Novel 3D Printing Inks with Non-Toxic Photoinitiators

Presented by Teoh Wee Yong, Darren

Supervised by Assoc Prof Terry W.J. Steele & Muhammad Naziruddin Bin Mohd Ali

Introduction

- The rise in the adoption of vat polymerization 3D printing in biomedical application is limited by the constrained selection of current monomer systems and initiators.
- An approach to overcome these limitations is to use renewable biocompatible monomers such as Acrylated Epoxidized Soybean Oil (AESO), which has relative non-cytotoxicity and has been observed to be able to undergo polymerization in 3D printing applications [1].
- Another approach is to test potential alternative photoinitiators like diazirines, which are organic compounds used for their carbene precursors and could initiate free-radical photopolymerization when irradiated with appropriate UV light.
- In particular, Trifluoromethylphenyl-diazirine (TPD) is a form of diazirine with relative stability, non-toxicity, and observed polymerization of acrylates in the presence of UVA-activated TPD [2].

Objectives

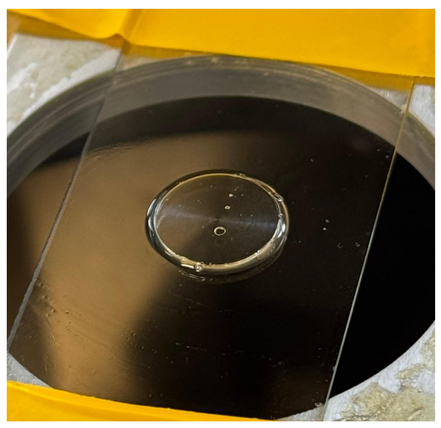
- Design a 3D printing UV-curable resin formulation that utilizes different functionality monomer systems (acrylates) with TPD as a photoinitiator.
- Characterizing the formulation's polymerization, viscoelastic, cytotoxicity and mechanical properties.
- Assessing the printing of the resin formulation on a 405 nm SLA 3D printer with different printing parameters.

Methodology

1. Photorheometry

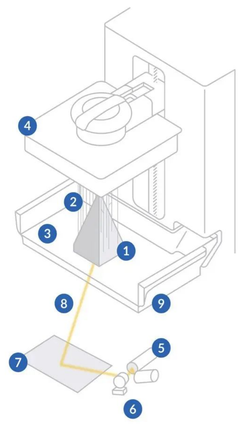
3 Testing phases:

- 1st stage: Steady-state viscosity.
- 2nd stage: Dynamic oscillatory strain measurement with LED UV source (365nm or 405nm) irradiation for 100 seconds (LIGHT ON at 30 seconds point, OFF at 130 seconds point) for a total exposure dose of 10 J.cm^{-2} (100 mW.cm^{-2}). Normal force acting on the steel probe was simultaneously measured.
- 3rd stage: Amplitude sweep of 1% to 1000% shear with an angular frequency of 10 rad.sec^{-1}.



