbersome and leads to significant material waste. Moreover, in the case of biocompatible polymers for medical devices, this way of work is not economically viable. Hence, this work covers the development of a light-box set-up for resin composition optimization of photo-polymer resins for VPAM technologies. The lightbox set-up comprises of four main components; an LED-array ($\lambda = 405$ nm), a light diffusor, a mask, and a sample holder. The effectivity of the set-up was validated using a novel biocompatible acrylate-end capped urethane-based poly(ethylene glycol) polymer (AUP). A photo-polymer resin was formulated by mixing the AUP with the photo-initiator lithium (2,4,6-trimethylbenzoyl) phenyl phosphonate and a photo-absorber. Photo-rheology was used to determine the optimal concentration of photo-initiator. Furthermore, in order to retain the biocompatible properties of the AUP material, two FDA-approved food dyes were chosen as the photo-absorber. The light-box set-up was used to determine the optimal concentration of photo-absorber. The results presented here show that the experimental set-up developed herein, allows for optimization of the resin composition for a given processing energy density using minimal amounts of resin. Moreover, the set-up can be used for processability evaluation, as well as quality control of newly synthesized photo-polymer resins.

Additive manufacturing, vat polymerization, photo-polymerization

1. Introduction

Stereolithographic (SLA) printing, invented in the early 1980s, is considered to be the first additive manufacturing technology to be developed. Over the years, other vat polymerization additive manufacturing (VPAM) technologies, such as digital light processing (DLP) and two photon polymerization, have emerged, all of which use the same basic principle; the consolidation of a photo-polymer resin through a photo-polymerization reaction [1]. Usually, the photo-polymerization takes place by means of a free radical polymerization reaction. Hence, the monomers and oligomers used in VPAM are often functionalized with acrylate groups, which can in turn participate in the polymerization reaction [2].

Photo-polymer resins used in VPAM technologies are composed out of three main constituents; monomers and oligomers, a photo-initiator, and a photo-absorbing species. Additives can be used to further alter the properties, such as the colour or mechanical performance, of the final parts [3]. Each constituent plays a crucial role in the polymerization reaction. Hence, finding the optimal balance between the three constituents is of key importance in setting up a stable process.

Optimizing the resin formulation is usually performed by constructing the so-called working curves [4]. These curves give the relation between the applied light energy dose and the curing depth of the resin. Benjamin et al. used this approach to determine the optimal photo-absorber concentration for PEG-based hydrogel resins for use with the SLA printing process [5]. However, constructing these curves leads to excessive material waste. Bennett proposed a test set-up that limits the required resin to produce the working curve samples [6]. However, using this set-up, only one formulation could be tested at a time.

Therefore, this work covers the development of an experimental light-box set-up which can be used for photo-polymer resin formulation for use in VPAM technologies. This set-up allows for optimization of the resin composition for a given processing energy density using minimal amounts of resin, for up to four formulations at the same time. To test this, the optimal photo-absorber concentration was determined for a resin based on a novel biocompatible acrylate-end capped urethane-based poly-(ethylene glycol) polymer (AUP).

2. Materials and methods

2.1. Materials

The acrylate-end capped urethane-based PEG macromer (AUP) was synthesized by the Polymer Chemistry and Biomaterials Group (PBM) at the University of Ghent following their patented procedures (WO 2017/005613 A1) [7]. Lithium (2,4,6-trimethylbenzoyl) phenyl phosphinate was synthesized using previously reported protocols [8]. The food dyes quinoline yellow (QY; E104; Sigma Aldrich; Belgium) and tartrazine (TAR; E102; Sigma Aldrich; Belgium) were selected as the photo-absorbing species in the resin formulation. Table 1 shows an overview of the resin formulations used in this work.

Table 1 Resin formulations used for the experiments.

AUP (m/m%)	Photo-initiator (mol%)	Photo-absorber (mg mL ⁻¹)
30	2	0.1 – 0.9

2.2. Light-box set-up

The experimental set-up for the determination of the photo-absorber concentration was fabricated using fused filament fabrication (FFF) with poly(lactic acid) filament. The lightbox set-up comprised of an LED-array, a light diffuser, a mask, and a sample holder. The LED-array consists of 48 UV-emitting LEDs ($\lambda = 405$ nm; Conrad; Belgium), which passes through a poly(methyl methacrylate) (PMMA) sheet acting as a light diffuser before passing through a square (1x1 mm) mask. The sample holder consists of a well which is filled with resin and covered with a glass slide (VWR; Belgium). Surface activation of the glass slides was performed through oxygen plasma treatment at 100 W for 3 minutes (Diener Plasma GmbH & Co. KG; Femto; Germany), in order to ensure bonding between the cured samples and the glass surface. The mask was mounted on the sample holder, which in turn was mounted on the test set-up. The optical irradiance of the test set-up was measured using a radiometer, equipped with a VISBG probe ($\lambda = 400$ -570 nm; Opsytec Dr. Gröbel RM-12; Germany), and was observed to be 1.33 mW cm⁻².

