Advanced Technologies for Hypersonic Propulsive, Energetic and Reusable Platforms
Technical Conference and Exposition
July 30, 2021

SYNTHESIS OF POLYMER RESINS WITH MECHANICALLY TUNABLE PROPERTIES FOR 3D PRINTING

Catalina Caramaschi Ratto
University of Central Florida
Orlando, FL

Ziyang Zhang
University of Central Florida
Orlando, FL

Dazhong Wu
University of Central Florida
Orlando, FL

ABSTRACT

This study gathers evidence from previously published with regards to materials, methods, and properties with the intent to review and synthesize resin(s) with the ability to tune its mechanical properties to include one or multiple desired properties in future papers. Resins with additional functions are very desirable and critical to the advancement of materials used in applications of or similar to soft robotics, medical devices, and more. Commercial resins serve a great purpose for basic uses with the catch that many do not possess the required properties to produce objects with complex geometric structures and/or additional functions. Many times, tuning is necessary but difficult or not possible to accomplish using resins found commercially. Synthesizing a novel resin formulation using materials found in previous literature would allow for easy tuning to combine multiple desired properties into one resin. The paper focuses mainly on shape memory and self-healing polymers with a brief mention of thermal and electrical conductivity capabilities as secondary interests.

Keywords: Stereolithography, Resin, Photopolymerization, Mechanically Tunable, Shape Memory, Self-Healing

NOMENCLATURE

SLA Stereolithography
DLP Digital Light Processing
VIS Visible Light
Additional Functions
Shape Memory
Self-Healing
Electrical Conductivity
Thermal Conductivity

1. INTRODUCTION

Additive Manufacturing (AM) or 3D Printing is a production process which allows for the fabrication of complex structures using a variety of methods and materials. It is used for a multitude of applications which include models, prototypes for medical devices, toys, vehicle parts, and such. For the purposes of this paper the respective resin formulations have potential applications like soft robotics, embedded electronics, flexible electronics, sensors and such. The figures shown in this paper were printed using the extrusion process of additive manufacturing. This refers to the process of printing in which the printer extrudes small amounts of liquid resin out of a resin tank layer by layer. The liquid resin is then cured by VIS (Visible) light or more commonly UV (Ultraviolet) light in order to ensure the object the least amount of liquid resin remains, so it is structurally sound. The resin may then be placed in an alcohol bath to remove any excess resin. Injection molding, fused deposition molding, selective laser sintering, injection electron beam melting are other known printing techniques. Stereolithography (SLA) and Digital Light Processing (DLP) are virtually the same with some minor differences. The most noticeable difference lies in the curing process. Stereolithography uses a laser beam to emit a small amount of light onto the resin in order to cure it. The Digital Light Processing printer uses a light reflecting off a mirror to cover the entire layer of resin leading to faster curing and overall printing times.

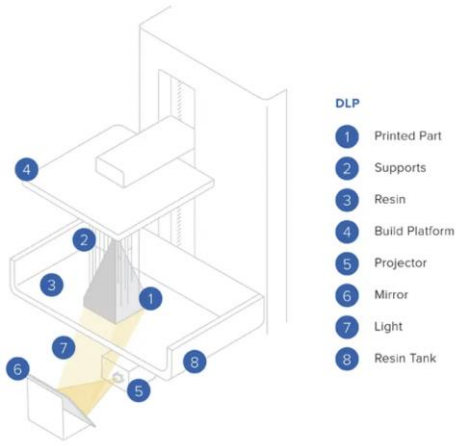

Figure 1. Visual representation of Digital Light Processing (DLP) printing technique. **[8]**

