

Resin Component Optimization for Green Strength of Photocrosslinked Resorbable Scaffolds Prepared by Continuous Digital Light Processing (cDLP) Additive Manufacturing

David Dean¹, Eric Mott¹, Xinyi Luo¹, Martha O. Wang², Charlotte E. Vorwald², Ali Siblani³, John P. Fisher²



¹Department of Neurological Surgery, Case Western Reserve University, Cleveland, OH 44106; ²Fischell Department of Bioengineering, University of Maryland, College Park, MD 20742; ³envisionTEC, Inc., Dearborn, MI 48120

Introduction

High resolution is one of the most important benefits of photocrosslinking methods for the manufacture of resorbable tissue engineering scaffolds. High resolution 3D printing allowing the production of thin walls in any orientation can help to ensure the *in vivo* resorption of polymeric scaffolds. Prior fabrication, the orientation of porous spaces may be designed on computer to facilitate the formation and ingrowth of host tissue and vasculature within the defect site. However, a predicted and reliable resorption of the scaffold may be needed if remodeling of the tissue is necessary for sufficient neo-tissue material properties, vascularization, and prevention of compartmentalizing the defect site.

Thus, the additive manufacture of resorbable scaffolds may create competing demands on material properties. First, it is necessary to have sufficient "green strength" (i.e., scaffold strength prior to post-fabrication curing) to clear unpolymerized polymer from the porous space without deforming the scaffold. Second, it is necessary for the scaffold to be weak enough to resorb by the time the neo-tissue filling the defect site must remodel.

additive photocrosslinked resolution manufacture of resorbable polymeric scaffolds requires one or more Type I or Type II initiators and possibly co-initiators to produce free radicals to sufficiently cause crosslinking both within and between layers. While within layer resolution is primarily dependent on pixel size, between-layer resolution commonly depends on the power of the mechanism used to deliver light and the use of light-blocking and/or -absorbing dyes.

Materials and Methods

PPF was prepared as previously described.² Diethyl fumarate, the monomer precursor to PPF, was used as a diluent in a 1.5:1 PPF:DEF ratio. These ingredients were combined with 3% Irgacure® 819 (BASF, Florham Park, NJ), the primary initiator, and 3% Irgacure 784 (BASF), a dye. Cylinders (3 mm diameter, 6 mm length) were rendered in an EnvisionTEC (Dearborn, MI) Perfactory Micro EDU via Continuous Digital Light Processing (cDLP). These cylinders were 3D printed using 90 (N=1), 180 (N=3), and 210 (N=5) seconds exposure per layer and set aside for mechanical testing without post-curing. One specimen (6 mm diameter, 12 mm length) was post-cured in a 3D systems (Rock Hill, SC) ProCureTM 350 UV chamber. Compression testing utilized an Instron (Norwood, MA) 8501 (Figure 1).

Results

Cylinders such as in Figure 1 were 3D printed (Figure 2a) to varying degrees of yield. The yield was observed to increase with exposure time.