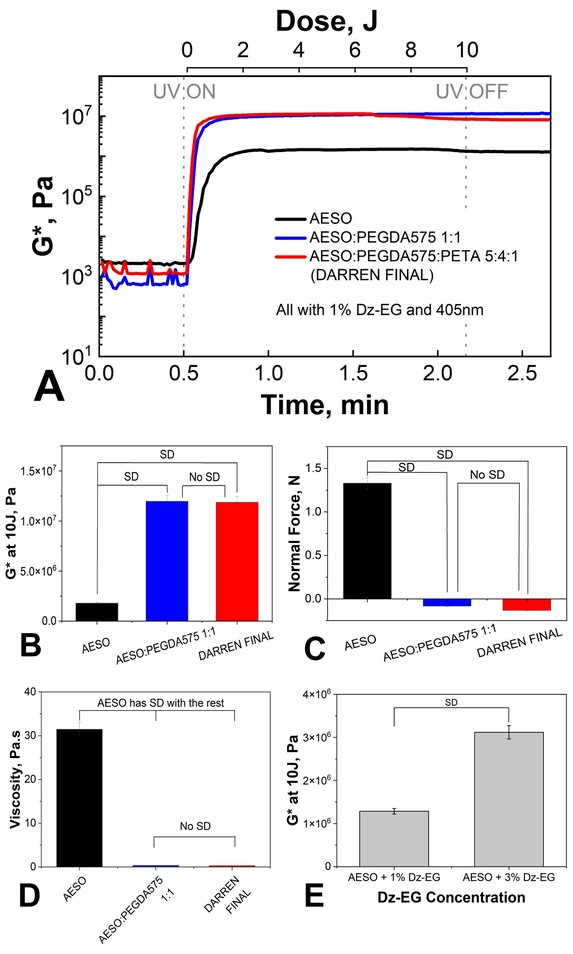
2. Other Experiments

- AlamarBlue Leachate Cytotoxicity Test
- Stereolithography 3D Printing using FormLabs Form 3B+ Printer
- Instron 5567 Mechanical Compression Testing

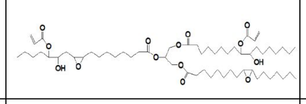
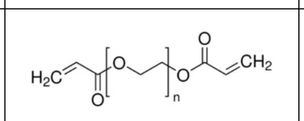
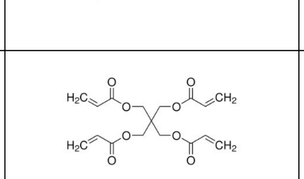
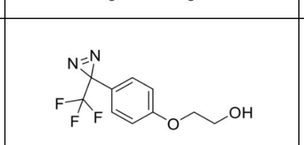


Results and Discussion

1. Photorheometry Testing

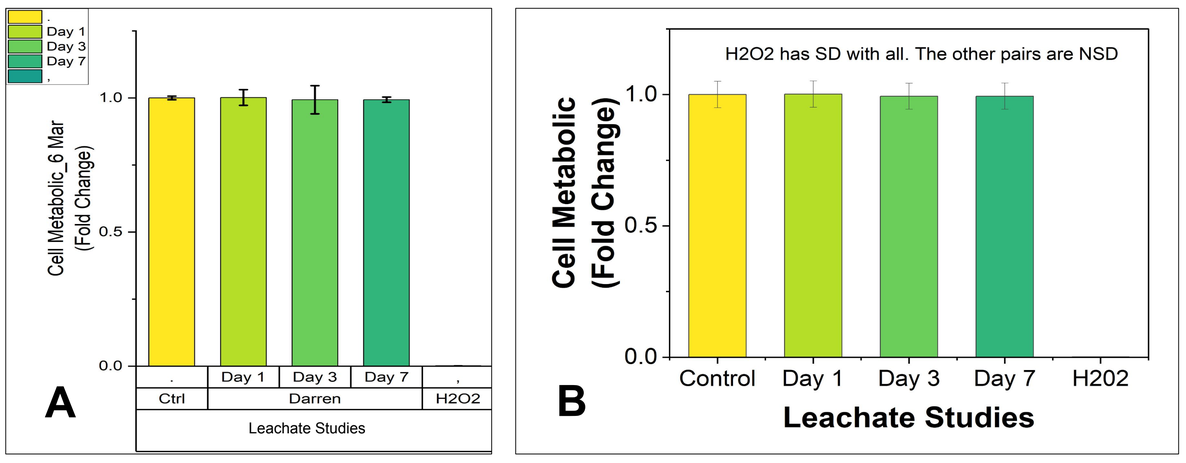


The 3D printing resin [DARREN FINAL] consists of 50% AESO, 40% PEGDA575, 10% PETA and 1% Dz-EG.