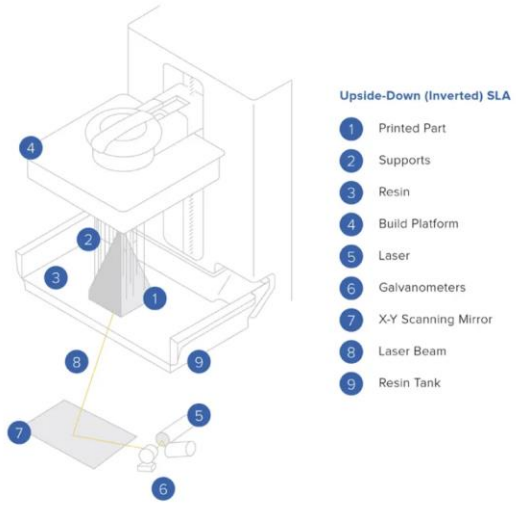

Figure 2. Visual representation of Stereolithography (SLA) printing technique. **[8]**

Resins used in SLA printing are mostly fossil fuel based and rather expensive. Synthesizing a resin from scratch or using bio-based materials allow for a greener and cheaper alternatively. The possibility of multiple healing cycles and ability to retain original shape of self-healing and shape memory polymers provides an offset the manufacturing costs of printing somewhat.

2. METHODS

The lab employs a Formlabs Form 2 3D printer equipped with a class-1 laser with a wavelength (λ) of 405 nm, 250 mW. The structures analyzed in this paper were printed using a wavelength between 385 nm and 405 nm. Tensile bars and rook tower prototypes are most commonly printed in order to conduct mechanical tests and optical analysis respectively.

3. DESIRABLE PROPERTIES

Viscosity, shrinking, cross-link density, Young's modulus, tensile strength, elongation at break etc. are important to keep in mind when looking for materials. Their high influence on mechanical properties and/or resulting additional functions

3.1 SELF-HEALING

Self-healing polymers are emerging as a popular and desirable material to use in additive manufacturing as they attain the ability to repair damage in order to prolong their life cycles and reliability. Their ability to mimic natural soft tissues is a great area of interest with protentional applications in areas of biomedical devices and tissue engineering as well as those stated in the introduction. Self-healing polymers can be described as an extrinsic type or intrinsic type, according to different healing mechanisms. **[7]** Intrinsic SHP's contain can heal damage to the printed object repeatedly rather than a single heal cycle for extrinsic as they typically possess reversable bonds such as dynamic covalent or non-covalent bonds.

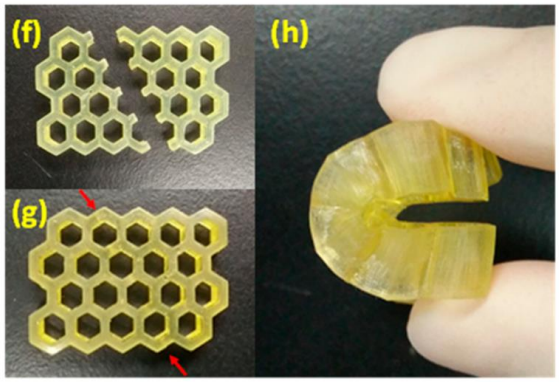

Figure 3. (f–h) Self-healing experiment of the honeycomb structure made with PUA-N_1. The fabricated honeycomb structure was cut into two parts and healed at 80 °C for 12 hours. The healed sample can then be freely bent. **[6]**