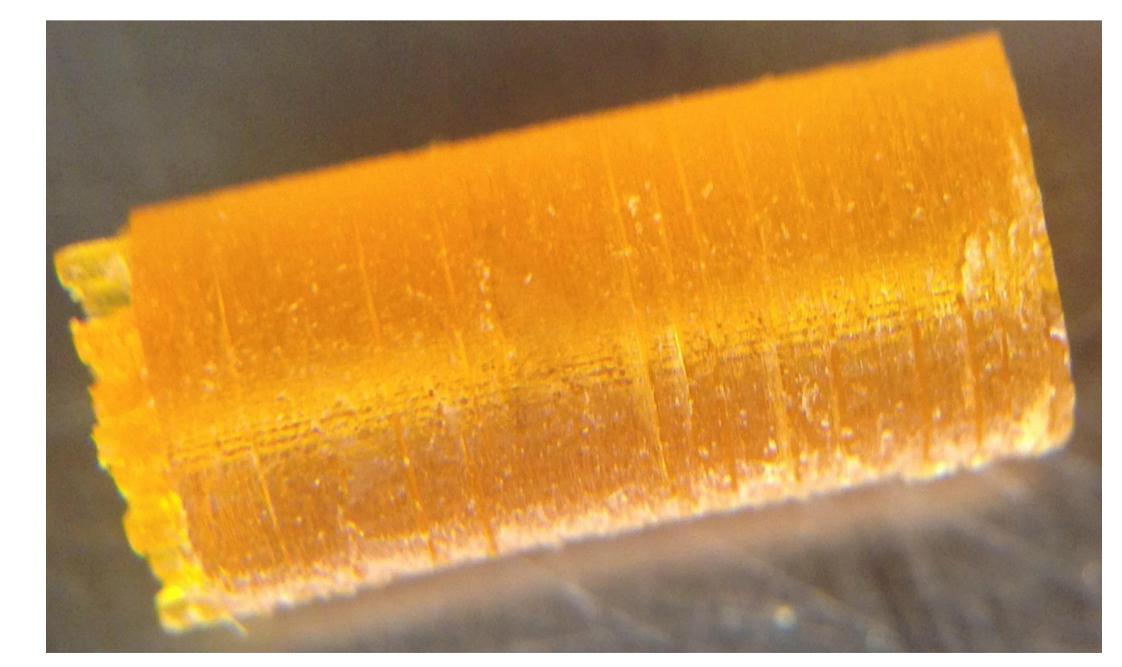


Figure 1. Example of 3mm x 6mm cylinder part 3D printed. Note that the supports have not yet been removed.

Specimens were tested to failure in an Instron rigged with self aligning fixture such as in Figure 2b. This ensured that compression occurred axially. Load was recorded through a load cell and strain was recorded using an externally mounted extensometer due to the specimen being too small to attach directly to. Results of this testing can be seen in Figure 3, which plots load versus displacement. From the slope, stiffness can be examined, which can then be correlated to modulus.





Figure 2. (a) Cylinder test specimens after being 3D printed in Perfactory Micro. (b) Specimen after being tested to failure under compression.

Load vs Displacement Displacement [mm] -2.5 **—**210 s **-**180 s **-90** s Layer Thickness Avg. Modulus (sample size) 23.7 MPa (1) 120 micron 124.8 MPa (3) 210 s 188.5 Mpa (5)

Figure 3. Mechanical Testing of 3D Printed PPF Cylinders: Strength vs. Exposure Time. MPa = megapascals.

Discussion

The interaction of resin components (e.g., polymer, initiator, and dye), influences green strength, postcured strength, and resolution. In our preparation of scaffolds from poly(propylene fumarate) (PPF), we have found that Irgacure 784 appears to act primarily as a dye allowing highly accurate scaffold fabrication. After clearing the pores, Irgacure 784 appears to act as an initiator during post-curing. Exposure time is correlated with gradually increasing green strength. Strength (Figure 1) increased dramatically, from under 200 MPa to almost 700 MPa, following post-curing.

References

- . Daicho Y, Murakami T, Hagiwara T, Maruo S. Opt Mater Exp 3(6), dx.doi.org/10.1364/OME.3.000875, 2013.
- 2. Kasper FK, Tanahashi K, Fisher JP, Mikos AG. Nat Protoc 4, 518, 2009.

Acknowledgements

Partial support for this research was provided by the Dept. of Neurological Surgery Research Foundation, Case Western Reserve University (CWRU) and NIH R01-DE013740 and R01-AR061460. Compression tests were done by Jay Bensusan in Dr. Clare Rimnac's laboratory, Dept. of Mechanical and Aerospace Engineering, CWRU.

Disclosures

DD, EM, MOW, AS, and JPF have submitted patent applications on these topics. DD received compensation from, and has an ownership stake in, Osteoplastics LLC.

Corresponding Author:

David Dean, Ph.D. Associate Professor, Department of Plastic Surgery The Ohio State University 460 West 12th Ave., 10th Floor, Rm. 1004 Columbus, OH 43210

Telephone: (614) 688-9044 E-mail: David.Dean@osumc.edu