Name	Structure	Ratio in Formulation
Acrylated Epoxidized Soybean Oil (AESO) 1200 g.mol^{-1}		50
Polyethylene glycol diacrylate (575 Mw) (PEGDA575) 575 g.mol^{-1}		40
Pentaerythritol tetraacrylate (PETA) 352.34 g.mol^{-1}		10
2-(4-[3-(trifluoromethyl)-3H-diazirin-3-yl]phenoxy)ethan-1-ol (Dz-EG) 246.06 g.mol^{-1}		1

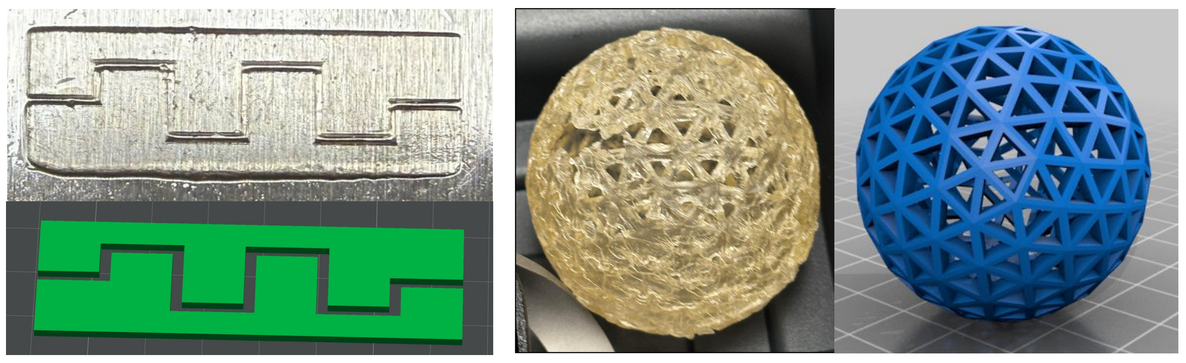
- Statistical difference: DARREN FINAL formulation has higher G*, minimal shrinkage and lower viscosity compared to pure AESO.
- Statistical difference: G* of 1% Dz-EG was ⅓ of G* of 3% Dz-EG. However, as Dz-EG was only provided in small quantities, the testing of Dz-EG in 3D printing formulations was limited to 1% for the project.

2. AlamarBlue Leachate Cytotoxicity

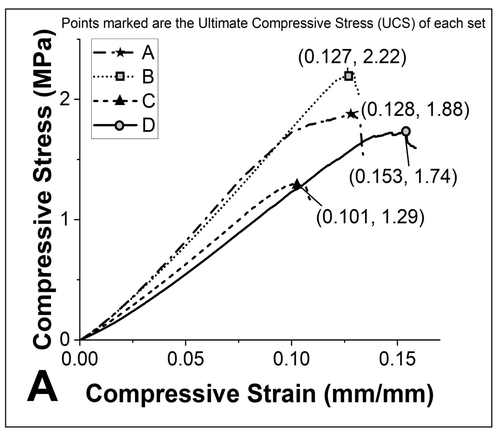


- Leachates showed relative non-cytotoxicity for DARREN FINAL formulation.

3. SLA 3D Prints (Microfluidic Channel & Ping Pong Ball)



4. Mechanical Compression Testing



Sample Set	Toughness (J/m^3)
A (UV and Heat Cured)	147212
B (UV Cured)	98998
C (No Curing)	90882
D (Heat Cured)	146210

- No statistical difference between the different post-curing methods for cylinders' mechanical properties (compressive stress, compressive strain and toughness).

Conclusion

- TPD can initiate the polymerization of acrylates with irradiation at 405 nm.
- The DARREN FINAL formulation was shown to be printable. However, the printing parameters need to be further refined to improve surface finishing and prevent over-curing.
- Post-curing using different types of post-curing methods was inconclusive and parts printed using other formulations need to be analyzed in further studies.

References:

[1] A. Bagheri and J. Jin, "Photopolymerization in 3D Printing," *ACS Applied Polymer Materials*, vol. 1, no. 4, pp. 593–611, Feb. 2019, doi: 10.1021/acsapm.8b00165.

[2] E. Ellis, I. Djordjevic, M. N. Bin Mohd Ali, and T. W. J. Steele, "Carbene-Based Bioadhesive Blended with Amine, Thiol, and Acrylate Liquid Additives," *ACS Applied Polymer Materials*, vol. 5, no. 2, pp. 1440–1452, Jan. 2023, doi: 10.1021/acsapm.2c01658.