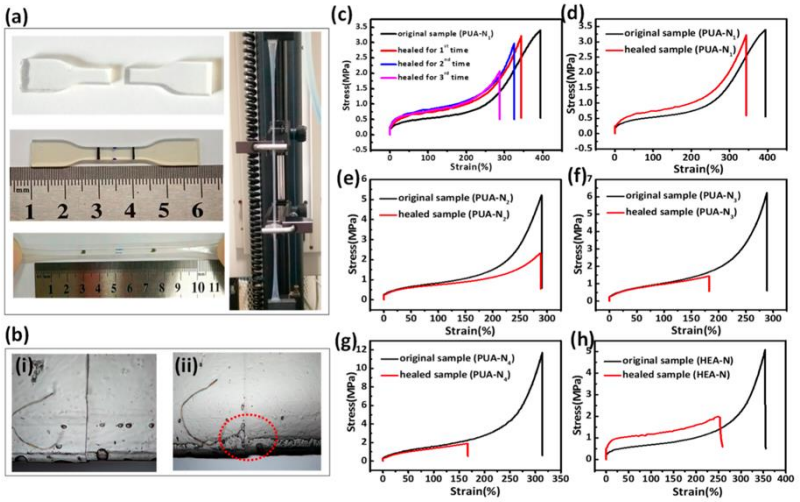

Figure 4. Mechanical properties of the UV-cured polyurethane acrylate elastomer. (a) Images of the tensile testing sample from PUA-N_1 cut into two parts, healed at 80 °C for 12 hours, and then stretched to a large deformation; (b) Optical microscope images of the healing portion of the tensile testing sample before and after the healing process, respectively; (c) Stress−strain curves of the original samples and the healed sample from PUA- N1 for three healing times; (d−h) Comparison of the mechanical properties of the samples from PUA-N_1, PUA-N_2, PUA-N_3, PUA-N_4, and HEA-N before and after the healing process, respectively. **[6]**

[6]

Table 1. Compositions, Viscosity of the Photopolymer Resins, and Content of Disulfide Bonds and Gel Content of the Obtained Elastomers

photoresins	PUSA (g)	PUHA (g)	HEA (g)	PI (g)	viscosity (cp, 25 °C)	disulfide contents (%)	gel contents (%)
PUA-N_1	10.0	0	10.0	0.4	4013	3.3	82.4
PUA-N_2	7.0	3.0	10.0	0.4	14210	2.3	83.0
PUA-N_3	5.0	5.0	10.0	0.4	26071	1.7	94.2
PUA-N_4	0	10.0	10.0	0.4	38840	0	96.2
HEA-N	0	0	20.0	0.4	5.4	0	99.0

Table S1. The mechanical properties of the original and healed samples and calculated healing efficiency of these elastomers. **[6]**

Samples	Original		Healed		Healing efficiency
	σ (MPa)	ε (%)	σ (MPa)	ε (%)	
PUA-N_1	3.39 ± 0.09	400.38 ± 14.26	3.22 ± 0.40	340.15 ± 15.52	95 %
PUA-N_2	5.19 ± 0.13	288.72 ± 6.19	2.41 ± 0.22	299.49 ± 11.90	47 %
PUA-N_3	6.18 ± 0.55	296.37 ± 24.77	1.44 ± 0.10	190.34 ± 9.45	23 %
PUA-N_4	11.71 ± 1.17	319.63 ± 11.56	1.87 ± 0.13	166.45 ± 16.08	16 %
HEA-N	5.14 ± 0.12	366.38 ± 9.82	1.78 ± 0.11	305.24 ± 9.02	36 %

While there are flaws to work out, it is important to note how vastly different the resulting resins can be with only a minor tune in composition.

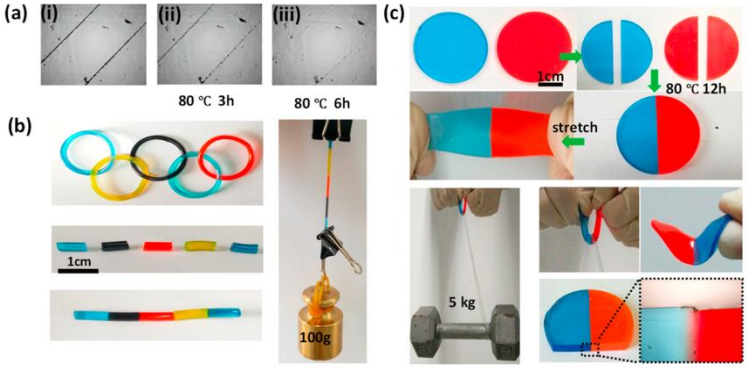

Figure 5. (a) Optical microscopy recorded during the scratch healing process of the elastomer prepared from PUA-N_1; (b) Images of the Olympic Rings pattern jointed by cylindrical samples with a diameter of 2 mm; the cylindrical samples were cut, reconnected, and healed at 80 °C for 12 h to get a new cylindrical sample; the healed cylindrical sample lifting a weight of 100 g; (c) Images of the colored PUA-N_1 samples cut into two pieces, connected, and healed for 12 h at 80 °C and, finally, subjected to first stretching manually to a large deformation and then to a 5 kg weight lifting test; optical microscope images of the healing interface of the healed PUA-N_1 sample. **[6]**

