Dual color tomographic volumetric printing for stiffness-graded scaffold

Wang, Bin; Engay, Einstom; Yang, Yi; Islam, Aminul

Published in:
European Society for Precision Engineering and Nanotechnology, Conference Proceedings

Publication date:
2023

Document Version
Publisher's PDF, also known as Version of record

Citation (APA):
Wang, B., Engay, E., Yang, Y., & Islam, A. (2023). Dual color tomographic volumetric printing for stiffness-graded scaffold. In O. Riemer, C. Nisbet, & D. Phillips (Eds.), *European Society for Precision Engineering and Nanotechnology, Conference Proceedings: 23rd International Conference and Exhibition, EUSPEN 2023* (pp. 119-120). euspen.

---

euspen's 23rd International Conference &
Exhibition, Copenhagen, DK, June 2023
www.euspen.eu

Dual color tomographic volumetric printing for stiffness-graded scaffold

Bin Wang [1], Einstom Engay [2], Yi Yang [3], Aminul Islam [1,*]

[1]*Department of Mechanical Engineering, Technical University of Denmark*
[2]*National Center for Nano Fabrication and Characterization, Technical University of Denmark*
[3]*Department of Chemistry, Technical University of Denmark*

biwang@dtu.dk

Abstract
This work provides a manufacturing strategy for the scaffold with heterogeneous mechanical properties via dual color tomographic volumetric printing (DCTVP). By initiating the polymerization of an acrylate and epoxy based multicomponent material using visible (λ~455 nm) and UV (λ~365 nm) light in parallel, a composite scaffold with graded stiffness can be produced within several minutes. The stiffness contrast of printed samples is proved to be tuneable through adjusting the precursor composition. The achieved modulus contrast ratio between the UV and visible light cured samples ranges from 88% to 825%.

Tomographic volumetric printing, Stiffness control, Gradient scaffold

1. Introduction

The worldwide incidence of bone disorders is escalating at an alarming rate, especially among elderly people and people with increased obesity and poor physical activity. Therefore, bone tissue engineering - the process for the regeneration of diseased or damaged bone is getting great attention from the scientific world [1]. One of the critical components for tissue engineering is scaffolds that act as artificial extracellular matrices to promote bone regeneration. Research demonstrated that the substrate stiffness gradient could be leveraged to cue cell migration and even differentiation, and it is thus highly valuable to create scaffolds with heterogeneous mechanical properties [2-3]. In recent decades, three-dimensional printing has been ascertained as a promising technology to manufacture the scaffold with complex structures and properties to better mimic the native bone tissue environment. Di Luca et al. were able to print discrete stiffness gradient scaffolds by sequentially depositing three different materials together [4]. Jelen et al. prepared the gradient structure by stacking two different homogeneous layers that were made of a mixture of varied concentrations of hydroxyapatite and gelatin [5]. However, traditional layer-by-layer printing processes show bottlenecks in scaffold manufacturing, such as the weak interface at the printing layers, the limitation in geometric complexity, and the long processing time. Tomographic volumetric printing is an emerging additive manufacturing method inspired by reversed computed tomography, which demonstrates the advantages of high printing speed, smooth surface finishes, and the fabrication of complex structures without any auxiliary support [6-7].

Our previous work already demonstrated stiffness gradients can be generated within workpieces with high precision by modulating the polymerization of interlaced material using two different light sources [8]. Inspired by that we here apply this method to produce a composite scaffold with graded stiffness and validated whether the graded stiffness could be granted to a scaffold via dual color tomographic volumetric printing (DCTVP). Besides, we explored how to expand the stiffness contrast by adjusting the precursor composition.

2. Methods and materials

For the current investigation, two light sources- 365 nm UV light source (VISITECH-LRS-4KA, Visitech, Norway) and 455 nm visible light source (Acer XD1270D, Acer, China) that work in parallel were installed in a tomographic volumetric 3D printing setting. A camera surveillance system (Grasshopper3 GS3-U3-28S5C, Point Grey Research Canada) was embedded into the setup to monitor and record the real printing process. The schematic representation of the setup is shown in Fig. 1. At the beginning of the printing process, the 2D calculated patterns of the target object in different angles are transferred into the projectors, then a series of projections are exposed to the rotating container filled with the photoresins. In the meantime, the 3D exposure energy dose starts to build up until each voxel within the material is cured into the solid.