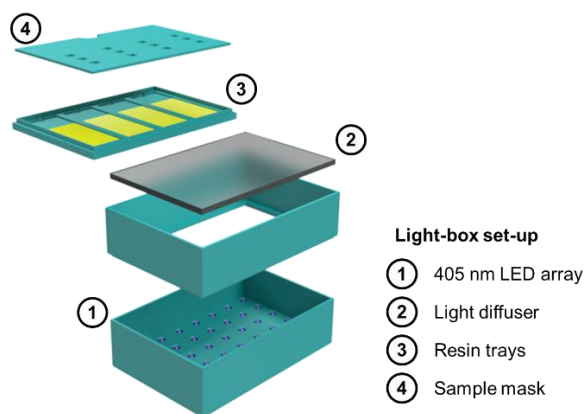


Figure 1. Light-box set-up for photo-polymer resin optimization, consisting of a LED-array ($\lambda = 405$ nm), a light diffuser, a mask, and a sample holder.

2.3. Photo-absorber concentration

The photo-absorber (QY; $\lambda_{\max} = 439$ nm or TAR; $\lambda_{\max} = 425$ nm) was added at 0.1, 0.3, 0.5, 0.7 and 0.9 mg mL⁻¹ concentrations, to a 30 m/m% AUP solution in ultrapure water containing 2 mol% LAP. The resin was exposed to the UV-light for 20 s, which resulted in an applied light energy dose of 26.6 mJ cm⁻², after which the glass slides were washed with ultrapure water (MQ;

Merck; Belgium) to remove excess resin, leaving only the cured square samples attached to the treated glass surface. Optical surface profilometry was performed to measure the thickness of the cured samples in both dry state as well as equilibrium swollen state.

3. Results and discussion

Figure 2 shows AUP films cured using the light-box set-up, with different concentrations of photo-absorber, quinoline yellow in this case. The samples prepared with no photo-absorber can be seen in the bottom right corner of the image. From this image, it is already clear that the addition of a photo-absorber affects the thickness, and thus the curing depth of the photo-polymer resin, as the samples prepared with photo-absorber added to the resin are clearly thinner. In order to quantify the thickness of these samples, optical surface profilometry was performed, the results of which are shown in Figure 3 and 4.



Figure 2. AUP samples cured with the light-box set-up. Increasing concentrations of photo-absorber results in visually thinner films.

Figure 3 shows the thickness of cured AUP samples measured using surface optical profilometry in function of Quinoline Yellow photo-absorber concentration. It is clear that the photo-absorber controls the light penetration into the photo-polymer resin, as the sample thickness decreases with increasing absorber concentrations following a power-law relationship. As with QY, the TAR photo-absorber shows a similar trend of the sample thickness in function of the absorber concentration (see Figure 4). Moreover, the thickness of the films increases in swollen state compared to the dry state. This is to be expected due to the nature of the hydrogel material. Hydrogels are polymer networks with a high affinity for water, hence are able to absorb multiple times their volume in water [9]. This highlights one of the main challenges when printing hydrogels using VPAM technologies. The AUP material is in a semi-swollen state during printing as it still swells upon cleaning in water after printing. Hence, determining the correct photo-absorber concentration is more challenging for these types of materials.

The QY dye formed aggregates in the AUP resins, pointing out the bad solubility of QY in water-based systems. Indeed, QY is representative of a large class of pigments. In its purest form, QY is insoluble in water-based systems, but soluble in nonpolar organic solvents [10]. The dye used in this work is the non-sulphonated, spirit soluble form of QY, rather than the sulphonated, water-soluble form. Hence the poor solubility in the water-based photo-polymer resin. On the other hand, the solubility of TAR appears to be better, as no aggregate formation of the photo-absorber were observed in the AUP resins. This is in accordance with the good water-solubility of TAR reported in literature [11]. Because of the better solubility, as well as an absorption peak wavelength ($\lambda_{\max} = 425$ nm) closer to the 405 nm wavelength used in the SLA printing process, TAR was chosen as the photo-absorber for the photo-polymer resin.