3.2 SHAPE MEMORY

Refers to the ability of a resin to retain its original shape after being deformed by thermal or manual agitation. SMP's main purpose is to retain the original shape printed with the external stimuli and extend the life cycle of a resin with optimal durability.

4. CONCLUSION

The overview presented today will have to be narrowed and reviewed precisely in order to continue with experimental plans. For the purposes of the paper, formulations including Diels-Alder reactions, hydrogen bonding, and dynamic covalent bonds seem to be most promising to achieve tunable resins with additional function(s). Self-healing (SHP) and shape memory polymers (SMP) can retain near almost original values of self-healing efficiency and ultimate tensile strength (UTS) recovery, with a potential for Young's modulus to significantly increase; This is dependent on the formulations of materials utilized and compositions.

ACKNOWLEDGEMENTS

We would like to kindly acknowledge the University of Central Florida, the National Science Foundation, the Department of Defense, and the HYPER Undergraduate Research Experience program at UCF.

REFERENCES

[1] Mirko Maturi, Carolina Pulignani, Erica Locatelli, Veronica Vetri Buratti, Silvia Tortorella, Letizia Sambri, and Mauro Comes Franchini. “Phosphorescent bio-based resin for digital light processing (DLP) 3D-printing” *Green Chem*., **2020**, 22, 6212

[2] Vincent S. D. Voet, Tobias Strating, Geraldine H. M. Schnelting, Peter Dijkstra, Martin Tietema, Jin Xu, Albert J. J. Woortman, Katja Loos, Jan Jager, and Rudy Folkersma. “Biobased Acrylate Photocurable Resin Formulation for Stereolithography 3D Printing” *ACS Omega* **2018** *3* (2), 1403-1408

[3] Jarno Guit, Marjory B.L. Tavares, Jerzy Hul, Chongnan Ye, Katja Loos, Jan Jager, Rudy Folkersma, and Vincent S.D. Voet “Photopolymer Resins with Biobased Methacrylates Based on Soybean Oil for Stereolithography” *ACS Applied Polymer Materials* **2020** *2* (2), 949-957

[4] Park et al. “A visible light-curable yet visible wavelength-transparent resin for stereolithography 3D printing” NPG Asia Materials (**2018**) 10: 82–89

[5] Dominika N. Lastovickova, Faye R. Toulan, Joshua R. Mitchell, David VanOosten, Anthony M. Clay, Joseph F. Stanzione III, Giuseppe R. Palmese, and John J. La Scala. “Resin, cure, and polymer properties of photopolymerizable resins containing bio-derived isosorbide” Journal of Applied Polymer Science **(2020)**

[6] Xinpan Li, Ran Yu, Yangyang He, Ying Zhang, Xin Yang, Xiaojuan Zhao, and Wei Huang, “Self-Healing Polyurethane Elastomers Based on a Disulfide Bond by Digital Light Processing 3D Printing”, *ACS Macro Letters* **2019** *8* (11), 1511-1516

[7] Alexander W. Bassett, Amy E. Honnig, Claire M. Breyta, Ian C. Dunn, John J. La Scala, and Joseph F. Stanzione, “Vanillin-Based Resin for Additive Manufacturing”, ACS Sustainable Chemistry & Engineering **2020** *8* (14), 5626-5635

[8] https://formlabs.com/blog/resin-3d-printer-comparison-sla-vs-dlp/