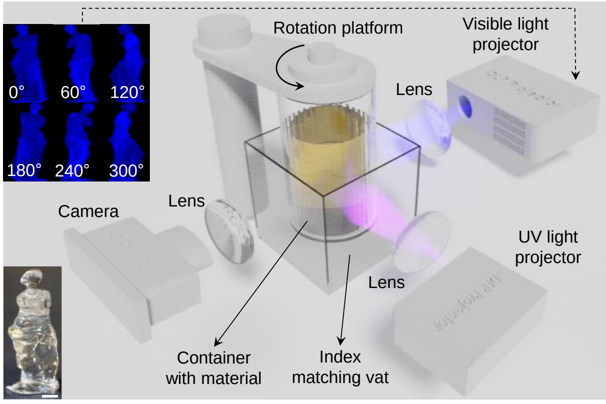

Figure 1. Experimental setup for DCTVP. Cured object showing at the bottom left corresponding to the input projections. Scale bar 5mm.

In this experiment, the resin used was a mixture of acrylate- and epoxy-based photosensitive resin with the functional photoinitiator added. The acrylate-based resin was prepared with the mixture of bisphenol A glycerolate diacrylate (BPAGDA) and poly(ethylene glycol) diacrylate (PEGDA, with Mn 250 or 700) with a volumetric ratio of 3:1, and 5 mM camphorquinone (CQ) and ethyl 4-dimethylaminobenzoate (EDAB) were added as the free radical photoinitiator (PI) and co-initiator, respectively. The epoxy-based resin was 3, 4-epoxycyclohexylmethyl 3, 4-

epoxycyclohexanecarboxylate (EEC) and 50 mg/ml cationic initiator triarylsulfonium hexafluoroantimonate salts (CAT2). Different combination ratios of acrylate-based monomers and epoxy-based monomers were formulated for the printing test as shown in Table 1. The materials used in this work had been proven cytocompatible [9]. Post-processing was conducted as depicted in our previous work [8].

Table 1. Materials composition.

Formula	Acrylate monomers (%)	Epoxy monomers (%)
AE-4-1	80	20
AE-3-1	75	25
AE-2-1	67	33

3. Results

The cubic structure (10x10x10 mm, through hole diameter 6.25 mm, Fig. 2A) was designed as the representative scaffold unit to demonstrate the stiffness control capacity of DCTVP. By using the two light sources in parallel, the scaffold with composite cubic structures could be readily manufactured with satisfactory geometrical fidelity (Fig. 2C-CAD design and 2D-printed part). The blue cubic on the top position of Fig. 2C represents the cube that was cured by the visible light with exposure time (ET) 440 s and the corresponding delivered light dose (LD) 1.2 J, and the bottom purple cubic represents the part that was cured by the UV light (ET: 480 s, LD: 7.3 J). Both parts were made using resin AE-3-1 (with PEGDA, Mn 250).

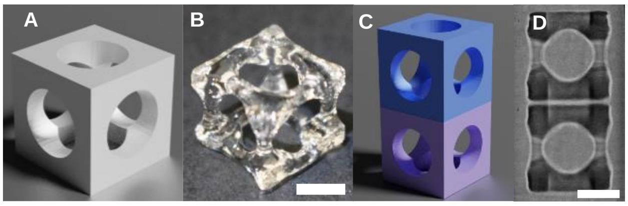

Figure 2. Stiffness control of the cubic structures. (A)&(B) Designed and printed-out cubes. (C) Cubic scaffold (D) A snapshot of the polymerized scaffold by the surveillance camera. Scale bar 5mm.

For direct evaluation of the inherent mechanical property gradient of the composite scaffolds and avoiding cutting the composite scaffold into two cubic units, another group of cubic structure were printed using two light sources individually and compressive test was carried out based on the single cubic unit (illustrated in Fig. 3A inset at the bottom left). As the stress-strain curve shows, the cubic structures cured with UV and visible light separately imparted different compressive strength. The UV induced structure, without post-curing, was stiffer than the one cured by visible light with the estimated modulus of 3.6 MPa and 590 KPa, respectively (solid lines in Fig. 3A, zoom in version shown in the inset at the top left). After post-curing, the corresponding modulus of both cubes were significantly improved and the UV cured parts had a higher modulus (253 MPa) compared with the parts cured by visible light (159 MPa).