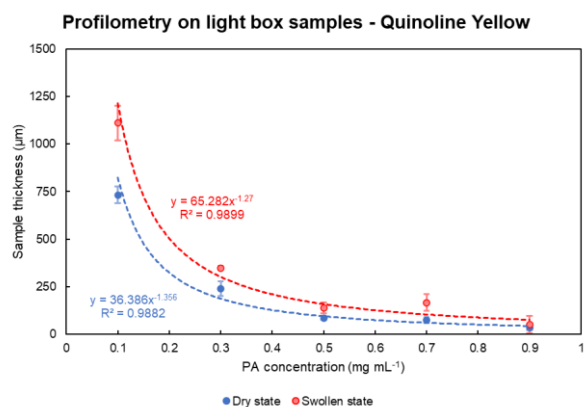


Figure 3. Results of the profilometry measurements of the cured films with quinoline yellow as the photo-absorber.

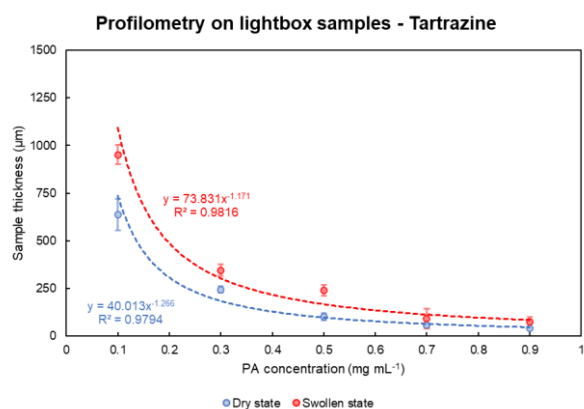


Figure 4. Results of the profilometry measurements of the cured films with tartrazine as the photo-absorber.

The TAR photo-absorber concentration for use in the SLA printing process, was determined by choosing a layer thickness, 100 µm in this case. Based on the plot in Figure 4, this corresponds to a TAR concentration between 0.49 and 0.77 mg mL⁻¹ (dry and wet state respectively) when processing with an applied light energy dose of 26.6 mJ cm⁻². Assuming a linear swelling behaviour and a 50% hydrated state of the AUP in the resin, the concentration of TAR for a chosen layer thickness of 100 µm should be 0.63 mg mL⁻¹. Figure 5 shows a first attempt at printing a generic sample. The final layers of the print detached from the sample. This could be either due to the weakness of the material, or due to insufficient adhesion between these layers. In the latter case, this would mean that that chosen absorber concentration is too high. Nevertheless, the sample was printed almost successfully, showing that the light-box is useful in determining an initial resin formulation for VPAM technologies, such as SLA.

There are, however, several limitations to the set-up presented in this work. First, the set-up uses a fixed light-source from which the wavelength cannot be altered, hence is only applicable for VPAM technologies using a 405nm light-source. Second, the experiments carried out here were performed for one applied energy dose. Ideally, multiple energy doses are used, allowing for the construction of the working curves. Finally, the thickness measurements using optical profilometry is rather cumbersome. An alternative measurement method could be used, such as simply using a calliper. Bennett has shown that there is minimal influence of the measurement method on the overall outcome of similar thickness measurements [6].

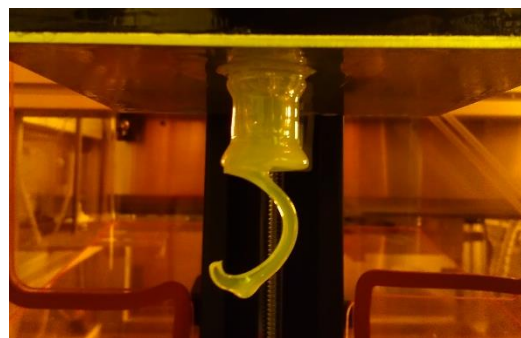


Figure 5. First attempt at printing a generic sample using the optimized resin formulation.

4. Conclusion

This work shows the development of a light-box set-up which is used to determine optimal resin formulations for VPAM technologies, such as SLA or DLP. The set-up was used to formulate a photo-polymer resin based on the AUP material. More specifically, the optimal concentration of photo-absorber was determined for use in the SLA printing process. Based on the profilometric thickness measurements, the optimal concentration of photo-absorber in order to print with a layer thickness of 100 µm, was 0.63 mg mL⁻¹. This resin formulation was used in printing pre-tests. The samples printed still showed several issues such as delamination between layers, however, the overall XY resolution and shape fidelity was improved. This work has shown that the light-box set-up is an easy, yet powerful tool to quickly formulate photo-polymer resins which can then be used for further optimization. Though, there is still room for improvement of this set-up, such as the use of a variable light-source and a timer-controlled exposure switch. Also, the thickness measurement method could be simplified by using callipers for example.

Acknowledgments

This work was supported by Research Foundation Flanders (FWO, Grant No. G083117N).

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