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Preliminary Study on 3D printing of PEGDA Hydrogels for Frontal Sinus Implants using Digital Light Processing (DLP)

Abstract: Digital Light Processing (DLP) enables high precision 3D-printing of photopolymers and holds promising potential for patient-specific implant solutions. On the material side, Poly(ethylene glycol) diacrylate (PEGDA) has emerged as an interesting material for use in biomedical applications. For adequate photopolymerization, a photoinitiator and a light absorber are necessary, using well-defined concentrations. This study shows preliminary results of DLP 3D-printing of different PEGDA hydrogel compositions with varying water content (90; 70; 50; 30; 10; 0 % w/w) as well as varying concentrations of a photoinitiator and a light absorber. Printing performance and accuracy are investigated by printing rectangular test samples as well as an anatomically customised tubular frontal sinus implant prototype. For basic mechanical characterisation, the hardness of the printed hydrogels is investigated using a Shore A durometer. The results show a decrease in printing accuracy and hardness with an increasing water content of the composition. There is a need to use a light absorber to reach high printing accuracy. This leads to a need for increasing photoinitiator concentration and prolonged light exposure to achieve proper printing performance.

Keywords: 3D-printing, digital light processing (DLP), PEGDA hydrogel, Orange G, LAP, frontal sinus implant, shore hardness

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1 Introduction

The technology of 3D printing holds promising potential for patient-specific implant solutions and prosthetics, as well as tissue engineering and bioprinting applications. There is a variety of different 3D printing processes. Photopolymerization 3D printing techniques such as Stereolithography (STL) or Digital Light Processing (DLP) solidify liquid photopolymers via light exposure, using a laser beam or a DLP projector respectively. They can be seen as methods offering the highest printing accuracy and precision [1]. Furthermore, photopolymerization 3D printing has minimal thermal impact on the photopolymers and enables extensive control over the polymerising process by means of varying the light exposing parameters as well as the material composition. Those possibilities are very beneficial in the context of establishing 3D printing processes for drug eluting devices.

On the material side, biocompatible polymers and hydrogels such as Poly(ethylene glycol) (PEG) and PEG diacrylate (PEGDA) [2][3], Poly-D,L-lactic Acid (PDLLA) [4] or Polyurethane (PUR) [1] are available for photopolymerization 3D printing processes. The variation of polymerization parameters and material compositions offers many possibilities to adjust the chemical and mechanical properties of the polymers [3]. A photoinitiator and light absorbers are typically necessary for a proper 3D printing process. These additives have to match the wavelength of the light source. It is important to note that these additives often have negative effects on the cytotoxicity and biocompatibility of the material composition. In this context, the photoinitiator Lithium phenyl-2,4,6-trimethyl benzoyl phosphinate (LAP) [5][6] and the light absorber Orange G dye [1] show good promise for high biocompatibility.

The current study focuses on a DLP 3D printing process using PEGDA-based hydrogels in combination with LAP and Orange G dye. Furthermore, this study also aims for 3D printing of a prototype of a novel frontal sinus implant, personalised to a patient's anatomy. That addresses a current limitation of frontal sinus implants available in the market, which usually are strictly tubular. In general, there is a growing demand for customised implants and medical devices that meet the anatomical needs of patients [7].

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2 Materials and methods

2.1 Materials

Photocurable PEGDA solutions were prepared using PEGDA of molecular weight of $M_n = 700$ g/mol (PEGDA₇₀₀) as matrix polymer, LAP as a photoinitiator and Orange G dye as a light absorber. LAP and Orange G concentration in PEGDA solution were varied as shown in Table 1. PEGDA solutions were diluted with distilled water (90, 70, 50, 30, 10 % w/w and no water content) to investigate DLP 3D-printing of PEGDA hydrogels. All substances were purchased from Sigma Aldrich Chemie GmbH, Munich, Germany. For comparative investigations of printing accuracy, the well-established E-Model light resin (envisionTEC GmbH, Gladbeck, Germany) was used.

Table 1: LAP and Orange G content in PEGDA solutions. The weight percentage is based on the mass of PEGDA in solution.

Composition	LAP % w/w	Orange G % w/w
c1	0,05	not included
c2	0,05	0,1
c3	0,1	0,1

2.2 DLP 3D-printing investigations

DLP 3D printing investigations were performed using a VIDA 3D printer (envisionTEC GmbH, Gladbeck, Germany). First, simple rectangular test samples, such as one Shore A hardness test sample (40 x 40 x 7 mm) and two flat test samples (54 x 10 x 2 mm), were printed. They were placed next to each other with a spacing of 3 mm (Figure 1 A) on the building platform. Second, a much more complex test sample of a frontal sinus implant prototype was built. That prototype is customised based on a patient's anatomical individualities. Consequently, it is a tubular structure with complex free-formed geometry that needs a support structure in order to be 3D printed (Figure 1 B).