Another important investigation made during this work was about the achievable stiffness contrast by changing the material formulation, specifically, adjusting the composite ratio of the epoxy-based and acrylate-based resins (with PEGDA, Mn 700). The resized dogbone specimens were printed with two different lights separately for the comparison of the compressive modulus (measurements were conducted on the grip section using ⌀ 2mm probe). The testing results are shown in Fig. 3B and Table 2. The UV cured objects demonstrated higher stiffness than the ones cured with visible light for all the three groups of material formulations as listed in Table 1. For resin AE-4-1 the tested compressive modulus contrast (how stiffer the parts printed with UV were compared to the parts printed with visible light) of the printed dogbone were relatively Low (88%). Whereas, the modulus contrast was noticeably higher with the increased amount of epoxy-based monomer. The corresponding modulus contrasts of the samples using resin AE-3-1 and resin AE-2-1 were 177% and 825%, respectively.

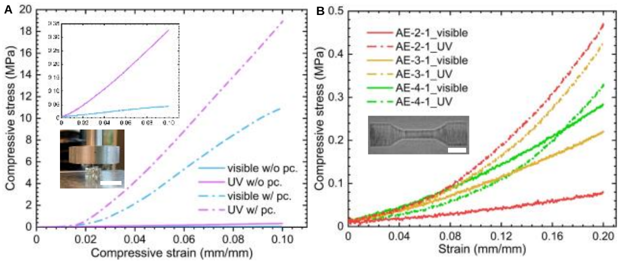

Figure 3. Representative stress-strain plot of the compressive testing results. (A) Cubic structures testing, the bottom left inset illustrates the real compressive testing, with scale bar 20 mm. (B) Dogbone testing, the inset is the printed dogbone illustration, with a scale bar of 5 mm.

Table 2. Compressive testing results.

Formula	Visible	UV	Contrast
AE-4-1	1.7 MPa (ET: 358 s; LD: 1.7 J)	3.2 MPa (ET: 684 s; LD: 15 J)	88%
AE-3-1	1.3 MPa (ET: 358 s; LD: 1.7 J)	3.6 MPa (ET: 594 s; LD: 13 J)	177%
AE-2-1	0.4 MPa (ET: 358 s; LD: 1.7 J)	3.7 MPa (ET: 684 s; LD: 15 J)	825%

Visible light is used to initiate the acrylate functional group but cannot trigger the epoxy polymerization, therefore, with decreasing acrylate content, the overall crosslinking density of the cured object is lowered, resulting in the lower modulus of the cured objects. For the UV light, increasing epoxy proportion enhances the cationic polymerization, therefore, prompting the formation of hard structure. The improved excitation of cationic photoinitiator also enhances the production of the free radical, leading to shorter curing time that limits the stiffer, interlaced polymer network. Moreover, if the epoxy resin ratio keeps rising, meaning the proportion of the acrylate monomers will be markedly decreased, which will increase the curing time of acrylate. Hence, this trade-off sets the limit for the stiffness contrast achieved by DCTVP and lay the foundation for future reserch and optimization.

4. Conclusion

This investigation demonstrated that the modulus contrast can be tuned considerably by adjusting the composition ratio of epoxy and acrylate monomers, paving the way for the application of DCTVP technology to customize functionally-graded scaffold for different application scenarios and opens up the scopes of further research and development. Although the cubic scaffold showed in thIs work only possess the discreate stiffness, it is noted that the combinatory utilization of visible and UV light sources can result in any targeted stiffness within the determined stiffness range.

References

[1] Vitković N, Stojković M, Majstorović V, Trajanović M and Milovanović J 2018 *CIRP Annals* **67** 1

[2] Bangasser B L et al. 2017 *Nat Commun.* **8** 1

[3] Engler A J, Sen S, Sweeney H L and Discher D E 2006 *Cell* 2006, **126** 4

[4] Di Luca A et al. 2016 *Biofabrication* **8** 1

[5] Jelen C, Mattei G, Montemurro F, De Maria C, Mattioli-Belmonte M and Vozzi G 2013 *Materials Science and Engineering: C* **33** 1

[6] Kelly B E, Bhattacharya I, Heidari H, Shusteff M, Spadaccini C M and Taylor H K 2019 *Science* **363** 6431)

[7] Loterie D, Delrot P and Moser C 2020 *Nat Commun.* **11** 1

[8] Wang B, Engay E, Stubbe P R, Moghaddam S Z, Thormann E, Almdal K, Islam A & Yang Y 2022 *Nat Commun.* **13** 367

[9] Schmidleithner C, Zhang R, Taebnia N, Larsen E K, Almdal K and Larsen N B 2022 *Adv. Mater. Technol.* **7** 6