PEGDA solutions were processed using a light exposure time per layer of 20 s and a layer height of 100 μ m (Z-resolution). Additionally, PEGDA solutions containing Orange G were processed with a doubled light exposure time of 40 s per layer to compensate the loss of light exposure intensity due to the absorbing agent. These relatively long light exposure durations per layer allow for low concentrations of photoinitiator and light absorber, which might have a positive

impact on biocompatibility. The wavelength of the DLP projector is 405 nm, which is in accordance with the absorption spectra of the used photoinitiator LAP and the light absorber Orange G. The XY printing resolution of the VIDA 3D printer is 73 μ m.

2.3 Shore A hardness measurements

Shore A hardness measurements were performed with DLP 3D printed Shore A hardness test samples using a durometer (HBA 100-0, Sauter GmbH, Balingen, Germany) following EN ISO 868:2003.

Figure 1: CAD design of the DLP 3D printing test samples: (A) rectangular test samples: Shore A hardness test sample (40 x 40 x 7 mm, pink) and two flat rectangular samples (54 x 10 x 2 mm, brown and blue) with a spacing of 3 mm. (B) frontal sinus implant prototype (length ~15 mm, green) with support structures (various coloured)

3 Results and discussion

3.1 DLP 3D-printing investigations

PEGDA material composition c1 with water contents of 70, 50, 30 and 10 % w/w have been successfully cured in a DLP 3D printing process. However, the test samples show insufficient printing accuracy. The simple rectangular test samples merged during the 3D printing, as shown in Figure 3.

Nevertheless, it can be seen that the merging effect decreases with decreasing water content, resulting in an increasing printing accuracy. The printing accuracy peaks for PEGDA solutions with a water content of $\leq 30\%$ w/w. PEGDA solution with 90 % w/w of water could not be cured at all using the described DLP parameters due to the high dilution of the photoinitiator. The printing investigations of the more complex test sample of a frontal sinus implant prototype show comparable results. In comparison to the prototype sample printed with E-Model light resin, it can be clearly seen that support structures are merged with prototype structures (Figure 4 A). Nevertheless, printing accuracy of the free-formed geometry is acceptable when using PEGDA solutions with a water content of $\leq 30\%$ w/w. Based on these results, the composition c2 with a water content of 30 % w/w was tested. No merging effect occurred during 3D printing. In comparison to composition c1 there is a need for a prolonged light exposure time of 40 s per layer for adequate photopolymerization. However, the printing process showed significant problems, such as insufficient adhesion of the specimens on the build platform. As a result, the frontal sinus implant prototype could not be printed using c2 material composition. The best printing performance was achieved with PEGDA solution c3 (water content 30 % w/w) using a prolonged light exposure time of 40 s per layer. The accuracy of the printed c3 PEGDA hydrogel prototype is comparable to E-Model light prototype (Figure 4 B and Figure 5). However, due to the relatively low M_n of the selected PEGDA₇₀₀ ($M_n = 700$), test samples seem to be brittle.

3.2 Shore A hardness measurements

Shore A hardness measurements are shown in Figure 2. Hardness peaks for PEGDA hydrogels with a water content of $\leq 30\%$ w/w. No significant increase of hardness could be

Figure 2: Shore A hardness measurements. Designation of PEGDA hydrogels (x-axis): cx-aa/bb: x $\triangleq$ configuration number; aa $\triangleq$ content of PEGDA₇₀₀ in hydrogel; bb $\triangleq$ content of water in hydrogel.

observed at lower water contents of the hydrogels. The presence of the light absorber Orange G results in a need for increased photoinitiator concentration as well as prolonged light exposure time to achieve similar values of Shore A hardness.

Figure 3: PEGDA hydrogel rectangular test samples DLP 3D-printed with c1 PEGDA solutions containing 70 % w/w (A) and 30 % w/w (B) of water. Printing accuracy increases with decreasing water content. Best accuracy has been reached under usage of Orange G as light absorber for c3 PEGDA- hydrogel (30 % w/w water, C).

4 Conclusion

This study demonstrates promising first results of DLP 3D printing of PEGDA hydrogels for frontal sinus implants. It was shown that printing accuracy and Shore A hardness decrease with increasing content of water in the PEGDA hydrogel. There is a need for controlling the penetration depth of light exposure for the printing of complex geometries like tubular or overhanging structures. The presence of the absorber agent Orange G has significant positive effects on the printing performance and accuracy for PEGDA hydrogels using a VIDA 3D printer. However, there is a need for an increased concentration of photoinitiator LAP and prolonged light exposure time.

It can be stated that the introduced material composition of PEGDA₇₀₀, the photoinitiator LAP and the light absorber Orange G is very promising for DLP 3D printing in the medical and pharmaceutical field as well as in the field of tissue engineering. Further investigations will aim for the characterisation and optimisation of mechanical properties, cytotoxicity tests as well as 3D printing of drug delivery devices.

Figure 4: Frontal sinus implants DLP 3D printed with c1 PEGDA hydrogel (30 % w/w water, A) and c3 PEGDA hydrogel (30 % w/w water, B). There is a need for a light absorber for printing complex geometries like hollow structures.

Figure 5: Frontal sinus implant made from commercially available resin E-Model light. The 3D printing accuracy using c3 PEGDA hydrogel (Figure 4 B) is comparable to accuracy that can be achieved with resin E-Model light.

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